SYNTHESIS, CHARACTERIZATION AND APPLICATION OF NANOPARTICLES FOR ENHANCED PERFORMANCE OF TEXTILES

A THESIS SUBMITTED TO
THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA
FOR THE AWARD OF THE DEGREE OF

DOCTOR OF PHILOSOPHY
IN
TEXTILE CHEMISTRY

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UNDER THE GUIDANCE OF
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DECLARATION

I here declare that the topic entitled ***"Synthesis, Characterization and Application of Nanoparticles for Enhanced Performance of Textiles"*** *which is submitted herewith to The Maharaja Sayajirao University of Baroda, Vadodara for the fulfillment of the award of the degree of* **DOCTOR OF PHILOSOPHY IN TEXTILE CHEMISTRY** *is the result of the work carried out by me in Textile Chemistry Department, Faculty of Technology & Engineering, The M. S. University of Baroda, under the able guidance of Dr. D. P. Chattopadhyay, Associate Professor, Department of Textile Chemistry, Faculty of Technology & Engineering, The M. S. University of Baroda, Vadodara.*

I further declare that the result of this work has not been previously submitted for any degree / fellowship.

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CERTIFICATE

This is to certify that, this thesis entitled,

Synthesis, Characterization and Application of Nanoparticles for Enhanced Performance of Textiles

Submitted by

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In partial fulfillment for the award of Doctorate degree
IN
TEXTILE CHEMISTRY

To The Maharaja Sayajirao University of Baroda, has been carried out under my supervision and guidance. The matter compiled in this thesis has not been submitted earlier for the award of any other degree or fellowship.

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TO
MY PARENTS

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List of publications

Review papers

1. Nano-particles & their uses in textiles. ***The Indian Textile Journal***, (ISSN 0019-6436), Dec.2007, vol. CXVIII, No.3, p. 23-31, By B.H.Patel & Dr D.P.Chattopadhyay.

Research Papers: Publications in national/ international research journals

2. Improvement in physical and dyeing properties of natural fibres through pre-treatment with silver nanoparticles. ***Indian Journal of Fibre & Textile Research***, (ISSN: 0971-0426), December. 2009, Vol. 34, P.368-373, By D P Chattopadhyay & B H Patel.
3. Effect of nanosized colloidal copper on cotton fabric, ***Journal of Engineered Fiber Fabrics,*** (ISSN 1558-9250), Vol. 5, Issue 3, July 2010, p 1-6, By D.P.Chattopadhyay & B.H.Patel.
4. Modification of Cotton Textiles with Nanostructural Zinc Particles, ***Journal of Natural Fibers***, (ISSN: 1544-046X (electronic) 1544-0478 (paper)), Volume 8, Issue 1, March 2011, Pages 39 – 47 By D. P. Chattopadhyay & B. H. Patel
5. Preparation, characterization and stabilization of nano sized copper particles, ***International Journal of Pure Sciences and Technology,*** ISSN: 2229-6107, vol. 9, No. 1, P- 1-8, 2012, D. P. Chattopadhyay & B. H. Patel.
6. Influence of copper nano-colloids on jute fibre, ***Textile Asia***, ISSN: 0049-3554, vol 43, No.11, December 2012, Pages 19-21, By D. P. Chattopadhyay & B. H. Patel.
7. Effect of Cu-nano colloid treatment on the properties of wool and Silk, ***Textile Review,*** ISSN No: 0974-2530 (Invited paper) By Debapriya Chattopadhyay and Bharat H. Patel.
8. Novel padding technique to prepare Ag-nano/silk composite fabric, (under communication) By D. P. Chattopadhyay & B. H. Patel

Research Papers presented in conferences

9. Improvement in the properties of cotton textiles through the application of synthesized Cu

Nanoparticles Workshop on synthesis and characterisaton of nano-structured materials (scnm-08).The M.S.University of Baroda, Gujarat, India. 30th march.2008. By B.H.Patel & D.P.Chattopadhyay.

10. Synthesis, Characterization and Application of Silver nanoparticles to textiles, Second National Conference on Advances in Chemicals for Textile Polymers – Application and Quality Assurance (ACTPAQ 2009), Department of Chemistry, PSG College of Technology, Coimbatore , 12-13 February 2009, By D.P.Chattopadhyay & B.H.Patel.

11. Introduction to nanotechnology in textiles and effect on environment & human health, U G C Sponsored National Conference on Environmental Sustainability of Textile Industry, 8-9 January 2009, International College for Girls, Jaipur, India, By: Dr. D P Chattopadhyay and B H Patel (Award :Best oral presentation)

12. Synthesis, characterization and application of Zinc nano to cotton textiles, International Conference on Nanoscience and Nanotechnology (ICONN-2010), 24 - 26 February 2010, SRM University, Chennai, INDIA By D.P.Chattopadhyay & B.H.Patel.

13. Preparation of improved performance silk fabric through application of Silver nanosol, International Conference Intelligent Science and Technology (IIST-2010), 18 - 19 March 2010, at Sun college of engineering and technology, Nagercoil, Tamilnadu, INDIA. D.P.Chattopadhyay & B.H.Patel,

14. Studies on synthesis and stabilization of nano-sized copper particles, March 28-29,2011, International Conference on “Latest Trends in Nanoscience & Nanotechnology” (ICNSNT 2011) at KBN College of Engineering , Gulberga , Karnataka , India, D. P. Chattopadhyay and B. H. Patel

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CONTENT

CHAPTER 1

GENERAL INTRODUCTION & LITERATURE SURVEY

1.1 INTRODUCTION

Abrupt of research activity is witnessed in recent years in the area of synthesis and fabrication of different size and shape of nanomaterials. Nanometer sized materials display many interesting optical, electronic, magnetic and chemical properties yielding applications in biological nanosensors, optoelectronics, nanodevices, nanoelectronics, information storage, catalysis and textiles.

Many textile industries and research organizations have already developed fabrics with distinguished properties. Nanotechnology is adding its labels to popular clothing brands with various products: Resists Spills, Resists Static, Coolest Comfort, and Repels and Releases Stains. Researchers all around the world looking at all sorts of metal additives and polymer additives, inorganic, organic materials to take them at nanoscale to impart lots of interesting properties to textiles. Nano-particles in functional textile finishing are thus widely reported [1-7].

In some typical textile finishing applications nano-particles can be substantially alter surface properties and also confer different functions to the textile materials as per Li, Lokyuen and Junyan [8]. The nano size particles offer a larger surface area compared to that of bigger particles. Being in the nanometer range, the particles are transparent, so they do not blur colour or alter brightness of textile substrates.

Nano-particles can be applied on textiles by two-stage process. Initially, there is the manufacture of new, stable nano-material, which must in the first instance be protected against properties defined by the size of the particles. The second step sees the creation of the foils, emulsions and dispersions that can be applied to the final textile product, in the most favorable case, by means of conventional finishing processes. Nano-particles are most commonly applied to textiles by coating using a composition of nano particles, a surfactant, ingredients and a carrier medium.

As quoted by Wang, et.al [9] in their study in 2004 that nano particles have large surface area to volume ratio, which makes it easy for them to attach to fiber or fabrics, and increase the durability of the functions imparted by the particles. In addition, the coatings of nano particles do not affect the breathability, and hand feel of the textile.

The commonest functions are wrinkle resistance, stain, soil and water repellency and anti static, anti bacterial and ultraviolet protection.

Nanotechnology has real commercial potential for the textile industry due to the fact that conventional materials and methods used to impart different properties to fabrics often do not lead to permanent effects, and will lose their functions after laundering or wearing.

It is believed that the use of nano-sized materials not only improves the existing properties but also introduces special properties to textile fiber materials. Thus the main purpose of this doctorial thesis is to develop simple techniques for the preparation of nano-sized materials and their application to common textile fibers.

In agreement with the aims defined for the present thesis, in the general introduction corresponding to chapter 1, a brief bibliographic revision is made concerning the most relevant topics related to the synthesis, stabilization, characterization and application of nano-sized materials to textiles. The second part contains the major results attained in the scope of this thesis. The third part presents a general discussion, major conclusions and gives some perspectives for continuing the work in this research field.

Thus, the organization of this thesis comprehends 3 major parts:

1st part: Theoretical considerations about synthesis, stabilization, characterization and application of nano-sized materials to textiles and aims of the work- Chapter 1.

2nd part: Major results, in the scope of this thesis. This section contains the experimental procedures, as well as the attained results and respective discussions- Chapters 2, 3, 4, and 5.

3rd part: General discussion, conclusions and future perspectives- Chapter 6.

1.2 HISTORY AND DEFINITION OF NANOTECHNOLOGY

These days, the word “nano” seems to be popping up everywhere. Wall Street, Hollywood, and major universities around the globe have all endeavored to associate their diverse enterprises with this word. “Nano” is a metric unit that means one billionth of a unit; as of late, it has been used most frequently in reference to nanotechnology.

The term, “nanotechnology” was not always used so broadly. K. Eric Drexler coined it in his 1986 book, Engines of Creation to refer to his theories for molecular manufacturing, following up on visionary ideas presented 27 years earlier by famed physicist, Richard Feynman. As the possibilities of molecular nanotechnology grew and excitement built in the scientific community many researchers began using the term for their own endeavors at the nanoscale, unrelated to molecular manufacturing.

Nanotechnology seeks to provide and apply knowledge of the behaviour of objects in the nanometer (nm) size range to the assembly of complex structures for use in a variety of practical applications. The tiniest substances promise to transform industry and create a huge market. In chemicals, cosmetics, pharmaceuticals, technology and textiles, businesses are researching and manufacturing products based on nanotechnology, which use bits of matter measured in billionths of a meter. The study of Chattopadhyay [10] in 2006 and Patel and Chattopadhyay [11] in 2007 stated that the technology, utilizing materials a thousand times smaller than the width of a human hair, is showing up in everything from auto parts to sunscreens and clothing. However, nanotechnology has been used to improve products that most of us use everyday. These include laundry detergent, 6-pack rings, and surgical tools.

What if we could inexpensively make things with every atom in the right place? For those unfamiliar with the nanotechnology, it means we could continue the revolution in computer hardware right down to molecular gates and wires -something that today's lithographic methods, which are used to make the computer chips, could never achieve. Additionally, we could inexpensively make very strong and very light materials according to the convenience. This may include shatterproof diamond in precisely the shapes we want and over fifty times lighter than steel of the same strength. We could make surgical instruments of such precision and deftness that they could operate on the cells and even molecules from which we are made-something well beyond today's medical technology.

Energy-efficient: Molecular manufacturing can be energy-efficient because the key feature of its basis productive mechanisms i.e. guiding the motion of the molecules using mechanical systems, impose no great energy cost. Almost all the molecularproduct and any manufactured product could be vastly proved by orders of its magnitude. Also the, bottom-up, manufacturing approach i.e. making materials and products from the bottom-up, that is building them up from the atoms and molecules, would require less material and create less pollution.

Inexpensive: Molecular manufacturing will be inexpensive because it uses small amounts of material and energy and its costs of capital, land and labor will be low. Capital will be inexpensive because molecular manufacturing systems can be quickly used to build additional molecular manufacturing systems. Land and labor will add little costs because little of either will be needed. Setting aside costs external to manufacturing, the instruct cost of products made by molecular manufacturing would typically be little more than the cost of the required raw materials and energy. Molecules to bring them together in new patterns and molecular machines systems can move molecules more efficiently than systems that subject them to fluid drag.

Dream or reality: whether the concept of molecular assembling is a distant dream or not, only time can say. Development of the ability to design protein molecules will open a path to the fabrication of devices to complex atomic specifications, thus overcoming the obstacle facing conventional micro technology. This path will involve construction of molecular machinery able to position reactive groups to atomic precision. It could lead to great advances in computational devices and in the ability to manipulate biological materials. Biologists are a good audience to present molecular nanotechnology (MNT), as they are intimately familiar with analogues of the proposed MNT programmable self-replicating machinery tools, possible with atomic precision construction, Chemists, on the other hand, synthesis larger and more complicated molecules that perform more complex physical tasks. Chemists and biologists together are in a better position to produce ever more complicated self-assembling molecular structures.

1.2.1 Present status of nanotechnology

Nanotechnology is a new and emerging technology which has radically changed the fields of physical sciences and engineering as posted by CSIR in 2007[12]. Nanotechnology deals with the ability to observe manufacture and manipulate materials that have novel properties, at a scale generally between 1 and 100 nanometres (nm). At this minute scale, nano-particles are affected by quantum effects and other physical and chemical properties in ways that are not significant at larger scales, reported by Breggin and Pendergrass [13]. Using modern technology, therefore, it is possible to expose matter to extreme conditions (such as extreme cold or a vacuum) which can then change its properties. A metal might become an insulator or a substance might be able to convert light into electricity.

In 2004, EC [15] in his study reported that when particles become very small (in the nano range) there are more atoms on the surface than inside the particle, and atoms on the surface may have different properties than those inside the particle. Similar finding was by Berger [14] in 2006, he stated that, due to their size, nanoparticles have much larger surface areas on which chemical reactions can take place, in comparison to macro particles of the same material, when the mass of the two sets of particles is the same. In same line Luther [16] in 2004 said that a particle with a 10nm diameter has approximately 20% of its atoms forming the surface, whereas a particle of 1nm in diameter has about 90% of its atoms forming the surface. The physical, chemical and biological properties of nanomaterials may thus differ fundamentally from those of larger particles. It is for these reasons that nanotechnology applications are numerous and many benefits have been demonstrated. Nanomaterials are currently in use in consumer products such as sun-screens and tennis rackets, stain-free clothing and paints

1.2.1.1 Advantages of nano-sized additions

The Nanocomposites 2000 conference (In November 2000, was held in Brussels. Organised by Emap's 'European Plastics) has revealed clearly the property advantages that nano-material additives can provide in comparison to both their conventional filler counterparts and base polymer. Properties which have been shown to undergo substantial improvements include:

- Mechanical properties e.g. strength, modulus and dimensional stability
- Decreased permeability to gases, water and hydrocarbons
- Thermal stability and heat distortion temperature
- Flame retardancy and reduced smoke emissions
- Chemical resistance
- Surface appearance
- Electrical conductivity
- Optical clarity in comparison to conventionally filled polymers

1.2.1.2 Fields of nanotechnology

Describing about the application areas of nanotechnology, Nass et.al. [17] in 2004 stated that Nanotechnology, Nano science can be applied to absolutely any field. It brings about hybridization in all fields of science, to get the best out of it. Today nanotechnology consists of the following major fields:

Table 1.1 Overview on applications of nanomaterial based products in different areas

Automotive industry o Lightweight construction o Painting (fillers, base coat, clear coat) o Catalysts o Sensors	**Chemical industry** o Coating system based on nanocomposites o Impregnation of papers o Switchable adhesives o Magnetic fluids	**Engineering** o Wear protection for tools and machines (anti-blocking coatings, scratch resistant coatings on plastic parts) o Lubricant-free bearings
Electronic industry o Data memory (MRAM , GMR-HD) o Displays OLED,FED) o Laser diodes o Glass fibers o Optical switch o Filters (IR-blocking) o Conductive, antistatic coatings	**Construction** o Thermal insulation o Flame retardants o Surfacefunctoinalized building materials for wood, floors, stone, roof tiles o Facade coatings	**Medicine** o Drug delivery systems o Active agents o Contrast medium o Medical rapid tests o Prosthese and implants o Antimicrobial agents and coatings o Agents in cancer therapy
Textile/fabrics/non-woven o Surface-processed textiles o Smart clothes	**Energy** o Fuel cells o Solar cells o Batteries o Capacitors	**Cosmetics** o Sun protection o Lipstick o Skin creams o Tooth paste
Food and drinks o Package materials o Storage life sensors o Additives o Clarification of fruit juice	**Household** o Ceramic coatings for irons o Odors catalyst o Cleaner for glass, ceramic, floor,windows	**Sports/outdoor** o Skin wax o Antifogging of glasses / goggles o Antifouling coatings for ship/boats o Reinforced tennis rackets and balls

1.2.1.3 Approaches

i) Top-down approach

The techniques generally used are grinding, cutting, spraying and etching. The top-down approach to nanotechnology has found a first application in research in the field of Micro-Electro-Mechanical System (MEMS). In MEMS, systems are building integrate electronic & mechanical component on a very small scale. Textile production can also benefit from development in the MEMS field.

Today we see textile processing methods in which clusters of objects are manipulated. E.g. in spinning or non-woven formation there is little or no control of individual fibers. Using MEMS, which can sense the position (sensors) and control the motion or position (actuators) of each in individual fibers, could lead to better. Stronger yam or non-woven structures with controlled properties. In weaving, warp tension of individual warp yams could be monitored and controlled by MEMS, leading first to warp yam break detection and to a decrease in warp brakes. Further MEMS could assist in or possibly repair the warp yam breaks, which would lead to a decrease in interventions and a higher production yield.

ii) Bottom-up approach

Bottom -up approaches have the potential to allow fundamentally new assembly and manufacturing processes at the atomic and molecular level? The opportunities for exploitation will expand, rather than narrow as the basic principles of the operation and tools are developed.

Bottom-up processes are less well developed in terms of their application, are less well developed, require more fundamental scientific study, and have far less certain outcomes in commercial terms. Some key processes under debate may never be realized. At best, their exploitation cycle will be relatively long.

1.2.2 Chemistry of nano materials

Nano-chemistry makes its contribution as it is a science that investigates, designs, synthesizes, and fabricates matter that are in the nanometer-size regime through molecular control of systems.

Since the beginning, chemists (or alchemists) had been attempting to transform matter, but these attempts could not have progressed without a proper theory or model, at least in part, to help in the design of the method of transformation. The Greek Philosophers Leucippus and Democritus had proposed (450 B. C.) the idea that matter must be made of smaller building blocks, 'the atomos', a proposition which could have just been a rational extrapolation of the observation that the beach looks solid when viewed from afar, but is in fact granular on closer inspection. In 1985, Holton, et.al [18] explained different transformation of some of the known substances observed, based on the atomic theory developed by Dalton in his opus “A New System of Chemical Philosophy (1808)”.

Chemistry succeeded as a science because it was able to develop techniques for 'handling' atoms and molecules. The typical size of the atom ? Order of magnitude, it is about 1 Angstrom (Å) in diameter or 0.0000001 of a millimeter. Clearly, too small to touch or handle individually. The 'handling' is really a logical manipulation of the atomic model. By knowing the reactivities of the elements and compounds, chemists had a way of peering into the properties of the individual atoms or the molecules that they are made of.

Thus now, we have a clearer understanding of the chemical reactivities of atoms or molecules, are able to predict the molecular shape and electronic properties, or predict how they will interact with light, electricity, magnetism or with other atoms, assess their stabilities and reactivities, and all of these with fairly good accuracy. These molecular properties are, in turn, related to the observed property of bulk matter. Bulk matter here is made of at least 1016 atoms or molecules in an assemblage that has a size that can be manipulated and handled in glass vessels or crucibles typically found in a chemical laboratory; a typical lab specimen size being of micro-or milligrams, grams or even kilograms in quantity, which is readily weighed using a laboratory balance.

In explaining, an observed behavior of bulk matter in terms of the properties of the molecules that it is made of. For instance: this author overheard an auto-mechanic trying to explain why battery acid spills on polyester pants do not readily burn into holes—so he explained: “it is because the acid did not easily absorb into the polyester fabric, unlike in cotton.” A fine observation and a good explanation at that, but is still lacking of a molecular explanation. Chemists would prefer to explain the observation based on the molecular constitution of the fabric and what its properties are: “that polyester is made of molecules that are less polar than cotton, and are therefore less water-liking than cotton, among other things to be considered.” In this perspective, a chemist could therefore 'design' a molecule whose property will be of a particular wettability, in contrast to forming a blend of cotton and polyester. The point is, chemical intuition is synonymous to molecular level understanding, and this is routinely used to rationalize observed bulk properties of matter and in the design of molecules for desired bulk properties.

In terms of forming new substances, synthetic chemists act like molecular engineers—designing and fabricating molecular structures of desired physico-chemical and electronic properties. They come up with steps to build a complex molecular structure in an atom-by-atom or molecular fragment-to-molecular fragment approach.

Whereas before, bulk behavior was routinely measured, nowadays, the observation data on properties of matter are not only limited to bulk behavior but also include those of matter made up of only a cluster of atoms—in the hundreds, thousands, or just a few million atoms bonded together in assembled structures whose final dimensions are only in the tens or hundreds of Angstroms, in other words in the nanometer size regime. These structures—which we may refer to as nanostructures—are not like the molecules of old, but are materials yielding behavior unlike their bulk counterparts. And as more of them are cropping up these days, new phenomena are being observed, and in turn, there is more impetus to create new ones and innovates methodologies for making them into various morphologies or modes of molecular organization. The motivation is both fundamental and practical.

- ***Fundamental:*** to discover and understand new phenomena exhibited by matter at these newly accessible dimensions, and
- ***Practical:*** to form them into useful something ; as novel electronic devices, as efficient drug delivery systems, as ultrasensitive sensors, as ultra-lightweight structural materials, as highly efficient alternative energy sources, as environmentally benign materials, or as new materials for an entirely new application.

1.2.3 Types of nanomaterial

1.2.3.1 Ultrathin films (Two-Dimensional Nanostructures)

We can try to spread the atoms on a flat surface to form a single layer, and thus we would have constructed an ultrathin film (or coating, if you will) which is only 1 Å thick and can cover roughly a square area of 1000 Å 2 or 1 μm^2 when compacted. The covered area is not nanometer-sized, but the film thickness is sub-nanometer, and thus, this film is within the realm of nanotechnology. This may be done in the lab by vaporizing the 106 atoms and allow them to adhere onto a solid substrate. In the lab, this technique is called atomic layer deposition as reported by George, et.al in 1996 [19]. It is important to note, however, that to form a single layer of atoms on a flat substrate is not trivial, because it may not be stable. Atoms at a surface or interface experience an imbalance of forces. Below and beside them, they have other atoms that pull them inward due to bonding interactions, and above them it is just air or vacuum. Nature abhors this imbalance—it is unstable, and thus, ordinarily, the surface atoms would seek ways to minimize this imbalance, to lower the surface energy. Clustering is one way to minimize surface energy. In fact, the growth of our film formed by vapor deposition would most likely start with clustering of atoms (nucleation) and this growing cluster may begin to coalesce with the other clusters to eventually form a continuous film. In this case, our film may not be mono-atomic in thickness but would turn out to be several atomic layers thick. Nonetheless, it may still be nanometer-thin and so we have a nanostructured system. The preparation of ultrathin films poses experimental and theoretical challenges, and thus many scientists are busying themselves with these concerns.

Another way would be for us to disperse the atoms into a solvent to form a solution, and from there, allow the atoms to spontaneously organize onto a solid substrate. Obviously, gravity would not do it—because they are too small to be settling down; there are other forces in solution that will keep them dissolved. The formation of our thin film will happen if there is a strong preferential attraction of our atoms to the substrate. What we hope to do here is to spontaneously crystallize our atoms onto a surface or interface: a self-assembling technique. Self-assembly is a generic term for forming nanostructures from a disordered state. This is a major technique, actually, that is widely used because it offers a generally straightforward manner of building nanostructures, and is amenable to mass production of the nano-material for commercial purposes. This is a bottom-up approach to nano-synthesis, because the structure is built in a manner that is one atom-at-a-time. If self-assembly were not possible, a bottom-up approach is not going to be efficient, if one is to build atom-by-atom mechanically. This methodology is opposed to the top-down approach, wherein one first makes a bulk material, and then its size is decreased by mechanical or some other means until the material is divided or fabricated into the nanometer size range.

1.2.3.2. Nanoparticles (Zero-Dimensional Nanostructures)

If the 106 atoms that we have are all in one solid mass, and are closed-packed in a particle, it will occupy a volume of about 6000 nm3 with a width or diameter of only about 18 nm. A million atoms make a nano-particle! Many everyday-life particles that we encounter are already nanometer in dimensions, such as the micelles formed by soap molecules in water, smoke particulates, or clay particles. In fact, nano-particles were used hundreds of years ago as colorants in Chinese vases or pigments in the stained glass windows of cathedrals in Europe. There is much renewed interests in nanoparticles because chemists and other researchers are able to characterize their behavior at higher precision using the advanced tools that are now available. There are also various ways to synthesize and stabilize them, and new possible applications are discovered.

1.2.3.3 Nanowires (One-Dimensional Nanostructures)

Going back to our starting 1 million atoms, we know that to produce a one-dimensional structure, we will need to align the atoms unidirectionally to make elongated structures. Based on the length of the nanostructure, it could be a nanowire or a nanorod. Bonding the atoms to make a linear polymer chain is not new, but this is possible only with elements that are amenable to extensive covalent linkages, otherwise, the structure will be unstable. For semiconductor or metallic elements, nanowires are made with nanometer-sized radii, such that the cross-section of the wire consists of hundreds or thousands of atoms. They may be formed by controlling the growth process, usually along preferred directions of crystallization or using a template to align the process.

1.2.3.4 Supramolecular assemblies

What was discussed so far are nanostructures that can be formed based on the dimensionality of the material that is produced. However, nanotechnology or nanochemistry is not limited to these types, and more often than not, the nanostructured system or material is a composite of various types. Ultimately, nanotechnology will approach molecular-level control of the device or material architecture. What is uniquely nanotechnology today is that the design is molecular in approach to form materials that are supramolecular assemblies as quote by Schneider, et.al [20] in 2000 is much of what is happening in biological cells, for example, is a molecular machinery of sorts that is responsible for the spontaneous copying, transcription, and reproduction of the DNA and proteins, for example. And some researchers have also begun to look at nature to come up with biologically-inspired nanomaterials. One such example stated by Podsiadlo, et.al, in 2005 [21] is a nacre-like nanostructured composite formed by layer-by-layer assembly of polymers and clay materials that are nanometer-spaced —the resulting structure is brickwork in the nanometer scale. Apart from this Schevchengko, et.al [22] engaged in nanocrystal research in 2006 also discovered that nanoparticles can form superlattices, and a group of researchers has already begun forming various types based on binary nano-particle superlattices. In similar lines Krishnamoorthy, et.al in 2006[23] states that Polymers also form nanostructure assemblies such as those used in nano-patterning using block copolymers (or polymers with two parts of the chain that are different in chemical composition) in a self-assembly approach.

1.2.4 General properties of nanoparticles

Because of its small size, the number of surface atoms becomes significant. The smaller the radius of the particle, the bigger is the fraction of surface atoms. For a spherical particle, the surface area As =4πr^2, whereas the volume of the particle is V = (4/3) πr^3. Thus, the surface area-to-volume ratio is As/V = 3/r, and since the number of surface atoms is proportional to the area exposed, then this ratio is proportional to the fraction of surface atoms in the particle. The smallest closed-packed cluster of spherical atoms is a 13-atom cluster wherein one atom is surrounded by 12 surface atoms (its coordination number). Here, the surface-to-volume ratio of atoms is very large at 92.3% (or 12/13). A 100-particle cluster will have a surface-to-volume ratio of 68.0%; a thousand, 38.4 %; and a million, 4.4%. For a micron-sized particle composed of 1011 atoms, the surface-to-volume ratio is 0.10%. Indeed, the nanometer-sized cluster will have significant surface energy. Recall that our surface atoms experience an imbalance of forces around them creating a surface energy that seeks to be minimized. Therefore, the surface energy and surface curvature become dominant factors that affect the overall shape, stability, and property of the nano-particle. Generally, the particle will be stable at or above a critical radius wherein the effect of surface energy is compensated by the overall free energy of the entire particle. Any smaller size means the surface atoms will have to reconstruct, melt away, or seek other ways to minimize surface energy. For example, the melting point for gold crystals was shown to have a dramatic decrease with decreasing radius of the crystal, especially right around 3-4 nm radius as stated by Burda et.al in 2005 [24].

Semiconductor nano-particles are also sometimes referred to as quantum dots or 'synthetic atoms' because of quantum confinement effects. When a particle is energetically excited, an electron leaves a hole creating an electron-hole pair that is called an exciton. Because of the small size of the particle, the electron-hole pair may still be 'bound' to each other thus creating electronic energy levels that are modeled after the electron-proton pair of a hydrogen atom. This is theoretically and experimentally observable for cases when the size of the nanocrystal is less than the corresponding Bohr radius of the bulk crystal. For nanocrystals, electronic properties become size-dependent, because the electronic energy level structure is quantized or discrete as opposed to the electronic band structures exhibited by bulk crystals. Therefore, nanocrystals are tunable opto-electronic elements. This is dramatically exhibited by the varying colors of colloidal dispersion, due to the sharp absorption lines of the excitons in the visible region of light. In 2005 Burda et.al. [24], found another very interesting property in this size regime is the discreteness of electron conductivity, wherein the observed current-voltage characteristics produce a staircase-like pattern due to individual tunneling of single electrons. This is different from the continuous curve predicted by Ohm's Law. Measurement of this effect may be done by connecting an SPM probe tip (specifically STM) on top of a nano-particle adsorbed on a metal. This behavior which is also known as Coulomb blockade or 'Coulombic staircase' offers a possibility for single electron transistors that may be part of future computing devices.

In his study on metallic nano particals, Burda, et.al.[24] stated that metallic nano-particles exhibit strong surface plasmon absorption that gives them the characteristic deep red color, such as Faraday's colloidal gold dispersion. Surface plasmon resonance arises from the coherent motion of electrons in the conduction band of the metal, which 'resonates' with light. This is another 'tunable' property, because the absorption band can shift in wavelength depending on the size of the metallic nanoparticle. Because colloidal gold is easily synthesized, and they are amenable to self-assembly interactions with molecules with thiol groups, they have been used a lot in various functionalized forms.

Of course, atoms can also bond with other atoms covalently to make molecules, and in this way, the bonding requirement by each atom is satisfied, that is, there is no dangling bond left at the surface. Nonmetallic elements generally do these to form a molecular species—small molecules or very large ones (polymers) which have extensive covalent bonding. Polymers are large molecules wherein each atom is covalently bonded to each other in a particular way, such as to form a very long chain that can fold into a random coil. The radius of the coil can go as high as several microns. Polymers are not new, but they also figure in a lot in nanochemistry because they make interesting nanostructures, may be used as agents to stabilize the system, as templates for nanostructure fabrication, and many other uses.

1.3 SYNTHESIS OF NANO-STRUCTURED MATERIALS

There are generally two approaches to synthesize nanostructure materials: top-down and bottom-up. Top-down methods reduce macroscopic particles to the nano scale size. Due to the lack of precise control over the experimental conditions, this route is usually not very well suited to the preparation of uniformly shaped particles; in addition, very small sizes are especially difficult to realize. On the contrary, bottom-up procedures are much better for generating uniform particles, of distinct size, shape, and structure. Bottom-up methods start with atoms that aggregate in solution or even in the gas phase to form particles of definite size, if appropriate experimental conditions are applied. However this bottom-up method always face the stability issue more than the top-down method because, in most of the cases, the particles are dispersed in aqueous suspension, the as-synthesized particles possess high mobility, and thus have better chance to collide with each other and form clusters or aggregations.

The synthesis of nano-structured materials from atomic or molecular sources depends on the control of a variety of nano-scale attributes desired in the final product. In general, the following four methods have been used to make nano-structured materials:

1 The first technique involves the production of isolated, ultrafine crystallites having uncontaminated free surfaces followed by a consolidation process either at room or at elevated temperature.
2 Chemical vapor deposition (CVD), physical vapor deposition (PVD), and some electrochemical methods have been used to deposit atoms or molecules of materials on suitable substrate.
3 By introducing defects in a formerly perfect crystal such as dislocations or grain boundaries, new classes of nano-structured materials can be synthesized. Subjecting the materials to high energy by either ball milling extrusion, shear, or high-energy irradiation may bring about such deformations.
4 The final approach used to make nano-structured materials is based on crystallization or precipitation from unstable states of condensed matter such as crystallization from glasses or precipitation from supersaturated solid or liquid solutions.

Although there are the general methodologies employed in the synthesis of nano-structured materials, several variants of these procedures have been developed to generate compounds or alloys with specific compositions and properties and also for optimized production. There are basically two broad areas of synthetic techniques for nano-structured materials, namely, physical methods and chemical methods.

1.3.1 Physical Methods

Several different physical methods are currently in use for the synthesis of commercial production of nanostructures materials. The first technique, and the most widely used, involves the synthesis of single-phase metals and ceramic oxides by the inert-gas evaporation technique, in this technique the generation of atom clusters by gas phase condensation proceeds by evaporating a precursor material, either a single metal or a compound, in a gas maintained at a low pressure. The evaporated atoms or molecules undergo a homogeneous condensation to form atom clusters via collisions with gas atoms or molecules in the vicinity of a cold-powder collection surface. The clusters once formed must be removed from the region of deposition to prevent further aggregation and coalescence of the clusters. These clusters are then removed from the gas condensation chamber either by natural convection of the gas or by forced gas flow. The advantage of this method lies in the ease of control on the particle size by changing the removal speed, and as the particles are located specifically in the precursor sites, they are not tending to aggregate easily. However, contaminations can be introduced during the load and unload of the materials. This approach is preferable when large particle quantity is needed, and the particle size is not required to be highly uniform.

Sputtering is another technique used to produce nano-structured materials' clusters as well as a variety of thin films. This method involves the ejection of atoms or clusters of designated materials by subjecting them to an accelerated and highly focused beam of inert gas such as argon or helium. The mechanism is somehow similar to the method above. The drawback is also the control of the uniformity of the particle size.

The third physical method involves generation of nano-structured materials via severe mechanical deformation. In this method, nano-structured materials are produced not by cluster assembly, but rather by structural degradation of coarser-grained structures induced by the application of high mechanical energy. The nanometer-sized grains nucleate within the shear bands of the deformed materials converting a coarse-grained structure to an ultrafine powder. The heavy deformation of the coarse materials is affected by means of a high-energy ball mill or a high-energy shear process. Although this method is very useful in generating commercial quantities of the material, it suffers from the disadvantage that contamination problems result from the sources of the grinding media. The synthesized particles also tend to aggregate because they are directly contact each other without any effective separation mechanism. Another concern about this approach is that the particles cannot be made as really small size nano-particles; the smallest size people get today is around 50 nm.

1.3.2 Chemical Methods

Chemistry has played a major role in developing new materials with novel and technologically important properties. The advantage of chemical synthesis is its versatility in designing and synthesizing new materials that can be refined into the final product.The primary advantage that chemical processes offer over other methods lies in good chemical homogeneity, as chemical synthesis offers mixing at the molecular level. Molecular chemistry can be designed to prepare new materials by understanding how material is assembled on an atomic and molecular level and the consequent effects on the desired material macroscopic properties. Basic understanding of the principles of crystal chemistry, thermodynamics, phase equilibrium, and reaction kinetics is important to take advantage of the many benefits that chemical processing has to offer.

Solution chemistry (wet chemistry) is used sometimes to prepare the precursor, which is subsequently converted to the nano-phase particles by nonliquid phase chemical reactions. Precipitation of solid from solution is a common technique for the synthesis of fine particles. The general procedure involves reactions in aqueous or nonaqueous solutions containing the soluble or suspended salts. Once the solution becomes supersaturated with the product, the precipitate is formed by either homogeneous or heterogeneous nucleation. After the nuclei are formed, their growth usually proceeds by diffusion. The growth rate of the nuclei after formation is very important in determining the formation of monodispersed particles. For instance, to prepare unagglomerated particles with a very narrow size distribution, all the nuclei must form at nearly the same time and subsequent growth must occur without further nucleation or agglomeration of the particles. In this regard, the selection of various chemicals, the determination of solution pH and chemical concentration as well as the reaction temperature are of extremely important to obtain fine particles.

In general, the particle size distribution, the physical properties such as crystallinity and crystal structure, and the degree of dispersion can be affected by reaction kinetics. In addition, the concentration of reactants, the reaction temperature, the pH, and the order of addition of reactants to the solution are also important. Even though a multielement material is often made by co precipitation of batched ions, it is not always easy to co precipitate all the desired ions simultaneously because different species may only precipitate at different pH. Thus, control of chemical homogeneity and stoichiometry requires a very careful control of reaction conditions.

However, there are certain difficulties in chemical processing. In some preparations, the chemicals are complex and hazardous. Contamination can also result from generation of the byproducts or side reactions in the chemical process. This should be minimized or avoided to obtain desirable properties in the final products. Agglomeration can also be a major cause of concern at any stage in the synthesis process and it can dramatically alter the properties of the materials. As an example, agglomeration frequently makes it more difficult to consolidate nano-particles to a fully dense compact. Finally, although many chemical processes are scalable for economical production, it is not always straightforward for all systems.

1.3.3 General physico-chemical methods for preparation of nano-sized material

There are several methods for creating nano-particles, including both attrition and pyrolysis. In attrition, macro or micro scale particles are ground in a ball mill, a planetary ball mill, or other size reducing mechanism. The resulting particles are air classified to recover nano-particles. In pyrolysis, a vaporous precursor (liquid or gas) is forced through an orifice at high pressure and burned. The resulting solid (a version of soot) is air classified to recover oxide particles from by-product gases.

There are several physico-chemical methods for preparation of nano-sized material mentioned as below

1. Vapour phase reaction,
2. Chemical vapour deposition,
3. Inert gas condensation,
4. Laser ablation,
5. Plasma spraying,
6. Spray conversion,
7. Sputtering,
8. Liquid-phase reaction methods,
9. Micro emulsion approach,
10. Sol-gel synthesis

1) Vapor phase or gas phase reaction

Most synthesis methods of nano-particles in vapor or gas phase are based on homogeneous nucleation in the vapor or gas phase and subsequent condensation and coagulation. Once nucleation occurs, remaining supersaturation can be relieved by condensation or reaction of vapor or gas-phase molecules on the resulting particles, and particle growth will occur rather than further nucleation. Therefore, to prepare small particles, one wants to create a high degree of supersaturation, thereby inducing a high nucleation density, and then immediately quench the system, either by removing the source of supersaturation or slowing the kinetics, so that the particles do not grow. In most cases, this happens rapidly (milliseconds to seconds) in a relatively uncontrolled fashion, and lends itself to continuous or quasi-continuous operation. This contrasts with many colloidal syntheses of nano-particles that are carried out in discrete batches under well-controlled conditions with batch times of hours to days. Finally, initiating homogeneous nucleation synthesis of nano-particles in the gas phase inside aerosol droplets can result in many nano-sized nuclei in the droplet, which upon drying will yield nano-particles.

The vapor may be generated by thermal, laser, electron beam, etc. evaporation. Different sources of energy can be used to decompose the precursor such as microwave plasma, laser pyrolysis, laser photolysis, combustion flame, etc. The study of Garry, et.al. in 2006 [25] revels that the size of the nano-particle is determined by the particle residence time, temperature of the vapor, precursor composition, and pressure. Low-temperature flames can also be used to supply the energy to decompose the precursors. Flame synthesis is most common for the production of oxides.

2) Chemical vapor deposition

In this approach, vapor phase precursors are brought into a hot-wall reactor under conditions that favor nucleation of particles in the vapor phase rather than deposition of a filmon the wall. It is called chemical vapor synthesis or chemical vapor condensation in analogy to the chemical vapor deposition (CVD) processes used to deposit thin solid films on surfaces. This method has tremendous flexibility in producing a wide range of materials and can take advantage of the huge database of precursor chemistries that have been developed for CVD processes. The precursors can be solid, liquid or gas at ambient conditions, but are delivered to the reactor as a vapor (from a bubbler or sublimation source, as necessary).

The catalytic vapor phase deposition of carbon was first reported in 1959, but it was not until 1993 that carbon nanotubes were formed by this process. In 2007, researchers at the University of Cincinnati (UC) developed a process to grow aligned carbon nanotube arrays of 18 mm length on a First Nano ET3000 carbon nanotube growth system. During CVD, a substrate is prepared with a layer of metal catalyst particles, most commonly nickel, cobalt, iron, or a combination. The metal nano-particles can also be produced by other ways, including reduction of oxides or oxides solid solutions. The diameters of the nanotubes that are to be grown are related to the size of the metal particles. This can be controlled by patterned (or masked) deposition of the metal, annealing, or by plasma etching of a metal layer.

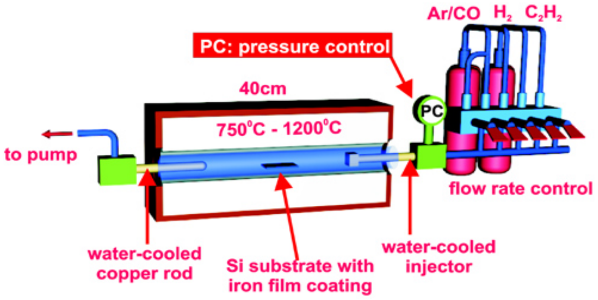

Figure 1.1 Thermal-CVD experimental set-up

There are many good examples of the application of this method in the recent literature. Ostraat et al. 2001, [26] have demonstrated a two-stage reactor for producing oxide-coated silicon nano-particles that have been incorporated into high-density nonvolatile memory devices. By reducing the silane precursor composition to as low as 10 parts per billion, they were able to produce non-agglomerated single-crystalline spherical particles with mean diameter below 8 nm. This is one of relatively few examples of a working microelectronic device in which vapor-phase synthesized nano-particles perform an active function. In other recent examples of this approach, Magnusson et.al. [27] produced tungsten nano-particles by decomposition of tungsten hexacarbonyl and Nasibulin et.al. [28] produced copper and copper oxide nano-particles from copper acetylacetonate. Another key feature of chemical vapor synthesis is that it allows formation of doped or multi-component nano-particles by use of multiple precursors. Schmechel et.al., [29] prepared nanocrystalline europium doped yttria (Y O: Eu3q) from organometallic yttrium and europium precursors. Senter et.al. [30] incorporated erbium into silicon nano-particles using disilane and an organometallic erbium compound as precursors. Srdic´ et.al. [31] prepared zirconia particles doped with alumina. It is also possible to make composite nano-particles where one material is encapsulated within another. A particularly promising approach to this is the sodium metalymetal halide chemistry used by Ehrman et.al. [32]. In this approach, a halide, such as SiCl, is reacted with sodiumvapor in a heated furnace to produce NaCl-encapsulated particles. For example $SiCl_4$ reacts with Na to produce NaCl-encapsulated Si particles. The salt-encapsulation can potentially be used to prevent agglomeration of the particles, and the salt can then be washed away in a post-processing step.

3) Inert gas condensation

Inert Gas Condensation (IGC) is the most versatile process in use today for synthesizing experimental quantities of nano-structured powders as stated by Kear and Strutt in 1995 and Oda et al. in1992 [33-34]. A feature of the process is its ability to generate non-agglomerated nano-powders, which are sinterable at relatively low temperatures. In IGC processing, an evaporative source is used to generate the powder particles, which are convectively transported to and collected on a cold substrate.

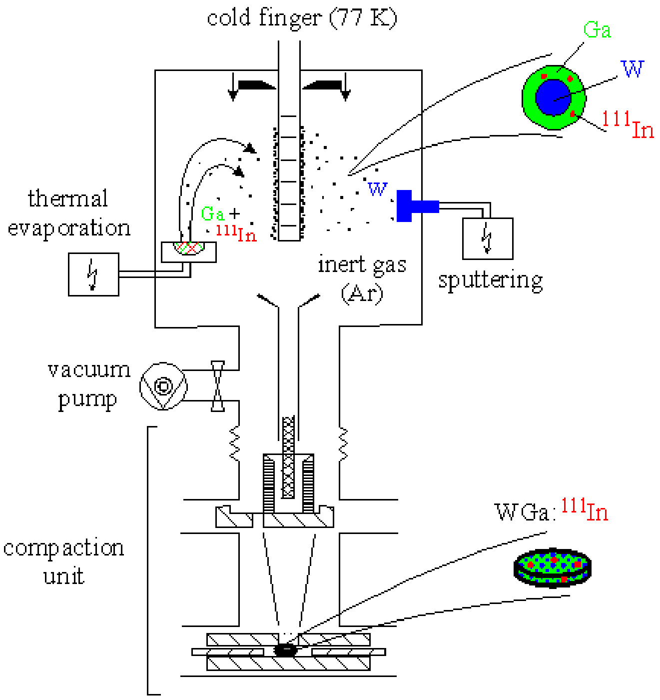

Figure 1.2 Inert Gas Condensation (IGC) experimental set-up

The nano-particles develop in a thermalizing zone just above the evaporative source, due to interactions between the hot vapor species and the much colder inert gas atoms (typically 1-20 mbar pressure) in the chamber. Ceramic powders are usually produced by a two-stage process: evaporation of a metal source, or preferably a metal suboxide of high vapor pressure, followed by slow oxidation to develop the desired n-ceramic powder particles.

4) Laser ablation

LASiS is the acronymous for Laser Ablation Synthesis in Solution and it is a commonly used method for obtaining colloidal solution of nano-particles in a variety of solvents. In the LASiS method, nano-particles are produced during the condensation of a plasma plume formed by the laser ablation of a bulk metal plate dipped in a liquid solution. LASiS is usually considered a top–down physical approach. In the past years, laser ablation synthesis in solution (LASiS) emerged as a reliable alternative to traditional chemical reduction methods for obtaining noble metal nano-particles (NMNp). LASiS is a ‘‘green’’ technique for the synthesis of stable NMNp in water or in organic solvents, which does not need stabilizing molecules or other chemicals. The so obtained NMNp are highly available for further fictionalization or can be used wherever unprotected metal nano-particles are desired. Surface fictionalization of NMNp can be monitored in real time by UV-visible spectroscopy of the plasmon resonance. However LASiS has some limitations in the size control of NMNp, which can be overcome by ‘‘chemical free’’laser treatments of NMNp. In the laser ablation process, a pulsed laser vaporizes a graphite target in a high-temperature reactor while an inert gas is bled into the chamber. Nanotubes develop on the cooler surfaces of the reactor as the vaporized carbon condenses. A water-cooled surface may be included in the system to collect the nanotubes. The laser ablation method yields around 70% and produces primarily single-walled carbon nanotubes with a controllable diameter determined by the reaction temperature.

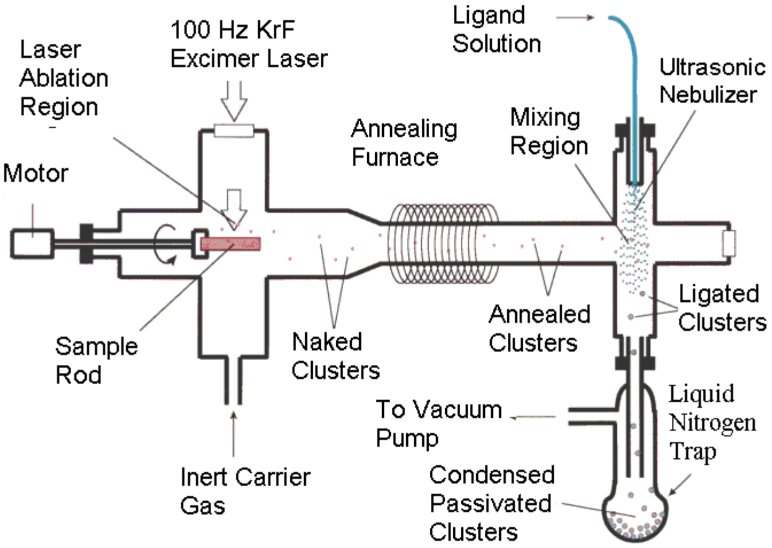

Figure 1.3 Working principle of Laser Ablation Synthesis system

Marine et. al. [35] presented a recent analysis of this method, in which they also reviewed its development. Nakata et.al. [36] used a combination of laser-spectroscopic imaging techniques to image the plume of Si atoms and clusters formed during synthesis of Si nano-particles. They investigated the dependence of the particle formation dynamics on the background gas, and found that it was substantial. Some other recent examples include the preparation of magnetic oxide nano-particles by Shinde et al. [37] titania nano-particles by Harano et al. [38] and hydrogenated-silicon nano-particles by Makimura et.al. [39]. However, it is more expensive than either arc discharge or chemical vapor deposition.

5) Plasma-enhanced chemical vapor deposition

PECVD is a process used to deposit thin films from a gas state (vapor) to a solid state on a substrate. Chemical reactions are involved in the process, which occur after creation of a plasma of the reacting gases. The plasma is generally created by RF (AC) frequency or DC discharge between two electrodes, the space between which is filled with the reacting gases. The plasma-enhanced chemical vapor deposition is widely used to produce thin films. The PECVD is the family of deposition processes, which are broadly defined as chemical vapor deposition. In conventional CVD the precursor gases are thermally decomposed by the temperature of 500-1000°C. However in the PECVD processes, they proceed at temperature that is much lower because the energetic electron gas of a plasma is capable of highly dissociating the feed gas. Even when the feed gas and the substrates that is near room temperature, the PECVD is useful for deposition on sensitive substrates that are damaged by high temperature or, in the case of semiconductor production, where dopant redistribution is an important concern. So, the rise of temperature is not desirable for such a process. The concurrent ‘ion bombardment of the PECVD film by the plasma may also modify the properties of film during the deposition process. There are two classes of PECVD process, which are commonly practiced.

i. Direct method
ii. Remote method

In the ‘direct method ‘PECVD, the precursor gases, inert gas dilutants, and the substrates are directly in the region. The formation of reactive species and deposition precursors occurs in the active plasma region by many possible ‘reaction pathways’. These pathways, include electron impact dissociation, dissociative collision with electronically excited atoms, and the reaction involving the products of recombination as well as the by product of the film formation. One of the greatest successes of PECVD is the deposition of polycrystalline films of diamond and cubic boron nitride.

Many methods have been used for the deposition of hydrocarbon precursors, including dc hot filament, oxygen-acetylene flame and the microwave direct and remote diamond deposition films.The substrate temperature for the production of PECVD diamond fall in the range of 400-900°C with the lower temperature of deposition requiring the addition of oxygen. The silicone dioxide and silicone nitride films have long been mainstay insulators in the electronics industry. The PECVD of SiO_2 at 300°C was accomplished introducing oxygen radicals from a weak, inductively coupled, plasma source in a tube furnace. SiH_4 dilute in N_2 was introduced down stream from the discharge at the inlet of the furnace.

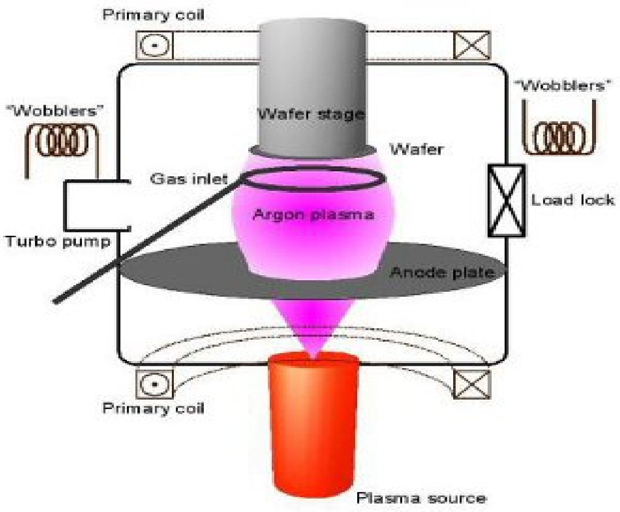

Figure 1.4 Working principle of Low-energy plasma-enhanced chemical vapour deposition [40].

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6) Spray pyrolysis (sp) methods

In addition to the methods listed above, spray pyrolysis (SP) methods are also promising for nano-particle preparation, in which the precipitation, thermolysis (i.e. calcinations) and sintering stages of powder synthesis can be integrated into a single continuous process. To prepare fine particles by SP, a starting solution is usually prepared by dissolving the metal salts of the product in the solvent.

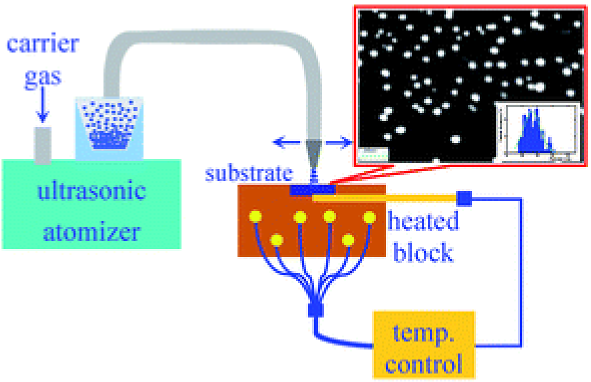


Figure 1.5 Direct spray pyrolysis process

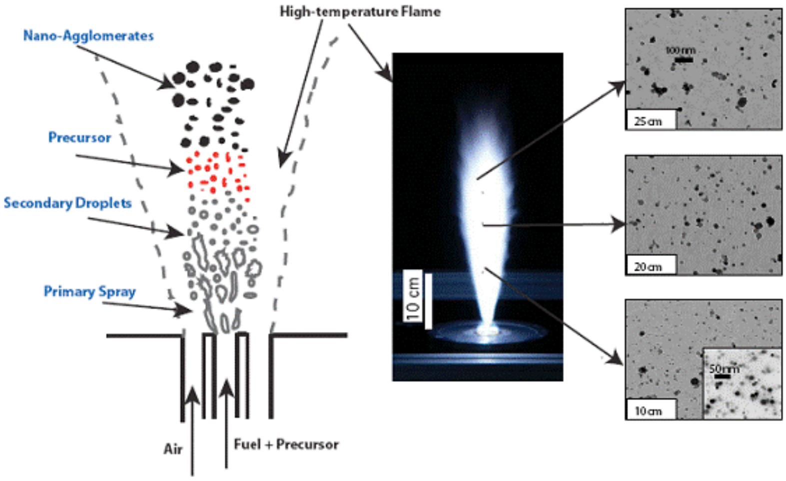


Figure 1.6 Flame-assisted spray pyrolysis process

The droplets are atomized from the starting solution with an atomizer, and the droplets are then placed in a furnace. A variety of activities may occur inside the furnace during formation of the final product including evaporation of the solvent, diffusion of solutes, drying, precipitation reaction between the precursor and surrounding gas, pyrolysis and sintering. Generally, a one droplet- to-one-product particle (ODOP) conversion is considered the typical particle formation mechanism in conventional spray pyrolysis (CSP) [41-42].

7) Sputtering Physical Vapor Deposition vacuum process

Sputtering is a Physical Vapor Deposition vacuum process used to deposit very thin films onto a substrate for a wide variety of commercial and scientific purposes. Sputtering occurs when an ionized gas molecule is used to displace atoms of a specific material. These atoms then bond at the atomic level to a substrate and create a thin film. Several types of sputtering processes exist, including: ion beam, diode, and magnetron sputtering. Angstrom Sciences specializes in Magnetron Sputtering Technology 43.

In a magnetron sputtering application, the high voltage is delivered across a low pressure gas (usually argon) in order to create high-energy plasma. This plasma emits a colorful halo of light often referred to as a "glow discharge" and consists of electrons (yellow) and gas ions (red). These energized plasma ions strike a target composed of the desired coating material. The force causes atoms to eject from the target material and bond with those of the substrate. Because sputtering takes place in a high-energy environment, it creates a virtually unbreakable bond between the film and its substrate at the atomic level, creating one of the thinnest, most uniform and most cost-effective films possible. So, given the right tools, researchers and engineers in a variety of industries can use this technique to create a whole new generation of smaller, lighter, more durable products.

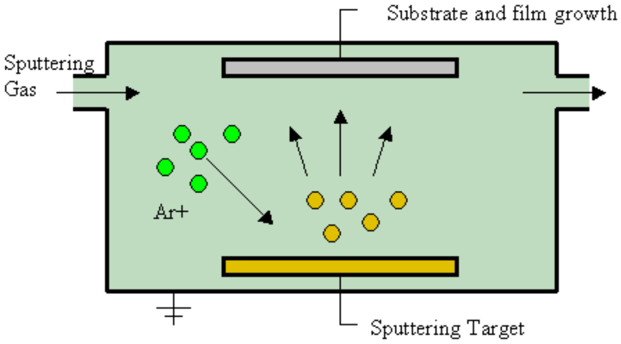


Figure 1.7 Sputtering; Physical Vapor Deposition vacuum process

8) Liquid-phase reaction methods

Many techniques for the preparation of nano-particles have been developed via the liquid phase route. It is important to develop a synthesis method in which particles have controlled characteristics including size, size distribution, morphology, agglomeration and composition. To be industrially relevant, the process needs to be low-cost and involve continuous operation and a high production rate. Silica (SiO_2) nano-particles, phosphors luminescent semiconductors (e.g., ZnO, CdSe) and metallic materials (e.g., Au, FePt) were fabricated using this technique. This novel techniques for preparing nano-particles were developed, especially those focusing on controlling the agglomeration. FePt nano-particles have been synthesized from a process involving the mixing of two precursor liquids, ferric acetyl ferric acetyl acetonate, Fe (acac) 3, and platinum acetyl acetonate, Pt (acac) 2, in a polyol solution of sodium hydroxide at high temperatures. The particle size was monodispersed without agglomeration. An ultrasonic field generator also was applied for preparation of FePt and Au nanoparticles [44].

9) Micro emulsion approach

The microemulsion approach is a sol–gel approach. This system has added surfactant in the nano-particle sol system. The surfactant forms an in situ cover on the nano-particles, which forms a so-called nano-particle core–shell colloid wisp. The inner core consists of nano-particles and the shell layer of surfactants. The microemulsion approach is excellent for the preparation of particles of small diameter, narrow size distribution and large specific surface area. The method requires that a properly matched microemulsion should be designed, and that suitable deposition system and economical post treatment be provided. Its composition should include nano-material precursors (organic reagents, e.g., metal alcoholic compound), surfactants and their matching additives. The greater the solubility capacity of the microemulsion for the organic reagents, the better the microemulsion is for obtaining a high yield rate of nano-particles. After the microemulsion system is prepared, measures should be taken to control the preparation conditions of nano-particles. These measures control the relative ratio of water/surfactant and pH value of the system in order to control the particle size. The nano-particles obtained from the microemulsion approach have core–shell structures, which have a direct effect on their subsequent applications.

Microemulsions are isotropic, thermodynamically stable dispersion of oil, water, surfactant and often cosurfactant. Microemulsion can be characterized as oil-in-water (O/W), water-in-oil (W/O) and bicontinuous system. Water-in-oil microemulsions are composed of nanometer-sized water droplets that are dispersed in a continuous oil medium and stabilized by surfactant molecules. These droplets can serve as nanoreactors for producing nano-particles as seen in figure 1.8 [45].

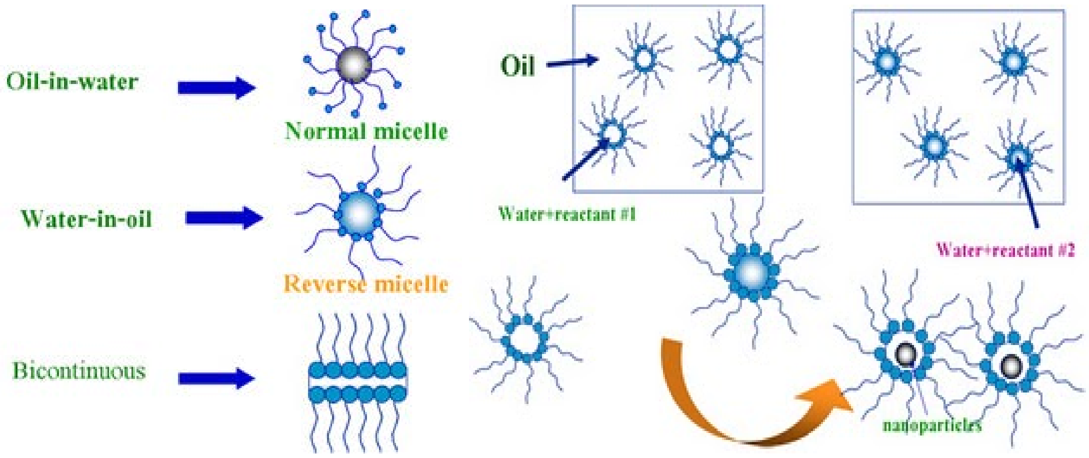


Figure 1.8 Synthesis of nanoparticle by micro emulsion technique

10) Sol gel synthesis method

The sol-gel process is a wet-chemical technique (also known as chemical solution deposition) widely used recently in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials (typically a metal oxide) starting from a chemical solution (sol, short for solution) which acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers. Typical precursors are metal alkoxides and metal chlorides, which undergo hydrolysis and polycondensation reactions to form either a network "elastic solid" or a colloidal suspension (or dispersion) – a system composed of discrete (often amorphous) submicrometer particles dispersed to various degrees in a host fluid. Formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution. Thus, the sol evolves towards the formation of a gel-like diphasic system containing both a liquid phase and solid phase whose morphologies range from discrete particles to continuous polymer networks.

In the case of the colloid, the volume fraction of particles (or particle density) may be so low that a significant amount of fluid may need to be removed initially for the gel-like properties to be recognized. This can be accomplished in any number of ways. The simplest method is to allow time for sedimentation to occur, and then pour off the remaining liquid. Centrifugation can also be used to accelerate the process of phase separation. Removal of the remaining liquid (solvent) phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification. The rate at which the solvent can be removed is ultimately determined by the distribution of porosity in the gel. The ultimate microstructure of the final component will clearly be strongly influenced by changes implemented during this phase of processing. Afterwards, a thermal treatment, or firing process, is often necessary in order to favor further polycondensation and enhance mechanical properties and structural stability via final sintering, densification and grain growth. One of the distinct advantages of using this methodology as opposed to the more traditional processing techniques is that densification is often achieved at a much lower temperature.

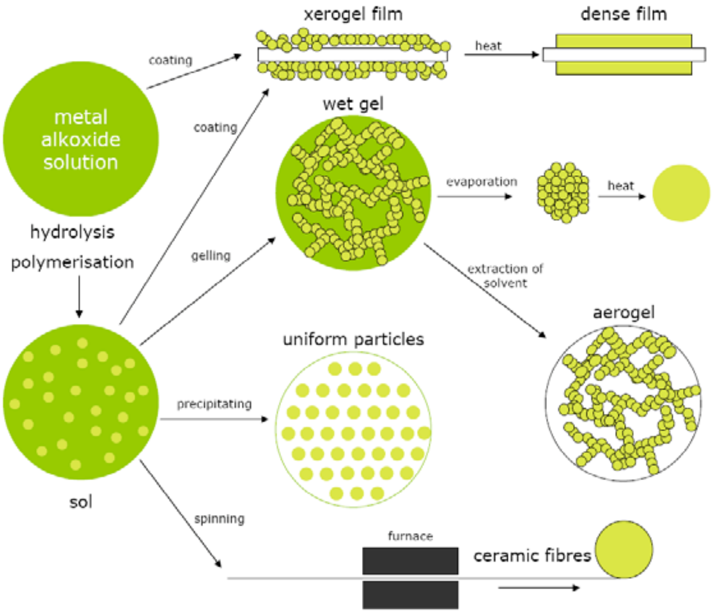


Figure 1.9 The sol gel principle [46]

The precursor sol can be either deposited on a substrate to form a film (e.g. by dip-coating or spin-coating), cast into a suitable container with the desired shape (e.g. to obtain a monolithic ceramics, glasses, fibers, membranes, aerogels), or used to synthesize powders (e.g. microspheres, nanospheres). The sol-gel approach is a cheap and low-temperature technique that allows for the fine control of the product's chemical composition. Even small quantities of dopants, such as organic dyes and rare earth metals, can be introduced in the sol and end up uniformly dispersed in the final product. It can be used in ceramics processing and manufacturing as an investment casting material, or as a means of producing very thin films of metal oxides for various purposes. Sol-gel derived materials have diverse applications in optics, electronics, energy, space, (bio) sensors, medicine (e.g. controlled drug release) and separation (e.g. chromatography) technology.

The sol-gel technique presents many processing merits for several material production methods, mainly owing to facility, versatility, purity, homogeneity and modifications of material properties by changing synthesis parameters The mean pore size, the interconnectivity and the pore size distributions can be controlled by changing the molar ratio water/precursor, type of catalyst or precursor, temperatures of gelation, drying, and stabilization. Moreover, the sol-gel technique is in-expensive and the silica xerogels produced are non-toxic materials.

1.3.4 Stabilization of Nanoparticles

In one of the studies by Wiese & Healy in 1970 and Miller & Zukoshi [47-48] in 1948 stated that, fine particles, particularly nanoscale particles, since they have large surface areas, often agglomerate to form either clusters or larger particles to minimize the total surface or interfacial energy of the system. When the particles are strongly stuck together, these hard agglomerates are called aggregates. Agglomeration of fine particles can occur at the synthesis stage, during drying and subsequent processing of the particles. Thus, it is very important to stabilize the particles against agglomeration at each step of particle production and powder processing.

Van der Waals [49] in 1873 stated that Agglomeration of fine particles is caused by the attractive van der Waals force and/or the driving force that tends to minimize the total surface energy of the system. So, repulsive interparticle forces are required to prevent the agglomeration of these particles. Hunter in 1989, Israelachvili in 1992 and Russel, et.al. [50-52] in 1990 talks about Two commonly methods used, namely, electrostatic and steric stabilization.

The main reasons for the stabilization of nano-particles are:

1) To prevent the uncontrollable growth of particles, but also
2) To prevent particle aggregation;
3) To control the particles growth rate;
4) To control particle size, and finally
5) To allow particle solubility in various solvents.

Generally there are two methods available for the stabilization of nano-particles;

a) By placing them in an inert environment;
    i.e. an inorganic matrix or polymer
b) By adding surface protecting reagents ;
    i.e. Organic ligands or Inorganic capping materials

a) By placing them in an inert environment

In the first technique of stabilization also known as Solid Phase Incorporated Reagents (SPHINER) technique, the nano-particles after reduction with aqueous solution, the particles are well separated from each other and stabilized inside the polymeric matrix, which prevents them from aggregation.

The mechanism of nano-particles stabilization with polymers can be explained by using the following two approaches:

1) Substantial increase of viscosity of the immobilizing media (the polymer matrix).

As follows from the Smoluchowsky equation, the rate constant of particle coagulation, kc, is inversely proportional to the viscosity of the media, i.e;

$$k_c = \frac{4kT}{\eta}$$

______________________ (1)

Here k stands for the Boltzman constant, and T is the temperature. A similar conclusion follows from the Stokes-Einstein equation, which permits to determine the diffusion coefficient of a spherical particle of radius r in a viscous medium stated by Cole, et, al. in 1997 [53].

$$D = \frac{kT}{6\pi\eta r}$$

_______________________ (2)

The mobility of Au nanoparticles in poly (t-butyl acrylate)/gold composite decreases by 2 or 3 orders of magnitude compared with that predicted by Stokes-Einstein equation. The authors ascribe this discrepancy to strong bridging interactions between Au-MNPs and the chain segments of the stabilizing polymeric matrix. As a result, the mobility of nanoparticles inside the polymer substantially decreases and the matrix, in turn, appears to be a somewhat “crosslinked” so that effective viscosity of the polymer increases by a factor of ~ 4 as stated by Cole, et,al. in 1999 [54].

2) Substantial decrease of the energy of particle-particle interaction in PSMNP systems (e.g., in polymer- nanoparticles composites) versus non-stabilized nanoparticles dispersions. The potential energy of attraction (Ur) between two spherical particles of radius r can be approximately described by the following simplified expression: where A is the effective Hamaker constant having the dimensions of energy, and lo is the minimum distance between particle surfaces. The value of the Hamaker constant A is known to be close to kT for polymer particles, while for the metal dispersions it is far higher as reported by Visser in 1972 [55] and Pomogailo in 1997 [56].

b) By adding surface protecting reagents;

The stabilizing agent can be either some ligands, capping agents and passivating agents or surfactants and polymers.

i) Electrostatic Stabilization

This method provides the dispersion by electrostatic repulsion. Most substances acquire surface electrical charges when brought in contact with a polar medium, resulting from one or more of the followings:

- Preferential dissolution and salvation of surface species followed by dissociation of some of these species.

- Lattice imperfection on solid surfaces.
- Adsorption of ions or impurities at the solid-liquid interface.

As the surface electrical charges are formed, an unequal charge distribution always exists between a particle surface and the solvent, which depicted in Figure 1.11.

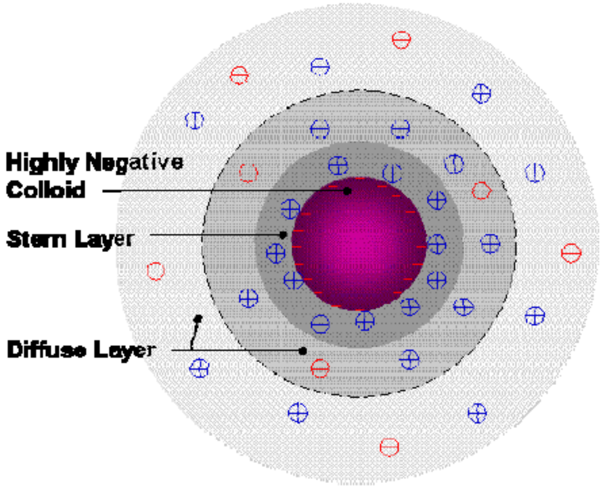


Figure 1.10 Distribution of electrical potential in the double layer region surrounding a charged particle showing the effective position of zeta potential

Gouy in 1910 and Chapman in 1913 [57-58] in their study found that, the surface charge influences the spatial distribution of ions or molecules in the surrounding solution, attracting ions of opposite charge but repelling ions of similar charge from the surface. Along with the thermal motion, this leads to the formation of the diffused electrical double layer, which consists of the charged surface, neutralizing counter-ions, and, farther from the surface, co-ions distributed in a diffused manner. The layer of counter-ions is known as Stern layer as found by Stern in 1924 [59], and the diffused layer can be visualized as a charged atmosphere surrounding the colloid.

The charge density at any distance from the surface is equal to the difference in concentration of positive and negative ions at that point. Charge density is greatest near the colloid and gradually diminished toward zero as the concentration of positive and negative ions equal each other. The thickness of this double layer depends upon the type and concentration of ions in solution.

The magnitude of the surface potential is related to the surface charge and the thickness of the double layer. As we leave the surface, the potential drops off roughly linearly in the Stern layer and then exponentially through the diffuse layer, approaching zero at the imaginary boundary of the double layer, as depicted in Figure 1.12. The potential measured at the interface of Stern layer and the diffuse layer is defined as zeta potential. The potential curve is useful because it indicates the strength of the electrical force between particles and the distance at which this force comes into play.

A charged particle will move with a fixed velocity in a voltage field. This phenomenon is called electrophoresis. The particle's mobility is related to the dielectric constant and viscosity of the suspending liquid and to the electrical potential at the boundary between the moving particle and the liquid. This boundary is called the slip plane and is usually defined as the point where the Stern layer and the diffuse layer meet. The Stern layer is considered to be rigidly attached to the colloid, while the diffuse layer is not. As a result, the electrical potential at this junction is related to the mobility of the particle and is called the zeta potential. Although zeta potential is an intermediate value, it is sometimes considered to be more significant than surface potential as far as electrostatic repulsion is concerned.

Therefore, electrostatic stabilization of dispersion occurs when the electrostatic repulsive force overcomes the attractive van der Waals forces between the particles. The stabilization method is very sensitive to the electrolyte concentration since a change in the concentration may destroy the electric double layer, which results in particle agglomeration.

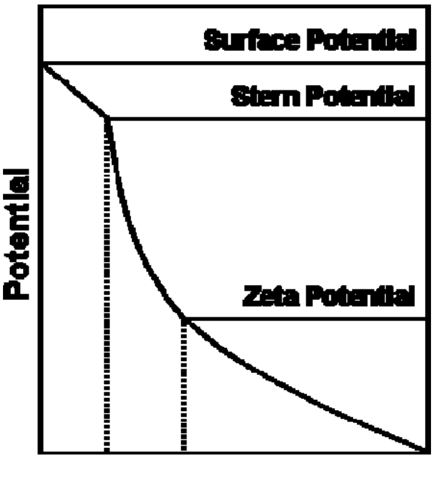


Figure 1.11 The numerical relationship between zeta potential and surface potential depends on the level of ions in the solution, as well as the ionic-ability of the solutes.

ii) Steric Stabilization

The second method of stabilization involves the steric forces. Surfactant molecules can adsorb onto the surfaces of particles and their lyophilic chains will then extend into the solvent and interact with each other. The solvent-chain interaction, which is a mixing effect, increases the free energy of the system and produces an energy barrier to the closer approach of particles. When the particles come into closer contact with each other, the motion of the chains extending into the solvent become restricted and produce an entropic effect. Steric stabilization can occur in the absence of the electric barriers, and is effective in both aqueous and nonaqueous media. It is less sensitive to impurities or trace additives than electric stabilization. The steric stabilization method is particularly effective in dispersing high concentrations of particles.

Another steric stabilization takes advantages of core-shell geometry; the stability of the colloid will be greatly determined by the nature of the shell material. Silica shell is broadly applied for this purpose. It has been observed that silica nano-particles in the size range of 10-100 nm possess a remarkable stability at very high salt concentration at pH >10.5, and even at their isoelectric point.

Comparing with the coating of a semiconductor with silica shell or coating a metallic nano-particle with metal shell, coating of metallic nano-particles with silica shell presents an additional difficulty, the lack of chemical affinity between the core and the shell materials. A procedure must be designed to overcome the very low tendency of the core and the shell materials to bond to each other. Several routes have been followed with better or worse results. Patil, Andres, and Otsuka [60] synthesized $Au@Si0_2$ and $Ag@Si0_2$ particles using a gas aggregation source. Though the technique can be employed to synthesize a whole range of particles, it suffers from many important disadvantages.

A much simpler procedure was used by Liz-Marzan and Philipse [61] for the synthesis of $Au@Si0_2$ particles. The procedure was based on the formation of nano-sized gold particles in the presence of small silica spheres, which led to heterocoagulation. The composite particles were then diluted with ethanol, where extensive growth was achieved by means of the Stober method as stated by Stbber, Fink and Bohn in 1962 [62], so that Au was embedded as a core. This synthetic route resulted in a mixture of unlabeled and labeled silica particles, with a low proportion of the coated particles.

Another method that has provided substantially better results was later designed by Liz-Martan [63], Giersig, [64], and Mulvaney [65]. The method was based on the use of silane coupling agents as surface primers to provide the nano-particle surface with silanol groups, and therefore to render the surface of noble metals compatible with silicate moieties. Once the surface had been modified, slow deposition of a thin silica shell was effected from a solution of active silica. Subsequent transfer into ethanol led to sudden condensation of unreacted silicate, which can yield nicely concentric $Au@Si0_2$

core shells. The shells could then be grown by careful addition of ammonia and tetraethoxysilane, resulting in monodisperse colloids.

The interest in core-shell nano-particles, is not just due to the enhancement of colloidal stability, but has been driven by the interest in creating nano-materials and nanostructures with unique, complex properties. The properties of interest are mainly optical, electronic, and magnetic as stated by Mulvaney, Giersig, and Henglein, 1993; Henglein, et.al., 1992; Johnson and Christy, 1972 [66-68].

1.4 CHARACTERIZATION TECHNIQUES FOR NANOSTRUCTURE

The morphological features of nano material and structures need to be determined in various stages of production such as size distribution, porosity, pore size distribution, surface structure and composition, which are critical to ensure the materials and structures are in nano scale to archive special properties as reported by Li, Lokyuen and Junyan in 2003 and also from website - *http://www.egr.msu.edu/cmsc/esem/index.html.; http://www.egr.msu.edu/cmsc/nano/index.html* [8, 69, 70]. Such structural feature can be characterized by a rang of techniques and instruments such as Particle Analyzer, Atomic Force Microscopy (AFM), Scanning Tunneling Microscopy (STM), Scanning Electron Microscopy (SEM), High Resolution Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES), Near Field Scanning Optical Microscopy (NSOM or SNOM), X-ray and Neutron Diffraction or other spectroscopic techniques.

The properties of nano materials and structures/composites also need to be measured to test whether specific and unique properties can be derived due to the nano scale structures. Properties characterization should be carried out in various aspects in relation to specific functions to be achieved such as in physics, mechanical, electrochemical, optical and thermal properties. Examples of properties “characterization techniques: property to be characterized techniques; Dynamic Time Resolved Techniques; Magnetic Scanning Electron Microscopy with Polarization Analysis (SEMPA); Surface Magnet – Optic Kert Effect (SMOKE) Spectroscopy; Spin-Polarized Low –Energy Electron Microscopy (SPLEEM); Magnetic Force Microscopy (MFM); Electrochemical Impedance Spectroscopy; Potential Sweep Method; Electrochemical Quartz Crystal Microbalance, Mechanical Electricity Method; Vibrating Reed Method; Thermal Diffractional Scanning Colorimeter(DSC).

Characterizing nano sized materials is an emerging field posing lot of challenges to scientists and technologists. Thus, nanotechnology has motivated the upsurge in research activities on the discovery and invention of sophisticated nano characterization techniques to allow a better control of morphology, size and dimensions of materials in nano range. The important characterization techniques used for nanotechnology research can be broadly categorized as follows;

1. Determination of size, shape and surface area
2. Determination of atomic structure and chemical composition

This section discusses the basic principle and applications of these instrumental techniques in the field of nanotechnology research in textiles.

1.4.1 Nano material Characterization by Microscopy

Optical microscopes are generally used for observing micron level materials with reasonable resolution. Further magnification cannot be achieved through optical microscopes due to aberrations and limit in wavelength of light. Hence, the imaging techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM/HRTEM), scanning tunneling microscopy (STM), atomic force microscopy (AFM), etc. have been developed to observe the sub micron size materials. Though the principles of all the techniques are different but one common thing is that they produce a highly magnified image of the surface or the bulk of the sample. Nanomaterials can only be observed through these imaging techniques as human eye as well as optical microscope cannot be used to see dimensions at nano level. Basic principles and applications of all these imaging techniques used in nanotechnology research are described below.

1.4.1.1 Scanning Electron Microscopy (SEM)

The scanning electron microscope is an electron microscope that images the sample surface by scanning it with a high energy beam of electrons. Conventional light microscopes use a series of glass lenses to bend light waves and create a magnified image while the scanning electron microscope creates the magnified images by using electrons instead of light waves, as found on website http:// www.purdue.edu/ REM/rs/sem.htm [71].

Basic Principle

When the beam of electrons strikes the surface of the When the beam of electrons strikes the surface of the specimen and interacts with the atoms of the sample, signals in the form of secondary electrons, back scattered electrons and characteristic X-rays are generated that contain information about the sample's surface topography, composition, etc. The SEM can produce very high-resolution images of a sample surface, revealing details about 1-5 nm in size in its primary detection mode i.e. secondary electron imaging. Characteristic X-rays are the second most common imaging mode for an SEM. These characteristic X-rays are used to identify the elemental composition of the sample by a technique known as energy dispersive X-ray (EDX). Back-scattered electrons (BSE) that come from the sample may also be used to form an image. BSE images are often used in analytical SEM along with the spectra made from the characteristic X-rays as clues to the elemental composition of the sample.

In a typical SEM, the beam passes through pairs of scanning coils or pairs of deflector plates in the electron column to the final lens, which deflect the beam horizontally and vertically so that it scans in a raster fashion over a rectangular area of the sample surface. Electronic devices are used to detect and amplify the signals and display them as an image on a cathode ray tube in which the raster scanning is synchronized with that of the microscope. The image displayed is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen.

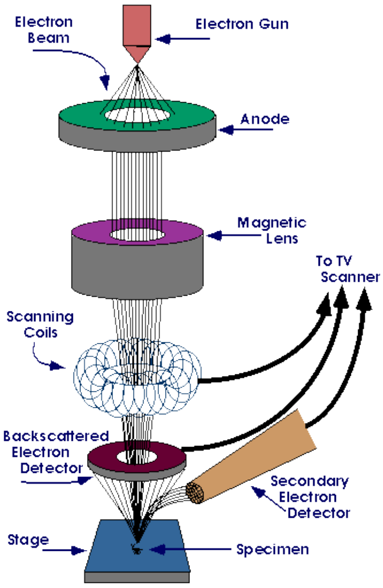


Figure 1.12 Schematic diagram of SEM

SEM requires that the specimens should be conductive for the electron beam to scan the surface and that the electrons have a path to ground for conventional imaging. Non-conductive solid specimens are generally coated with a layer of conductive material by low vacuum sputter coating or high vacuum evaporation. This is done to prevent the accumulation of static electric charge on the specimen during electron irradiation. Non-conducting specimens may also be imaged uncoated using specialized SEM instrumentation such as the "Environmental SEM" (ESEM) or in field emission gun (FEG) SEM operated at low voltage, high vacuum or at low vacuum, high voltage.

Applications

The SEM shows very detailed three dimensional images at much high magnifications (up to x300000) as compared to light microscope (up to x 10000). But as the images are created without light waves, they are black and white. The surface structure of polymer nanocomposites, fracture surfaces, nanofibres, nano-particles and nanocoating can be imaged through SEM with great clarity. As very high resolution images of the dimension 1 - 5 nm can be obtained, SEM is the most suitable process to study the nanofibres and nanocoatings on polymeric/textile substrate as advocated by Joshi & Viswanathan in 2006; Joshi et al., 2006; Klajn et al.,2007 [72-74].

Marcato et al. in 2005 and Ma et al. in 2001 [75-76] also, recommandes the SEM technique to view dispersion of nanoparticles in the bulk and on the surface of nanocomposite fibers and coatings on yarns and fabric samples.

1.4.1.2 Energy Dispersive X-ray Analysis (EDX)

Energy dispersive X-ray analysis is a technique to analyze near surface elements and estimate their proportion at different position, thus giving an overall mapping of the sample.

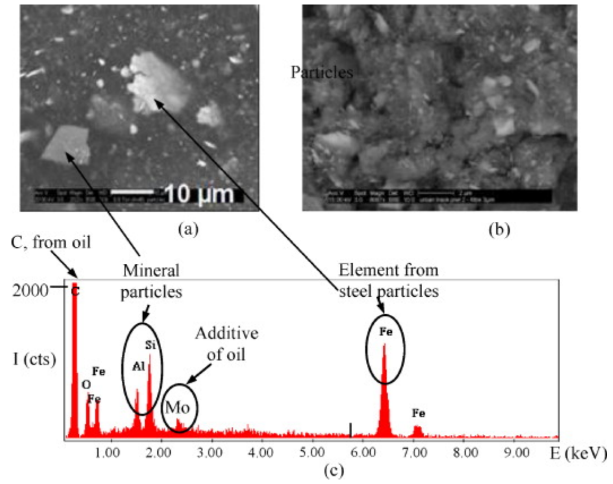


Figure 1.13 Elemental analysis of nanoparticles by EDX.

Basic Principle

This technique is used in conjunction with SEM. An electron beam strikes the surface of a conducting sample. The energy of the beam is typically in the range 10-20keV. This causes X-rays to be emitted from the material. The energy of the X-rays emitted depends on the material under examination. The X-rays are generated in a region about 2 microns in depth, and thus EDX is not truly a surface science technique. By moving the electron beam across the material an image of each element in the sample can be obtained. Due to the low X-ray intensity, images usually take a number of hours to acquire.

Applications

The composition or the amount of nano-particles near and at the surface can be estimated using the EDX, provided they contain some heavy metal ions. For example, the presence of Au, Pd and Ag nano-particles on surface can easily be identified using EDX technique. Elements of low atomic number are difficult to detect by EDX, The Si-Li detector protected by a beryllium window cannot detect elements below an atomic number of 11 (Na). In windowless systems, elements with as low atomic number as 4 (Be) can be detected. EDX spectra have to be taken by focusing the beam at different regions of the same sample to verify spatially uniform composition of the bimetallic materials. Figure shows the elemental analysis of nano-particles can be verified by EDX as reported by Sano et al. in 2002 [77].

1.4.1.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen and interacts as passes through the sample. An image is formed from the electrons transmitted through the specimen, magnified and focused by an objective lens and appears on an imaging screen.

Basic Principle

The contrast in a TEM image is not like the contrast in a light microscope image. In TEM, the crystalline sample interacts with the electron beam mostly by diffraction rather than by absorption. The intensity of the diffraction depends on the orientation of the planes of atoms in a crystal relative to the electron beam; at certain angles the electron beam is diffracted strongly from the axis of the incoming beam, while at other angles the beam is largely transmitted.

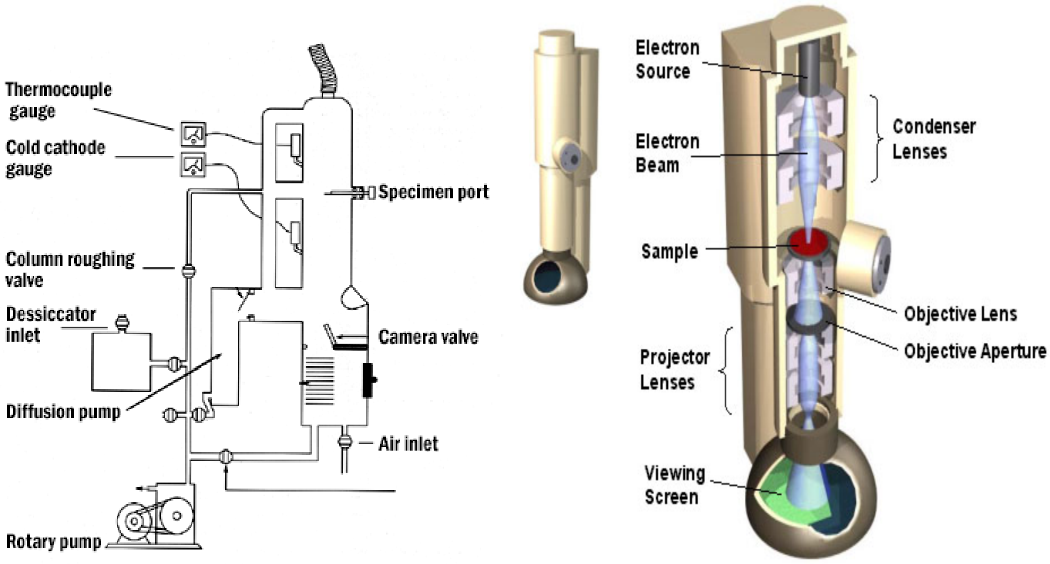


Figure1.14 Schematic of a transmission electron microscope

Modern TEMs are equipped with specimen holders that allow to tilt the specimen to a range of angles in order to obtain specific diffraction conditions. Therefore, a high contrast image can be formed by blocking electrons deflected away from the optical axis of the microscope by placing the aperture to allow only unscattered electrons through this produces a variation in the electron intensity that reveals information on the crystal structure. This technique, particularly sensitive to extended crystal lattice defects, is known as 'bright field' or 'light field'. It is also possible to produce an image from electrons deflected by a particular crystal plane which is known as a dark field image.

The specimens must be prepared as a thin foil so that the electron beam can penetrate. Materials that have dimensions small enough to be electron transparent, such as powders or nanotubes, can be quickly produced by the deposition of a dilute sample containing the specimen onto support grids. As polymeric nanocomposites or the textile samples are not as hard as metals, they are cut into thin films (< 100 nm) using ultra-microtome with diamond knife at cryogenic condition (in liquid nitrogen).

Applications

The TEM is used widely both in material science/metallurgy and biological sciences. In both cases the specimens must be very thin and able to withstand the high vacuum present inside the instrument. For biological specimens, the maximum specimen thickness is roughly 1 micrometer. To withstand the instrument vacuum, biological specimens are typically held at liquid nitrogen temperatures after embedding in vitreous ice, or fixated using a negative staining material such as uranyl acetate or by plastic embedding.

The properties of nanocomposites depend to a large extent on successful nanolevel dispersion or intercalation/exfoliation of nanoclays, therefore monitoring their morphology and dispersion is very crucial. TEM images reveal the distribution and dispersion of nano-particles in polymer matrices of nanocomposite fibres, nanocoatings, etc. The extent of exfoliation, intercalation and orientation of nano-particles can also be visualized using the TEM micrograph

1.4.1.4 High Resolution Transmission Electron Microscopy (HRTEM)

High resolution transmission electron microscopy is an imaging mode of the transmission electron microscope that allows the imaging of the crystallographic structure of a sample at an atomic scale.

Basic Principle

As opposed to conventional microscopy, HRTEM does not use absorption by the sample for image formation, but the contrast arises from the interference in the image plane of the electron wave with itself. Each imaging electron interacts independently with the sample. As a result of the interaction with the sample, the electron wave passes through the imaging system of the microscope where it undergoes further phase change and interferes as the image wave in the imaging plane. It is important to realize that the recorded image is not a direct representation of the samples crystallographic structure.

Applications

Because of its high resolution, it is an invaluable tool to study nanoscale properties of crystalline material. At present, the highest resolution possible is 0.8 A. At these small scales, individual atoms and crystalline defects can be imaged.

1.4.1.5. Atomic Force Microscope (AFM)

The atomic force microscope is ideal for quantitatively measuring the nanometer scale surface roughness and for visualizing the surface nano-texture on many types of material surfaces including polymer nanocomposites and nanofinished or nanocoated textiles. Advantages of the AFM for such applications are derived from the fact that the AFM is nondestructive technique and it has a very high three dimensional spatial resolution.

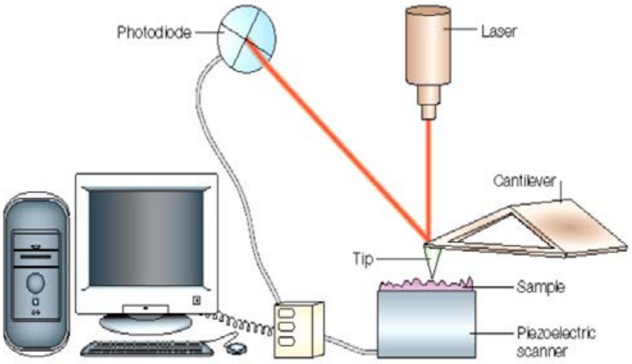


Figure 1.15 Schematic representation of the components of an atomic force microscope

Basic Principle

The basic principle and applications of atomic force microscopy have been the subject of a number of excellent reviews as reported by Rynders et al., 1995; Wei & Wang, 2004; Poletti et al., 2003 [78-80]. In atomic force microscopy, a probe consisting of a sharp tip (nominal tip radius is in the order of 10 nm) located near the end of a cantilever beam is raster scanned across the surface of a specimen using piezoelectric scanners. Changes in the tip specimen interaction are often monitored using an optical lever detection system, in which a laser is reflected off of the cantilever and onto a position-sensitive photodiode. During scanning, a particular operating parameter is maintained at a constant level, and images are generated through a feedback loop between the optical detection system and the piezoelectric scanners. There are three scan modes for AFM, namely contact mode, non contact mode and tapping mode. In contact mode, the tip scans the specimen in close contact with the surface of the material. The repulsive force on the tip is set by pushing the cantilever against the specimen's surface with a piezoelectric positioning element. The deflection of the cantilever is measured and the AFM images are created. In non-contact mode, the scanning tip hovers about 50-150 A above the specimen's surface. The attractive forces acting between the tip and the specimen are measured, and topographic images are constructed by scanning the tip above the surface. Tapping mode imaging is implemented in ambient air by oscillating the cantilever assembly at its resonant frequency (often hundreds of kilohertz) using a piezoelectric crystal. The piezo motion causes the cantilever to oscillate when the tip is not in contact with the surface of a material. The oscillating tip is then moved towards the surface until it begins to tap the surface. During scanning, the vertically oscillating tip alternately contacts the surface and lifts off, generally at a frequency of 50,000-500,000 cycles/s. As the oscillating cantilever begins to intermittently contact the surface, the cantilever oscillation is reduced due to energy loss caused by the tip contacting the surface. The reduction in oscillation amplitude is used to measure the surface characteristics.

Applications

The use of this new tool is of importance in fundamental and practical research and development of versatile technical textiles for a variety of applications. Atomic force microscopy can be used to explore the nanostructures, properties, and surfaces and interfaces of fibres and fabrics. For example, structural characteristics of nanofibre materials, nanolevel surface modification of textile surfaces (by plasma or LTV eximer lamp, etc) can be easily assessed by this sophisticated technique. AFM provides powerful tools for nondestructive characterization of textiles. A possible way to investigate the effect of processing on the morphology of the textile surfaces is given by AFM as reported by Sakurai et al. in 2007 [81]. Changes in the morphology of surface modified textile samples can also be quantified by root-mean-square (rms) surface roughness and surface area values.

1.4.1.6 *Scanning Tunneling Microscopy (STM)*

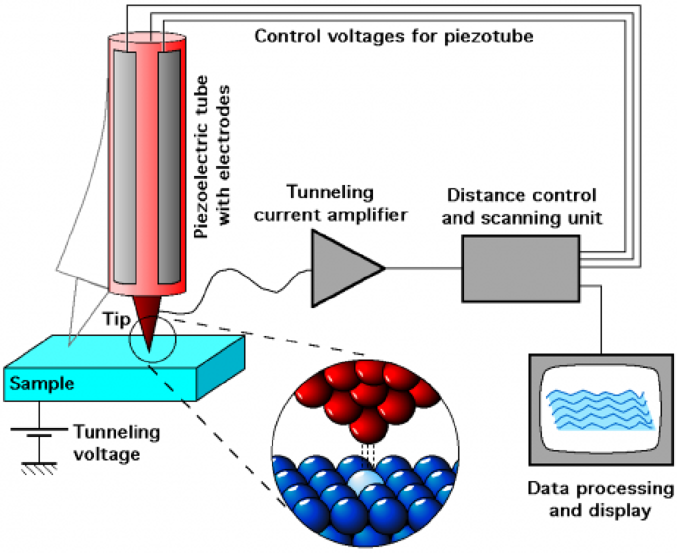


Figure 1.16 A schematic view of a scanning tunneling microscope (STM).
Source : http:// www.answers.com/topic/scanning-tunneling-microscope [82].

Scanning tunneling microscopy is an instrument for producing surface images with atomic-scale lateral resolution, in which a fine probe tip is scanned over the surface of a conducting specimen, with the help of a piezoelectric crystal at a distance of 0.5-1 nm. and the resulting tunneling current or the position of the tip required to maintain a constant tunneling current is monitored

Basic Principle

The principle of STM is based on the concept of quantum tunneling. When a conducting tip is brought very near to a metallic or semi-conducting surface, a bias between the two can allow electrons to tunnel through the vacuum between them F or low voltages, this tunneling current is a function of the local density of states at the Fermi level of the sample. Variations in current as the probe passes over the surface are translated into an image. For STM, good resolution is considered to be 0.1 nm lateral resolutions and 0.01 nm depth resolutions. They normally generate images by holding the current between the tip of the electrode and the specimen at some constant value by using a piezoelectric crystal to adjust the distance between the tip and the specimen surface, while the tip is piezoelectrically scanned in a raster pattern over the region of specimen surface being imaged by holding the force, rather than the electric current, between tip and specimen at a set-point value. Atomic force microscopes similarly allow the exploration of nonconducting specimens. In either case, when the height of the tip is plotted as a function of its lateral position over the specimen, an image that looks very much like the surface topography results. The STM can be used not only in ultra high vacuum but also in air and various other liquid or gas, at ambient and wide range of temperatures. STM can be challenging technique, as it requires extremely clean surfaces and sharp tips.

Applications

Scanning tunneling microscopy is a powerful tool in nanotechnology and nanoscience providing facilities for characterization and modification of a variety of materials. STM is successfully used to detect and characterize materials like carbon nanotubes (single-walled and multi-walled) and graphine layer. The instrument has also been used to move single nanotubes or metal atoms and molecules on smooth surfaces with high precision as reported by Terrones et al., 2004; Meier et al., 2004 [83-84].

1.4.2 Nano materials Characterization by Spectroscopy

1.4.2.1 Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique used in condensed matter physics and chemistry to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering of monochromatic laser light. The laser light interacts with phonons or other excitations in the system resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the phonon modes in the system.

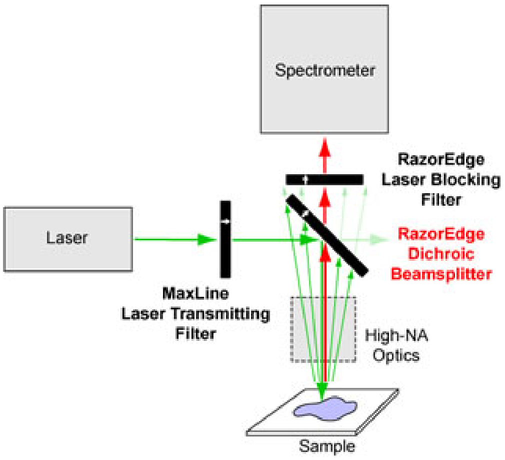


Figure 1.17 A schematic of Raman spectroscopy

Basic Principle

The Raman effect occurs when light impinges upon a molecule interacts with the electron cloud of the bonds of that molecule and incident photon excites one of the electrons into a virtual state. For the spontaneous Raman Effect, the molecule will be excited from the ground state to a virtual energy state, and relax into a vibrational excited state, which generates stokes Raman scattering. If the molecule was already in an elevated vibrational energy state, the Raman scattering is then called anti-stokes Raman scattering. A molecular polarizability change or amount of deformation of the electron cloud, with respect to the vibrational coordinate is required for the molecule to exhibit the Raman effect. The amount of the polarizability change will determine the Raman scattering intensity, whereas the Raman shift is equal to the vibrational level that is involved.

Applications

Raman spectroscopy is commonly used in chemistry, since vibrational information is very specific for the chemical bonds in molecules. It therefore provides a fingerprint by which the molecule can be identified in the range of 500-2000 cm1. Raman gas analyzers have many practical applications. For instance, they are used in medicine for real-time monitoring of an aesthetic and respiratory gas mixture during surgery. In solid state physics, spontaneous Raman spectroscopy is used to characterize materials, measure temperature, and find the crystallographic orientation of a sample. The polarization of the Raman scattered light with respect to the crystal and the polarization of the laser light can be used to find the orientation of the crystal. As stated by Gouadec & Colomban, 2007 [85].

Raman active fibres, such as aramid and carbon, have vibrational modes that show a shift in Raman frequency with applied stress. Polypropylene fibres also exhibit similar shifts. The radial breathing mode is a commonly used technique to evaluate the diameter of carbon nanotubes. As reported by Eitan et al., 2007 [86].

1.4.2.2 Ultraviolet-Visible (UV-VIS) Spectroscopy

Ultraviolet spectrophotometers consist of a light source, reference and sample beams, a monochromator and a detector. The ultraviolet spectrum for a compound is obtained by exposing a sample of the compound to ultraviolet light from a light source, such as a Xenon lamp.

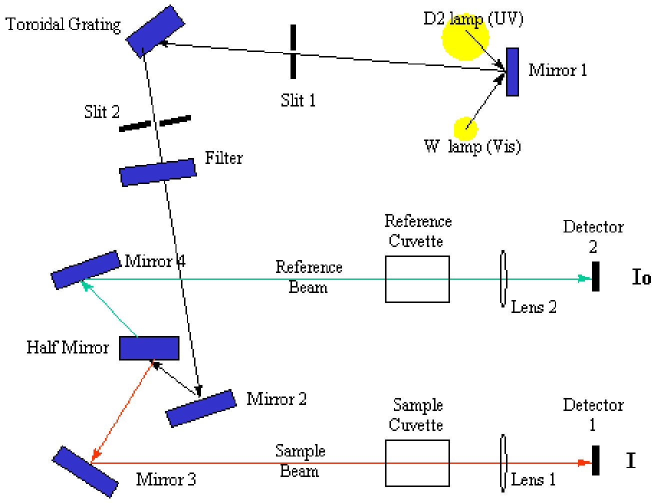


Figure 1.18 A schematic of Ultraviolet-Visible (UV-VIS) Spectroscopy

<u>Basic Principle</u>

The reference beam in the spectrophotometer travels from the light source to the detector without interacting with the sample. The sample beam interacts with the sample exposing it to ultraviolet light of continuously changing wavelength. When the emitted wavelength corresponds to the energy level which promotes an electron to a higher molecular orbital, energy is absorbed. The detector records the ratio between reference and sample beam intensities (MI). The computer determines at what wavelength the sample absorbed a large amount of ultraviolet light by scanning for the largest gap between the two beams. When a large gap between intensities is found, where the sample beam intensity is significantly weaker than the reference beam, the computer plots this wavelength as having the highest ultraviolet light absorbance when it prepares the ultraviolet absorbance spectrum, as per reported on website http:// www.science of spectroscopy.info/edit/index.php [87].

Applications

In certain metals, such as silver and gold, it has been found by Patakfalvi, Oszko & De'ka'iiy in 2003; Pal, Tak & Song in 2007; Mock et al. in 2002 [88-90] that, the plasmon resonance is responsible for their unique and remarkable optical phenomena. Metallic (silver or gold) nano-particles, typically 40-100 nm in diameter, scatter optical light elastically with remarkable efficiency because of a collective resonance of the conduction electrons in the metal known as surface plasmon resonance. The surface plasmon resonance peak in UV absorption spectra is shown by these plasmon resonant nano-particles. The magnitude, peak wavelength, and spectral bandwidth of the plasmon resonance associated with a nano-particle are dependent on the particle's size, shape, and material composition, as well as the local environment.

Besides biological labeling and nanoscale biosensing silver nano-particles have received considerable attention to the textile and polymer researchers due to their attractive antimicrobial properties. The surface plasmon resonance peak in absorption spectra of silver particles is shown by an absorption maximum at 420-500 nm. The surface peaks vary with size, shape and concentration of the metallic nano-particles. This shape of the nano-particles can be identified by observing the corresponding peak as reported by Brause, Moeltgen & Kleinermanns, 2002; MuLvaiiey, 1996; Mie, [91-93].

1.4.3 Characterization of Nano materials by X-ray

1.4.3.1 Wide Angle X-Ray Diffraction

X-rays are electromagnetic radiation similar to light, but with a much shorter wavelength (few Angstrom). They are produced when electrically charged particles of sufficient energy are decelerated. In an X-ray tube, the high voltage maintained across the electrodes draws electrons toward a metal target (the anode). X-rays are produced at the point of impact, and radiate in all directions.

Basic Principle

If an incident X-ray beam encounters a crystal lattice, general scattering occurs. Although most scattering interferes with itself and is eliminated (destructive interference), diffraction occurs when scattering in a certain direction is in phase with scattered rays from other atomic planes. Under this condition the reflections combine to form new enhanced wave fronts that mutually reinforce each other (constructive interference). The relation by which diffraction occurs is known as the Bragg's law or equation as per Sosa, Noguez & Barrera, 2003 [94]. As each crystalline material including the semi crystalline polymers as well as metal and metal oxide nano-particles and layered silicate nanoclays have a characteristic atomic structure, it will diffract X-rays in a unique characteristic diffraction order or pattern.

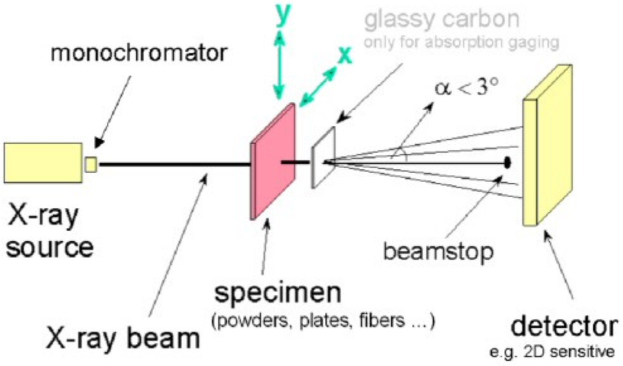


Figure 1.19 Schematic of Wide Angle X-Ray Diffraction

Applications

X-ray diffraction data from polymers generally provide information about crystallinity, crystallite size, orientation of the crystallites and phase composition in semi crystalline polymers. With appropriate accessories, X-ray diffraction instrumentation can be used to study the phase change as a function of stress or temperature, to determine lattice strain, to measure the crystalline modulus, and with the aid of molecular modeling to determine the structure of polymer.

Besides the above mentioned characterization this sophisticated technique can also be used to characterize polymer layered silicate (clay), silicate nanoclay interest both in characterize polymer layered nanocomposites, Polymer/layered composites have attracted great industry and in academia, because they often exhibit remarkable improvement in materials properties at very low clay content (3-6 wt %), when compared with virgin polymer or conventional composites. The use of organoclays as precursors to nanocomposite formation has been extended into various polymer systems (thermoset and thermoplastic) including epoxy and others.

For true nanocomposites, the clay nanolayers must be uniformly dispersed and exfoliated in the polymermatrix. The structure of polymer/layered silicates composites has typically been established using wide angle X-ray diffraction (WAXD) analysis. By monitoring the position, shape and intensity of the basal reflections from the distributed silicate layers, the nanocomposite structure (intercalated or exfoliated) may be identified. In an exfoliated nanocomposite, the extensive layer separation associated with the delamination of the original silicate layers in the polymer matrix results in the eventual disappearance of any coherent X-ray diffraction from the distributed silicate layers. On the other hand Ray & Okamota in 2003 [95], for intercalated nanocomposites, the finite layer expansion associated with the polymer intercalation results in the appearance of a new basal reflection corresponding to the larger gallery height. Organophilic clay (also known as nanoclay) can be obtained by simply the ion-exchange reaction of hydrophilic clay with an organic cation such as an alkyl ammonium or phosphonium ion to make it compatible with polymeric matrix. The inorganic ions, relatively small (sodium), are exchanged with more voluminous organic onium cations as per Lagaly G [96]. This ion-exchange reaction results in widening the gap between the single sheets, enabling organic cations chain to move in between them. This increase in d-space or degree of exfoliation of the polymer nanocomposite can be obtained from Bragg equation. The X-ray diffractograms by Patel et al. in 2006 [97] of the organoclay reveals a shift in the position of [001] planes (26 changed from 5-7° to 4-32°), indicating an increase in the basal spacing of these planes. The increase is relatively large from 1-5 nm to 2 06 nm and confirms the occurrence of organic molecule intercalation between silicate platelets.

1.4.3.2. X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy is a quantitative spectroscopic surface chemical analysis technique used to estimate the empirical formula or elemental composition, chemical state and electronic state of the elements on the surface (up to 10 nm) of a material. XPS is also known as ESC A, an abbreviation of electron spectroscopy of chemical analysis.

Basic Principle

X-ray irradiation of a material under ultra-high vacuum (UHV) leads to the emission of electrons from the core orbital of the top 10 nm of the surface elements of the material being analyzed. Measurement of the kinetic energy (KE) and the number of electrons escaping from the surface of the XPS material gives the XPS spectra. From the kinetic energy, the binding energy of the electrons to the surface atoms can be calculated. The binding energy of the electrons reflects the oxidation state of the specific surface elements. The number of electrons reflects the proportion of the specific elements on the surface.

As the energy of a particular X-ray wavelength used to excite the electron from a core orbital is a known quantity, we can determine the electron binding energy (BE) of each of the emitted electrons by using the following equation that is based on the work of Ernest Rutherford (1914):

$$E_{\text{binding}} = E_{\text{photon}} - E_{\text{kinetic}} - \Phi$$

Where, E_{binding} is the energy of the electron emitted from one electron configuration within the atom; E_{photon}, the energy of the X-ray photons being used; E_{kinetic}, the kinetic energy of the emitted electron as measured by the instrument; and 0, the work function of the spectrometer (not the material).98(Crist, 2005)

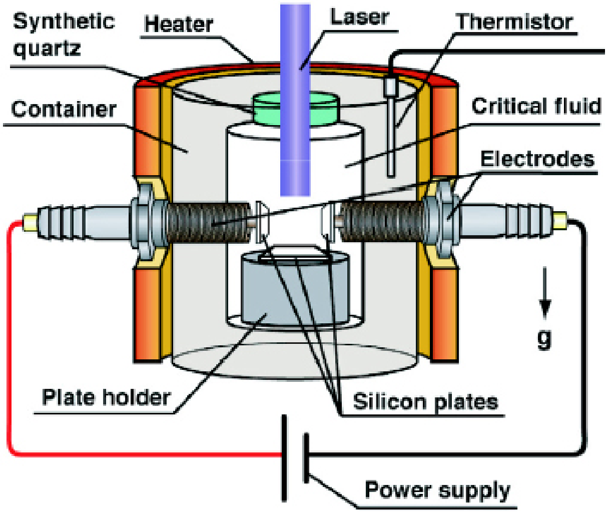


Figure 1.20 Schematic view of X-Ray Photoelectron Spectroscopy

Applications

XPS is used to determine the elements and the quantity of those elements that are present within -10 nm of the sample surface. It also detects the contamination, if any, exists in the surface or the bulk of the sample. If the material is free of excessive surface contamination, XPS can generate empirical formula of the sample and the chemical state of one or more of the elements can be identified. Moreover, the technique can be used to determine the thickness of one or more thin layers (1-8 nm) of different materials within the top 10 nm of the surface. It can also measure the uniformity of elemental composition of textile surfaces after nanolevel etching, finishing or coating of the surfaces. The only limitation is that it cannot detect hydrogen (Z=l) or helium (Z=2), because these two elements do not have any core electron orbitals, but only valence orbitals.

1.4.3.3. Particle Size Analyzer

There are different techniques for the measurement of particle size and its distribution (PSD) such as sieve analysis, optical counting methods, electro resistance counting methods, sedimentation techniques, laser diffraction methods, dynamic light scattering method, acoustic spectroscopy, etc. Among them dynamic light scattering is mostly used for obtaining size distribution of nano-particles

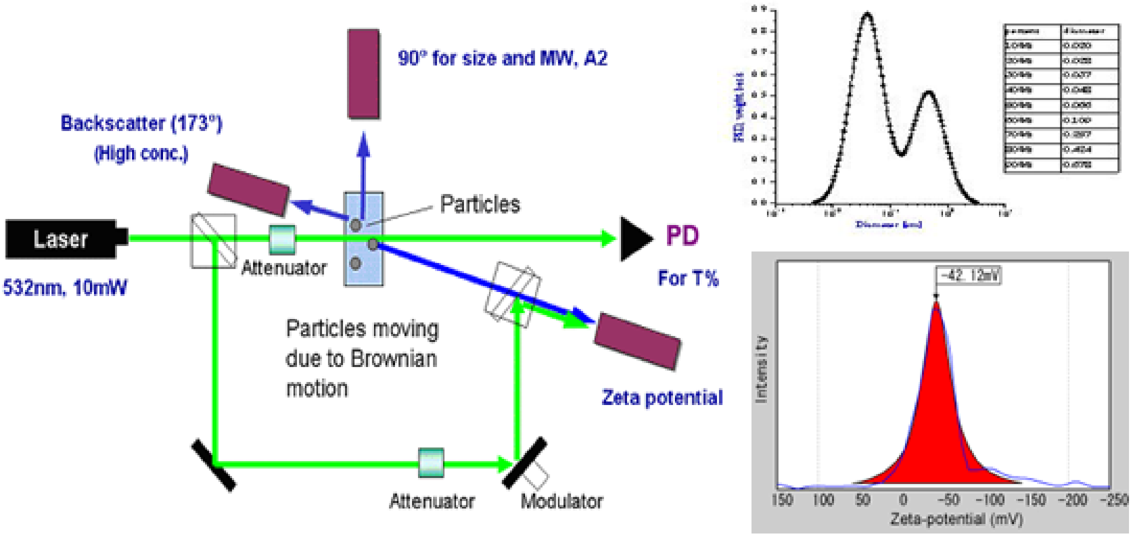


Figure 1.21 Schematic view of Zeta Particle Size Analyzer

Basic Principle of Dynamic Light Scattering (DLS)

Dynamic light scattering, sometimes referred to as photon correlation spectroscopy (PCS) or quasi-elastic light scattering (QELS) is a noninvasive, well-established technique for measuring the size of molecules and particles typically in the submicron region, and with the latest technology lower than 1 nanometre. Particles, emulsions and molecules in suspension lower than undergo Brownian motion. This is the motion induced by the bombardment of solvent molecules that themselves are moving due to their thermal energy. If the particles or molecules are illuminated with a laser, the intensity of the scattered light fluctuates at a rate that is dependent upon the size of the particles as smaller particles are "kicked" further by the solvent molecules and move more rapidly. Analysis of these intensity fluctuations yields the velocity of the Brownian motion and hence the particle size (radius r_k) using the Stokes-Einstein relationship, from http://www.physics.emory.edu/~weeks/lab/papers/sendai2007.pdf [99], as shown below:

$$r_k = \frac{kT}{6\pi\eta D}$$

Where, ***k*** is the Boltzmann's constant; ***T***, the temperature in K; ***η***, the solvent viscosity; and ***D***, the diffusion coefficient

Applications

Silver, titanium, silica and zinc oxide nano-particle are often used in textile substrates to get improved functionality of the nano-particle finished textile materials. The enhanced property is dependant on the size of the applied nano-particles, which generally have a tendency to agglomerate. Therefore, size and size distribution study of the nano-particle in the dispersion as well as suspension is important before applying to the textile substrates as stated by Joshi, Bhattacharyya and Wazed in 2008 [100].

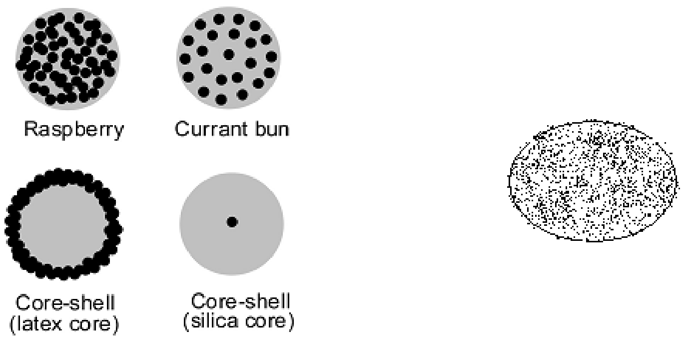
1.5. APPLICATION TECHNIQUES

However, there are number of methods used for the application of nano-particles to textile materials. The nano-particles can be applied to textiles at different stages such as:

1) Filament or fibre preparation stage
2) During finishing stage
3) During Garment processing

1.5.1 Filament or Fibre Preparation Stage

Sols can be used as basic solution for the spinning of fibres. By this method, simple glass fibres are prepared by dry spinning of silica sols, quoted by Peltola et al.,2001; Celzard et al., 2002) [101-102]. By spinning directly from appropriate sols, inorganic composite fibres can be prepared, not only based on pure SiO_2 but also on other metal oxides or mixtures of both. Amalvy , et. al [103] has basically described two different kinds of sol-gel based fibres :– inorganic/organic or pure inorganic composite fibres, the Schematic representation of the possible Nanocomposite particle morphologies as see below in figure.



Polymer/ silica composite

silica composite

Figure 1.22 Schematic Representations of the Possible Nanocomposite Particle Morphologies

Polymer-based organic/inorganic nanocomposites have gained increasing attention in the field of materials science. Inorganic/organic nanocomposite materials combine the advantages of the inorganic material and the organic polymer. Various inorganic nanoscale materials including silicate, metal nano-particles, metal oxides, and semiconductors have been used to prepare polymer/inorganic nanocomposite materials.

In recent years, polymer/SiO_2 nanocomposites have attracted substantial academic and industrial interest. Many potential and practical applications of this type of nanocomposites in the fields of coatings, flame-retardant materials, and photo resist materials, and optical devices have been reported. There are essentially four different approaches to use for synthesize polymer-silica nanocomposites as stated by Jianan Zhang, et.al., in 2008 [104].

1) Melt intercalation
2) Solution method
3) In situ polymerization. From Ahmadi et al., 2004 [105]
4) Electro spinning. From http://www.worldscibooks.com/materialsci/6961.html [106].

1.5.2 Finishing Stage

a) Pad-dry-cure and Spray finishing method:

The application of nanosols to the textile materials can be carried out by conventional procedures used for textile finishing. Such procedures are mainly simple dipping, padding or spraying processes, foam finishing. Even printing processes using nanosols can be realized on textiles. Probably the simplest method is dipping of a textile sample into the nanosol.

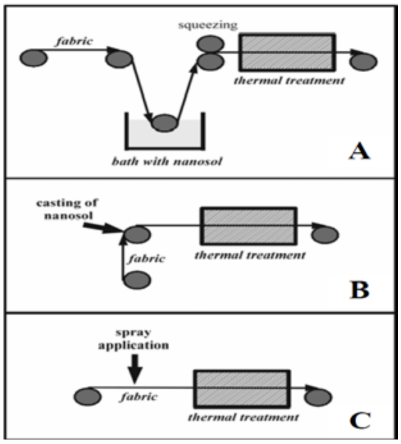


Figure 1.23 Schematic drawing of nanosol finishing of textiles by conventional application techniques, A: padding, B: casting, C: spraying. Source http: //217.218.200.220 /c/ document_library/ LFE-12410.pdf [107]

The fabric is immersed in the sol, remains there for a certain time, it is taken out and it either dries under the ambient conditions or it is thermally cured in an oven or a stenter frame. For certain applications or finishing full penetration of the textile by the sol is not necessary. As an example, repellence might only be needed on one side of the product. In these cases the sol application cannot be carried out by dipping or padding. For this the casting of the nanosol or a spray application treating only one side of the textile fabric is useful methods. The above mentioned application techniques are depicted schematically in Figure 1.23.

b) Foam Finishing Method:

One important application method for chemical finishes is the use of foam to apply the finish to the fabric. By replacing part of the water in the chemical formulation with air, the amount of water added to the fabric can be significantly reduced. In addition, surfactants are included in the formulation to be foamed. Even if they are carefully selected, they may cause effect reduction of repellent finishes. The chemical formulation is mixed with air in a foam generator producing high volumes of foam that can be applied to fabrics in a number of ways. The ratio of liquid to air in foam is referred to as the 'blow ratio', Terlingen in 1993 [108] has conveniently determined by Equation:

$$\text{blow ratio} = \frac{1}{\text{foam density}}$$

c) Plasma Technology:

Before going on into the uses of plasma, it's important to understand what it is. Simply put, plasma is nothing more than ionized gas. When a surface is exposed to plasma a mutual interaction between the gas and the substrate takes place. The surface of the substrate is bombarded with ions, electrons, radicals, neutrals and UV radiation from the plasma while volatile components from the surface contaminate the plasma and become a part of it, as per website "aasimahmed.files.wordpress.com/.../a-review-of-plasma-treatment-for-application-on-textile-substrate-aasim-ahmed.pdf" [109].

The electrons in the plasma are able to cleave covalent chemical bonding. Therefore, physical and chemical modification of surfaces of various substrates is possible. It is through the use of these in different combinations and on different substrate that the vast variety of outcomes which are possible through plasma treatment can be achieved. The mechanism of plasma modification as shown in figure 1.24.

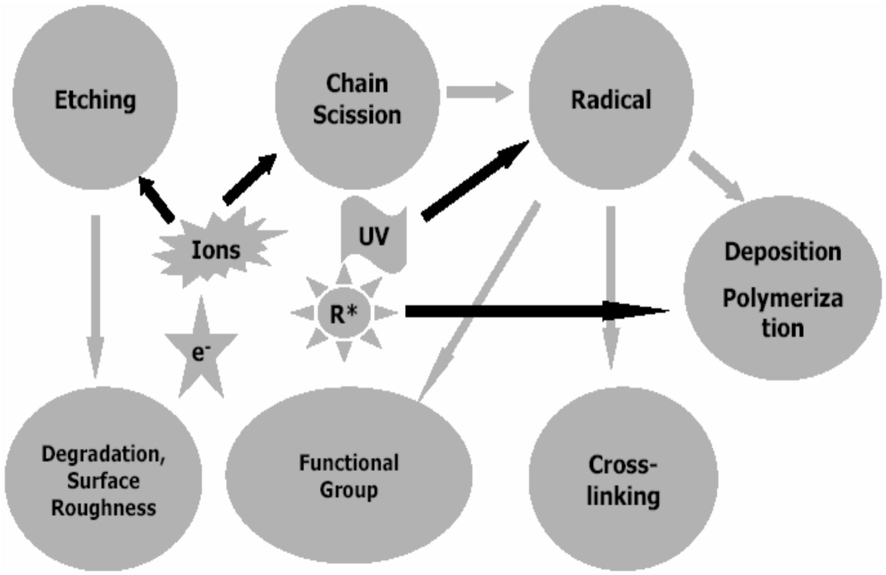


Figure 1.24 Mechanism of plasma-substrate interaction

Coating, deposition or polymerization Coating and layering are synonymous terms for applying films on textiles substrate by using plasma activated gasses. The main advantages of plasma treatment are the extremely short treatment time and low application temperatures; water or solvents respect to drying steps after plasma finishing can be avoided as per Hua Zou, et al., in 2008 [110].

1.5.3 Garment processing stage

Applying chemical finishes to garments is usually accomplished using exhaustible finishes (softeners, antimicrobials, ultra violet (UV) absorbers, and so on), which are added to the bath of the garment processing machine after all other garment wet processing steps have been completed. However, occasionally, a non-exhaustible finish such as an easy care finish is desired. Special procedures have been developed for this situation. One approach is to extract as much water as possible from the garments and then immerse them into the finish solution, either in a separate trough or in the garment machine itself, followed by further extraction, drying and curing. A second approach is to spray a precise amount of finish solution into the garment processing machine after water extraction. Even distribution of finish is accomplished by rotating the garments long enough to allow the finish to migrate throughout the garment. Drying and curing complete the process. Both methods have been demonstrated commercially, but the spray procedure requires fitting existing garment machines with the precision spraying attachment, while the immersion procedure involves less capital investment, but consumes more chemical finish [107].

1.5.4 Characterization of polymer nano composites

The characterization methods used in the analysis of the chemical structure, microstructure and morphology, as well as the physical properties, of the nanocomposites are varied. To fully understand structure-property relationships, several characterization techniques are often employed. The properties of the nanocomposites strongly depend on their composition, the size of the particles, interfacial interaction, etc. The interfacial interaction between polymer and silica (which depends on the preparative procedure) strongly affects the mechanical, thermal, and other properties of the nanocomposites.

TEM, SEM, and AFM are three powerful microscopy techniques to observe the morphology of nanocomposites. Crystallization behaviors of the silica nanoparticle-filled composites are usually studied by DSC. The chemical structure of polymer/silica nanocomposites is generally identified by FTIR and solid-state NMR spectra. Thermal properties of materials are change with temperature. They are studied by thermal analysis techniques, which include DSC, TGA, DTA, dielectric thermal analysis, since one of the primary reasons for adding inorganic fillers to polymers is to improve their mechanical performance, and the mechanical properties of polymer nanocomposites are most concerned. Therefore, it is usually necessary to characterize the mechanical properties of nanocomposites from different viewpoints. Several criteria, including tensile strength, impact strength, flexural strength, hardness, fracture toughness, and so forth, have been used to evaluate the nanocomposites as per Russell, et al., in 2002 [111].

1.6 NANO TEXTILE RELATED RESEARCH

Nanotechnology is an emerging interdisciplinary technology that has been booming in many areas during the recent decade. Nanotechnology endeavours are aimed at manipulating atoms, molecules and nano-size particles in a precise and controlled manner in order to build materials with fundamentally new organization and novel properties.

Nanotechnology is called a “bottom up” technology by which bulk materials can be built precisely in tiny building blocks, different from traditional manufacture “top down” technology. Therefore, resultant materials have fewer defects and higher quality. The fundamentals of nanotechnology lie in the fact that properties of substances dramatically change when their size is reduced to the nanometre range. When a bulk material is divided into small size particles with one or more dimension (length, width or thickness) in the nanometre range or even smaller, the individual particles exhibit unexpected properties, different from those of the bulk material. It is known that atoms and molecules possess totally different behaviours than those of bulk materials; while the properties of the former are described by quantum mechanics, the properties of the latter are governed by classic mechanism. With only a reduction of size and no change in substance, fundamental characteristics such as electrical conductivity, colour, strength and melting point can all change. Therefore nanomaterials show promising application potentials in a variety of industrial branches such as chemistry, electronics, medicine, automotive, cosmetics or the food sector. For example, ceramics, which normally are brittle, can easily be made deformable when their grain size is reduced to the low nanometre range. Moreover, a small amount of nanosize species can interfere with matrix polymer bringing up the performance of resultant system to an unprecedented level. These are the reasons why nanotechnology has attracted large amounts of research activity and media attention

For the present study literatures were sorted according to the possible textile-functions which the research group tried to achieve. For each function, the papers were then reviewed with regard to used NP, applied production methods and the integration into the textile matrix in the finished fabric. In some of the studied papers, the incorporated structure or particles which were called "nano" by the authors were far bigger than 100nm and therefore actually out of the scale which is defined in section 1.2. The resulting nano-particles are integrated into a fibrous web, comprised of bigger, interrelated structures. We assumed that in these cases, the potential risks of an exposure to nano-particles or nanostructures would not be bigger than in conventional textiles.

1.7 APPLICATION FIELDS AND COMMERCIAL PRODUCTS

The possible commercial applications described in section 1.2. are based on propositions made in the examined research papers and on an Internet research for manufactures who claim to use nanoengineering in their products. The Internet research was conducted by reviewing different existing online consumer inventories and nanotechnology related news pages. A list of the screened inventories and pages is added in the Appendix. Information about the used NP or the nanostructure in the commercially available products is based on statements of the manufacturer. Commercial products for industrial clients as for example nanoengineered coating agents or textile additives are included into the listed applications, not included are textile coating or impregnation agents for the end consumer, as their not considered being "textile products".

1.7.1 Nano engineered textiles and their commercial applications

The following chapter describes the nanotechnology related research on the Web of Science with the aim to draw a spectrum of the textile functions which might be achieved trough nanoengineering. It points out the different NP and production methods that are currently under investigation. The mechanism that leads to the desired effect is shortly described for each textile function together with the incorporated NP/nanostructure, the textile matrix, the applied production method and the form in which the NP occurs in the finished fabric. An overview on which NP can be used to achieve a certain textile function is given in following section.

The commercial applications of the different functional textiles described in the chapter are based on the propositions in the examined research papers and on an Internet research for available nanoengineered consumer goods. The proposed products are assigned to the following product groups: Apparel, protective clothing, interior trim and upholstery, sports and leisure, household, cosmetics, medical appliances, construction materials, industrial uses and auxiliary/intermediate products for industrial processes. The last product group includes all products which are not sold directly to the end consumer but which are purchased by industrial clients and used during the production process of a nanoengineered end product. Examples for such auxiliary or intermediate products would be textile additives, fabrics that are processed on into apparel or furniture, or also licenses for the use of a certain production procedure or technology.

1.7.1.1 Conductive textiles

Antistatic or electromagnetic shielding functions in textiles can be achieved by increasing the conductivity of the fibers. Synthetic textile polymers, as for example polypropylene (PP) or polyethylene (PE), generally have a rather low electric conductivity and therefore act as isolators. To be able to create a conductive material which still shows the in terms of manufacturing favorable mechanical properties of the polymers, small metal particles, conductive polymers (e.g. polypyrrole, polyanilline, polythiophen) or also carbon nanoparticles (Carbon Nanotubes (CNT), Carbon Black (CB)) can be included into the polymer matrix quted by Lubben in 2005 [112].

One example for the possibility to increase the conductivity of textiles by using metal NP is the work of Wei, Q.F., et al., in 2006 [113] where the production of a nanostructured copper-coating on the surface of polypropylene (PP) and polyamide (PA) fibers led to better surface conductivity. As reported by Hwang, Muth, and Ghosh, in 2007 [114] the same effect can be achieved by the dispersion of CB particles into a polymer solution and subsequent electrospinning. For the integration of CNT into textile relevant polymers, efforts have been made by research groups around the world Gottschalk, 2006 [115]. Chang, et al., 2005; Hagenmueller, et al.,2003; Dalton, et al.,2004 [116-118] stated that most of the examined research papers focused on the effect on the mechanical properties, as for example increased tensile strength or higher elasticity, but it is also possible to produce fibers with increased electrical conductivity trough the integration of CNT.

Table 1.2 Nano materials and techniques available for conductive textiles

NP / Nano-structure	Textile material	Production method	Integration into the textile matrix
Cu	PP/ PA	Physical vapor deposition: sputter coating	Homogeneous Cu-layer, some nm thick
CB (in dispersion: 400-1700nm)	Polyurethane (PU)	Electrospinning of PU dispersion with CB	CB-nanoparticles in nm thin PU fibre
CNT	Not specified	Dip or spray coating of finished textile	Some SWCNT cluster on the fibre surface
	PP	Dip-coating with polyaniline / CNT dispersion	CNT in polyaniline matrix and as composite layer on and in PP hollow fibre
	-	Wet spinning of dispersive CNT / polyaniline solution	Polyaniline CNT composite fibre
Polypyrrole	Viscose, Wool	Vapor or solution Polymerization of polypyrrole on the textile	Homogenous layer of polypyrrole on the fabric, partial penetration of polypyrrole into fibre interior, Aggregates of polypyrrole on the fibre surface, complete penetration of polypyrrole into interior of fibre.
	Wool	Hand brushing , dip or spray coating of finished textile with a polypyrrole emulsion	Non homogeneous, nanoporous polypyrrole layer
Polyaniline	Polyester	Solution polymerization	Polyaniline layer on PET fibre

Panhuis, M.I.H., 2006 [119] reports that such fiber were produced in different research projects by using polyaniline composites with incorporated CNT: Spinks, et al., 2006 [120] and Mottaghitalab, Spinks, & Wallace, 2005 [121] obtained fibers with increased conductivity trough the production of a CNT containing polyaniline dispersion and subsequent wet spinning. Spinks, G.M., et al., 2005 [122] achieved the same effect by dip-coating hollow PP fibers with CNT containing polyaniline dispersion. Hecht, Hu, and Gruner in 2007 [123] obtained textiles with increased conductivity trough dip and spray coating the finished fabric with a dispersive CNT solution. Another possibility is the coating of finished textiles with nano-thin layers of conductive polymers, as for example polypyrrole or polyaniline. Polypyrrole was either applied by hand brushing, by dip- or spray- coating the finished textile with a nanoparticulate emulsion. Foitzik, Kaynak and Pfeffer, 2006 [124] or by solution- or vapor polymerization of the polypyrrole on the textile surface by Dall'Acqua, et al., 2006 [125]. Polyaniline was applied by solution polymerization by Armes, et al., 1991 [126].

Possible applications

Conductive textiles could find applications in the following product groups: Apparel, interior trim and upholstery, protective clothing and products for industrial uses. In the apparel sector, conductive textiles can be used to produce antistatic clothing, Lubben, 2005; Kohler, et al.,2007 [112,169]. Furthermore, they might be used to develop "smart-clothes" with integrated sensors which could for example measure heart rate or body movements. The conductive textiles might thereby take the role of the sensor (textiles that increase or decrease their conductivity, e.g. when stress is applied) or be used to transmit electronic signals form other sensors to integrated electronic devices, Kim, and Lewis,2003 [170]. In the product group related to interior trim and upholstery, conductive fabrics could be used to produce antistatic furniture textiles as per Nanotex., 2007 [171]. Another possible application would consist in the production of carpets or floor coverings with electromagnetic shielding functions which could protect underlying electronic devices, Bekaert, 2007 [172]. In industrial processes, conductive textiles could find applications in antistatic dust filters and bulk containers which would prevent explosions caused by spark discharges, Bekaert, 2007 [172]. Possible applications in the production of protective clothing include suits for the protection of static discharges or clothing with electromagnetic shielding functions by Mahltig, Haufe, and Bottcher, 2005 [134].

Available products

Related to the above described product groups, the following commercially available goods could be found on the Internet: Auxiliary products include production methods that yield antistatic and conductive textile properties or additives that promise the same effect stated by Nanotex. 2007; Eeon technology, 2007;nanogate, 2007 [171,173,174]. Eeon technology, 2007 [173] declares to use polypyrrole and polyaniline. Consumer end products could be found in the apparel sector where nanoengineered clothing is available in form of antistatic jackets, pants, caps and gloves, Lands End, 2007 [175]. Sensatex, 2007 [176] furthermore offers "SmartShirts" made of conductive fabric with included sensors to measure heart rate, body temperature or respiration.

1.7.1.2 Reinforced textiles

Nanotechnology can be used to change and improve the mechanical properties of textile fibers according to the corresponding application. Such properties include increased tensile strength, elasticity or fiber stiffness collectively stated by Hagenmueller, et al., 2003; Poncharal, et al., 1999; Stegmaier, 2006; Kalarikkal, Sankar, and Ifju, 2006 [117,127-129]. These properties can lead to the production of stronger or more elastic textiles or increase the tear and wear resistance of a fabric.

The probably most investigated way of improving the mechanical properties of textiles trough nanoengineering is the integration of CNT which was found to increase tensile strength or elasticity significantly as observed by Chang, et al., 2005; Hagenmueller, et al.,2003; Dalton, et al.,2004; Poncharal, et al., 1999; Miaudet, et al.,2005 [116-118, 127,130]. Hagenmueller, et al., 2003 [117] stated that CNT reinforced fibers were produced by melt compounding CNT with polystyrene (PS) and polypropylene (PP) or the production of a CNT-PP Masterbatch, Chang, et al., 2005 [116], both followed by melt spinning. Miaudet, et al., 2005 [130] uses the co-flowing of a CNT dispersion during solution spinning to produce reinforced polyvinyl-alcohol (PVA) fibers. Dalton, et al., 2004 [118] reports the production of PVA-CNT-composite fibers with increased strength by a modified solution spinning process. CNT can also be applied to the fabric by spray-coating or simply dipping the textile into a CNT solution Hecht, Hu, and Gruner, 2007 [123].

Table 1.3 Nano materials and techniques to enhance mechanical properties of textiles

NP/ Nanostructure	Textile material	Production method	Integration into the textile matrix
CNT	PVA	Co-flowing stream of CNT-dispersion during solution spinning	No information
	PVA	modified solution spinning process of CNT dispersion	PVA coated CNT
	PS, PP	melt compounding and subsequent melt spinning	PS CNT composite
	not specified	dip or spray coating of finished textile	Network of CNT clusters on fibre surface
ZnO	Cotton	coating of finished fabric by dip pad dry cure method	ZnO NP coating
Al_2O_3	not specified	dip coating of finished fabric	Single Al_2O_3 particles on the surface
SiO_2	polyester	coating of finished fabric by sol-gel process	Nanoporous SiO_2 coating as a crosslinked network
Polybutylacrylate (PBA)-NP1)	not specified	production of PBA/PS nanocomposite by two stage solution polymerization; dip coating of the finished fabric with aqueous dispersion of the obtained composite	PBA/PS nanocomposite coating

Apart from CNT, also other NP were reported to alter or improve the mechanical properties of the textile fibers. The appliance of a ZnO nanoparticle based coating was observed to increase the stiffness of a fabric. The coating was thereby applied by dipping the fabric into a nanodispersive ZnO solution and a subsequent dry-pad-cure process by Yadav, et al., 2005 [131]. Kalarikkal, Sankar, and Lfju, 2006 [132] used a similar process to provide different textile materials with a nanoparticulate Al_2O_3 coating which led to an increase in fracture toughness. To optimize the mechanical properties of carpet backings, Campos, et al., 2006 [133] used a PS - composite containing polybutylacrylate (PBA)-NP as coating. Mahltig, Haufe, and Bottcher, 2005 [134] furthermore reports the possibility to increase the abrasion stability of polyester by treating the finished fabric with a SiO_2 coating. The coating is produced trough a sol-gel process which involves the production of a nanoparticulate SiO_2 dispersion.

Possible applications

Reinforced fibers could find applications in the apparel industry, the fabrication of upholstery, in geotextiles Lubben, 2005 [112], industrial textiles or the production of protective clothing by Mahltig, Haufe, and Bottcher, 2005 [134]. In the apparel industry and upholstery sector, such fibers might be used to produce tear-and wear-resistant clothes or furniture textiles. Their application in the production of protective clothing could furthermore lead to the development of stronger and more lightweight safety harnesses and bullet proof vests, Ward,2003 [167]. In a lightweight military battle suit which is able to withstand blasts and which is currently under development, reinforced fibers would fulfill a similar function as web.mit.edu [177]. Nano-reinforced fibers could also be used to produce stronger and more durable Geotextiles which are used in the construction sector for sealing, isolation or erosion control by Lubben, 2005 [112]. In industrial textiles, the nano-reinforced fibers could find applications in filters or sieves with improved abrasion stability, as they are used in paper production as per Mahltig, Haufe, and Bottcher, 2005 [134].

Available products

In the conducted Internet research, the following two commercially available products could be found: CNT-reinforced fibers for antiballistic purposes (e.g. bullet proof vests or doors) US global Nanospace, 2007 [178] and CNT containing polymer additives for the production of reinforced textiles Zyvexpro Materials,2007 [179].

1.7.1.3 Antibacterial textiles

According to Mahltig, Haufe, and Bottcher, 2005 [134], biocidal textiles can basically be divided into three groups:

1) Textiles with photoactive properties
2) Textiles with non diffusible biocides
3) Textiles with controlled release of the embedded biocide

One example for the first group would be the coating of a fabric with TiO_2 Daoud, Xin, and Zhang, 2005 [135]. Trough the absorption of light, the valence electrons of TiO_2 can be lifted into a higher energetic state, which produces excited charge carriers, an electron and a positively charged electron-hole. The positively charged holes can cause the oxidation of organic molecules while the electrons can react with oxygen and lead to the formation of hyperoxid radicals which also attack and oxidize the cell membranes of microorganisms as per Parkin, and Palgrave, 2004 [136]. The described photocatalytic process can lead to the degradation of stains, so that TiO_2 can also be used for the production of self cleaning textiles.

Table 1.4 , Nano materials & techniques for antibacterial textiles

NP /Nanostructure	Textile matrix	Production method	Integration into the textile matrix
Ag	polyester, cotton, spandex	coating of finished textile by dip-pad-dry-cure method	some Ag NP on textile surface, partial diffusion into the textile
	PA , silk	production of Ag/PP Masterbatch, melt spinning	PA/Ag nanocomposite in PP matrix
	PP	melt compounding of Ag/PP	PP/Ag nanocomposite in PP matrix
	PP	production of Ag/PP Masterbatch, melt spinning	PP/Ag nanocomposite in PP matrix
	not specified	acetylene/Ag coating of finished fabric: Plasma polymerization of acetylene with co-sputtering of Ag-NP	some Ag NP on nanoporous acetylene coating
TiO_2	Cotton, Cellulose fibers	coating of finished fabric by sol gel process	TiO_2 NP on textile surface Some TiO_2 NP on cotton
	Cotton	coating of finished fabric by plasma enhanced chemical vapor deposition	1 nm TiO_2 coating on fiber
Ag + TiO_2	Cotton	coating of finished textile by dip-pad-dry-cure method	Some Ag NP on textile surface
ZnO	Cotton	coating of finished textile by dip-pad-dry-cure method	Starch matrix coating with ZnO NP
Chitosan-polybutylacrylate	Cotton	Production of NP with a PBA core and a chitosan shell,	PBA chitosan NP coating

(PBA)-NP1)		coating of finished textile with these NP by dip-pad-dry cure method	
SiO_2 matrix with embedded biocides	not specified	Addition of biocides to Si nanosol, coating of finished textile by sol-gel process	Nanoporous SiO_2 coating as a crosslinked network

In the textiles of the second group, the biocide is immobilized in the textile-matrix itself or in the matrix of a coating. The antibacterial effect is then caused by the interaction between the positively charged biocide and the negatively charged cell membranes which damages the microorganism and inhibits their growth and reproduction as reported by Mahltig, Haufe, and Bottcher, 2005 [134].

The third group is comprised of coatings where the biocides (e.g. triclosan, Ag^+, Cu^{2+}) diffuse out of the matrix. In the case of metallic antibacterial agents, the nanoparticles in the matrix are oxidized by air. The formed cations then diffuse out of the matrix and lead to the inhibition of bacterial growth, Mahltig, Haufe, and Bottcher, 2005 [134].

In the majority of the examined research papers [135,137-145], Ag, TiO_2 or a combination of both NP were used to achieve a biocidal effect. In a research paper by Vigneshwaran, et al., 2006 [146], the desired effect in the textile is reached trough the integration of ZnO nanoparticles while Ye, et al., 2005 [147] uses Chitosan Core-Shell-NP to obtain an antibacterial coating for cotton fabrics. Mahltig, Haufe, and Bottcher, 2005 [134] furthermore mentions the possibility of including different organic (e.g. Triclosan, chitosan) or inorganic biocides (Ag, Cu), into the matrix of a silica coating.

In most of the examined research papers, TiO_2 is applied to the textile by sol-gel processes Daoud, and Xin, 2004; Qi, et al., 2006; Bozzi, Yuranova, and Kiwi, 2005; Daoud, and Xin, 2004 [138,139,144,148]. In a first step, a TiO_2 dispersion with a particle size of about 50 nm, a so called nanosol, is prepared by Mahltig, Haufe, and Bottcher, 2005 [134]. The fiber, yarn or finished fabric is then dipped into the nanosol which leads to the aggregation of the particles on the textile surface and the formation of a solvent-containing lyogel layer. The lyogel is then heated to remove the solvent and a solid, porous xerogel layer is obtained by Mahltig, Haufe, and Bottcher, 2005 [134]. The antibacterial coatings mentioned by Mahltig, Haufe, and Bottcher, 2005 [134], where the biocides are embedded into a Si-matrix are also the result of sol-gel processes. Yuranova, 2006; Vigneshwaran, et al., 2006 [140,146] and Lee, Yeo, and Jeong, 2003 [141] use different dip-pad-dry-cure methods to provide the textile with an antibacterial Ag, Ag/TiO_2 or ZnO coatings. The textile is dipped into a nanosol and afterwards dried and heated to remove the solvent. Dubas, Kumlangdudsana, and Potiyaraj, 2006 142 obtains an antibacterial coating using a layer by layer deposition method where the finished fabric is dipped sequentially into an Ag-nanosol and a polyelectrolyte solution. Other possible methods to produce an antibacterial coating include the co-sputtering of Ag-NP during plasma polymerization Hegemann, Hossain, and Balazs, 2007 [143] or the deposition of TiO_2 NP by chemical vapor deposition Szymanowski, H., et al., 2005 [149]. In contrast to procedures in which NP are applied as a coating, it is also possible to incorporate them at an earlier stage of the manufacturing process, for example trough direct melt compounding of Ag and the textile polymer as per Jeong, Yeo, and Yi, 2005 [145] or the production of Ag /PP Masterbatches and subsequent melt spinning, Yeo, Lee, and Jeong, 2003 [137].

Possible applications

The product groups with possible applications for antibacterial textiles include apparel, interior trim and upholstery, sports and leisure, automotive interiors, protective clothing, medical textiles and cosmetics. In apparel-, interior trim- and automotive applications, these functional textiles could be used to produce "self-cleaning" or "anti-odour" clothes, furniture textiles or automotive interiors, Daoud, and Xin,2004 [138]. In household products, antibacterial textiles could possibly be incorporated into kitchen clothes, sponges or towels. In the medical sector, possible products include antibacterial wound dressings, patient dresses, bed lines or reusable surgical gloves and masks, Daoud, and Xin,2004; Sun, 2006 [138,180]. Further thinkable applications are protective face masks and suits against biohazards by Sun, 2006 [180] or cosmetic products as antibacterial face masks or toothbrushe as per Mahltig, Haufe, and Bottcher, 2005 [134] .

Available products

With exception of the products related to the automotive sector, commercially available goods could be found for all of the above mentioned applications. In the apparel sector, antibacterial or self-cleaning shoe insoles, socks, underwear a Poloshirts can be purchased by various manufacturers as per Goodweaver Textile; United Textile Mills; AgActive; Nanobabies; Song Sing Nanotechnology; Nanoinfinity Nanotech [181-186]. As examples for products related to interior trim and upholstery, antibacterial bed sheets and baby blankets were found by AgActive ; Greenyarn technology [187,188]. In the product group related to the medical sector, biocidal wound dressings are available as per Smith and Nephew [189] while cosmetic appliances include toothbrushes and face masks as per Nanover; Song Sing Nanotechnology; Nanoinfinity Nanotech [185,186,190]. Also available are protective face masks against bacterial and viral infections, Emergency filtration products inc. [191]. Various companies furthermore offer their industrial clients textile treatment technologies, additives or fabrics with antibacterial properties. Thomson Research Associates [192] offers an antibacterial textile treatment which is used on a wide range of products including antibacterial underwear, kitchen sponges or clothes, bed sheets, towels, carpets or sport helmet paddings. Nanopool [193] and Nanogate [194] both offer antibacterial coating technologies, while antibacterial polymer masterbatches are available from Murray, 2006 [195]. Antibacterial fabrics which can be processed into outdoor clothing or household products were developed by HeiQ Materials Ltd [196] and Polartec [197].

1.7.1.4 Self cleaning textiles

"Self cleaning" properties in textiles can basically be achieved by three different processes. One is the integration of NP that act as photocatalyst and are able to degrade organic dirt and stains as per Parkin, and Palgrave, 2004 & Yeo, Lee, and Jeong, 2003 [136,137]. (Section A) The second method is the production of superhydrophobic surfaces which provide stain and grime repellency and are "self-cleaned" by the rolling water drops that collect dust and other debris, Yeo, Lee, and Jeong, 2003; Feng, et al.,2002 [137,151] (Section B). Furthermore, antiadhesive surfaces with repellent properties towards specific compounds or substances, as for example proteins, can be designed trough nanoengineering as per Mahltig, Haufe, and Bottcher, 2005 [134] (Section C).

A) Photocatalytic coatings

In the examined research papers, stain degrading properties in textiles were achieved by coating the fabric with nanoparticulate TiO_2. A TiO_2 nanosol was produced and applied to the fabric by the dip-pad-dry-cure technique. The textile fabrics were comprised of cotton, wool-polyamide and polyester fibers by Parkin, and Palgrave, 2004; Bozzi, Yuranova, and Kiwi, 2005; Yuranova, 2006; Jeong, Yeo, and Yi, 2005 [136,139,140,145] then exposed to light, the electrons of TiO_2 are lifted into an excited state and electron/hole pairs in the valence band region are formed which leads to the formation of superoxid and hydroxyl radicals as per Parkin, and Palgrave, 2004 [136]. These radicals are then able to oxidize organic material adsorbed at the surface and lead to the degradation of stains. As the formed radicals also attack the membranes of microorganisms, textiles which are coated with TiO_2 also show antibacterial effects.

Table 1.5 Nano materials & techniques for self cleaning textiles

NP /Nanostructure	Textile matrix	Production method	Integration into the textile matrix
TiO_2	cotton, wool/PA, polyester	coating of finished fabric by sol gel process	TiO_2 NP on textile surface some TiO_2 NP on Cotton

B) Hydrophobic surfaces

Attempts to produce super hydrophobic textile surfaces have been made by research groups trough the integration of CNT, silica-NP (Si-NP) and fluoro containing polymer-NP, Yu, et al., 2007; Huang, Chao, and Liao, 2004; Zhang, 2003 [152-154]. In all three cases, the NP were applied to the textile fabric in form of a coating: Zhang, 2003 [154] produced an emulsion containing fluoroacrylate copolymer NP which was then applied as a coating to nylon and polyester fabrics. Si-NP were applied to cotton fabrics by the production of a nanosol and a subsequent dip-pad-dry-cure-process as per Krogman, et al.,2007 [155]. In the third case, hydrophobic properties could be achieved by producing artificial lotus leaf structures on cotton fiber-surfaces trough the application of modified CNT using a common dip-dry-cure method by Yu, et al., 2007 [152].

Table 1.6 Nano materials & techniques for hydrophobic textiles

NP /Nanostructure	Textile matrix	Production method	Integration into the textile matrix
CNT	Cotton	coating of finished textile by dip-dry-cure method	absorbed CNT on Cotton Network of CNT cluster around every fibre
CNT grafted with Polybutylacrylate (PBA)	Cotton	grafting of CNT with PBA, coating of finished textile by dip-dry-cure method	absorbed CNT on Cotton PBA shells penetrate in cotton and forming a durable linkage
SiO_2 (*SiO_2 particles after the coating: 60-200nm*)	Cotton	production of SiO_2 nanodispersion, coating of finished textile by dip-pad-dry-cure method	some SiO_2 aggregates on cotton

fluoroacrylate-NP	polyester, PA	coating of finished textile with nanodispersive fluoroacrylate-polymer emulsion	Fluoroacrylate Coating

C) Surfaces with antiadhesive properties

Mahltig, Haufe, and Bottcher, 2005 [134] reports the production of antiadhesive wound dressings by coating viscose fabrics with a modified SiO_2 coating.

Table 1.7 Nano materials & techniques for antiadhesive textiles

NP /Nanostructure	Textile matrix	Production method	Integration into the textile matrix
SiO_2 matrix with embedded hexadecyl-triethoxysilane	Viscose	Addition of hexadecyl-triethoxysilane to Si-nanosol, coating of finished textile by sol-gel process	SiO_2 network matrix

Possible applications

Textiles with anitadhesive properties could find applications in dirt repellent or self cleaning apparel and furniture as per Liu, Y., et al.,2007 [150]. Also part of this group of functional textiles are hydrophobic materials as per Zhang, J.,et at.,2003 [154] which could be used in waterproof sports or outdoor clothing. Schoeller Textile AG [199] proposes the production of vascular grafts or arterial prostheses with blood platelet adhesion resistant properties as application for the developed protein coated cotton. Consumer goods could therefore possibly be found in the following products groups: Apparel, sports and leisure, interior trim and upholstery and medical appliances.

Available products

For the products proposed by the research papers, providers of the following consumer goods were found: Stain repellent, quick drying apparel, Shenzhen Kangnami clothing ; Woodrow Wilson International NanoTousers ; Woodrow Wilson International Stain resistant tie; NanoTsunami; Woodrow Wilson International Super stain resistant Gripper Cushions, [200-204] or furniture Franz Ziener GMBH [205] and waterproof, grime repellent outdoor clothing, by Beyond clothing; Woodrow Wilson International Bike and Hike Pants; Schoeller Textile AG, [206-208]. Apart from these applications, the following commercial end products were found: Esasy to clean luggage as stated by

Pro Idee [209], water repellent umbrellas by Percent AG [210] and cleaning clothes with dirt repellent properties by nanoproofed [211]. Furthermore, various auxiliary products for industrial production processes are commercially available. Nanotec [212] offer coating technologies for easy to clean, stain repellent textile surfaces while industrial coating agents, which promise the same effect can be purchased from Nano-X [213] and Globetrotter Ausrustung [214].

1.7.1.5 Hydrophilic textiles

As described in sub section 4, nanoengineering can lead to the production of hydrophobic surface, but also the opposite, the development of hydrophilic surfaces is possible. Apart from the attempts to obtain moisture absorbing functions in a textile which are described in this paragraph, hydrophilic surface modifications can also improve the dyeing properties of a fabric. The research papers related to this topic are described in section 4. One possibility to obtain a textile with moisture absorbing functions might be the integration of TiO_2 which increases the water absorbance at the surface through a photocatalytic process. The "electron holes" that emerge when TiO_2 valence electrons are lifted into an excited state oxidize lattice oxygen, leaving vacancies that can be filled by absorbing water as per Mahltig, Haufe, and Bottcher, 2005 [134]. Krogman, et al., 2007 [155] obtained hydrophilic properties by the deposition of thin films of TiO_2 alternating with poly(dimethyldiallylammonium chloride) (PDAC) on polyethylene fibers by a layer by layer deposition method.

Table 1.8 Nano materials & techniques for hydrophilic textiles

NP / Nano-structure	Textile matrix	Production method	Integration into the textile matrix
TiO_2	PE	layer by layer deposition	coating with negative loaded TiO_2-NP layer and positive loaded poly(dimethyldiallyl-ammonium chloride) (PDAC)

Possible applications

In the examined research papers no propositions for commercial applications of nanoengineered textiles with moisture absorbing properties were made. Thinkable commercial products could be found in the apparel and sports industry where these textiles might be used to produce quick drying, transpiration wicking sports- or outdoor clothing.

Available products

For the above described applications, various commercial products could be found on the Internet. They include various moisture wicking outdoor jackets, caps and trousers by Woodrow Wilson International: New Balance [215] as well as sport pants, moisture absorbing underwear or water shorts, by Edi Bauer; Nanotex [216,217]. NanoTsunami [218] furthermore offers the technology for the production of fabrics which can be incorporated into all kinds of outdoor or sport clothing and promises to show moisture wicking properties.

1.7.1.6 Dyeability

In connection with the dyeing of textiles, nanoengineering can fulfill the following functions:

- Nanoparticulate pigments can directly be used as dyes, Li, D. and G. Sun, 2007 [156].
- Textile surfaces can be treated with nanostructured coatings to render them hydrophilic and improve their colourability, Bozzi, Yuranova, and Kiwi, 2005, [144].
- Dyes can be included into nano-thin coatings to improve bleaching resistance and leaching stability, Mahltig, Haufe, and Bottcher, 2005 [134].

The use of nanoparticles as dyes is reported by Li, D. and G. Sun, 2007 [156] where cotton, acrylic, and nylon fibers are dyed with surface modified carbon black (CB). The hydrophobic CB particles were thereby modified to obtain carboxylic surface structures which made the absorption of the CB to the textile fibers possible. To improve the colourability of textiles surfaces, Hegemann, Hossain, and Balazs, 2007 [143] produces a hydrophilic nano-thin coating trough plasma polymerization of C_2H_2 mixed with ammonia, the resulting hydrophilic coating and the included functional groups can enable substrate independent dyeing. After coating the surface of polyester fabrics, the textile was dyed with acid dyestuffs. Without surface modification, this would be impossible due to the lack of amino groups on the polyester surface which are needed for the dye-fiber reaction mechanism of this group of dyestuffs Hegemann, Hossain, and Balazs, 2007 [143].

Table 1.9 Nano materials & techniques for improving dyeability

NP / Nanostructure	Textile matrix	Production method	Integration into the textile matrix
SiO_2 matrix with embedded dyes or UV absorbers	not specified	addition of UV-absorbers to Si nanosol, coating of finished textile by sol-gel process	nanoporous SiO_2 matrix with dye and UV absorber
CB	polyamid, cotton, acrylic fibers	dying of finished textiles with CB by exhaustion process	CB with COOH for hydrogen bonding to cellulose
nanoporous hydrocarbon coating	polyester	coating of finished textile by plasma polymerization	nanoporous, crosslinked hydrocarbon network with nitrogen functional groups (a-C:H:N)

As mentioned above, nanoengineering can also be used to improve the bleaching resistance and leaching stability of textiles dyes Mahltig, Haufe, and Bottcher, 2005 [134]. These properties can be achieved trough the integration of dyes into an inorganic nanosol (silica or metal-oxid nanosols) which is then applied to the textile as a coating. The immobilization of the dye in the nanosol matrix significantly reduces the leaching fastness Mahltig, Haufe, and Bottcher, 2005 [134]. Particularly good results can be achieved by using mixed metal oxide nanosols (e.g. aluminium or titanium oxides in a silica oxide sol) which are able to form complexes with anionic dyes. In terms of bleaching resistance, the nanosol-dye-coatings can be optimized by the addition of an organic UV-absorber to the nanosol Mahltig, Haufe, and Bottcher, 2005 [134].

Possible applications

The examined research papers do not make any propositions for commercial applications of textiles with improved colourability. Such fabrics could theoretically be incorporated into all kinds of clothing or furniture textiles as well as into textile outdoor products, e.g. tent- or parasol-fabrics. The corresponding product groups would therefore include apparel, interior trim and upholstery as well as the sports and leisure.

Available products

For these applications, no commercially available products could be found in the conducted Internet research.

1.7.1.7 UV-blocking textiles

The UV blocking properties of textiles can be improved by the integration of metal particles, dyes, pigments or the application of a UV-absorbing finish to the fabric as per Vigneshwaran, 2007 [157]. The examined research paper all focus on the application of such finishes to achieve the desired effect. Yadav, et al., 2006 [131] reports the application of a nanoparticulate ZnO- finish to cotton fabrics by means of a dip-pad-dry-cure-method. A similar coating, where soluble starch was added during the synthesis of ZnO-NP to inhibit their agglomeration also led to enhanced UV-blocking, as reported by Vigneshwaran, et al.,2006 [146]. Another possibility to produce cotton fabrics with UV-blocking properties is their coating with a nanoparticulate TiO_2 film by sol-gel-process using the dip-pad-dry-cure method as stated by Daoud, and Xin,2004 [148].

Apart from the options described above by Mahltig, Haufe, and Bottcher, 2005 [134], further mention the possibility of including organic UV absorbers (e.g. benzotrialzoles) into a Si-nanosol which can then be applied to the fabric using sol-gel techniques.

Table 1.10 Nano materials & techniques for UV-blocking textiles

NP / Nano-structure	Textile matrix	Production method	Integration into the textile matrix
ZnO	cotton	coating of finished fabric by dip-pad-dry-cure method	no information
TiO_2	cotton	coating of finished fabric by sol gel process	Some TiO_2-NP on the fibers
SiO_2 matrix with embedded UV-absorbers	not specified	addition of UV-absorber to Si- nanosol, coating of finished textile by sol-gel process	nanoporous SiO_2 coating as a crosslinked network with UV absorbers

<u>Possible applications</u>

In the examined research papers, no propositions for commercial applications of UV-blocking textiles are made. Possible commercial applications could probably be found in apparel and sports wear with integrated sun protection or in the production of sun shields or parasols.

Available products

The following commercial applications could be found in the examined consumer inventories: In the sports and apparel sector, NanoTsunami [218] offers UV-blocking bathing NanoTsunami [218]. Further commercial applications were found in the product group related to auxiliary products for industrial processes: nanogate [219] and Tianjin Tianfang Investment Holding CO. [220] offer coating systems for the production of UV-blocking textiles while Luko International Technology [221] directly sells a fabric with the same properties that can be processed into Shirts or Sweaters. Nanogate [219] reports the launch of an industrial coating agent which leads to UV-blocking properties when applied to textile fabrics.

1.7.1.8 Flame retardant textiles

The integration of several kinds of nanocomposites have been found to cause flame retarding effects, Zhang, and Horrocks,2003 [158]. Due to its low price, many research projects focused on the production of montmorillonite-nanoclay containing composites to achieve these properties, Bourbigot, et al.,2004; Zhang, et al.,2006; Devaux, Rochery, and Bourbigot, 2002; Bourbigot, Devaux, and Flambard,2002; Marosi, et al.,2003 [159-163], but also boroxosiloxanes or Sb_2O_3 containing nanocomposites were reported to inhibit the combustion process, Zhang, and Horrocks,2003 [158]. A further possible method seems to be the use of CNT which led to enhanced flame retardance when incorporated into a ethylene-vinyl acetate (EVA) polymer-matrix as per Marosi, et al.,2003 [163]. The exact mechanism of the combustion inhibition caused by the nanoclays is not yet known, but it is presumed that while the polymer matrix is burned and gasified during combustion, the incorporated nanoclays accumulate at the surface and form a barrier to oxygen diffusion, thereby slowing down the burning process as per Zhang, and Horrocks,2003 [158]. According to Zhang, and Horrocks, 2003 [158], the integration of nanoclay-composites alone is not sufficient to provide a fabric with reliable combustion protection: The nanoclays do slow down the burning process and enhance the char formation, but they have no effect on the ignition tendency and after flaming properties.

Table 1.11 Nano materials & techniques for flame retardant textiles

NP / Nano-structure	Textile matrix	Production method	Integration into the textile matrix
montmorillonite	PA	melt blending and melt	exfoliated nanoclay

		spinning	
	PU, cotton	melt blending of PU and nanoclay, application of resulting nanocomposite as coating to cotton fabric	PU nanoclay matrix as cotton coating
	styrene acrylonitrile	melt blending and screw extrusion	intercalated and exfoliated nanoclays in styrene acrylonotrile matrix
	PP	melt compounding	no information
	PP	melt blending and compression molding	no information
Sb_3O_2	not specified	not specified	no information
Boroxosiloxane	PP	melt blending and compression molding	no information
CNT	ethylene-vinyl acetate (EVA)	melt blending of CNT and EVA	CNT in EVA matrix

Recent research indicates, that optimized properties can be achieved by combining the nanocomposites with low concentrations of conventional flame retardants, Zhang, et al.,2006; Marosi, et al.,2003 [160,163]. For the integration of the described nanocomposites into textile fabrics, mainly two process pathways are possible, Devaux, Rochery, and Bourbigot, 2002 [161]. For both application pathways, the nanoclay or nanoparticle is melt blended with the polymer material, Bourbigot, et al.,2004; Zhang, et al.,2006; Devaux, Rochery, and Bourbigot, 2002; Bourbigot, Devaux, and Flambard,2002; Marosi, et al.,2003 [159-163]. Before this process, the nanoclays have to be modified by replacing the (sodium-) cations found between the clay layers with other, sufficiently organophilic ions to make the integration and dispersion of the nanoclays in the polymer matrix possible as per Zhang, and Horrocks,2003 [158]. One possibility to incorporate these nanocomposites into textiles is by melt spinning them into yarns which can subsequently be knitted or woven to textile fabrics, Bourbigot, Devaux, and Flambard,2002 [162]. The second possibility is to apply the produced polymer-nanoclay composite as a coating to finished textiles Devaux, Rochery, and Bourbigot, 2002; Bourbigot, Devaux, and Flambard,2002 [161,162], as for example cotton or polyester fabrics.

Possible applications

In the examined research papers, no propositions for commercial applications of nanoengineered flame retardant textiles are made. Conventional flame retardant textiles already find application in a wide range of industrial branches as in the automotive or apparel industry, the manufacturing of interior trim and upholstery or the production of protective clothing. Examples for possible products would therefore include apparel made of synthetic textiles, protective clothing, carpets and other interior trim fabrics, seat cushions or linings for automotive interiors.

Available products

For the above mentioned applications, no consumer end products containing nano-engineered textiles were found in the Internet research. Concerning the offer of auxiliary products for industrial processes, nanoengineered, flame retardant textile additives for synthetic polymers are available from Woodrow Wilson Internatonal ,Nanorama [223] while a industrial coating agent for the production of flame retardant fabrics is sold by Nanocor [222].

1.7.1.9 Controlled release of active agents, drugs or fragrances

Nanoengineering can be used to produce fibers that act as carriers for drugs, fragrances or other active agents and enable the controlled release of the incorporated species. Research projects with the aim to produce antibacterial fabrics trough the controlled release of a biocidal agent are described in previous section, projects where the active species are not a biocide are described in this section. Persico, Carfagna, and Musto,2006 [166] used a montmorillonite-nanoclay as carrier for cosmetic jojoba oil substances to produce nylon fibers which could find applications in skin care products.

Table 1.12 Nano materials & techniques for textiles with controlled release of active agents

NP / Nano-structure	Textile matrix	Production method	Integration into the textile matrix
SiO_2 matrix with embedded active agents	not specified	addition of active agents to Si nanosol, coating of finished textile by sol-gel process	nanoporous SiO_2 coating as a crosslinked network
Montmorillonite	PA	melt compounding	exfoliated nanoclay in PA matrix

The jojoba oil and nanoclays were incorporated into the polyamid-matrix by direct melt compounding. Mahltig, Haufe, and Bottcher, 2005 [134] report the possibility of producing fibers with controlled release of different agents (e.g. drugs, ethereal oils, or insect repelling fragrances) by including them into a SiO_2-Nanosol coating.

Possible applications

Fibers with controlled release of fragrances or oils could find applications in apparel, cosmetics, home textiles, outdoor fabrics or medical appliances. Possible products would include cosmetic pads with integrated skin care products, insect repellent textiles for clothing or outdoor fabrics, medical textiles with therapeutical properties (e.g. drug releasing wound dressings) or so called fragrance emitting clothing or home-textiles, Mahltig, Haufe, and Bottcher, 2005 [134].

Available products

Commercially available products were found only in the cosmetic sector where Woodrow Wilson Internatonal, Nano Gold Mask [224] and Aspen Aerogels [225] offer facial masks with integrated cosmetics substances.

1.7.1.10 Insulating textiles

Possible applications

In the examined research papers, no propositions for commercial applications of nanoengineered insulating textiles are made. In the industrial sector, conventional textiles with insulating properties are used for the isolation of various technical appliances as for example steam vessels, pipelines or boilers. Furthermore, they can be used as construction material to reduce heat losses in houses and buildings. Thinkable applications of textiles with enhanced insulating properties might also be found in the apparel industry were these textiles could be used to produce jackets, pants, shoes or insoles for outdoor uses at low temperatures.

Available products

Daiichi Orimono Co. [226] offers different thermal insulating textiles for all of the above mentioned applications. Available consumer end products containing these fabrics include insulating blankets for exhausting channels, industrial vessels or boilers as well as mountain jackets and thermal shoe insoles.

1.7.1.11 Luminescent textiles

Possible applications

In the examined research papers, no propositions for commercial applications of insulating textiles are made. Luminescent textiles could possibly find application in apparel or interior trim and upholstery for the production of clothing or home textiles with special optical properties as for example fluorescence or color-changing effects.

Available products

In the researched consumer inventories, one example for an available commercial product was found at Daiichi Orimono Co. [226] who offers textiles with color changing effects.

1.8 ECONOMICAL AND ENVIRONMENTAL ASPECTS

The production of nanomaterials is undergoing exponential growth, their effects on biota, environmental fate and behaviour are still only partially understood. The environmental impacts of nanotechnology have become an increasingly active area of research. The problem is that it is difficult to extrapolate experience with bulk materials to nanoparticles because their chemical properties can be quite different. For instance, anti-bacterial silver nanoparticles dissolve in acids that would not dissolve bulk silver, which indicates their increased reactivity. Size is the general reason why nanoparticles have become a matter of discussion and concern. The very small dimensions of nanoparticles increases the specific surface area in relation to mass, which again means that even small amounts of nanoparticles have a great surface area on which reactions could happen. Size can cause specific toxic response if for instance nanoparticles will bind to proteins and thereby change their form and activity, leading to inhibition or change in one or more specific reactions in the body. Besides the increased reactivity, the small size of the nanoparticles also means that they can easier be taken up by cells and that they are taken up and distributed faster in organism compared to their larger counterparts. Due to physical and chemical surface properties all nanoparticles are expected to absorb to larger molecules after uptake in an organism via a given route of uptake. Some nanoparticles such as fullerene derivates are developed specifically with the intention of pharmacological applications because of their ability of being taken up and distributed fast in the human body, even in areas which are normally hard to reach – such as the brain tissue. Fast uptake and distribution can also be interpreted as a warning about possible toxicity, however this need not always be the case. Some nanoparticles are developed with the intension of being toxic for instance with the purpose of killing bacteria or cancer cells, and in such cases toxicity can unintentionally lead to adverse effects on humans or the environment. The structure of nanoparticles has been shown to have a profound influence on the toxicity of nanoparticles. In a study comparing the cytotoxicity of different kinds of carbon-based nanomaterials concluded that single walled carbon nanotubes was more toxic that multi walled carbon nanotubes which again was more toxic than C_{60}.

The unique properties of nanomaterials have attracted not only scientists and research workers but also businesses, because of their huge economic potential. The national science foundation reports that nano-related goods and services will increase to a US 1 trillion dollars market by 2015. This amount is larger than the combined businesses of the telecommunications and information technology industries. Several hundred billion Euros is forecast to be created by nanotechnology in the next decade.

The actual turnover depends very much on the definition of when a product was produced using nanotechnology (components or production methods). VDI-TZ ZTC (2004) compiles estimates from different analysts. These estimates range from USD 900 million for the world market volume of nanotechnological products in 2005 to a trillion USD for the world market volume of nanotechnically influenced products in the year 2015. The same authors expect an exponential growth of the world market in nanotechnological products. According to a study by the US market research institute LuxResearch, products in which nanotechnology is used make up only 0.1 percent of global goods production. By 2014 this share will rise to around 15 percent.

The nano materials markets could expand to 4 billion dollars by 2007. It was believed that 2 million new employment opportunities would be created in order to meet the worldwide annual production demand of 1 trillion dollars in 10-15 years.

Nanotechnology may impart favourably on the environment as well. By using less resource without sacrificing performance, nanotechnology may save raw materials and also upgrade quality of life.

1.9 PERSPECTIVE AND AIMS OF THE WORK

Recently, the ability to scale up the synthesis to bulk scale will gain increasing importance as more applications are established. However most of the synthetic methods either yielded particles of irregular shape with wide size distribution and required high temperature and pressure condition or produce particles with reduced catalytic activity and inability to reuse the particles. In view of the above limitations, attempt has been made to synthesis silver, copper and zinc nano particles through a simple one-phase aqueous route.

There are various conventional chemical means for improving the functional and performance properties of textile materials. But many of these methods suffer from other side effects like a finishing treatment may affect the hue/ tone of coloured textiles as reported by Chattopadhyay & Kaushik ,1994 [227]. Most importantly many chemical treatments for improving functional properties of textiles adversely influence their breathability or hand feel. Whereas nanotechnology can provide high durability for fabrics, because nano-particles have a large surface area-to-volume ratio and high surface energy, thus presenting better affinity for fabrics leading to an increase in durability of the function. In addition, a coating of nano-particles on fabrics will not affect their feel. Smart textile concept is easily achievable by utilizing nanotechnology. The morphological features of nano material and structures need to be determined in various stages of production such as size distribution, porosity, pore size distribution, surface structure and composition, which are critical to ensure the materials and structures are in nano scale to archive special properties, as stated by Li and Sun, 2003; Li, Lokyuen & Junyan , 2003; Patel & Chattopadhyay,2007 [5,8,11].

Looking to the huge potential of utilizing ‘nano’-concept in textiles the actual research done in this field is really seems to be in its embryo stage. Under this background the proposed research will concentrate on the following areas:-

a) Establishing suitable methods for synthesizing metal nano-particles or their compounds in nano form. The study further extended to the preparation of cellulose nano material.
b) Studies on stabilization of these particles
c) Characterizations of nano-particles for their size and size distribution
d) Applications of these synthesized nano-particles to common textile fibers like cotton, polyester, wool etc.
e) Studies on the effects of these particles on desired and relevant properties

1.10 REFERENCES

1. S. Amberg-schwab, D.Ulrikeweber, Functional Coatings Using Nanotechnology, *International Textile Bulletin*2004, 50, 1.

2. J.W.Gilman, et al. In Chemistry and Technology of Polymer additives, Edited by A.K.Malaika, S.A.Golovoy and C.A.Wilkie, Blackwell Science Inc., Malden, Mass., 1999, 249.
3. F. Qinguo, S.C.Ugbolue, A.R.Wilson, Y.S.Dar, and Y.Yang, Nanoclay-modified, polypropylene dyeable with acid and disperse Dyes, *AATCC Review*, 2003,3, 6, 25.
4. J.Chen, and N.Tsubokawa, Electric properties of conducting composite from poly(ethylene oxide) and poly(ethylene oxide)-grafted carbon black in solvent vapor, *Polymer Journal*, 2000,32,9, 729.
5. D. Li and G. Sun, Coloration of polyester and acrylic fabrics with carbon black nanoparticles. *AATCC Review*, 2003, 3, 12, 19.
6. Soane, S.David., US Patent, no.6, 607, 994, 2003.
7. A.V.Shivaprakash and M.Mohankumar, *Man-made Textiles in India*, 2005, 47, 2, 75.
8. Li, L.Lokyuen and H. Junyan, *Textile Asia*, 2003, 34, 11, 26.
9. Y.W.Wang, C.W.M.Yuen, M.Y.S.Leung, S.K.A.Kuand, H.L.I.Lam, Nanotechnologies in textiles, *Textile Asia*, 2004,35, 5,27.
10. D. P. Chattopadhyay, Nanotechnology-the emerging trends, *Textiles* (The Textile Institute), 2006,1, 21-24.
11. B.H.Patel and Dr D.P.Chattopadhyay, Nano-particles & their uses in textiles. *The Indian Textile Journal*, Dec.2007, 118, 3, 23-31.
12. CSIR, ScienceScope: Emerging Research Areas, Understanding and controlling the basis building blocks, *CSIR publication*, June 2007.
13. L .Breggin and J. Pendergrass, Where does the nano go? End of life regulation of nanotechnologies. Woodrow Wilson International Center for Scholars. *Project on Emerging Nanotechnologies*, PEN 10, July 2007.
14. M. Berger, Nanotechnology Risks – The Real Issues. *NanoRisk* , 2006,1,1, 1-8.
15. European Commission (EC), Nanotechnology: Innovation for tomorrow’s world EUR 21151EN 2004. [Online] Available: www.cordis.lu/nanotechnology
16. W. Luther, Ed: Industrial application of nanomaterial: chances and risks, *Future Technologies*, 2004, 54, 1-112.
17. R.Nass, R. Campbell, F. Schuster, W. Luther, Technological analysis- Industrial application of nanomaterials-chances and risks, *Future Technologies Division*, (August)2004, 54.

18. G. Holton and S. G. Brush, Introduction to Concepts and Theories in Physical Science, 2/e, *Princeton University Press*, 1985.
19. S. M.George, A. W. Ott, and J. W. Klaus. Surface Chemistry for Atomic Layer Growth, *J. Phys. Chem.*,1996,100, 13121-13131.
20. H. J. Schneider and A. K. Yatsimirski, Principles and Methods in Supramolecular Chemistry, Wiley, 2000.
21. P. Podsiadlo, S. Paternel, J. M. Rouillard, Z. Zhang, J. Lee, J. W. Lee, E. Gulari, and N. A. Kotov, Layer-by-layer assembly of nacre-like nanostructured composites with antimicrobial properties, *Langmuir*,2005, 21,11915-11921.
22. E. V.Schevchengko, D. V. Talapin, C. B. Murray, and S. O.'Brien, Structural Characterization of Self-Assembled Multifunctional Binary Nanoparticle Superlattices, *J. Am. Chem. Soc.*, 2006,128,3627.
23. S.Krishnamoorthy, C. Hinderling, and H. Heinzelmann, Nanoscale patterning with block copolymers, *Materials Today,* 2006,9 , 40-47.
24. C.Burda, X. Chen, R. Narayanan, and M. A. El-Sayed, The chemistry and properties of nanocrystals of nifferent shapes. *Chem. Rev.* , 2005, 105, 1025-1102.
25. Garry Glaspell, Vapor-phase synthesis of metallic and intermetallic nano-particles and nanowires:Magnetic and catalytic properties, *Pure appl. chem.,* 2006,78,9, 1667-1689.
26. M.L. Ostraat, J.W. De Blauwe, M.L. Green, L.D. Bell, H.A Atwater, R.C. Flagan, Ultraclean two-stage aerosol reactor for production of oxide-passivated silicon nano-particles for novel memory devices, *J. Electrochem. Soc.* 2001,148, G265 –G270.
27. M.H. Magnusson, K. Deppert, MalmJ-O, Single-crystalline tungsten nanoparticles produced by thermal decomposition of tungsten hexacarbonyl, *J. Mater. Res*., 2000,15,1564 –1569.
28. A.G. Nasibulin, O. Richard, E.I. Kauppinen, D.P. Brown, J.K. Jokiniemi, I.S. Altman, Nano-particle synthesis by copper (II) acetylacetonate vapor decomposition in the presence of oxygen, *Aerosol Sci. Technol.*, 2002,36, 899 – 911.
29. R. Schmechel, M. Kennedy, H. von Seggern, Luminescence properties of nanocrystalline Y O :Eu3q in different host materials, *J. Appl. Phys.*, 2001, 89, 1679 –1686.
30. R.A. Senter, Y. Chen, J.L. Coffer, L.R. Tessler, Synthesis of silicon nanocrystals with erbium-rich surface layers, *Nano. Lett*, 2001,1,383 –386.

31. V.V. Srdic´, M. Winterer, A. Moller, G. Miehe, H.Hahn, Nanocrystalline zirconia surface-doped with alumina; chemical vapor synthesis, characterization, and properties, *J Am Ceram. Soc.*, 2001, 84, 2771 –2776.
32. S.H. Ehrman, M.I. Aquino-Class, M.R. Zachariah, Effect of temperature and vapor-phase encapsulation on particle growth and morphology, *J. Mater. Res.*, 1999,14,1664 –1671.
33. B. H. Kear, and P. R. Strutt, Chemical processing and applications for nanostructured materials*, Nanostruct. Materials*, 1995, 6, 227–236.
34. M.Oda, E.Fuchita, M.Tsuneizumi, S.Kash, and C.Hayashi, Gas deposition films of ultra fine particles, *Nanostruct. Materials*, 1992, 1, 203–206.
35. W. Marine, L. Patrone, B. Luk'yanchuk, M. Sentis, Strategy of nanocluster and nanostructure synthesis by conventional pulsed laser ablation, *Appl. Surf. Sci.* 2000,154,155,345 –352.
36. Y. Nakata, J. Muramoto, T. Okada, M. Maeda, Particle dynamics during nanoparticle synthesis by laser ablation in a background gas, *J. Appl. Phys.*, 2002,91,1640 –1643.
37. S.R. Shinde, S.D. Kulkarni, A.G. Banpurkar, R. Nawathey-Dixit, S.K. Date, S.B. Ogale, Magnetic properties of nanosized powders of magnetic oxides synthesized by pulsed laser ablation, *J. Appl. Phys.*, 2000,88,1566 –1575.
38. A. Harano, K. Shimada, T .Okubo, M. Sadakata, Crystal phases of TiO ultrafine particles prepared by laser ablation of solid 2 rods, *J. Nanoparticle Res.*, 2002,4,215 –219.
39. T. Makimura, T. Mizuta, K. Murakami, Laser ablation synthesis of hydrogenated silicon nanoparticles with green photoluminescence in the gas phase, *Jpn. J. Appl. Phys.*, 2002,41, L144 – L146.
40. Information from website; http://www.triv.org.uk/~danny/LEPECVD.html
41. A.María Montero, R.María Gennero de Chialvo and C.Abel Chialvo, Preparation of gold nanoparticles supported on glassy carbon by direct spray pyrolysis *J.Mater. Chem.,* 2009, 19, 3276-3280.
42. Information from website; http://mmehta.public.iastate.edu/
43. T.Masuda, Y. Miyaguchi,M.Tanimura,Y.Nishioka, K.Suu,N.Tani,Development of PZT sputtering method for mass-production, Applied Surface Science, 2001,169,170, 539-543.
44. Kikuo Okuyama Wei-Ning Wang, Ferry Iskandar, Technology Innovation in the Nanoparticle Project Synthesis of Nanoparticles and Nanocomposites Department

of Chemical Engineering, Graduate School of Engineering, Hiroshima University1 Metals and metal oxides nano-particles

45. Information from website; http://future-nanotech.blogspot.com/2007/04/how-to-synthesize-nanoparticles.html
46. Information from website;http://www.centexbel.be/solgel-treatment
47. G.R. Wiese and T.W. Healy, *Trans. Faraday Soc.*, 1970, 66, 490.
48. K.T. Miller and C.F. Zukoski, Semiconductor nanoparticles, physical, chemical and catalytic aspects, *Elsevier*, Amsterdam, 1948, 23-57.
49. J.H. van der Waals, Ph.D Thesis, University of Leiden, 1873.
50. R.J. Hunter, *Foundations of Colloid Science*, Oxford Univ. Press, New York, 1989.
51. J.N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, San Diego, 1992.
52. W.B. Russel, D.A. Saville, and W.R. Schowalter, *Colloidal Dispersions*, Cambridge Univ. Press, Cambridge, U.K. 1990.
53. D.H. Cole, K.R. Shull, L.E. Rehl, P. Baldo, Metal-polymer interactions in a polymer/ metal nanocomposites, *Phys. Rev. Let.*, 1997,78, 5006–5009.
54. D.H. Cole, K.R. Shull, P. Baldo, L. Rehn, Dynamic properties of a model polymer/metal nanocomposite: gold particles in poly(tert-butyl acrylate), *Macromolecules*, 1999,32, 771–779.
55. J. Visser. On Hamaker constants: a comparison between Hamaker constants and Lifshitz-van der Waals constants, *Adv. Colloid Interface Sci.*, 1972,3, 331,
56. D. Pomogailo, Polymer-immobilized nanoscale and cluster metal particles, *Uspekhi Khimii (Russ. Chem. Rev.)*, 1997, 66, 750.
57. G. Gouy, Radium, *Phys. Chem.* 1910, 9, 457.
58. D.L. Chapman, A contribution to the theory of electrocapillarity, *Philos. Mag.*, 1913, 25, 475.
59. O.Z. Stern, Elements of electricity and electro-chemistry, *Electrochemistry*, 1924, 30, 508.
60. A.N. Patil, D.Y. Paithankar, N. Otsuka and R.P. Andres, *Z. Phys. D* , 1993, 26, 135.
61. L. M. Liz-Marzan and A. P. Philipse, Synthesis and optical properties of gold-labeled silica particles, *J. Phys. Chem.*, 1995, 99, 15120.
62. W. Stbber, A. Fink and E. Bohn, *J. Colloid Interface Sci.* , 1962, 26, 62.

63. L. M Liz-Marza'n, A. P. Philipse, Synthesis and optical properties of gold-labeled silica particles, *J. Colloid Interface Sci.*, 1995, 176, 459.

64. L. M.Liz-Marza'n, M Giersig, P. Mulvaney, Solid State Communications, *J. Chem. Soc, Chem. Commun.*,1996, 731.

65. L. M.Liz-Marza'n, M Giersig, P. Mulvaney, Synthesis of nanosized gold-silica core-shell particles, *Langmuir*,1996, 12, 4329.

66. P. Mulvaney, M. Giersig, and A. Henglein, Surface chemistry of colloidal gold: deposition of lead and accompanying optical effects, *J. Phys. Chem.*, 1993, 97, 7061.

67. A. Henglein, P. Mulvaney, A. Holzwarth, T.E. Sosebee, and A. Fojtik, Ber. Bunsenges, *Phys. Chem.* , 1992, 96, 754.

68. P.B. Johnson and W. Christy, Optical constants of noble metals, *Phys. Rev.,* B, 1972, 6, 4370.

69. http://www.egr.msu.edu/cmsc/esem/index.html.;

70. http://www.egr.msu.edu/cmsc/nano/index.html

71. http://www.purdue.edu/REM/rs/sem.htm.

72. M. Joshi and V. Viswanathan, High-performance filaments from compatibilized polypropylene/clay nanocomposites, *J.AppI. Polvm. Sci.,* 2006, 102, 3, 2, 164.

73. M. Joshi, B. Butola, G. Simon and N.Kukalevab, Rheological and viscoelastic behaviour of HDPE/ Octa methyl POSS nanocomposites, *Macromolecaies,* 2006, 39, 1839.

74. R. Klajn, K. J. M .Bisbop, M. Fialkowski, M. Paszewski, J. C. Campbell Chris, T. P. Gray and A. B. Gtzybowski, Comparison of antibacterial properties of all-silver, AgMUA/AgTMA , *Science,* 2007,316, 5S22, 261.

75. P. D. Marcato, G. De SoLiza, O. L. Alves, E. Esposito and N. Duraii, http://www .e n promer2005.equfrj.br/iuikle o/p dfs/1156_ marcato.prn.pdf.

76. J. Ma, Z. Qi and Hu Youliang, Synthesis and characterization of polypropylene/clay nanocomposites, *J. Appl. Potym. Sci.,* 2001,82, 3611.

77. N. Sano, H. Wang, I. Alexandrou, M. ChhowaLla, K. B. K. Teo and C. A. J. Amaratunga, *J. Appl. Phys.,* 2002, 92, 51, 2783.

78. R. M. Rynders, C. R. Hegedus and A. G. Cilicinski, Characterization of particle coalescence in waterborne coatings using atomic force microscopy, *J. Coat. Technol.,* 1995, 667, 845, 59.

79. Q. F. Wei and X. Q. Wang, AFM Characterisation of Technical Fibres, *J. Industrial Text.,* 2004,34,1,51.

80. G. Poletti, F. Orsini, A. R. Addamo, C. Riccardi and E. Selli, *Appl scie.* 2003, 12l9, 311.

81. M. Sakurai, M. Tona, S. Takabashi, H. Watanabe, N. Nakamura, N. Yoshiyasu, C. Yaraada, S. Ohtani, H. A. Sakaue, Y. Kawase, K. Mitsuraori, T. Terui and S. Mashiko, Nuclear instruments and methods [Physics Research Section 3]: *Beam Interactions with Materials and Atoms,* 2007, 257, 1-2, 297.

82. Information from; http:// www.answers.com/topic/scanning-tunneling-microscope ? cat=technology.

83. M. Terrones, A. Jorio, M. Endo, A. M. Rao, Y. A. Kim, T. Hayashi, H. Terrones, J. C. Charlier, G. Dresselbaus and M. S. Dresselhaus, New directions in nanotube science, *Materials Today*, 2004,1, L0, 30.

84. J. Meier, J. Schiotz, P. Liu, J. K. NtMskov and U. Stimming, Nano-scale effects in electrochemistry, *Chem. Phys. Lett*., 2004, 390, 4-6, 440.

85. G. Gouadec and P. Colomban, Raman spectroscopy of nanostructures and nanosized materials, *Prog. in Crvstal Growth and Charac. of Mat.*, 2007,53,1, 1.

86. A. Eitan, F. T. Fisher, R. Andrews, L. C. Brinson and L. S. Schadler, Reinforcement mechanisms in MWCNT-filled polycarbonate, *Compos Sci. Technol.*, 2006, 66, 9, 1162.

87. http://www.scienceofspectroscopy.info/edit/index.php?title=Image:UV-VIS.gif..

88. R. Patakfalvi, A. Oszko and I. De'ka'iiy, *Colloids and Surf A: Physicochem Eng Aspects,* 2003, 220, 45.

89. S. Pal, Y. K .Tak and J. M. Song, Does the antibacterial activity of silver nanoparticles, *Appl Environ Microbiol*, 2007,19,1.

90. J. J. Mock, M. Barbie, D. R. Sraich, D. A. Schultz and S. Schultz, Shape effects in plasmon resonance of individual colloidal silver, *J. Chem. Phys.*, 2002, 116, 15, 6755.

91. R .H. Brause, Moeltgen and K. Kleinermanns, Characterization of laser spectroscopy and STM/SEM microscopy, *Appl. Phys. B-Lasers Opt.*, 2002, 75, 711.

92. P. MuLvaiiey, Surface plasmon spectroscopy of nanosized metal particles, *Langmuir,* 1996, 12, 788.

93. G. Mie, Beitrage zur optik truber medien speziel kolloidaler metallosungen, *Ann. Phy.*, 1908, 25 , 377.

94. I.O. Sosa, C. Noguez and R. G. Barrera, Optical Properties of Metal Nanoparticles with Arbitrary Shapes, *J. Phys. Chem. B.*, 2003, 107, 6269

95. S. Ray and M. Okamoto, Polymer/layered silicate nanocomposites: a review from preparation to processing, *Prog. Polym. Sci.*, 2003,28,153.
96. G. Lagaly, Interaction of alkylamines with different types of layered compounds, *Solid State Ionics*, 1986,22, 43.
97. A. H. Patel, R. S. Somani, H. C. Bajaj and R. V. Jasra, Nanoclays for polymer nanocomposites, paints, inks, greases , *Bull. Mater. Sci.*, 2006, 29,2, 133.
98. B .V. Crist, Annotated Handbooks of Monochromatic XPS Spectra. PDF of Vol. 1 and 2 (XPS International LLC, Mountain View, CA, USA), 2005.
99. http://www.physics.emory.edu/~weeks/lab/papers/sendai2007.pdf.
100. M Joshi, A Bhattacharyya and S Wazed Ali, Characterization techniques for nanotechnology applications in textiles, *Indian Journal of Fibre and Textile Research,* 2008, 33, 3, 304-317.
101. Peltola, Influence of sol and stage of spinnablity on in vitro bioactivity and dissolution of sol-gel-derived SiO_2 fibers, *Biomaterials*, 2001, 22,589-598.
102. Celzard, Applications of the sol-gel process using well-tested recipes, *J. Chem. Educ.*, 2002, 79, 854-859.
103. M. J. Amalvy, Polymer/Silica nanomaterial preparation, characterization, properties, and. Applications, *Mater. Chem.* 2002, 12, 697.
104. Jianan Zhang, Preparation and characterization of polymer/silica nanocomposites via double In Situ miniemulsion polymerization, *Chem. Rev.* 2008,108, 3893–3957.
105. S. J. Ahmadi , Review Synthetic routes, properties and future applications of polymer-layered silicate nanocomposites, *Journal of materials science,* 2004, 39, 1919-1925.
106. Information from website; http://www.worldscibooks.com/materialsci/6961.html
107. Informationfromwebsite;http://217.218.200.220/c/document_library/get_file?p_l_id=18503&folderId=21410&name=DLFE-12410.pdf
108. J. G. A. Terlingen, Introduction of functional groups at polymer surfaces by glow discharge techniques, University of Twente: Enschede, 1993.
109. Information from website; aasimahmed.files.wordpress.com/.../a-review-of-plasma-treatment-for-application-on-textile-substrate-aasim-ahmed.pdf
110. Hua Zou, Polymer/Silica Nanocomposites: Preparation, Characterization, Properties, and Applications, *Chem. Rev.* 2008, 108, 3928–3947.

111. Russell, et al., Nanotechnologies and the shrinking world of textiles, *Textile Horizons*, 2002, 9/10,7-9.

112. J.Lubben, Funktionale Fasern und Textilien, tec21 [Functional fibers and textiles.]: Fachzeitschrift fur Architektur, Ingenieurwesen und Umwelt, 2005,41, 10-13.

113. Q.F.Wei, et al., Surface characterization of functional nanostructures sputtered on fiber substrates, *Surface & Coatings Technology*, 2006,201,3-4, 1821-1826.

114. J.Hwang, J. Muth, and T. Ghosh, Electrical and mechanical properties of carbon-black-filled, electrospun nanocomposite fiber webs, *Journal of Applied Polymer Science,* 2007, 104,4, 2410-2417.

115. A.Gottschalk, Environmental and health impacts of carbon nanotubes (carbon nanotubes). Draft risk assessment with special consideration of potential applications in textile fibers. Stuttgart: Fraunhofer IRB Verlag, 2008.

116. T.E.Chang, et al., Microscopic mechanism of reinforcement in single wall carbon nanotube/polypropylene nanocomposites, *Polymer*, 2005,46,2, 439-444.

117. R.Hagenmueller,et al., Production and characterization of polymer nanocomposites with highly aligned single walled carbon nanotubes, *Journal of nanoscience and nanotechnology*, 2003, 3,1-2,105-110.

118. A.B. Dalton, et al., Continuous carbon nanotube composite fibers: properties, potential applications, and problems, *Journal of Materials Chemistry*, 2004, 14,1,1-3.

119. M.I.H.Panhuis, Carbon nanotubes: enhancing the polymer building blocks for intelligent materials, *Journal of Materials Chemistry*, 2006, 16,36, 3598-3605.

120. G.M. Spinks, et al., Carbon-nanotube-reinforced polyaniline fibers for high-strength artificial muscles, *Advanced Materials,* 2006, 18,5, 637.

121. V. Mottaghitalab, G.M. Spinks, and G.G. Wallace, The influence of carbon nanotubes on mechanical and electrical properties of polyaniline fibers, *Synthetic Metals,* 2005, 152,1-3,77-80.

122. G.M.Spinks, et al., Actuation behaviour of layered composites of polyaniline, carbon nanotubes and polypyrrole, *Synthetic Metals*, 2005, 151,1,85-91.

123. D.S.Hecht, L. Hu, and G. Gruner, Electronic properties of carbon nanotube/fabric composites, *Current Applied Physics*, 2007, 7,1,60-63.

124. R.C.Foitzik, A. Kaynak, and F.M. Pfeffer, Application of soluble poly (3-alkylpyrrole) polymers on textiles, *Synthetic Metals*, 2006, 156,7-8, 637-642.

125. L. Dall'Acqua, et al., Vapor phase polymerisation of pyrrole on cellulose-based textile substrates, *Synthetic Metals*, 2006, 156,5-6, 379-386.

126. S.P.Armes, et al., Morphology and structure of conducting polymers, *Langmuir*, 1991, 7, 7, 1447-1452.

127. P. Poncharal, et al., Electromechanical Resonances of Carbon Nanotubes. *Science*, 1999, 283, 5407, 1513-1516.

128. T. Stegmaier, Nanopartikel - Anwendungen und mogliche Risiken, Institut fur Textil und Verfahrenstechnik Denkendorf: Stuttgart,2006.

129. S.G. Kalarikkal, B.V. Sankar and P.G. Ifju, Effect of Cryogenic Temperature on the Fracture Toughness of Graphite/Epoxy Composites, *Journal of engineering materials and technology*, 2006, 128, 2,151-157.

130. P.Miaudet, et al., Hot-drawing of single and multiwall carbon nanotube fibers for high toughness and alignment, *Nano Letters*, 2005, 5, 11, 2212-2215.

131. A.Yadav, et al., Functional finishing in cotton fabrics using zinc oxid nanoparticles, *Bulletin of Material Sciences*, 2006, 29, 6, 641-645.

132. S.G.Kalarikkal, B.V. Sankar, and P.G. Lfju, Effect of cryogenic temperature on the fracture toughness of graphite/epoxy composites, J*ournal of Engineering Materials and Technology-Transactions of the Asme*, 2006, 128, 2, 151-157.

133. G.Campos, et al., Development of new carpet backings based on composite polymer particles, *Journal of Reinforced Plastics and Composites,* 2006, 25, 18, 1897-1901.

134. B.Mahltig, H. Haufe, and H. Bottcher, Functionalisation of textiles by inorganic sol-gel coatings. *Journal of Materials Chemistry,* 2005, 15, 41, 4385-4398.

135. W.A.Daoud, J.H. Xin, and Y.H. Zhang, Surface functionalization of cellulose fibers with titanium dioxide nanoparticles and their combined bactericidal activities. Surface Science, 2005, 599, 1-3, 69-75.

136. I.Parkin and R. Palgrave, Self-cleaning clothes, *Journal of Materials chemistry,* 2004, 15, 1689-1695.

137. S.Y Yeo, H.J. Lee, and S.H. Jeong, Preparation of nanocomposite fibers for permanent antibacterial effect, *Journal of Materials Science*, 2003, 38, 10, 2143-2147.

138. W.A.Daoud and J.H. Xin, Nucleation and growth of anatase crystallites on cotton fabrics at low temperatures, *Journal of the American Ceramic Society,* 2004, 87, 5, 953-955.

139. K.H.Qi, et al., Self-cleaning cotton, *Journal of Materials Chemistry*, 2006, 16, 47, 4567-4574.

140. T.Yuranova, et al., Performance and characterization of Ag-cotton and Ag/TiO2 loaded textiles during the abatement of E-coli., *Journal of Photochemistry and Photobiology a-Chemistry*, 2006, 181, 2-3, 363-369.

141. H.J.Lee, S.Y. Yeo, and S.H. Jeong, Antibacterial effect of nanosized silver colloidal solution on textile fabrics, *Journal of Materials Science,* 2003, 38, 10, 2199-2204.

142. S.T.Dubas, P. Kumlangdudsana, and P. Potiyaraj, Layer-by-layer deposition of antimicrobial silver nanoparticles on textile fibers, *Colloids and Surfaces a-Physicochemical and Engineering Aspects*, 2006, 289, 1-3, 105-109.

143. D.Hegemann, M.M. Hossain, and D.J. Balazs, Nanostructured plasma coatings to obtain multifunctional textile surfaces, *Progress in Organic Coatings*, 2007, 58, 2-3, 237-240.

144. A.Bozzi, T. Yuranova, and J. Kiwi, Self-cleaning of wool-polyamide and polyester textiles by TiO_2-rutile modification under daylight irradiation at ambient temperature, *Journal of Photochemistry and Photobiology a-Chemistry*, 2005, 172, 1, 27-34.

145. S.H.Jeong, S.Y. Yeo, and S.C. Yi, The effect of filler particle size on the antibacterial properties of compounded polymer/silver fibers, *Journal of Materials Science*, 2005, 40, 20, 5407-5411.

146. N.Vigneshwaran, et al., Functional finishing of cotton fabrics using zinc oxide-soluble starch nanocomposites, *Nanotechnology*, 2006, 17, 20, 5087-5095.

147. W.J. Ye, et al., Novel core-shell particles with poly (n-butyl acrylate) cores and chitosan shells as an antibacterial coating for textiles, *Polymer*, 2005, 46, 23, 10538-10543.

148. W.A.Daoud and J.H. Xin, Low temperature sol-gel processed photocatalytictitania coating, *Journal of Sol-Gel Science and Technology,* 2004, 29, 1, 25-29.

149. H.Szymanowski, et al., Plasma enhanced CVD deposition of titanium oxide for biomedical applications, *Surface & Coatings Technology*, 2005, 200, 1-4, 1036-1040.

150. Y.Liu, et al., Artificial lotus leaf structure from assembling carbon nanotubes and their application in hydrophobic textiles, *Journal of Materials chemistry*, 2007, 17, 11, 1071-1078.

151. L. Feng, et al., Super-hydrophobic surfaces; from natural to artificial, *Advanced Materials*, 2002, 14, 24, 1856-1860

152. M.Yu, et al., Superhydrophobic cotton fabric coating based on a complex layer of silica nanoparticles and perfluorooctylated quaterny ammonium silane coupling agent, *Applied surface science*, 2007, 253, 3669-3673.

153. P.Y.Huang, Y.C. Chao, and Y.T. Liao, Preparation of fluoroacrylate nanocopolymer by miniemulsion polymerization used in textile finishing, *Journal of Applied Polymer Science*, 2004, 94, 4, 1466-1472.

154. J.Zhang, P.France, A.Radomyselskiy, S.Datta, J.Zhao, and W.V.Ooij, Hydrophobic cotton fabric coated by a thin nanoparticulate plasma film, *Journal of Applied Polymer Science*, 2003, 88.

155. K.C.Krogman, et al., Automated process for improved uniformity and versatility of layer-by-layer deposition, *Langmuir*, 2007, 23, 6, 3137-3141.

156. D. Li and G. Sun, Coloration of textiles with self-dispersible carbon black nanoparticles, *Dyes and Pigments*, 2007, 72, 2, 144-149.

157. N.Vigneshwaran, Nanotechnology finishing in textiles, 2007, 26.10.2006 [cited 26.07.2007].

158. S. Zhang and A.R. Horrocks, A review of flame retardant polypropylene fibres, *Progress in Polymer Science*, 2003, 28, 11, 1517-1538.

159. S.Bourbigot, et al., Solid state NMR characterization and flammability of styrene-acrylonitrile copolymer montmorillonite nanocomposite, *Polymer*, 2004, 45, 22, 7627-7638.

160. S.Zhang, et al., Flammability, degradation and structural characterization of fibre-forming polypropylene containing nanoclay-flame retardant combinations, *Polymer Degradation and Stability,* 2006, 91, 4, 719-725.

161. E. Devaux, M. Rochery and S. Bourbigot, Polyurethane/clay and polyurethane/POSS nanocomposites as flame retarded coating for polyester and cotton fabrics, *Fire and Materials*, 2002, 26, 4-5, 149-154.

162. S.Bourbigot, E. Devaux, and X. Flambard, Flammability of polyamide-6 /clay hybrid nanocomposite textiles, *Polymer Degradation and Stability*, 2002, 75, 2, 397-402.

163. G.Marosi, et al., Fire retardancy effect of migration in polypropylene nanocomposites induced by modified interlayer, *Polymer Degradation and Stability*, 2003, 82, 2, 379-385.

164. G.Beyer, Short communication: Carbon nanotubes as flame retardants for polymers, *Fire and Materials,* 2002, 26, 6, 291-293.

165. P.Anna, et al., Intumescent flame retardant systems of modified rheology, *Polymer Degradation and Stability*, 2002, 77, 2, 243-247.

166. P.Persico, C. Carfagna, and P. Musto, Nanocomposite fibers for cosmetotextile applications, *Macromolecular Symposia,* 2006, 234, 147-155.

167. D. Ward, Small scale technology with the promise of big rewards, *Tech. Text. Int.,* 2003, 12, 2, 13

168. Aspen Aerogels, Exhaust Duct Heat Loss Reduced by 50 Percent, 2006, [cited 1.08.2007]; Available from: http://www.aerogel.com/markets/c_exhaust.html.

169. A.Kohler, et al., Studying the potential release of carbon nanotubes throughout the application life cycle, unpublished, draft from July 2007, *Technology and Society*, Empa St. Gallen.

170. Y.K.Kim and A.F. Lewis, Concepts for energy-interactive textiles, *Mrs Bulletin,* 2003, 28, 8, 592-596.

171. Nanotex, Fabric to the Next. 2007 [cited 2007 22.08.2007]; Available from: http://www.nano-tex.com/index_noflash.html.

172. Bekaert, Innovative textiles by Bekaert. 17.03.2004 [cited 9.05.2007]; Available from: http://www.bekaert.com/bft/Products/Innovative%20Textiles.htm.

173. Eeon technology, EeonTexTM Conductive Textiles. [cited 22.08.2007]; Available from: http://www.eeonyx.com/prodsp.html.

174. Nanogate, Dielektrika unter Strom. [cited 22.08.2007]; Available from: http://www.nanogate.de/de/produktveredelung/funktionen/nanoadd/elektrisch-leitfaehig.php?PHPSESSID=aae7c8415e14e06254ff250691318264.

175. Lands End, ThermaCheck® Scarf [cited 22.08.2007]; Available from: http://www.landsend.com/cd/fp/prod/0,,1_2_1931_51997_151350_128897_5:view=-1,00.html?sid=0622107012275149920&CM_MERCH=SRCH.

176. Sensatex, Sensatex, Inc. Seamless technology. [cited 22.08.2007]; Available from: http://www.sensatex.com/.

177. MIT Institute for soldier nanotechnologies, Research on energy absorbing materials. [cited 8.05.2007]; Available from: http://web.mit.edu/isn/research/team01/index.html.

178. US global Nanospace, About US Global Nanospace. [cited 9.10.2007]; Available from: http://www.usgn.com/.

179. Zyvexpro Materials, Additives and Concentrates. [cited 9.10.2007]; Available from: http://www.zyvexpro.com/products/applications.htm.

180. G.Sun, Halamine Chemistry and it s applications in biological and chemical protective textiles, in Presentation on the NanoEurope conference, St.Gallen. 2006, Division of Textiles and Clothing, University of California, USA.

181. Goodweaver Textile co.LTD, Goodweaver textile. [cited9.10.2007]; Available from: http://www.goodweaver.com/.

182. United Textile Mills Co.LTD, I-Tex "Silver Nano" - Anti Bacterial Polo-Shirt [cited9.10.2007]; Available from: http://www.unitedtextilemills.com/index.asp#.

183. AgActive, Sports Anklet Sock. [cited 9.10.2007]; Available from: http://www.agactive.co.uk/index.cfm/fuseaction/produ.

184. Nanobabies, Nanobabies. [cited 9.10.2007]; Available from: http://nanbabies.com/SupportProductsStore.htm.

185. Song Sing Nanotechnology Co.LTD. Nano Silver Products. [cited 9.10.2007]; Available from: http://www.ssnano.net/ehtml/0418b.php.

186. Nanoinfinity Nanotech Co, LTD, Healthy deodorant series products. [cited 9.10.2007]; Available from: http://www.nano-infinity.com.tw/product01.htm.

187. AgActive, 100% cotton sheet sets. [cited 9.10.2007]; Available from: http://www.agactive.co.uk/index.cfm/fuseaction/product.display/ProductID8/.htm.

188. Greenyarn technology LTD, Greenyarn technology: Weaving togheter a healthy tomorrow.[cited 9.10.2007]; Available from: http://www.Greenyarn.com/ technology.htm.

189. Smith and Nephew, Acticoat Product Line. [cited 9.10.2007]; Available from: http://wound.smith-nephew.com/us/node.asp?NodeId=2867.

190. Nanover, Nanover WetWipes. [cited 9.10.2007]; Available from: http://www.nanogist.com/English/products/tissue.htm.

191. Emergency filtration products inc. Emergency filtration products, [cited 9.10. 2007]; Available from: http:// www. Emergencyfiltration .com/ Products/ NanoMask.htm.

192. Thomson Research Associates, Using Ultra fresh. [cited 10.10.2007]; Available from:http://www.ultra-fresh.com/tra/Content/Using_Specific/using_apparel1.cfm.

193. Nanopool, Nanopool. [cited 10.10.2007]; Available from: http:// www. nanoingermany.com/smr/content/company/company_id/88/exhibition_id/16/ subexhibition/ 0/.

194. Nanogate, Ist keimfrei, bleibt keimfrei. [cited 9.10.2007); Available from: http://www.nanogate.de/de/produktveredelung/funktionen/nanoadd/antimikrobiell.php.

195. J.Murray, Introducing a Novel Nanosilver Additive for Antimicrobial Textile Functionality, in Presentation at the NanoEurope conference, 2006,

196. HeiQ Materials Ltd, St.Gallen, Microban, Home Products.[cited 10.10.]2007; Available from: http:// www.microban.com/ americas/products/ category.html ? lang =en&CategoryID=1&SubcategoryID=200.

197. Polartec, Forward Fabric, [cited 10.10.2007]; Available from: http://www.polartec.com/. Woodrow Wilson International Center for Scholars Scholars. Antibacterial Silver Athletic and Lounging Socks. [cited 10.10.2007]; Available from: http://www.nanotechproject.org/index.php? id=44& action=view&product_id=1198.

198. A.G.A.Coombes, et al., Lactic acid-stabilised albumin for microsphere formulation and biomedical coatings, Biomaterials, 2001, 22, 1, 1-8.

199. Schoeller Textile AG, schoeller®-dynamic, The comfortable one. [cited 9.10.2007; Available from:http://www.schoeller-textiles.com/default.asp? cat1ID=128&cat2ID=126& pageID=69 & emotionstate =0 & emotionID =8 &langID=2.

200. Shenzhen Kangnami clothing wholesale center center, Water-supply magic oil neckties [cited 9.10.2007]; Available from: http://translate.google.com/translate? u=http%3A%2F%2Fdetail.china.alibaba.com% 2Fbuyer%2 Fofferdetail %2 F41040846. zhtml &langpair=zh%7Cen&hl=en&ie=UTF8.

201. Woodrow Wilson International Center for Scholars, NanoTousers by Pro-Idee GmbH&co. KG. [cited 9.10.2007]; Available from: http:// www.nanotechproject.org/ index.php? id=44&action=view & product_id = 1287.

202. Woodrow Wilson International Center for Scholars, Stain resistant tie by Brooks Brothers. [cited 9.10.2007].

203. NanoTsunami, Nano-Tex Adds Knits, Outerwear to Its Performance Apparel Roster [cited 9.10.2007]; Available from: http://www.voyle.net/ Nano%20 Textiles/ 2005%20 Textiles/ Textiles-2005-0009.htm.

204. Woodrow Wilson Internatonal Center for Scholars.Super stain resistant Gripper Cushions by Improvements. [cited 9.10.2007]; Available from: ttp://www.nanotechproject.org index.php?id=44&action=view&product_id=1058.

205. Franz Ziener GMBH, Ziener Technik: Nano Tex. [cited 9.10]-2007; Available from: http://www.ziener.de/Technik/technik_aqua.php.

206. Beyond clothing, Featured new products. [cited 9.10.2007]; Available from: http://beyondclothing.com/; http://www.schoeller-textiles.com/default.asp? cat1ID=128& cat2ID=126& pageID=69& emotionstate=0& em otionID=8&langID=2.

207. Woodrow Wilson International Center for Scholars, Bike and Hike Pants by Jack Wolfskin. [cited 9.10.2007]; Available from: http://www.nanotechproject.org /index.php? id=44&action=view&product_id=1404.

208. Schoeller Textile AG. Nanosphere, [cited 9.10.2007; Available from: http://www.schoeller-textiles.com/nanosphere/main.asp? Site = nanosphere & language = english & webpageID=255.

209. Pro Idee, Give it a shake and it s dry. [cited 8.10.2007]; Available from: http://www.proidee.co.uk/shop/SID_vgThzuGoexUuvTmwJhzj7adSkBB2/F=produkt _formular/P=02_GB_HPN570366/K=02_GB_120057.

210. Percent AG, Nanotechnology solutions. [cited 8.10.2007]; Available from: http://ch.percenta.com/special-celo-reinigungstuch.php.

211. Nanoproofed, nanoproofed® protection Leder und Textil Versiegelung. [cited 9.10.2007]; Available from: http://www.nanoproofed.de/reload.html?home.htm.

212. Nanotec. Nanoprotex, [cited 9.10.2007]; Available from: http:// www.nanotec. com.au / nanoprotex.htm.

213. Nano-X, Markenportfolio. [cited 9.10.2007]; Available from: http://www.nano-x.de/ deutsch/portfolio.htm.

214. Globetrotter Ausrustung, Nanodry. [cited 9.10.2007]; Available from: http:// www. globetrotter.de /de/shop/search.php? suchfeld =Nanodry&GTID=bb468a2220f61b968bf13541024b8e68a34.

215. Woodrow Wilson International Center for Scholars, New Balance Womans Sky Crop by New Balance. [cited 9.10.2007]; Available from: http://www. nanotechproject. org/ index.php? id = 44 &action = view & product_id=1120.

216. Edi Bauer, 8" Water Short. [cited 9.10.2007]; Available from: http:// www.eddiebauer.com/eb/product.asp?cm_cg=T319&product_id=29068&.rand =disabled.

217. Nanotex, Coolest comfort. [cited 9.10.2007]; Available from: http://www.nano-tex.com/ applications/apparel_P3.html.
218. NanoTsunami, Nanophase launches textil and non-woven nanoengineered products. [cited 9.10.2007]; Available from: http: // www.voyle.net /Nano% 20Textiles/ 2005%20Textiles /Textiles-2005-0004.htm.
219. Nanogate, Licht und Schatten. [cited 9.10.2007]; Available from: http:// www. nanogate.de/ de/produktveredelung/funktionen/nanobarrier/uv-schutz.php.
220. Tianjin Tianfang Investment Holding CO, Sell Nano Antibiotic and Deodorizing Shirting Fabric. [cited 9.10.2007]; Available from: http://rongze.en.alibaba.com/offerdetail/ 52555693/ Sell_Nano_Antibiotic _and_ Deodo rizing_ Shirting_ Fabric.html.
221. Luko International Technology, Produktserie Nanofin. [cited 9.10.2007]; Available from: http://www.luko-international.de/index.php?id=72.
222. Nanocor, Nanomer® Nanoclays [cited 9.10.2007]; Available from: http://www. nanocor.com/ products.asp.
223. Woodrow Wilson Internatonal Center for Scholars, Nanorama - Nano Gold Mask Pack by Lexon Nanotech, Inc. [cited 9.10.2007]; Available from: http://www.nanotechproject.org/ index.php?id=44&action=view&product_id=1407.
224. Woodrow Wilson Internatonal Center for Scholars, Nano Gold Mask by Quan Zhou Hu Zheng Nano Technology Co., Ltd.®. [cited 10.10.2007]; Available from: http:// www. nanotechproject.org/ index.php.
225. Aspen Aerogels, Aspen Aerogels: Products. [cited 10.10.2007]; Available from: http://www. aerogel.com/products/overview.html.
226. DAIICHI ORIMONO CO.LTE, Morphotex. [cited 10.10.2007]; Available from: http://www. dicros.co.jp/e/textile03.html.
227. D. P. Chattopadhyay and D.P.Kaushik, *The Indian Textile Journal*, 1994, October, 66-68.

CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF METALLIC NANOPARTICLES

2.1 INTRODUCTION

In recent decades, nanotechnology has attracted scientists from many different fields. The fundamentals of nanotechnology lie in the fact that properties of substances dramatically change when their size is reduced to the nanometer range, as reported by Chattopadhyay, 2006 and Patel & Chattopadhyay, 2007 [1-2]. When a bulk material is divided into small size particles with one or more dimensions (length, width, or thickness) in the nanometer range or even smaller, the individual particles exhibit unexpected properties which are different from those of the bulk material. Metal nano-particles, due to their special properties and also small dimensions, find important applications in optical, magnetic, thermal, sensoric devices, catalysis, etc. The optical properties of small metal nano-particles are dominated by the collective oscillation of conduction electrons resulting from the interaction with electromagnetic radiation. These properties are mainly observed in Au, Ag, and Cu, because of the presence of free conduction electrons. Such particles are under active research because they posses interesting physical properties differing considerably from that of the bulk phase as reported by Chattopadhyay and Patel, 2009 [3]. It comes from the small sizes and high surface/volume ratio. The most common method employed for the synthesis of metal nano-particles is the reduction of metal ions in solution as reported by Chattopadhyay and Patel, 2009, 2010 and Jana, Wang and Sau, 2000 [4, 5, 6]. However, the control of size and shape at the nanometer level is a real problem, as the mechanism of size/shape control is still left largely unresolved.

Attempts have been made to develop a simple method for synthesizing metal nano-particles of Copper, Silver and Zinc in colloidal solution form. Metallic nano-particles were prepared in aqueous solution by chemical reduction method using sodium borohydride as reducing agent. The metallic nano particles produced was either immediately capped with sodium lauryl sulphate (SLS) or trisodium citrate (TSC). The stability of nano-particles in the dispersion was monitored through the analysis of absorbance spectra at different stages during the process of synthesis. The stability of the nano-particles dispersed in aqueous medium was also examined at different time intervals. Their stability was examined in presence of various capping agents used. The size and size distribution of the particles were investigated by particle size analyzer. The morphology of the particles synthesized was examined by particle size analyzer and atomic force microscope (AFM) studies. A novel in-situ stabilization (i.e. the particles were formed and stabilized in-situ in fiber matrix itself) technique has also been developed and analyzed.

2.2 MATERIALS

Various chemicals and material used for the study are listed in Table 2.1 and 2.2. The polyester fabric supplied by Kiran Threads, Vapi (Gujarat) was mild scoured (5% soap Lisaapol L, and 2% soda ash at boil for 15 min.) and thoroughly washed with distilled water before use.

Table: 2.1 Chemical specifications

Sr no	Name	Formula	Grade	Mol.wt. gm/mol	Supplier
1	Copper sulphate	$CuSO_4.5H_2O$	AR	249.68	Sd Fine chemicals.
2	Silver sulphate	$AgSO_4.5H_2O$	AR	311.80	Sd Fine chemicals.
3	Zinc nitrate	$Zn\ (NO_3)\ _2.6H_2O$	AR	297.47	Sd Fine chemicals.
4	Sodium borohydride	$NaBH_4$	AR	37.83	Sd Fine chemicals.
5	Tri-sodium citrate	$C_6H_5Na_3O_7.2H_2O$	AR	294.10	Sd Fine chemicals.
6	Sodium lauryl sulphate	$CH_3(CH_2)_{11}OSO_3Na$	AR	288.38	Qualigens Fine Chemicals
7	Lissapol L	-	LR	284	Suvidhenath Chemicals

Table: 2.2 Polyester material specifications

Sample	Material Specification						
	Count/Denier						
	Warp	Weft	Ends/inch	Pick/inch	Type weave	Wt.gm/sq.m.	Thickness (mm)
100%	128d	146d	90	72	Plain	109.7	0.21

polyester							

2.2.1 Equipments

Three metallic nanoparticles namely, Cu, Ag and Zn in colloidal form were synthesized by chemical reduction technique. For the synthesis and characterization of these nano particles various equipments were used. Name and make of the equipments are listed below.

- Reaction Chamber (In-house designed) with N_2 gas supply unit and high speed magnetic stirrer as shown in figure 2.1. Experiment was carried out at Department of Textile Chemistry, The M.S. University of Baroda.
- Laboratory two bowl padding mangle: (EEC Pvt. Ltd., Mumbai). Experiment was carried out at Department of Textile Chemistry, of The M.S. University of Baroda.
- Spectrophotometer (interphased with computer colour matching system): Spectra scan 5100 (RT) (Premier color scan instrument), India test was performed at Department of Textile Chemistry, The M.S. University of Baroda.
- SEM/EDX Model JSM-5610 LV Japan, with oxford Inca Software for characterizing surface morphology and elemental analysis of nano particles, The test was performed at Department of Metallurgical and materials Engineering, The M.S. University of Baroda.
- UV-VIS Spectrophotometer (Shimadzu UV-2450, Japan): for determining absorbance of nano colloidal solution, at the Department of Applied Chemistry, The M.S. University of Baroda.
- Particle Size analyzer: MAL 501131, DTS version UK, Malvern Instrument was used for analysis the particle size. Test was performed at Department of Pharmacy, The M.S. University of Baroda.
- AFM; Easy Scan 2, Nanosurf AG, Switzerland, was used to examine morphology of nanoparicles deposited on glass plate.
- X-ray fluorescence spectrometer (EDX 800 Simadzu, Japan); For quantitative and qualitative elemental analysis of the polymer nano composite materials. Test was performed at Department of Metallurgical and materials engineering, The M.S. University of Baroda.

2.2.2 Reaction chamber designed and used

The reaction chamber designed and used for the synthesis of nano particles is shown in figure 2.1. As seen in the figure, the experiment setup consists of the actual reaction chamber, nitrogen gas supply unit with pressure gauge, magnetic stirrer and stainless steel clamp.

Figure 2.1 Experimental setup; reaction chamber with N_2 gas supply

The reaction chamber was made of toughened glass with a capacity of 500 ml. The glass chamber was equipped with three inlets. One for the introduction of nitrogen gas in the reaction mixture, the constant pressure of the nitrogen gas was ensured and monitored through the pressure gauge. Other inlet contains burette along with knob for the insertion of reducing agent inside the chamber. The third inlet was for the insertion of capping agent but initially it was kept closed. The reaction chamber was placed on magnetic stirrer, which ensures constant stirring throughout the experiment. The chamber was kept erect on the magnetic stirrer with the help of clamp. The schematic animated model of the chamber is shown in figure 2.2.

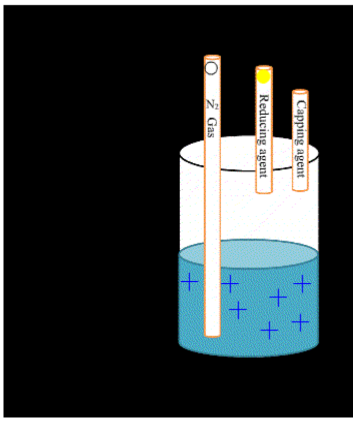


Figure 2.2 Schematic presentation of Reaction proceeding in reaction chamber

2.3 EXPERIMENTAL METHODS

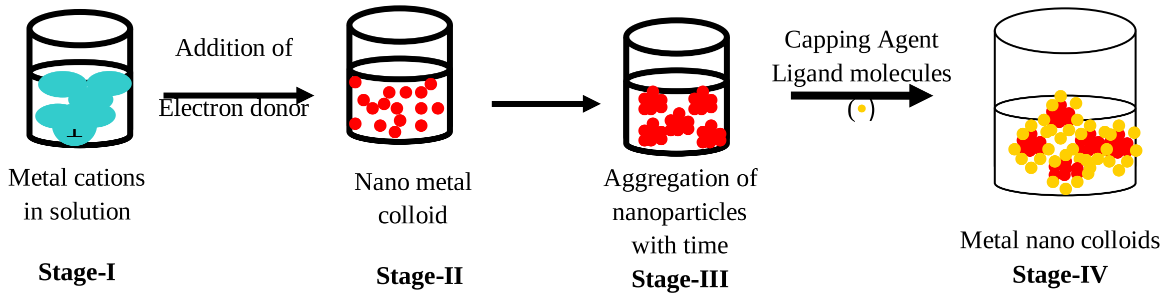
2.3.1 Preparation of copper nano colloids by chemical reduction technique

Metal nanoparticles, due to their special properties and also small dimensions, find important applications in optical, magnetic, thermal, sensoric devices, SERS (surface enhanced Raman scattering), catalysis, etc. The optical properties of small metal nanoparticles are dominated by the collective oscillation of conduction electrons resulting from the interaction with electromagnetic radiation. These properties are mainly observed in Au, Ag, and Cu, because of the presence of free conduction electrons.These particles are under active research because they posses interesting physical properties differing considerably from that of the bulk phase. It comes from the small sizes and high surface/volume ratio. The most common method employed for the synthesis of metal nanoparticles is the reduction of metal ions in solution. However, the control of size and shape at the nanometer level is a real problem, as the mechanism of size/shape control is still left largely unresolved.

In this work, an attempt has been made to analyze formation of Cu nanoparticles from copper salt at different stages of synthesis as well as after storing for variable time in atmospheric condition. The effect of time after synthesis on the shape and size of these particles was investigated using Particle size analyzer, SEM and AFM systems. Further, the effect of trisodium citrate as stabilizer for the nano particles was also investigated.

2.3.1.1 Preparation technique

Copper nanoparticles were prepared in aqueous solution by chemical reduction technique using sodium borohydride as reducing agent to reduce copper sulphate to metallic nano copper. In a typical set, 100 ml of $1x10^{-3}$ M $CuSO_4$ ($CuSO_4.5H_2O$, 0.3 gm, 4.17 mmol in 100ml water) solution was purged with N_2 gas for 10 min to remove the dissolved oxygen. 10 ml of $2x10^{-3}$ M aqueous solution of sodium borohydride ($NaBH_4$, 0.1gm, 3.83 mmol in 50ml water) was then added drop wise to it under constant stirring in nitrogen atmosphere. The colour of the solution was changed to dark yellow on gradual addition of reducing agent indicating the formation of copper nanoparticles. 10 ml of ($1x10^{-3}$ M) sodium lauryl sulphate or tri-sodium citrate ($C_6H_5Na_3O_7.2H_2O$, 0.1gm, 29.41mmol in 100ml water) was added and allowed to stir for another 10 min for capping of the nanoparticles. Distilled water was used for preparing the solutions of all the chemicals. Scheme 1 gives schematic presentation of Cu nano particle formation and their stabilization by capping agent. The absorbance of nano colloidal solution was recorded using UV-visible spectrophotometer at different stages of synthesis.



Scheme 1 Schematic process diagram of synthesis

2.3.1.2 *Stabilization study of copper nano particles*

The stability of copper nano colloid in absence of capping agent at different time intervals viz, after 12 hrs, 24 hrs 72 hrs and 4 weeks was examined by monitoring its absorbance in UV-VIS spectrophotometer. The effect of time after synthesis on the shape and size of these particles were investigated using particle size analyzer, SEM and AFM systems. Further, the effect of capping agents on the stability of nano particles were studied using two types of stabilizers viz. sodium lauryl sulphate and tri-sodium citrate.

Finally, a novel in-situ synthesis and stabilization technique was adopted i.e. the particles were formed and stabilized in-situ within the fiber matrix itself.

2.3.1.3 *In situ synthesis and stabilization technique*

The cleaned (100%) polyester fabric was used for this experiment. The fabric was first padded with chilled 2x10^{-3} M reducing agent (sodium borohydride solution) using 2-dip-2-nip padding technique at 70% padding expression at room temperature on laboratory two bowl padding mangle. The wet fabric was then further padded with 1x10^{-3} M copper salt ($CuSO_4$) solution using again 2-dip-2-nip padding technique. Finally, the fabric is cured in the curing chamber at 180 ˚C for 60 seconds.

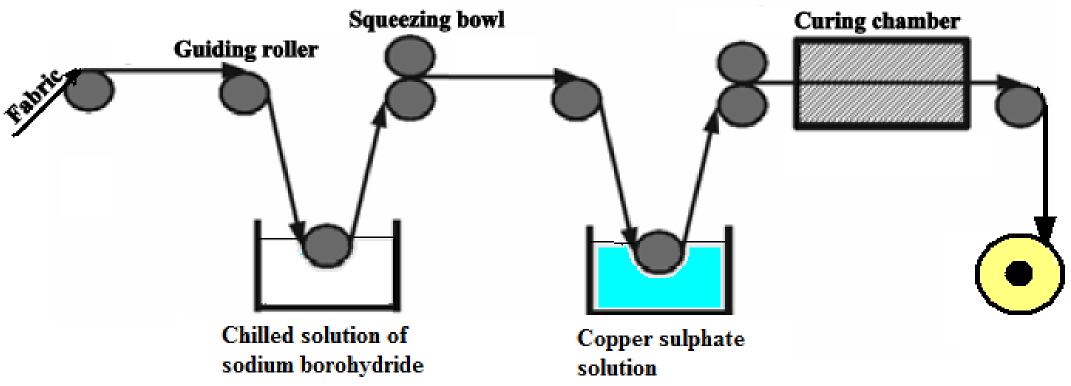


Figure 2.3 Schematic process design for in situ synthesis of metallic nano on textile

2.3.1.4 Characterization of copper nano particles

UV-visible spectrophotometery

The absorbance of nano colloidal solution was recorded using UV-visible spectrophotometer in the wavelength range: 300 nm to 700 nm.

Particle size analyzer

The particle size and size distribution of Cu nano particle were measured using particle size analyzer. The instrument was based on the diffraction/scattering of laser beam by particle in stable suspension. The statistical graph was formed using laser granulometries statistical method.

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy was used to characterize the nano particles shape and size. SEM image was formed using transmitted electrons (instead of the visible light) which can produce magnification up to 1, 00,000 X with resolution up to 100A^o. Stabilized solution of copper nano coated aluminum sheet was dried and illuminated under scanning electron microscope. Scanned images with different magnification and resolution were recorded on computer.

Elemental analysis by Oxford-Inca software on SEM

The elemental analysis of the synthesized copper nano particles was performed on scanning electron microscope (SEM) using Oxford Inca Software. The copper nano particles were deposited on carbon coated aluminum sheet and further coated with gold. EDX analysis of these samples was carried out using Oxford-Inca software on scanning electron microscope. The instrument reports the presence of elements in pure and oxide state qualitatively.

Atomic Force Microscopy (AFM)

Morphology of Cu nanoparicles deposited on glass plate was examined with the help of AFM operated in a contact mode (cantilever force constant 3 N/m).

Determination of colour of the colloidal solution

The changes in colour of the colloidal solution were examined and recorded using spectrophotometer interphased with computer colour matching system.

X- Ray fluorescence spectroscopy (EDX)

For the elemental analysis of polyester fabric before and after in-situ generation of copper nano technique were performed by X-ray fluorescence spectrometer (EDX 800

Simadzu, Japan). The instrument reports the presence of elements in pure and oxide state both qualitatively and quantitatively.

2.3.2 Preparation of silver nano colloids by chemical reduction technique

Metallic silver colloids were first prepared more than a century ago. Ag nanoparticles can be synthesized using various methods, such as chemical, electrochemical, γ-radiation, photochemical, laser ablation, etc. [10,11]. The most popular preparation of Ag colloids is chemical reduction of silver salts by sodium borohydride or sodium citrate. This preparation is simple, but the great care must be exercised to make stable and reproducible colloid. The purity of water and reagents and cleanliness of the glassware are critical parameters. Solution temperature, concentrations of the metal salt and reducing agent and reaction time influence particle size. Controlling size and shape of metal nanoparticles remains a challenge. The size-induced properties of nanoparticles enable the development of new applications or the addition of flexibility to existing systems in many areas, such as catalysis, optics, microelectronics and textiles.

Silver nano is a trademark name of an antibacterial technology which uses silver nanoparticles in washing machines, refrigerators, air conditioners, air purifiers and vacuum cleaners. Antimicrobial effect of silver nanoparticles on textiles has already been shown by various researchers [12-15]. In this section of the present chapter experimental results of the synthesis of silver nano particles by reduction of silver salt ($AgSO_4$) with sodium borohydride in the presence of tri-sodium citrate are discussed. The stability of the nano Ag particles dispersed in aqueous medium was investigated at different time intervals.

2.3.2.1 Preparation technique

The 100 ml solution of $1x10^{-3}$ M $AgSO_4$, kept in the earlier discussed reaction chamber (Figure 2.1), was slowly reduced by drop-wise addition of very dilute chilled solution of sodium borohydride in a nitrogen atmosphere. During the process of reaction the solution mixture was stirred vigorously with the help of magnetic stirrer. When the colour of the solution turned to light yellow, 5 ml of $1x10^{-3}$ M trisodium citrate were added drop by drop with constant stirring. Distilled water was used for preparing the solutions of all the chemicals.

2.3.2.2 Stabilization study of silver nano colloidal particles

The formation of Ag nanoparticles from silver salt at different stages of synthesis as well as their stability after storing for variable time in atmospheric condition has been monitored using UV-VIS spectrophotometer. Stability of synthesized Ag nano colloid in air (in absence of capping agents) was recorded at different time intervals i.e. after 12 hrs, 24 hrs 72 hrs and 4 weeks. The effect of capping agents on the stability of Ag nano colloidal particles was studied using TSC (Electrostatic stabilization).

2.3.2.3 In-situ synthesis and stabilization technique

The cleaned polyester fabric was used for this experiment. The fabric was first padded with chilled $2x10^{-3}$ M reducing agent (sodium borohydride solution) using 2-dip-2-nip padding technique at 70% padding expression at room temperature on laboratory two bowl padding mangle. The wet fabric was then further padded with $1x10^{-3}$ M silver salt ($AgSO_4$) solution using again 2-dip-2-nip padding technique

Finally, the fabric is cured in the curing chamber at 180 ˚C for 60 seconds. The fabric samples were thoroughly washed.

2.3.2.4 Characterization of silver nano colloidal particles

UV-visible spectrophotometery

The absorbance of silver nano colloidal solution was recorded using UV-visible spectrophotometer in the wavelength range: 300 nm to 700 nm.

Particle size analyzer

The particle size and size distribution of Ag nano particle were measured using particle size analyzer. The instrument was based on the diffraction/scattering of laser beam by particle in stable suspension. The statistical graph was formed using laser granulometries statistical method.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy was used to characterize the Ag nano particles shape and size. SEM image was formed using transmitted electrons (instead of the visible light) which can produce magnification up to 1, 00,000 X with resolution up to $100A^o$. Stabilized solution of silver nano coated aluminum sheet was dried and illuminated under scanning electron microscope. Scanned images with different magnification and resolution were recorded on computer.

Elemental analysis by Oxford-Inca software on SEM

The elemental analysis of the synthesized silver nano particles was performed on scanning electron microscope (SEM) using Oxford Inca Software. The silver nano particles were deposited on carbon coated aluminum sheet and further coated with gold. Elemental analysis of samples using Oxford-Inca software on scanning electron microscope reports the presence of elements in pure and oxide state qualitatively.

Determination of colour of the colloidal solution

The changes in colour of the silver colloidal solution were examined and recorded using spectrophotometer interphased with computer colour matching system.

X- Ray fluorescence spectroscopy (EDX)

For the elemental analysis of polyester fabric before and after in-situ generation of silver nano technique were performed by X-ray fluorescence spectrometer (EDX 800 Simadzu, Japan). The instrument reports the presence of elements in pure and oxide state both qualitatively and quantitatively.

2.3.3 Preparation of zinc nano colloids by chemical reduction technique

Quality of human life is highly influenced by the progress of technology and progress of technology depends on developments in novel material and their processing techniques. At present most of material processing technology are based on top-down technique. Recently, numbers of work have been reported on the developments of nano sized materials and their effect. Havaneak, (2003) [17]; Efras and Rosen (2003) [18] has reported that most of the novel devices of the future will be based on properties of nanomaterials [19]. Furthermore, Dutta and Sugunan (2004) [20]; Gates et.al (2004) [21] has also mentioned that the traditional approaches is not sufficient to achieve size selective nano particles. Various techniques of nano synthesis has been reported in chapter 2, in case of preparation of zinc nano particles , controlled precipitation from precursor dissolved in a solution is most popular.

In this work, zinc nano particles were prepared by wet chemical method. After synthesis the particles were stabilized with tri-sodium citrate. Stability of particles was observed in atmospheric condition and also under different light sources. Finally the synthesized nano particles were examined by particle size analyzer, their morphology and micro structure were observed and elementally detected through scanning electron microphotography.

2.3.3.1 Preparation technique

Zinc nano-particles were prepared by wet chemical method using zinc nitrate and sodium borohydride as reducing agent and tri-sodium citrate as stabilizing agent. 100 ml solution of Zinc nitrate (1 x 10^{-3} M), kept in reaction chamber (Figure 2.1), was slowly reduced by drop wise addition of 5 ml solution of sodium borohydride (2 x 10^{-3} M). During the process of reaction the solution mixture was stirred vigorously. As the drop wise addition of sodium borohydride solution completed, 5 ml of 1 x 10^{-3} M tri-sodium citrate were added drop by drop with vigorous stirring. The reaction was allowed to proceed for 2 hours after complete addition of tri-sodium citrate. Distilled water was used for preparing the solutions of all the chemicals.

2.3.3.2 Stabilization study of zinc nano colloidal particles

The synthesized Zn nano colloidal particles (in absence of capping agent) has been monitored with computer colour matching system after storing for variable time in atmospheric condition. Stability of synthesized Zn nano colloid in air was recorded after different time intervals i.e. freshly prepared, after storing for 48 hrs and after storing for 72 hrs, without capping.

2.3.3.3 In-situ synthesis and stabilization technique

100 % polyester fabric samples were impregnated and padded with very dilute chilled solution of 2 x 10^{-3} M sodium borohydride ($NaBH_4$, M.W. 37.83, 0.1gm, in 50 ml water) using automatic padding mangle using 2-dip-2-nip padding technique at 70% padding expression on laboratory two bowl padding mangle. The wet sample was further padded with the solution of 1 x 10^{-3} M Zinc nitrate ($Zn (NO_3)_2.6H_2O$, M.W. 297.47) using 2-dip-2-nip padding technique (Figure 2.3). The padded substrates were air dried and finally cured at 180 ˚C for 60 seconds in curing oven. The fabric samples were thoroughly washed.

2.3.3.4 Characterization of zinc nano colloidal particles

UV-visible spectrophotometery

The absorbance of zinc nano colloidal solution was recorded using UV-visible spectrophotometer in the wavelength range 300 nm to 700 nm.

Particle size analyzer

The particle size and size distribution of Zn nano particle were measured using particle size analyzer. The instrument was based on the diffraction/scattering of laser beam by particle in stable suspension. The statistical graph was formed using laser granulometries statistical method.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy was used to characterize the Zn nano particles shape and size. SEM image was formed using transmitted electrons (instead of the visible light) which can produce magnification up to 1, 00,000 X with resolution up to 100A^{o}. Stabilized solution of zinc nano coated aluminum sheet was dried and illuminated under scanning electron microscope. Scanned images with different magnification and resolution were recorded on computer.

Elemental analysis by Oxford-Inca software on SEM

The elemental analysis of the synthesized zinc nano particles was performed on scanning electron microscope (SEM) using Oxford Inca Software. The zinc nano particles were deposited on carbon coated aluminum sheet and further coated with gold. Elemental analysis of samples using Oxford-Inca software on scanning electron microscope reports the presence of elements in pure and oxide state qualitatively.

Determination of colour of the colloidal solution

The changes in colour of the zinc colloidal solution were examined and recorded using spectrophotometer interphased with computer colour matching system.

X- Ray fluorescence spectroscopy (EDX)

For the elemental analysis of polyester fabric before and after in-situ generation of zinc nano technique were performed by X-ray fluorescence spectrometer (EDX 800). The instrument reports the presence of elements in pure and oxide state both qualitatively and quantitatively.

2.4 RESULTS AND DISCUSSION

This section interprets the findings on synthesis, characterization and stabilization of copper nano particle.

2.4.1. Synthesis of colloidal copper nano particles

Copper nano particles were prepared by chemical reduction of copper salt as discussed earlier. The change in colour of the copper sulphate solution was captured at different stages during synthesis of copper nano colloid. Figure 2.4 shows how the blue-green colour of the copper sulphate solution gradually changed at different stages during synthesis. The optical properties of metal nanoparticles depend strongly upon the particle size and shape as reported by Mulvaney, 1996 [9]. The formation of nano sized Cu was noticed by the change in the optical properties of the reaction solution. The blue-green colours of $CuSO_4$ solution gradually change to intense yellow when the particle size of copper was reduced to nano level. The Cu nano particles in the solution were analyzed by particle size analyzer. The particles were also observed using SEM and AFM. The presence of Cu was detected by Energy dispersive X-ray spectroscopy (EDX).

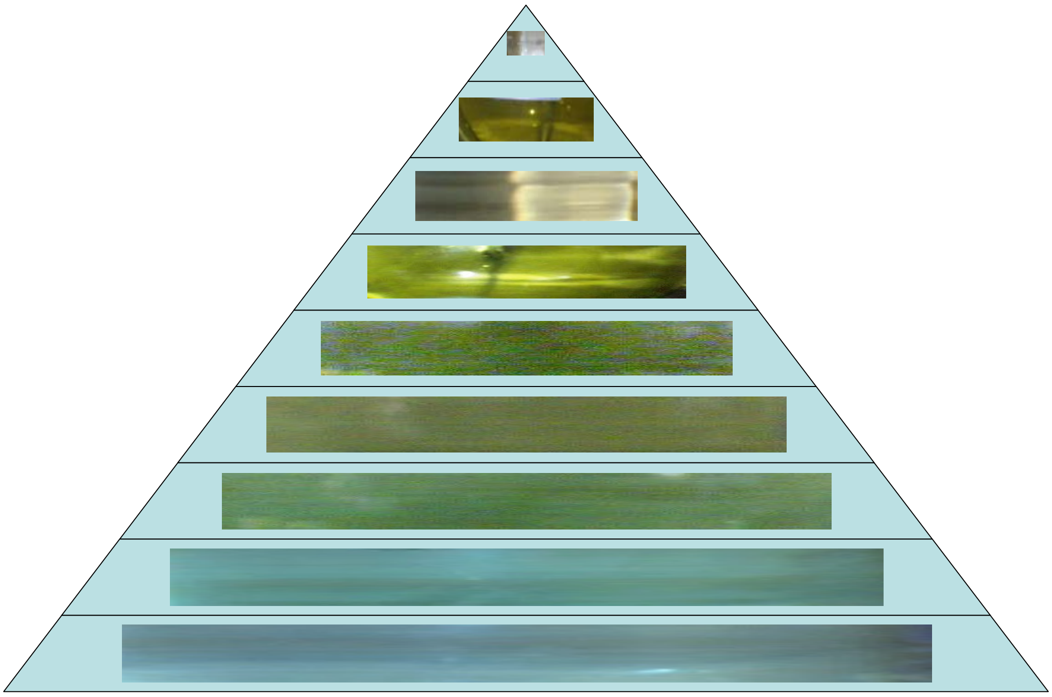


Figure 2.4 Progressive colour change of copper sulphate solution during the preparation of copper nano particles.

2.4.1.1 Studies on stability of synthesized copper nano colloidal solution in atmospheric condition

The stability of the copper nano colloid in absence of any capping agent stored for 24 hours in atmospheric condition was examined using particle size analyzer, SEM and AFM. The results are compared with the results of the freshly prepared copper nano colloid kept in similar environment. Particle size analysis gives an idea of the changes in size and size distribution of the particle with time. Nano particles are prone to cluster with time. The specialities of the nano particles are associated to its size. With increases in size its specialities also get reduced and after a certain point it starts behaving like normal (bulk) metal atoms. It is seen from the figure 2.5(a) and 2.5(b) that the size of the majority of the nanoparticles when prepared fresh was about 70 nm but after storage for 24 hours the same was increased to about 400 nm. This is due to the aggregation of nanoparticles which resulted a broadening of peak as seen in Figure.2.5 b. The inset photographs show the change in colour.

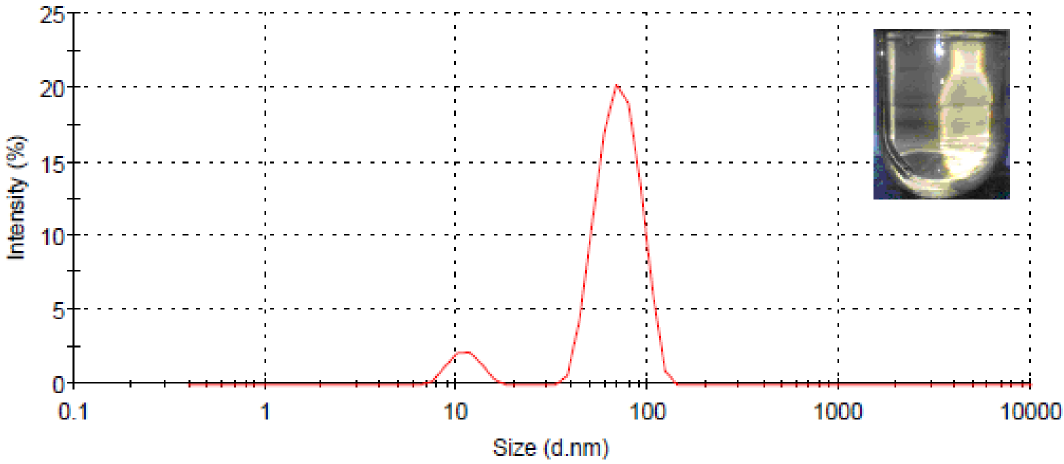


Figure 2.5 (a) Particles Size and their distribution for freshly prepared Cu nano colloids

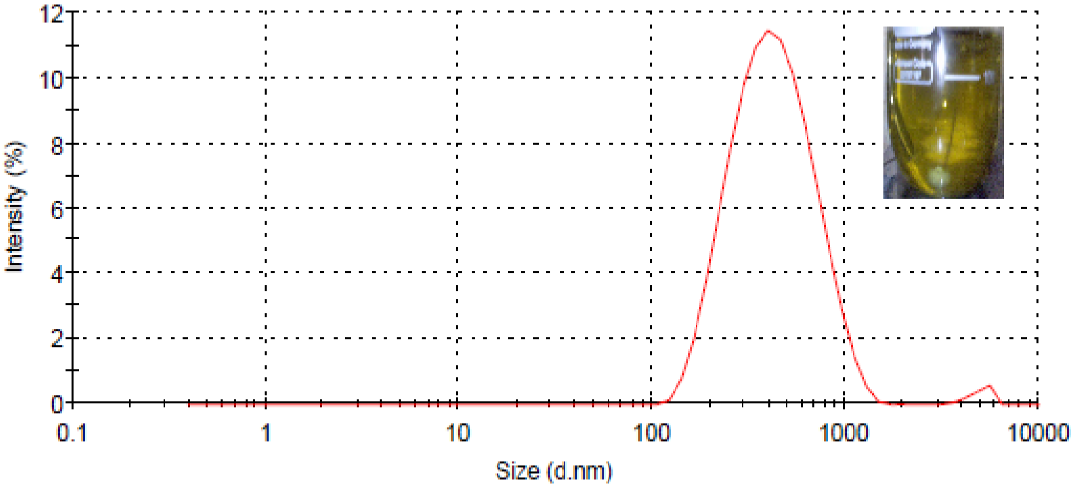


Figure 2.5 (b) Particles Size and their distribution after storing for 24 hours

Stability of the nano Cu particles colloid (in absence of capping agents) in atmosphere was not satisfactory as observed from the change in colour. Scanning electron micrographs of freshly prepared Cu nano particles and after storing for 24 hours in air are represented in figure 2.6. From the SEM photograph we can see that the size of nanoparticles is increased, after 24 hours, which is also supported by the atomic force microscopic images presented in figure 2.7.

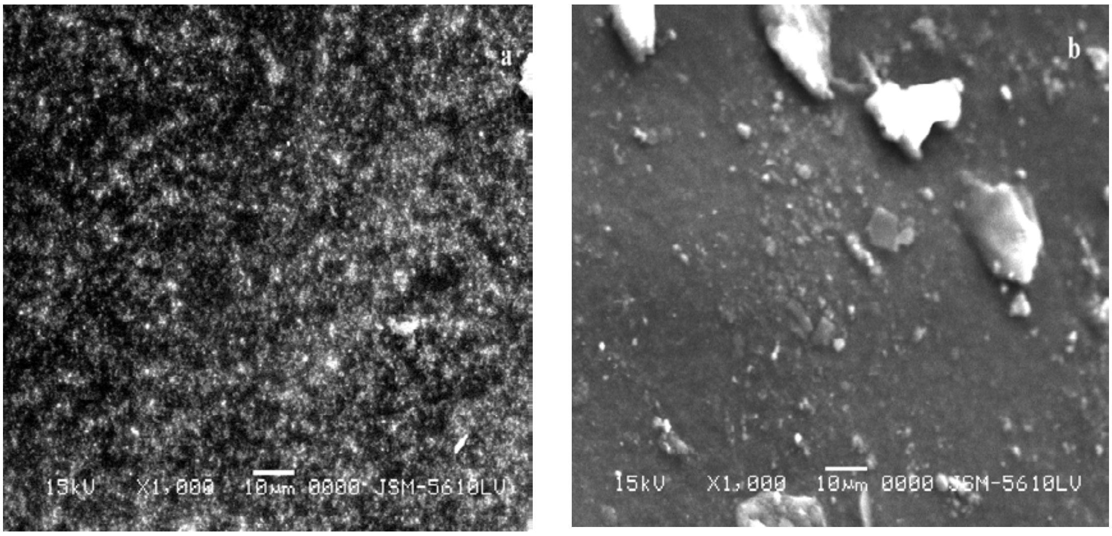


Figure 2.6 Scanning Electron Microscope (SEM) images of synthesized copper nano particles [(a) Freshly prepared; (b) After 4 week of Synthesis]

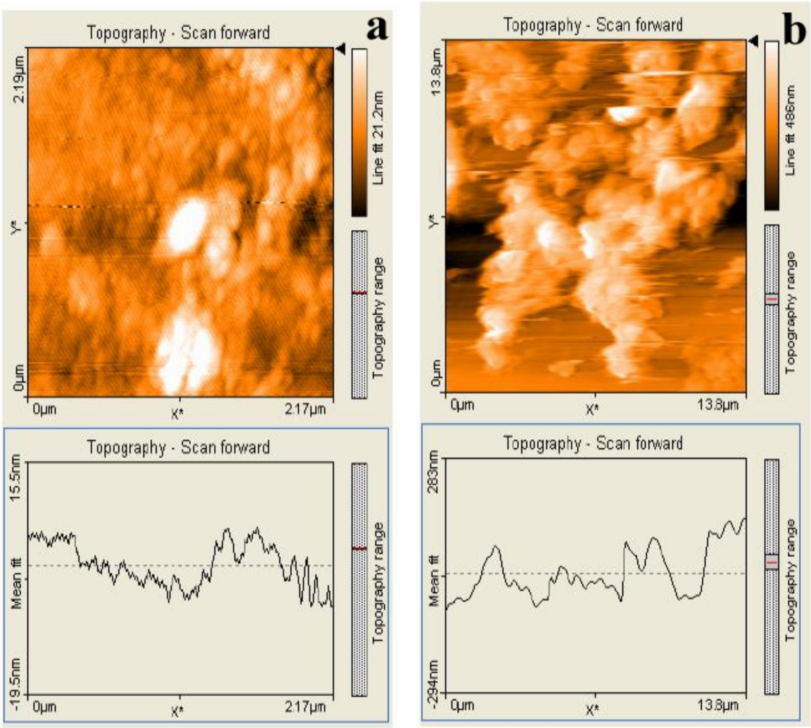


Figure 2.7(a) Atomic force microscopic image of freshly prepared Cu nano colloids and (b) After storing over 24 hrs.

Cu nanoparticles because of their high reactivity tend to form aggregates. The tendency of getting aggregated was therefore controlled by the stabilizer or capping agents reported in the following section.

2.4.1.2 Stability with different capping agents

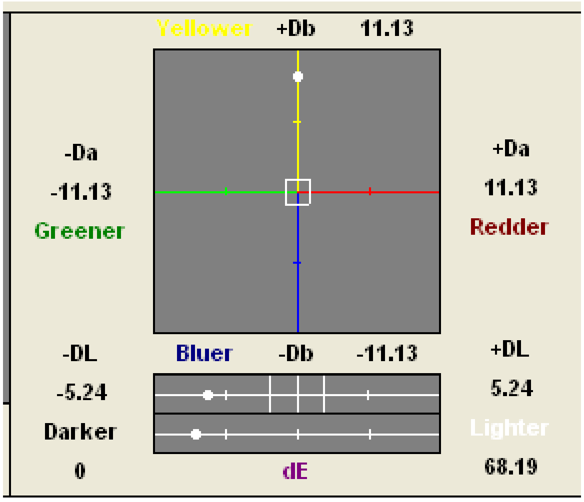
We have seen in the previous section that the stability of copper nano colloid get affected with time. It was found that even after 24 hours the size of the particles, ranged between 200-1000 nm due to aggregation (Figure 2.5). To enhance the stability of the copper nano colloid two methods of stabilizations were investigated i.e. Steric Stabilization (SLS) and Electrostatic stabilization (TSC).

(A) Effect of Steric Stabilization (SLS)

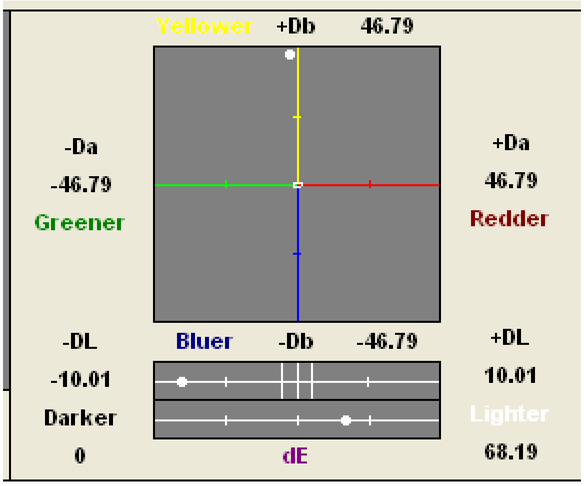
During the synthesis of copper nano particles as the colour of solution change to yellow the Cu nano colloidal particles were stabilized with the addition of Sodium Lauryl Sulphate (SLS) ($1x10^{-3}$ M). In the present experiment the steric stabilization of colloidal particles was achieved by attaching SLS macromolecules to the surfaces of the copper nano particles.

To check the efficiency of SLS as stabilizing agent for Cu nano colloid, we have examined and recorded the variation of colour of the SLS stabilized Cu nano colloids at different time intervals using computer colour matching system (CCM). The results recorded at different time intervals are shown in figure 2.8. There was no significance change in colour up to 48 hrs, but after that the colour changed to light green and further storing for 72 hrs the colour was changed to greener blue. The steric stabilization was thus not found to be very effective in arresting particle aggregation for a longer time as evaluated from the change in colour of the copper nano colloid with time.

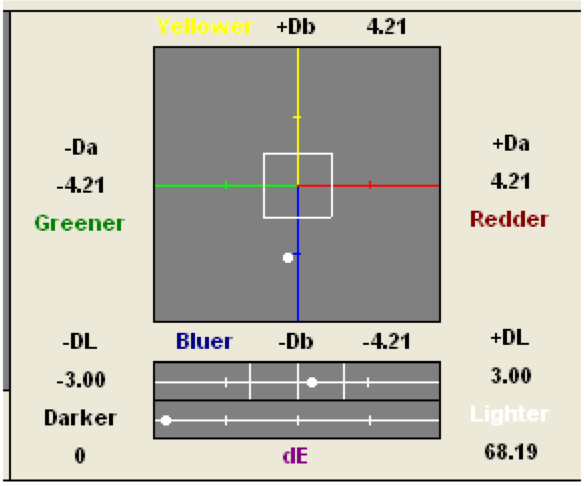
Colour Difference **Image at time interval**



SLS Stabilized Cu nano (Fresh)



SLS Stabilized Cu nano (After 48 hrs)



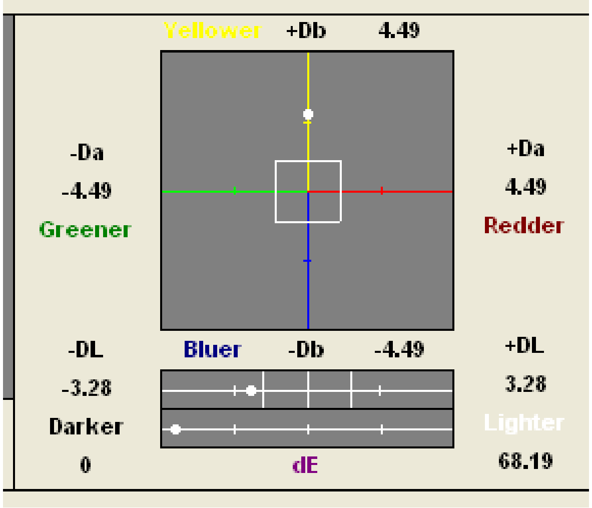
SLS Stabilized Cu nano (After 72 hrs)

Figure 2.8 Change in colour of the SLS stabilized Cu nano colloidal solution on storage in atmospheric condition for different time intervals.

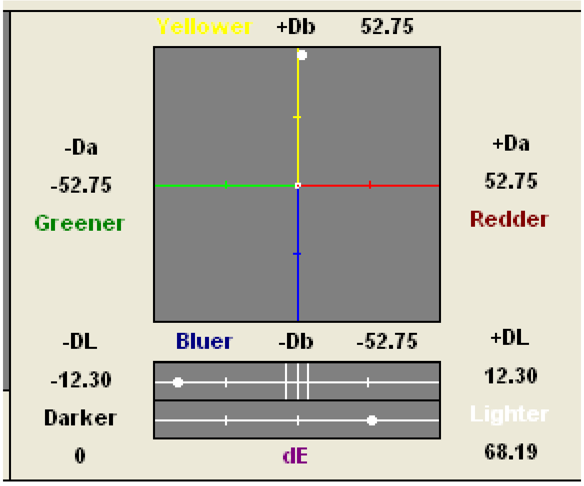
(B) Effect of Electrostatic stabilization (TSC)

Figure 2.9 shows the colour difference and actual photographs of the TSC stabilized freshly prepared copper nano colloid and stored for 72 hours and 4 weeks. From the

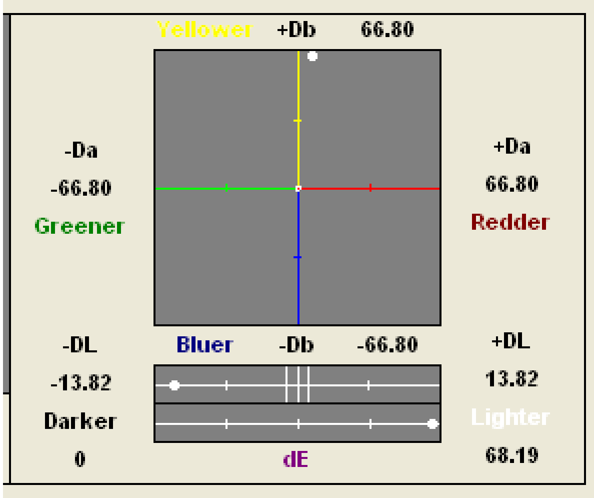
Colour Difference **Image at time interval**



TSC Stabilized Cu nano (Fresh)



TSC Stabilized Cu nano (After 72 hrs)



TSC Stabilized Cu nano (After 4 weeks)

Figure 2.9 Colour difference in TSC stabilized Cu nano colloidal solution on storage in atmospheric condition

figure it is seen that in contrast to SLS stabilized solution the colour of the TSC stabilized copper stored for 72 hours is more yellowish which indicates a better stabilization in the latter case. After 4 weeks, the colour is changed to redder side. Cu nano particles get surrounded by the citrate ions released from tri-sodium citrate and each sphere of Cu the nano particles surrounded by the citrate anions repelled each other and prevented further aggregation of the nano particle.

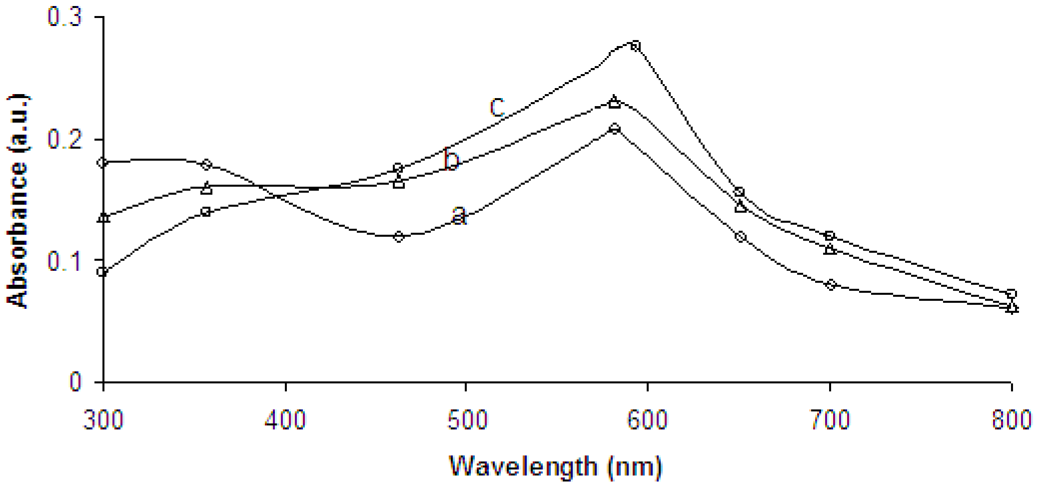


Figure 2.10 UV-VIS spectra of TSC capped Cu nano colloids of various time intervals [Time after synthesis: (a) 12 hours, (b) 18 hours and (c) 24 hours]

The stability of the TSC capped copper nano colloid was then assessed by examining the absorbance spectras of the solution for finer time intervals viz. 12 hours, 18 hours and 24 hours. From figure 2.10 (a & b) it is found that there was no change in λ_{max} value for storing the solution for 12 hours and 18 hours but the colour intensity was increased after 18 hours as seen from the increase in absorbance value. As the particles gain size, the absorption peak usually shifts towards redder side as we find in Figure 2.10 c. Increase in absorption indicates that the quantity of Cu nanoparticles increased. The stable position of absorbance peak in Figure 2.10 a and 2.6 b indicate that new particles do not aggregate. During the initial trial experiments when Cu nanoparticles were synthesized without the addition of stabilizing agent, the yellow colour of the solution was persisted for few hours only in atmospheric condition. Further work, therefore, confined to TSC stabilized nano colloids.

2.4.1.3 Characterizations of synthesized and TSC stabilized copper nanoparticles

Figure 2.11 (a, b and c) represent the absorption spectra of different stages during the formation of Cu nanoparticle colloid from copper sulphate solution. It is seen from the inset photographs of the absorbance curves that how a blue green solution of copper sulphate gradually turned to yellow indicating the formation of Cu nanoparticles.

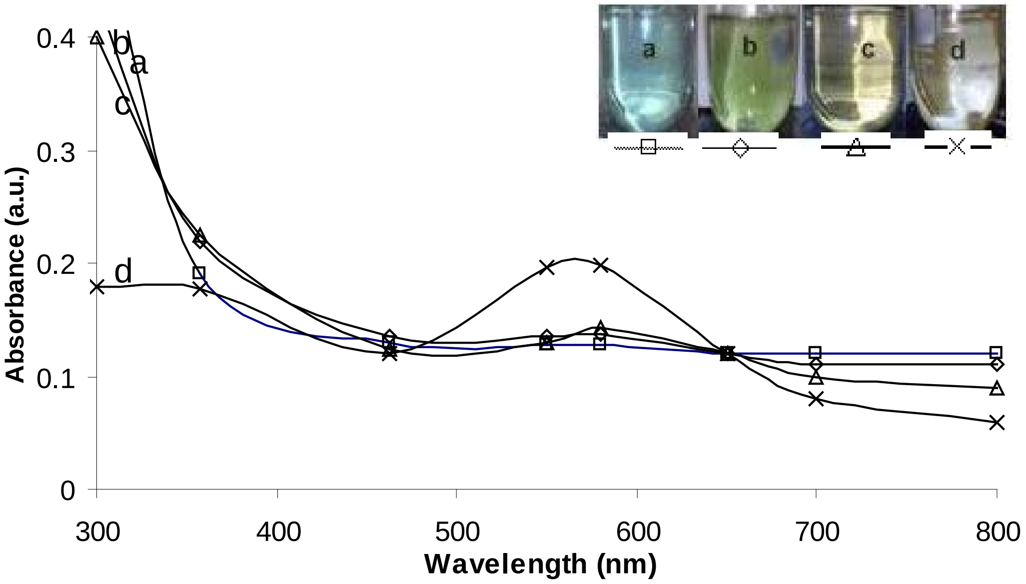
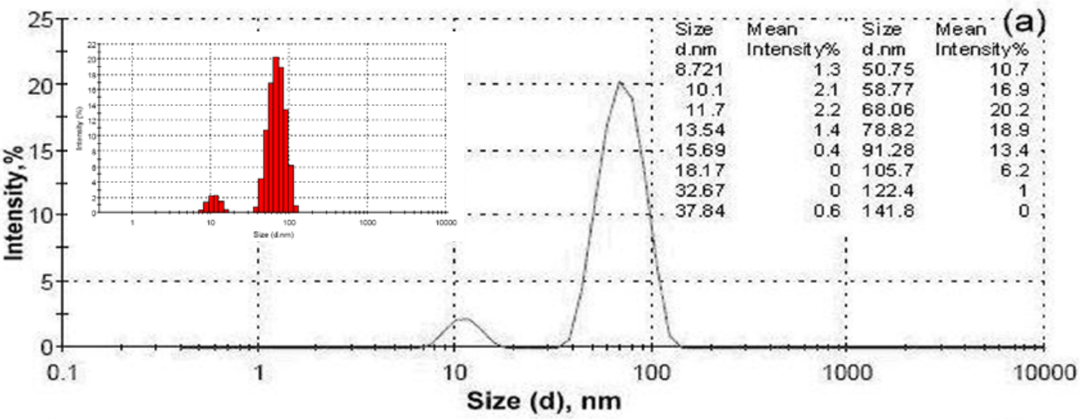


Figure 2.11 The UV-VIS spectrums of Cu nano colloids at different stages of synthesis [(a) Stage 1: Cu salt solution, (b) Stage 2: After the addition of reducing agent, (c) Stage 3: formation of Cu nano colloids and (d) Stage4: TSC stabilized Cu nano colloids.]

The shifting of blues-green color of $CuSO_4$ solution to intense yellow is due to the surface plasmon resonance, with a significant contribution from the interband transition which produces yellow colour hydrosol having maximum absorption at 580 nm (Figure 2.11 c & d) indicating nano Cu particles generation. The plasmon resonance of Cu nano particles was also observed at near 580 nm by Kazakevich et al [7]. Metals with free electrons possess plasmon resonances in the visible spectrum, which give rise to such intense colours. These properties are mainly observed in Au, Ag, and Cu because of the presence of free conduction electrons. The electric field of the incoming radiation induces the formation of a dipole in the nanoparticle. A restoring force in the nanoparticle tries to compensate for this, resulting in a unique resonance wavelength as reported by Henglein [8]. The wavelength of oscillation depends on a number of factors, among which particle size and shape, as well as the nature of the surrounding medium, are the most important factors.[9]

The particle size and size distribution of the prepared and stabilized Cu colloid were analyzed on Malvern instrument. Figure 2.12 (a) shows the intensity size distribution of Cu nano particles dispersed in water.



Size d.nm	Mean Intensity%	Size d.nm	Mean Intensity%
8.721	1.3	50.75	10.7
10.1	2.1	58.77	16.9
11.7	2.2	68.06	20.2
13.54	1.4	78.82	18.9
15.69	0.4	91.28	13.4
18.17	0	105.7	6.2
32.67	0	122.4	1
37.84	0.6	141.8	0

Figure 2.12 Particles Size and its distribution for synthesized and TSC stabilized Cu nano colloids; (a) by Intensity

The first peak at around 10 nm was arised from dispersion; the peak position at around 70 nm arises from stabilized Cu nano particles. Elemental analysis of gold coated Cu nano particles were performed on oxford Inca softwar using Scanning Electron Microscope (SEM). Figure 2.13 (a) shows the image analysis results of Cu nano particles. The elemental analysis results presented in Figure 2.13 (b) confirms the presence of copper particles. Peaks for carbon, gold, sodium also observed which got contaminated during the preparation of sample for elemental analysis.

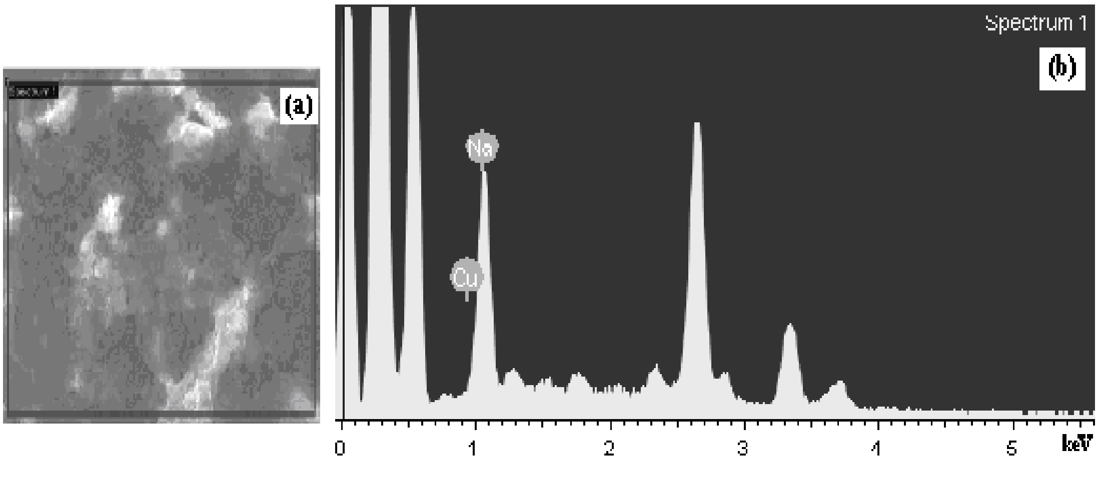
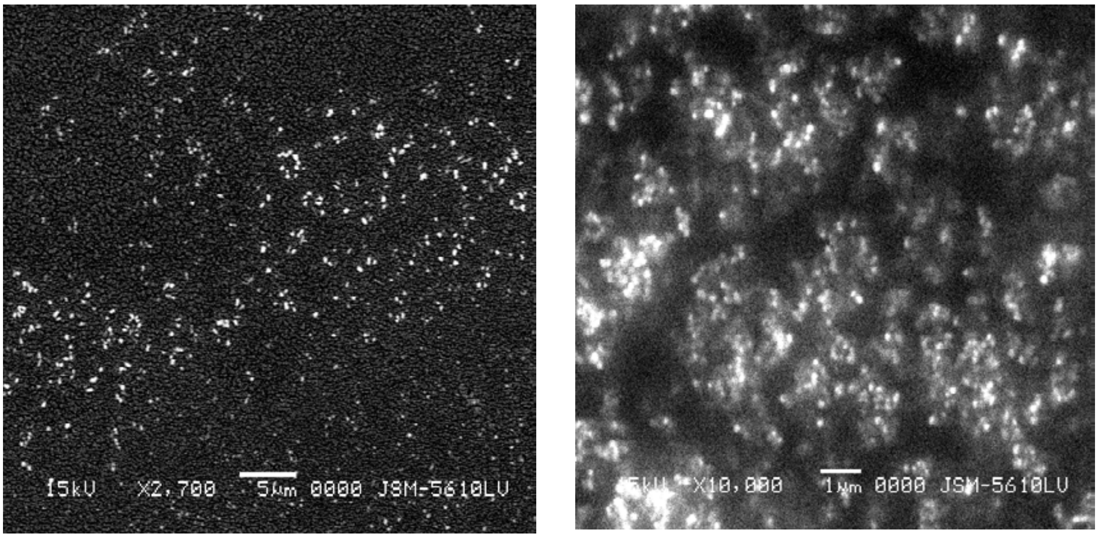
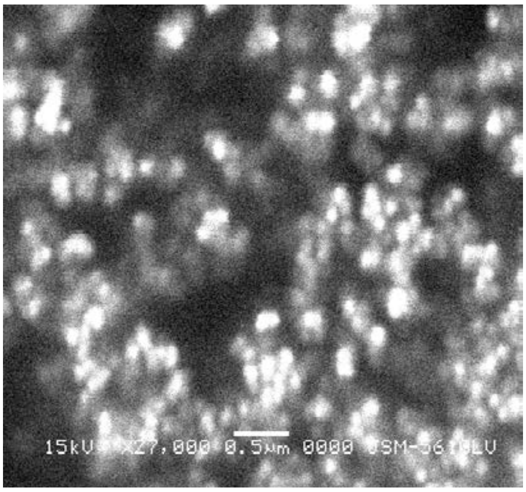


Figure 2.13 (a) SEM image of selected area of gold coated Cu nano particles (b) Elemental analysis of the synthesized particles using Inca software.

Figure 2.14 shows the scanning electron micrographs of stabilized Cu nano particles deposited on carbon coated aluminum sheet. From the images observed at 2700X, 10000X and 27000X it seems that the synthesized Cu nano particles were roughly spherical in shape.



Cu Nano@ 2700 X **Cu Nano@ 10000 X**



Cu Nano@ 27000 X

Figure 2.14 Scanning Electron Microscope (SEM) images of copper nano particles

The average size as seen from the scale of the photograph is about 60-100 nm which is also in agreement with the size distribution found using particle size analyzer

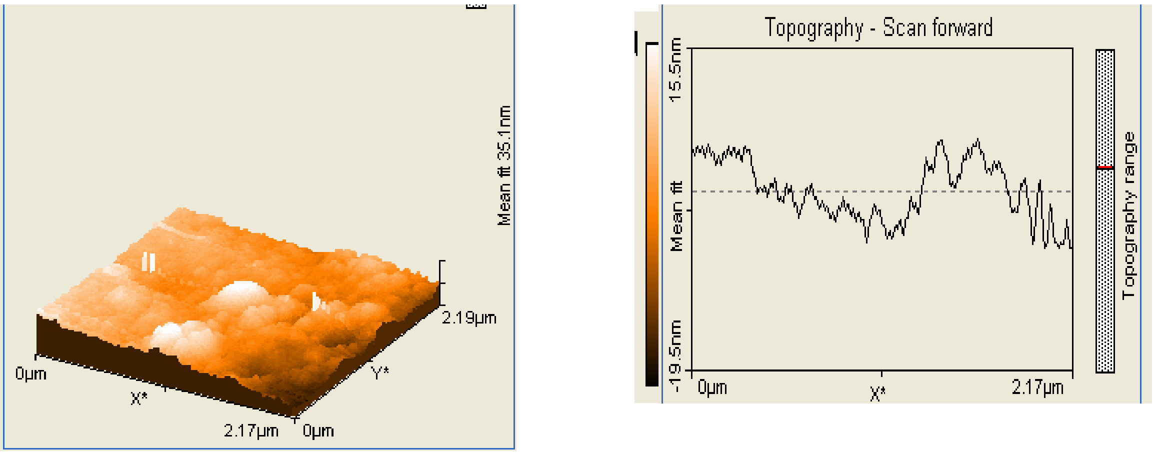
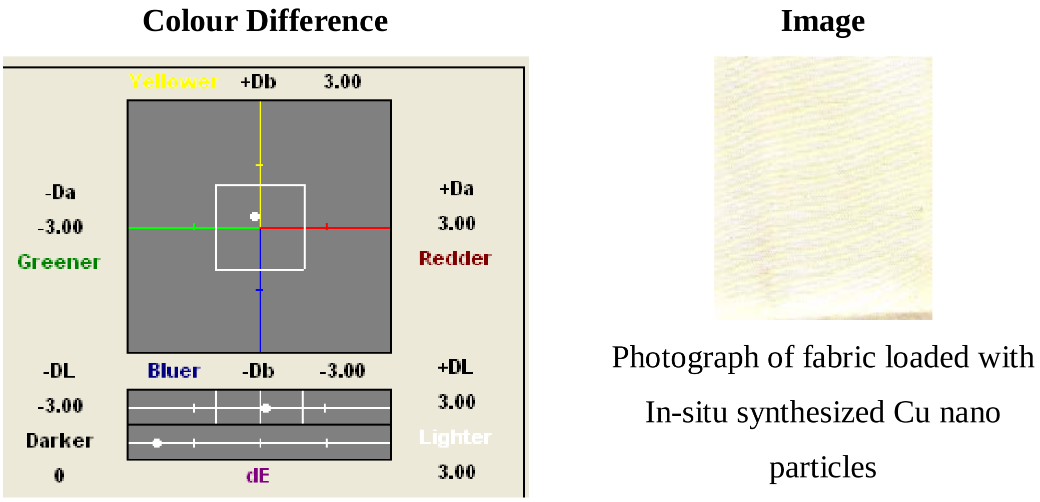


Figure 2.15 Atomic Force Microscopic image and topography of synthesized and TSC stabilized Cu nano colloids

The copper nano particles were deposited on glass plate for observation under atomic force microscopy (AFM). The size of nano Cu particles as seen from the scale on the AFM image (Figure 2.15) and topography lies below 100 nm, which also supports the results, obtained using particle size analyzer and SEM.

2.4.1.4 In situ formation and stabilization of copper nanoparticles on polyester fabric

As discussed in section 2.1.2, the in-situ synthesis and stabilization of the copper nano particles were done by impregnating polyester fabric first with chilled sodium borohydride followed by padding with copper sulphate solution and finally in-situ synthesis of nano particles and their locking in the fibre structure were done by curing at high temperature 180 °C for 60 seconds. Figure 2.16 shows the image and CCM colour coordinate of the fabric loaded with in-situ synthesized copper nano particles. Scanning electron microphotographs of the untreated and treated polyester are shown in figure 2.17. The surface deposited nano particles are seen in the SEM image of the treated polyester fabric.


Colour Difference

Image

Photograph of fabric loaded with In-situ synthesized Cu nano particles

Figure 2.16 Colour difference values of copper nano loaded polyester fabric

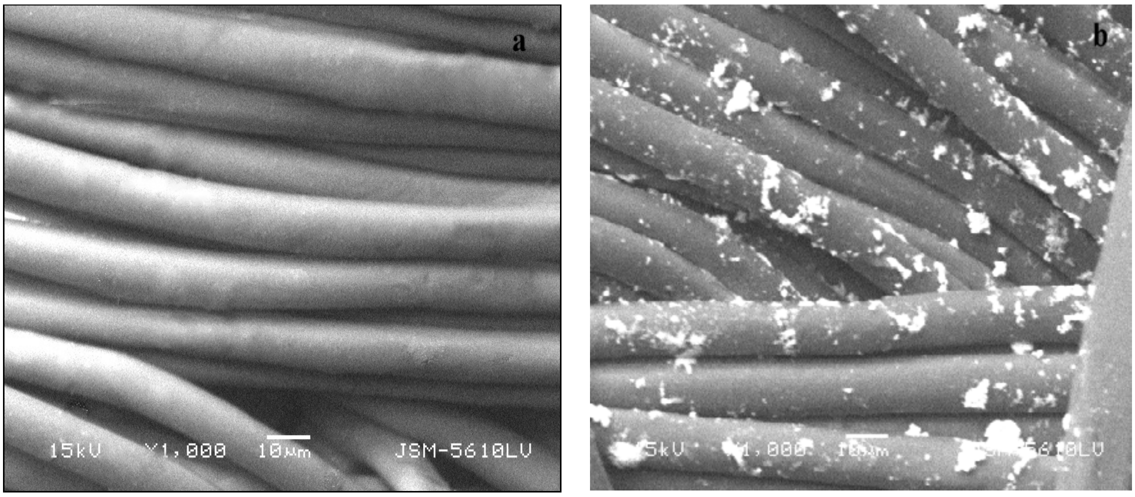


Figure 2.17 Scanning Electron Microscope (SEM) images of (a) normal polyester fabric and (b) in-situ synthesized and stabilized copper nano particles on polyester fabric

The amount of copper as element in the polymer structure was detected and measured using an X-ray fluorescence spectrometer (EDX 800 Simadzu, Japan). The operating X-ray source voltage and current were 35 kV and 26 mA respectively. Registration time was 30 s and the investigated area was 78.5 mm^2.

Both the treated and untreated polyester were analyzed on X- ray fluorescence spectroscopy for the detection and measurement of elemental copper respectively. The amount of copper found in the treated polyester was about 0.36 µg against nil for untreated one.

Table 2.3 Amount of copper detected on 78.5 mm^2 polyester with XRF

Structure	Amount of copper , µg
PET	Nil
Cu/PET fabric	0.36

2.4.2 Synthesis of colloidal silver nanoparticles

Silver nano colloidal particles were synthesized from silver salt by chemical reduction technique. The reduction of silver salt to silver nano particles was observed at different stages by computer colour matching system. The change in the colour of silver salt solution with the addition of reducing agent is shown in Figure 2.18. The progressive changes in the colour of the solution during the synthesis of silver nano particles were captured using computer colour matching system.

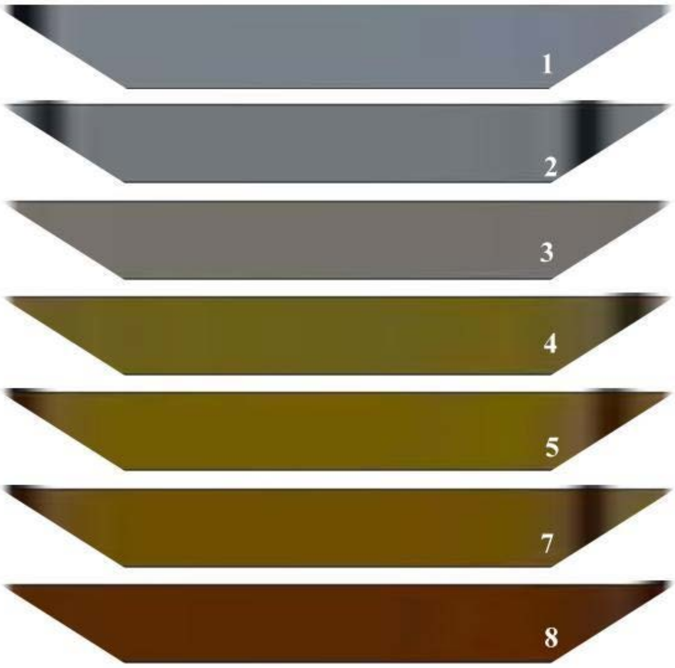


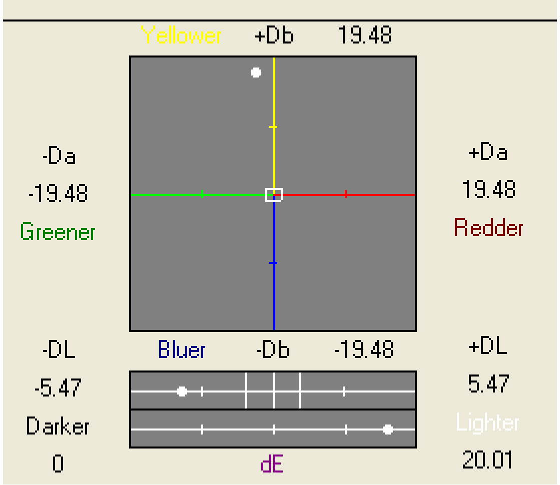
Figure 2.18 Progressive colour change of silver sulphate solution during the preparation of silver nano particles.

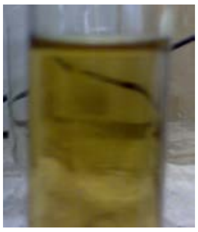
Figure 2.18 shows (i.e. stage 1-8) the gradual change in colour of silver salt during synthesis. Stage 1 presents the colour of silver sulphate solution before the addition of reducing agent. As the reaction proceeds i.e. with gradual addition of reducing agent, the colour of silver salt solution gradually changed to yellow (stage 7). After the addition of stabilizer TSC, colour of the solution was turned orange (stage 8) [15].

2.4.2.1 Change in colour of the synthesized silver nano colloid stored in atmospheric condition without stabilizing agent

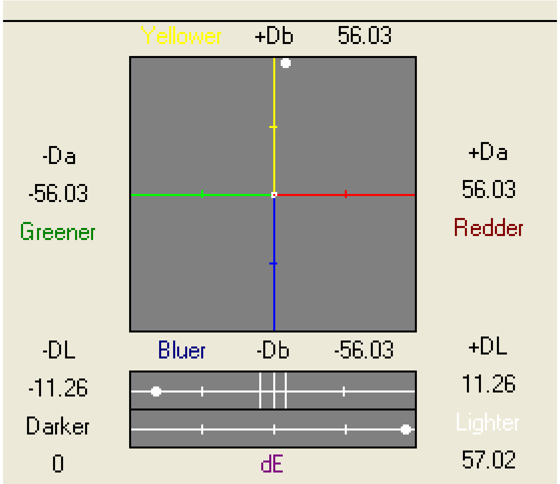
After synthesis, silver nano colloidal particles (in absence of capping agent) were analyzed for its change in colour using CCM system at different time intervals i.e. (i) just after synthesis, (ii) after storing for 48 hrs, and (iii) after storing for 72 hrs in atmospheric condition. From the results presented in Figure 2.19, it can be seen that even after storing for 72 hrs in atmospheric condition the colour of solution shifted towards red. But after 4 week of storing time the colour of the colloidal solution, changed to black.

Colour Difference **Image at time interval**

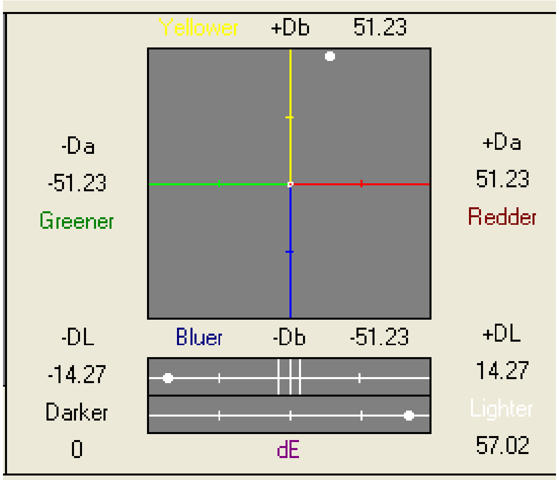




Ag nano (Freshly prepared)



Ag nano (after storing for 48 hrs)



Ag nano (after storing for 72 hrs)

Figure 2.19 Colour difference in Ag nano colloidal solution on storage in atmospheric condition (in absence of capping agent)

2.4.2.2 Stability of the TSC capped silver nano colloids in atmospheric condition

For examining the stability of the TSC capped nano silver colloid stored in atmospheric condition, the absorption spectra of the colloid were recorded measured at different time intervals viz. after 1 h, 2 weeks and 4 weeks which are shown in Figure

2.20. The UV-VIS spectrums recorded after different time intervals are shown in Figure 2.20 (a, b and c).

It is found that the stabilized silver nano colloidal solution gives an absorbance peak at 445 nm due to plasmon resonance of the nanoparticles. Similar observation was also reported by Šileikaitė et al [15]. The plasmon peak and the full-width of half-maximum (fwhm) depend on the extent of colloid aggregation.[8]

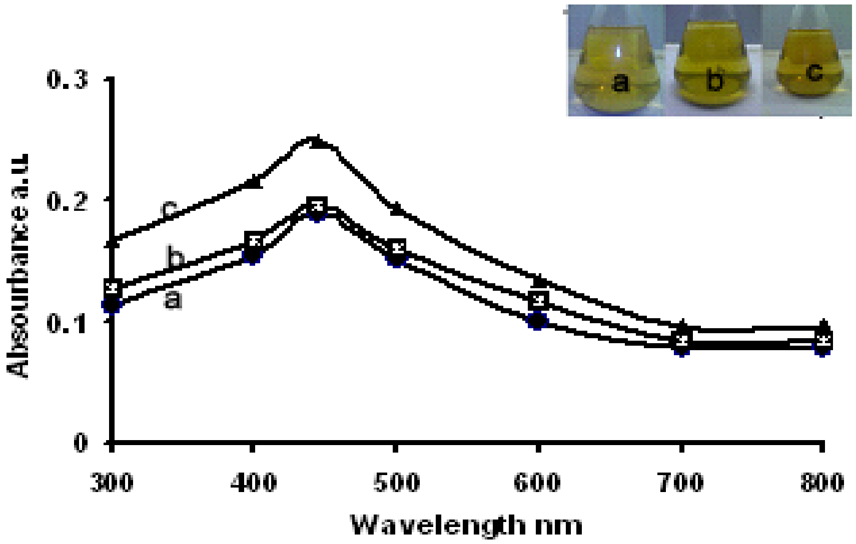


Figure 2.20 UV-VIS spectra of Ag colloids [time after synthesis: (a) 1 h, (b) 2 weeks and (c) 4 weeks]

There was no change in the peak position found even after storing for 4 weeks. The inset photograph (Figure. 2.20) shows that there is no reasonable change in the colour of the colloidal solutions except little darkening of colour when stored for 4 weeks. The stable position of the absorbance peak (λ_{max}) indicates that the particles do not aggregate. The increase in absorbance value after storing for 4 weeks is indicative of increase in concentration of the nanoparticles through the generation of new particles.

2.4.2.3 Characterizations of synthesized and TSC stabilized colloidal silver nanoparticles

Nano sized Ag particles in colloidal form prepared by chemical reduction technique were characterized for their size, shape and elemental analysis. The particle size and size distribution of stabilized nano Ag colloid were analyzed on Malvern instrument. Figure 2.21 shows the intensity size distribution of Ag nanoparticles dispersed in water. The first peak at around 110 nm arises from the dispersion.

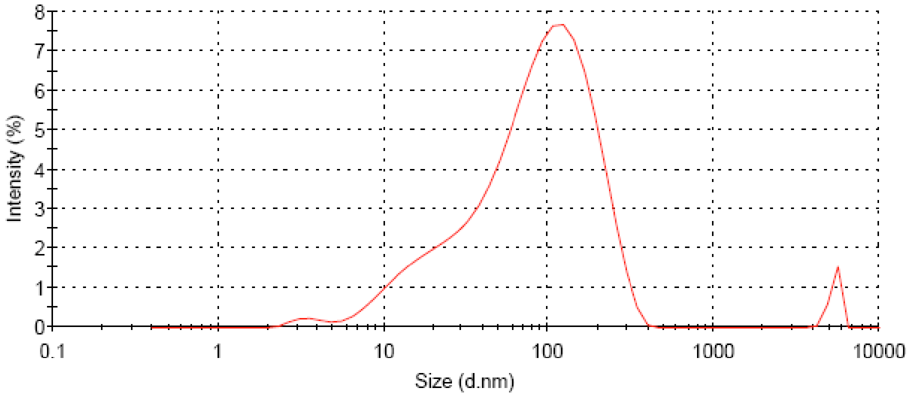


Figure 2.21 Particle size distribution of stabilized Ag nanoparticles by intensity

The peak positioned at 4 microns was arised from the stabilized Ag nanoparticles. The presence of the second peak has resulted in the *Z*-average diameter for this sample increasing to 62.06 nm. It is also evident from the particle size analysis that most of the nano particles are in the range of 60 nm to 120 nm.

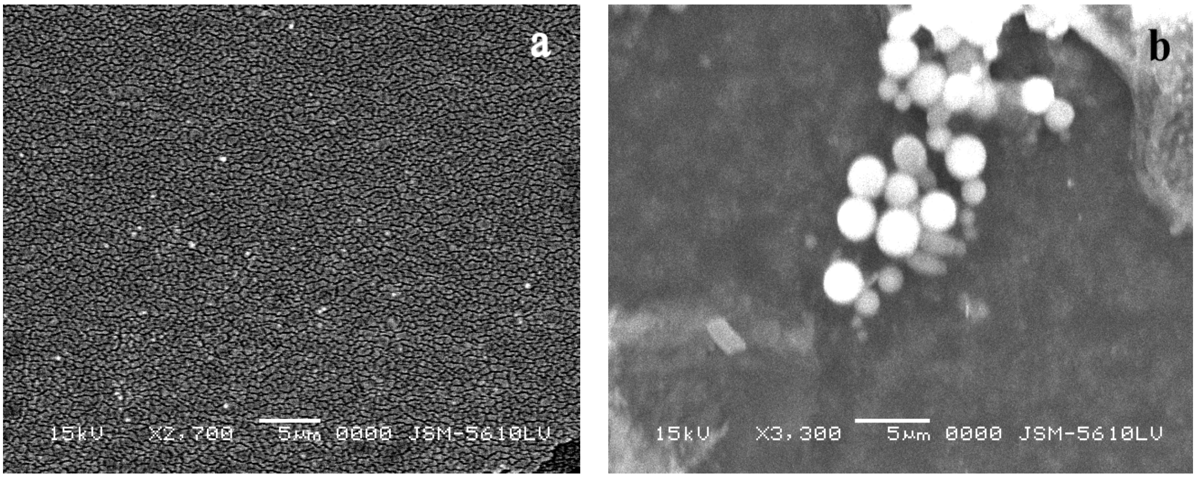


Figure 2.22 Scanning electron microphotographs of silver nanoparticles (a) deposited on carbon coated aluminum sheet and (b) coated with gold and deposited on carbon coated aluminum sheet

Figure 2.22a shows the scanning electron microphotographs of stabilized Ag nanoparticles deposited on carbon coated aluminium sheet. The average size as seen from the scale of the photograph is approximately below 90-100 nm which also supports the size obtained using particle size analyzer. Figure 2.22b represents the microphotographs of the gold coated Ag nanoparticles. It can be seen from the figure that the shape of the gold coated particles is spherical and the size of nanoparticles is increased by 500 – 800 nm due to the gold coating.

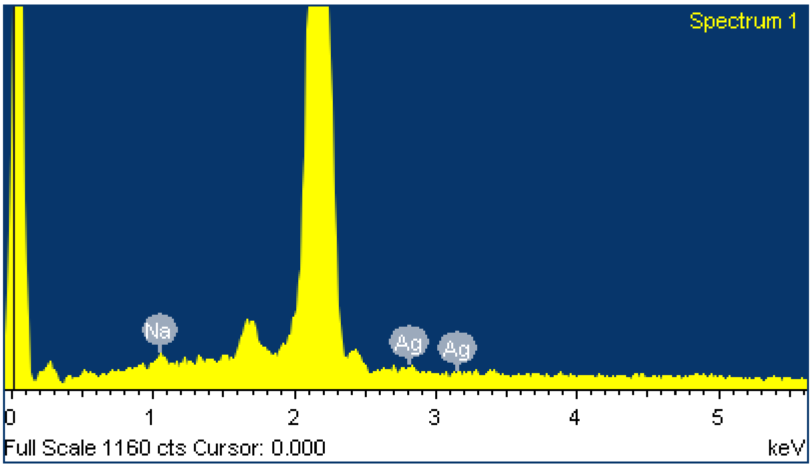
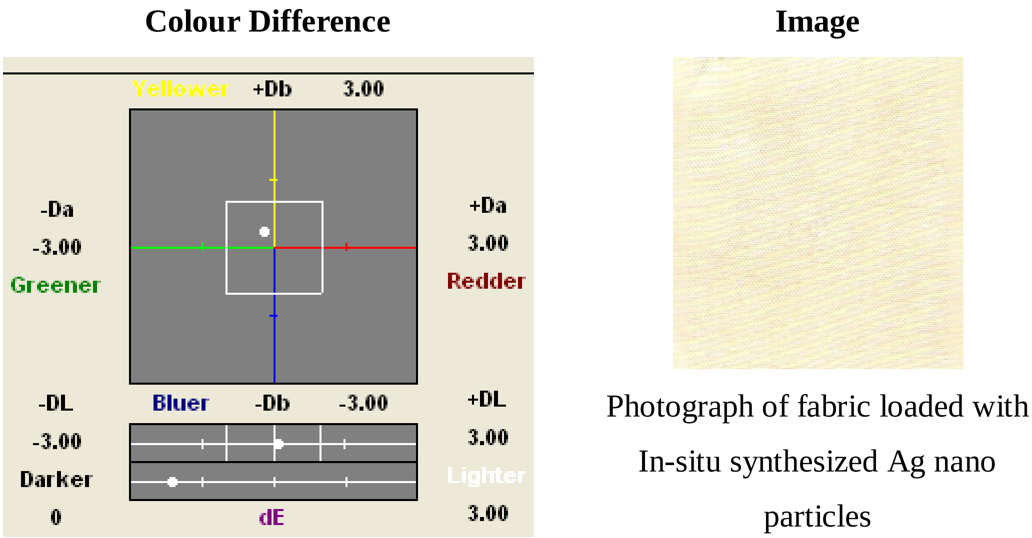


Figure 2.23 Elemental analysis result of silver nanoparticles deposited on carbon coated aluminum sheet and further coated with gold

Elemental analysis of gold coated nanoparticles was performed on the scanning electron microscope using special software. The result observed in this test is shown in Figure 2.23. Presence of silver is confirmed by the elemental analysis curve. The peaks for carbon, gold and sodium have also been observed.

2.4.2.4 In situ formation and stabilization of silver nanoparticles on polyester fabric

The in-situ synthesis and stabilization of the silver nano particles were done by impregnating polyester fabric first with chilled sodium borohydride followed by padding with silver sulphate solution and finally in-situ synthesis of nano particles and their locking in the fibre structure were done by curing at high temperature 180 °C for 60 seconds. Figure 2.24 shows the image and CCM colour coordinate of the fabric loaded with in-situ synthesized silver nano particles. It can be seen from the figure that the colour of polyester fabric after synthesis of silver nano by in-situ technique was turned to yellow. Scanning electron microphotographs of the untreated and treated polyester are shown in figure 2.25. The surface deposited nano particles are seen in the SEM image of the treated polyester fabric.


Colour Difference

Image

Photograph of fabric loaded with In-situ synthesized Ag nano particles

Figure 2.24 Colour difference values of Ag nano loaded polyester fabric

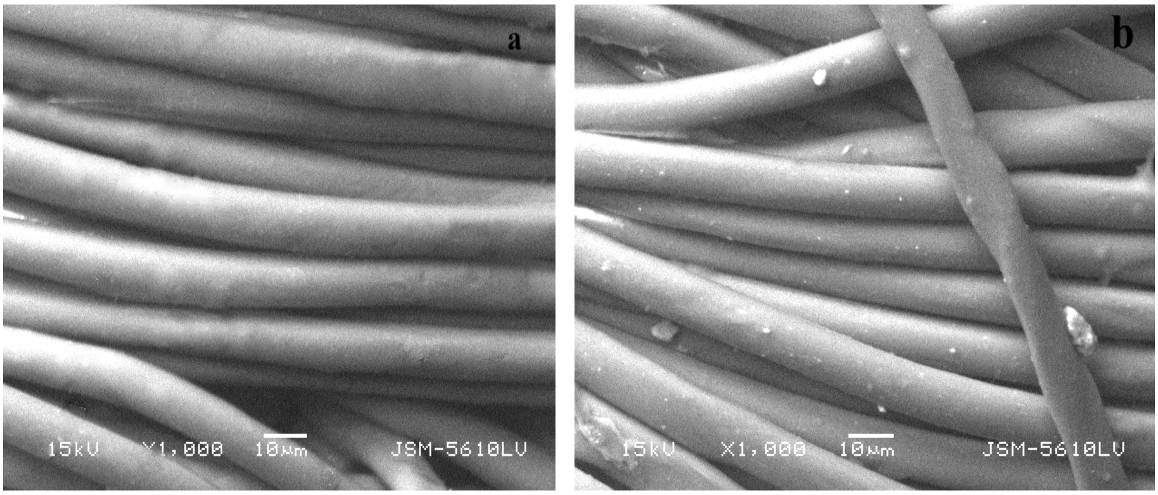


Figure 2.25 Scanning Electron Microscope (SEM) images of (a) normal polyester fabric and (b) in-situ synthesized and stabilized silver nano particles on polyester fabric

The amount of silver as element in the polymer structure was detected and measured using an X-ray fluorescence spectrometer (EDX 800 Simadzu, Japan). The operating X-ray source voltage and current were 35 kV and 26 mA respectively. Registration time was 30 s and the investigated area was 78.5 mm^2. From Table 2.4 it can be seen that the amount of silver found in the treated polyester was about 0.273 µg against nil for untreated one.

Table 2.4 Amount of silver detected on 78.5 mm^2 polyester with XRF

Structure	Amount of copper , µg
PET	Nil
Ag/PET fabric	0.273

2.4.3 Synthesis of colloidal zinc nanoparticles

Zinc nano colloidal particles were synthesized from zinc salt by chemical reduction technique. The absorption spectrum of the prepared colloidal solution dispersed in water is shown in Figure 2.26. It is found that the solution after synthesis gives an absorbance peak at 370 nm. Similar observation at ~375 nm was also reported by Zhang, et al (2002) [22]. Figure 2.26 (a, b and c) represent the absorption spectra of different stages during the formation of zinc nanoparticle colloid from zinc salt solution. It is seen from the absorbance curves that how a clear solution of zinc salt gradually turned to milky white indicating the formation of zinc nanoparticles.

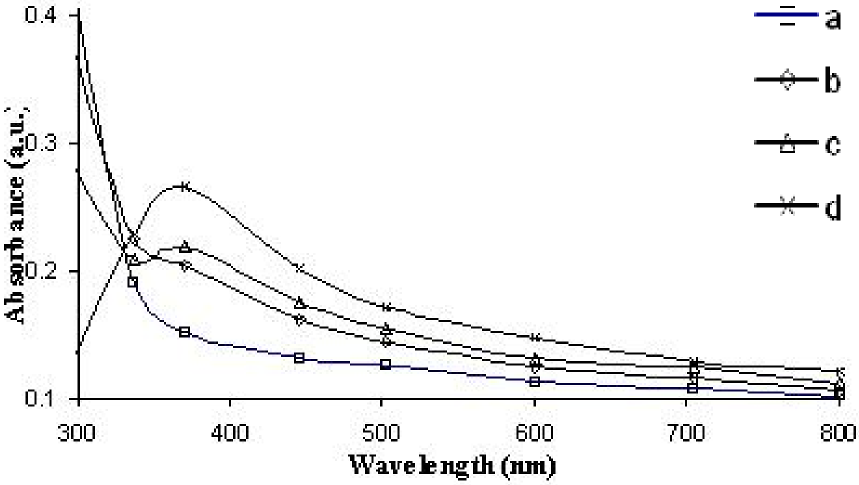
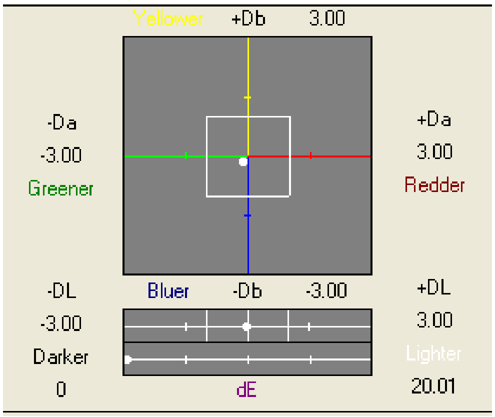


Figure 2.26 The UV-VIS spectrums of Zn nano colloids at different stages of synthesis [(a) Stage 1: Zn salt solution, (b) Stage 2: After the addition of reducing agent, (c) Stage 3: formation of Zn nano colloids and (d) Stage4: TSC stabilized Zn nano colloids.]

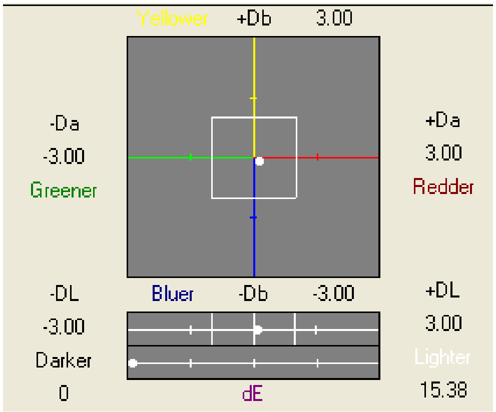
2.4.3.1 Stability of the synthesized zinc nano colloid stored in atmospheric condition without stabilizing agent

After synthesis, zinc nano colloidal particles were stored in atmospheric condition for different time intervals, i.e. (i) for 48 hrs and (ii) storing for 72 hrs in atmospheric condition. The colour difference evaluated by CCM and corresponding photographs of the solution given in Figure 2.27, it can be seen that after storing for 72 hrs in atmospheric condition the intensity of the solution was slightly changed. But after that the bigger particles settled down at bottom of the flask and the solution become clear.

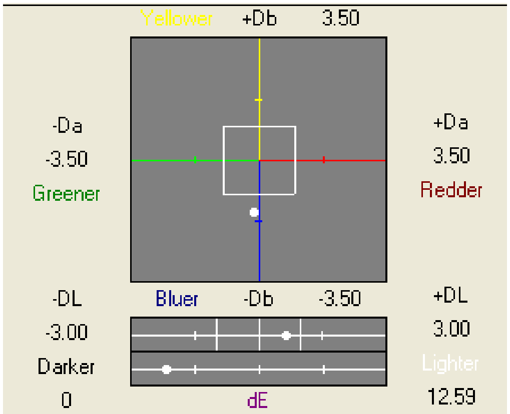
Colour Difference **Image at time interval**



Zn nano (Freshly prepared)



Zn nano (after storing for 48 hrs)



Zn nano (after storing for 72 hrs)

Figure 2.27 Colour difference in Zn nano colloidal solution on storage in atmospheric condition without capping

2.4.3.2 Characterizations of synthesized and TSC stabilized colloidal zinc nanoparticles

Zinc particles were prepared by reduction of zinc salt and stabilized with citrate anions. The nano Zn particles in the solution were characterized for their size, shape and elemental analyses

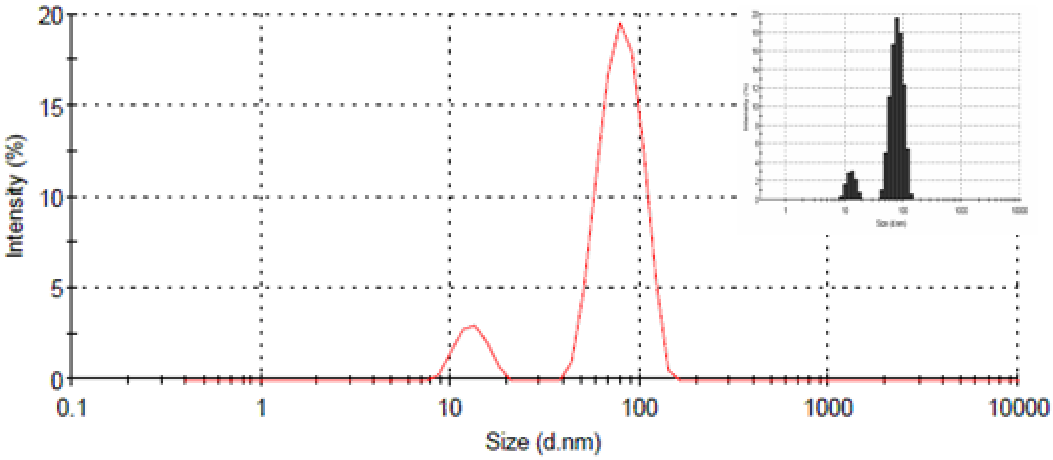


Figure 2.28 Particle size distribution of stabilized Zn nanoparticles by intensity

The particle size and size distribution of the prepared and stabilized Zn colloid were analyzed on Malvern instrument. Figure 2.28 shows the intensity size distribution of Zn nano-particles dispersed in water. The first peaks at around 15 nm arise from dispersion; this peak represents nano particles of size 13.14 nm diameter. The presence of second peak has resulted in the average diameter of 81.62 nm. Figure 2.29 shows the scanning electron micrographs of Zn nano-particles The average size as seen from the scale of the photograph is below 100 nm which is in agreement with the size distribution found using particle size analyzer.

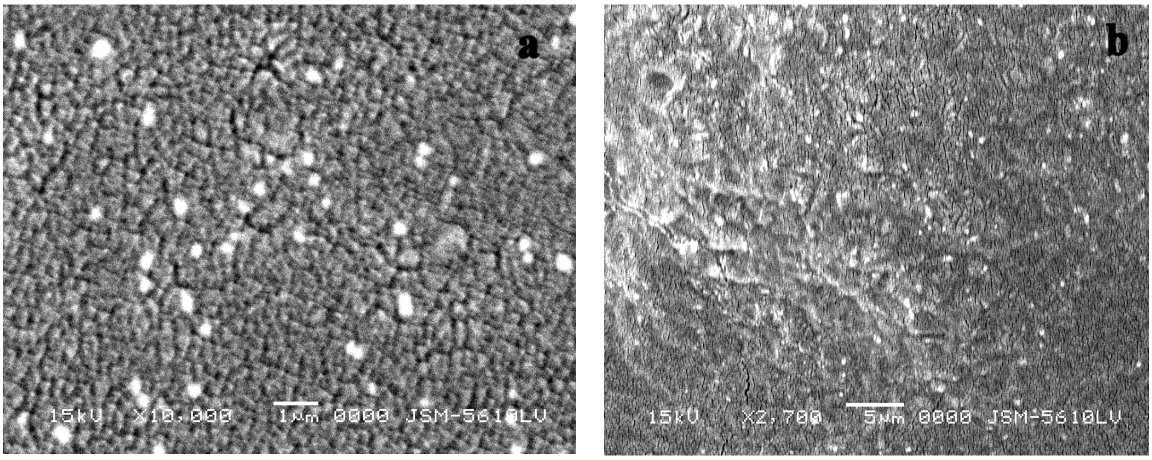


Figure 2.29 Scanning electron microphotographs of silver nanoparticles (a) deposited on carbon coated aluminum sheet and (b) coated with gold and deposited on carbon coated aluminum sheet

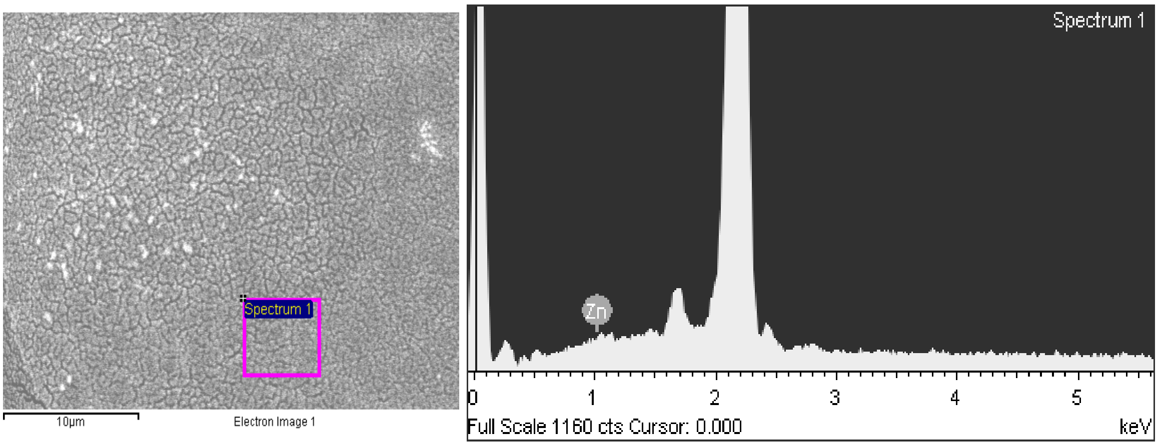


Figure 2.30 SEM micrograph and EDX spectrum of selected area of nano-particles deposited carbon coated aluminium sheet and further coated with gold.

Figure 2.30 represents the elemental analysis result which confirms the presence of zinc. Peaks for carbon, gold, sodium also were observed which are used for the preparation of sample for elemental analysis.

2.4.3.3 In situ formation and stabilization of zinc nanoparticles on polyester fabric

As shown in the Figure 2.3 an experimental set up was designed for the continuous synthesis and simultaneous application of Zn nano particles to polyester fabric. The SEM microphotograph of treated polyester fabric (Figure 2.31) confirms the uniform deposition of nano particles on the surface of the fabric. The SEM image also confirms that the average size of the synthesized Zn nanoparticles is remaining below 100 nm and the shape of the particle is spherical.

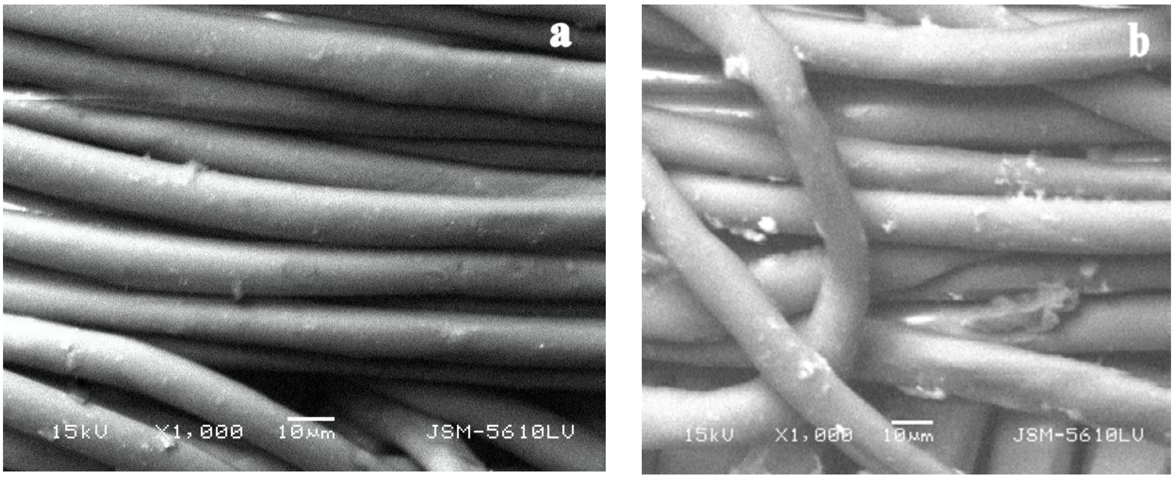


Figure 2.31 Scanning Electron Microscope (SEM) images of (a) normal polyester fabric and (b) in-situ synthesized and stabilized zinc nanoparticles on polyester fabric

The amount of zinc as element in the polymer structure was detected and measured using an X-ray fluorescence spectrometer (EDX 800 Simadzu, Japan). The operating X-ray source voltage and current were 35 kV and 26 mA respectively. Registration time was 30 s and the investigated area was 78.5 mm^2.

Table 2.5 Amount of zinc detected on polyester fabric with XRF

Structure	Amount of zinc, µg
PET	Nil
Zn/PET fabric	0.228

The results given in Table 2.5 show that the amount of zinc found on treated polyester was about 0.228 µg against nil for untreated one.

2.5 REFERENCES

1. D. P. Chattopadhyay, Nanotechnology-the emerging trends, *Textiles*, 2006, 33, 21-24.
2. B. H. Patel and D.P.Chattopadhyay, Nano-particles & their uses in textiles, *The Indian Textile Journal*, 2007, 118, 23-31.
3. D. P. Chattopadhyay and B. H. Patel, Improvement in physical and dyeing properties of natural fibres through pre-treatment with silver nanoparticles, *Indian Journal of Fibre & Textile Research*, 2009, 34, 368-373.
4. D.P.Chattopadhyay and B.H. Patel, Modification of Cotton Textiles with Nanostructural Zinc Particles, *Journal of Natural Fibers*, 2011, 8, 39-47.
5. D.P.Chattopadhyay and B.H.Patel, Effect of nanosized colloidal copper on cotton fabric, *Journal of Engineered Fiber Fabrics*, 2010, 5, 1-6.
6. N.R. Jana, Z. L. Wang, T. K. Sau, and T. Pal, Seed-mediated growth method to prepare cubic copper nanoparticles, *Current Science*, 2000, 79, 1367-1370
7. P.V.Kazakevich, V.V.Voronov, A.V.Simakin and G. A.Shafeev, Production of copper and brass nanoparticles upon laser ablation in liquids, *Quantum Electron*, 2004, 34, 951-956.
8. A.Henglein, Physicochemical properties of small metal particles in solution: "microelectrode" reactions, chemisorptions, composite metal particles, and the atom-to-metal transition, *J. Phys. Chem.*, 1993, 97, 5457–5471.

9. P.Mulvaney, Surface plasmon spectroscopy of nanosized metal particles, *Langmuir*, 1996, 12, 788-800.
10. I. M. Yakutik, G. P. Shevchenko and S. K. Rakhmanov, The formation of monodisperse spherical silver particles, *Colloids Surfaces A: Physicochem Eng Aspects,* 2004,.242, 175 – 179.
11. K. Patel, S. Kapoor, D. P. Dave and T. J. Mukherjee, Synthesis of Pt, Pd, Pt/Ag and Pd/Ag nanoparticles by microwave-polyol method, *J. Chem Sci,* 2005, 117, 1, 3 – 6.
12. L. Razafimahefa, S. Chlebicki, I. Vroman and E. Devaux, Effect of nanoclays on the dyeability of polypropylene nanocomposite fibres, *Coloration Technol,* 2008, 124, 2, 86-91.
13. M. Radetić, V. Ilić, V. Vodnik , S. Dimitrijević, P. Jovančić, Z. Šaponjić and J. M . Nedeljković, The antibacterial effect of silver nanoparticles deposited on corona treated polyester and polyamide fabrics, *Polym. Advanced Technol*, 2008, 19, 12, 1816-182
14. N. L. Lala, R. Ramaseshan , L. Bojun, S. Sundarrajan , R. S. Barhate, L. Ying-jun and S. Ramakrishna, "Fabrication of nanofibers with antimicrobial functionality used as filters: protection against bacterial contaminants, *Biotechnol Bioeng,* 2007, 97, 6, 1357-1365.
15. A. Šileikaitė, I. Prosyčevas, J. Puišo, A. Juraitis and A. Guobienė, Analysis of silver nanoparticles produced by chemical reduction of silver salt solution. *Mater. Sci. (Medžiagotyra),* 2006, 12, 4, 287-291.
16. S. Yamamoto, K. Fujiwara and H. Watari, "Surface-enhanced Raman scattering from oleate-stabilized silver colloids at a liquid/liquid interface, *Anal. Sci.,* 2004, 20, 1347 – 1352.
17. K. Havanscak, Nanotechnology at present and its promises in the future, *Materials Science Forum,* 2003 , 414-415, 85-94.
18. A. L. Efros and M. Rosen, The electronic structure of semiconductor nanocrystals, *Annu. Rev. Mater. Sci.*, 2003, 30, 475-521.
19. J. Dutta and A. Sugunan, "Colloidal self-organization for nanoelectronics" in B. Y. Majlis, and S. Shaari (Ed.) *IEEE international conference on semiconductor electronics,* 2004, A6-A11, Kuala Lampur.
20. B. D. Gates, Q. Xu, J. C. Love, D. B. Wolfe, and G. M. Whitesides, Unconventional nanofabrication, *Annu. Rev. Mater. Res.*, 2004, 34, 339-372.

21. H. Zhang, Z. Wang, L. Zhang, Y. Li, J. Yuan, and S. Yan, Chemical synthesis and characterization of Cu doped ZnS nano-powder, *J. Mater. Sci. Lett.*, 2002, 21, 1031-1033.
22. M. Bruchez Jr., M. Moronne, P. Gin, S. Wiess, and A. P. Alivisatos, Semiconductor nanocrystals as fluorescent biological labels, *Science*, 1998 , 281, 2013-2016.

CHAPTER 3

APPLICATION OF NANO COLLOIDS TO TEXTILES

3.1 INTRODUCTION

Nano structured entities have extraordinary properties, when introduced to textile fiber they generate special properties or cause enhancement of existing properties. Nano-size particles of Pd/Pt, Ag and Fe can be applied on textiles to impart antibacterial, conductive magnetic properties and remote heating properties. Silver has been used for the treatment of medical ailments for over 100 years due to its natural anti-bacterial and anti-fungal properties. Nano-silver particles are widely applied in socks to prohibit the growth of bacterial. In addition, nano-silver can be applied to a range of other healthcare products such as dressings for burns, scald, and skin donor and recipient sites. Nano-silver particles can be applied on textiles by padding method with good laundering durability [1]. Hoon Joo Lee and Song Hoon Jeong [2] have reported that nano-sized silver colloids and nano-silver treated polyester nonwovens have good bacteriostasis. Water based and ethanol based nano-silver colloids with spherical nano-particals of diameter 2-5 nm can be applied to polyester nonwoven fabric. It has been reported thet the growth of bacteria colonies is absolutely inhibited with only 10 ppm colloidal silver nano-particles. Nano-size particles of TiO_2, ZnO, Al_2O_3, and MgO are a group of metal oxide that posses photo catalytic ability, electrical conductivity, UV absorption, and photo-oxidizing capacity against chemical and biological species [3]. Intensive research involving the nono-particles of metal oxides have been focusing on antimicrobial, self decontaminating, and UV blocking functions for both military protection gears and civilian health products. Nylon fiber filled with ZnO nano-particles can provide UV shielding function and reducing static electricity of nylon fiber. A composite fiber with nano-particles of TiO_2/MgO can provide self-sterilizing function as reported by L.Qian [4]. TiO_2 and MgO nano-particles can be entrapped into textile fibers during the spinning process or incorporated into a textile material via normal textile finishing methods with a resultant material having chemical and biological protective performance [5]. He, Junhui et.al.2003, has stated that cellulose fiber filled with nano-particles of metal oxides (such as TiO_2) from *in situ* synthesis can be used as a catalyst in fuel cells [6].

In this section, the effects of application of synthesized nanoparticles to textiles materials are reported. The synthesized Ag, Cu and Zn nanoparticles were applied to various natural fiber fabrics like cotton, wool, jute and silk by exhaust and pad-dry-cure technique (PDC). The treated fabric surfaces were characterized using scanning electron microscopy (SEM) and X-ray fluorescence spectroscopy. The treated and untreated fabric samples were tested for various properties like dyeability, colour fastness, antimicrobial properties etc.

3.2 MATERIALS AND EXPERIMENTAL METHODS

The experimental plan was based on application of synthesized and TSC capped metallic nanoparticles i.e. Cu, Ag and Zn by exhaust and pad–dry-cure methods. The treated fabric samples were then characterized by various techniques. Finally, the changes properties, due to the nano treatment were evaluate by various standard methods.

3.2.1 Fabric

Cotton, wool, silk and jute fabrics with specification as given in Table 3.1 were supplied by Kiran Threads, Vapi (Gujarat) for the study. All the fabric were mild scoured (5% soap Lisaapol L, and 2% soda ash at boil for 15 min.) before use. The procured fabric was further thoroughly washed, neutralized and air dried.

Table 3.1 Specification of cotton, wool and silk fabrics

Fabric	Weave	Ends/ inch	Picks/ inch	Weight g/m^2
Cotton	Plain	112	72	118
Wool	Plain	80	60	65
Silk	Plain	84	62	29
Jute	Plain	13	10	165.11

3.2.2 Dyes and chemicals

Three commercial direct dyes, namely C.I. Direct Red 9 (D1), C.I. Direct Blue 67 (D2) and C.I. Direct Green 6 (D3), three acid dyes likes Acid orange R- AD1, Acid navy blue- AD2 and Acid rose 6B- AD3, three natural colourants *Azadirachta indica* -ND1, *Lawsonia inermis* -ND2 and *Ocimum sanctum* -ND3 and synthesized and TSC capped metallic nano colloids i.e. Cu, Ag and Zn colloids as described in chapter 2 were used for this study without further purification. Gram positive Staphylococcus aureus (Lab collection) was used for evaluation of antimicrobial property test as per ASTM E-2149 method.

3.2.3 Equipments used for the work reported in this section

- Laboratory Constant temperature shaking water bath (Alliance enterprise, India) for the application of nano material and dyes at Department of Textile Chemistry, The M.S. University of Baroda.
- Laboratory two bowl automatic padding mangle (EEC, India) for the application of nano material and dyes at Department of Textile Chemistry, The M.S. University of Baroda.
- Launder-ometer (Digi.wash, Paramount Scientific Instruments., India). For the evaluation of washing fastness at Department of Textile Chemistry, The M.S. University of Baroda.
- Xenon arc Fadometer, (FDA-R, Atlas, U.S.A.). For the evaluation of light fastness property of dyed textiles at Department of Textile Chemistry, The M.S. University of Baroda.
- Sasmira crease recovery tester (India) for AATCC Test Method 66-2003 at Department of Textile Chemistry, The M.S. University of Baroda.
- Prolific stiffness tester (India) AATCC Test Method 115-2005 at Department of Textile Chemistry, The M.S. University of Baroda.
- Spectrophotometer interphased with computer colour matching system; Spectra scan 5100 (RT) (Premier colour scan instrument), India test was performed at Department of Textile Chemistry, The M.S. University of Baroda.
- Tensile strength tester: (LRY Model, Lloyd, U.K), for measuring breaking load of fabric samples. The tests were performed at Department of Textile Engineering, The M.S. University of Baroda.
- Air permeability test: Metefem, type-FF12/A, no: 8838_002, made in Hungary, for measuring the air permeability of fabric. Tests were performed at Department of Textile Engineering, The M.S. University of Baroda
- SEM Model JSM-5610 LV Japan, for characterizing surface morphology, size and shape, The tests were performed at Department of Metallurgical and materials engineering, The M.S. University of Baroda.
- X-ray fluorescence spectrometer (EDX 800 Simadzu, Japan). For quantitative and qualitative elemental analysis of the polymer nano composite materials. The tests were performed at Department of Metallurgical and materials engineering, The M.S. University of Baroda.

- UV-VIS Spectrophotometer (600LC, Japan): for spectral analysis of UV transmission percentage, at the Department of Applied Physics, The M.S. University of Baroda.
- Antimicrobial test equipments: AATCC Test Method 30-2004, test was performed at Department of Textile Chemistry, The M.S. University of Baroda.
- Antibacterial test equipments: Incubator cum oven, Laminar air flow (Hexatec Instruments Pvt. Ltd. Mumbai: Model: HIPL-042), Autoclave Equitron (Sr.No. NC11GC-2824), Shaker Incubator and UV spectrophotometer, tests were conducted at Department of Microbiology, (Genone Research Centre), The M.S. University of Baroda.
- Electrical surface resistivity test: KEITHLEY-614 Electrometer MET/K/16B, USA, for measuring electrical surface resistivity of cotton and polyester fabric sample as per AATCC test method 76-2005 at the Department of Applied Physics, The M.S. University of Baroda.

Experimental design

The experiments were designed to apply metallic nano sol to cotton, wool, silk and jute fabrics, and to study the effects of nano treatment on the functional performance of the fabric. The experiments were divided into two parts as follow:-

1) Application of copper, silver and zinc nanoparticles to cotton, wool, silk and jute fabric by both exhaust and pad-dry cure techniques.
2) Evaluation of changes occurred in functional properties of textiles due to the treatment and their comparison with the respective untreated textiles.

3.3 EXPERIMENTAL METHODS

3.3.1 Preparation of textile fabrics for nano treatment

To remove the finish and other hydrophobic impurities from all the four selected fabrics i.e. cotton, wool, silk and jute, they were treated in the bath containing 5gpl non-ionic detergent (Lissapol N) and 2 gpl sodium carbonate for 30 minutes at 80 ^{0}C temperature. Then the fabrics were washed thoroughly in running water, neutralized and again washed thoroughly in running water. Finally, the pH of fabrics was checked to neutral.

3.3.2 Treatment of natural textiles with copper, silver and zinc nano colloids

3.3.2.1 Exhaust method

The synthesized nano-colloidal solution was applied to cotton, wool, silk and jute fabric samples using exhaust method on a constant temperature shaking water bath. The fabric samples were treated for one hour at 40°C keeping a material –to-liquor ratio of 1:50. The temperature was then raised to 80°C over 30 min. the treated fabric samples were thoroughly washed, neutralized and dried in air.

3.3.2.2 Pad –dry –cure method

Nano-colloidal solutions were applied to cotton, wool, silk and jute fabric samples by dipping them in the dispersion for 10 min and then padded on an automatic two bowl padding mangle which was running at 15 rpm with a pressure of 1.75 Kg/cm^2 using 2-dip-2-nip padding sequence at 70% expression. The padded substrates were air dried and finally cured at 120 ˚C for 20 min in a preheated curing oven.

3.3.3 Testing and Analysis

3.3.3.1 Fabric characterization

The treated and untreated samples were examined using scanning electron microscope and X-ray fluorescence spectrometer. Before physical testing the samples were dried and conditioned at 65± 2 % RH and 27 ± 2°C temperature.

Determination of Tensile Properties

2 cm x8 cm fabric samples were tested at 100 mm/min traversing speed for the determination of breaking load, breaking elongation, stress and strain. The test was performed as per B.S. 2576:1959 (B.S. Handbook No. 11, p.249)

Figure 3.1 Lloyd tensile strength testers.

Determination of crease recovery angle

The test specimen was folded and compressed under controlled condition of defined force to create a folded angle. The specimen was then suspended in an instrument for a controlled recovery; the recovery angle was then examined. The test was performed as per AATCC test method 66-2003.

Figure 3.2 Wrinkle recovery angle tester

Determination of bending length

The stiffness in terms of bending length of nano treated and untreated samples were measured as per AATCC Test Method 115-2005 using Prolific stiffness tester (India).

3.3.3.2 Determination of absorbency

Drop test method

Absorbency of nano treated and untreated fabric sample were evaluated using AATCC Test Method 79-2000. The test was conducted in a standard atmospheric condition. Before the test the samples were kept in standard atmosphere having a relative humidity of 65 ± 2% at 21 ± 1°C for 2 hours. The sample was first mounted in the embroidery hoop for making the surface free from wrinkles without distorting the structure of the material, then the hoop was placed the tip of the burette and allowed one drop of distilled water to fall on the cloth.

Figure 3.3 Drop test setup

And by using a stopwatch, the time required for the surface of the liquid to lose its specular reflectance was measured. Five tests were conducted for each sample. The average of five readings is reported here.

Wicking test

The test samples were prepared with 17cm x 2.5 cm in coarse wise direction. One end of the sample was suspended vertically, on the support behind scale with the help of a clip. The load was attached to the other end of the specimen. A 5gm hanging weight was loaded on the fabric to keep it under tension. Higher than this weight can close the capillaries and inhibit flow through the fabric. A beaker was filled to 300 ml tap water and placed below the sample (figure 3.4). The sample was then immersed into the water kept in beaker up to 3mm mark from the bottom edge of the sample. In each test, observation of water column were made for 1min, 5min and 10min. Five tests were conducted for each sample. For each sample an average of five readings was taken into account. Wicking behavior of treated and untreated samples were thus evaluated. The test is based on T-PACC standard method.

Figure 3.4 Wicking test instrument

3.3.3.3 Evaluation of water repellency

Spray Test

Water repellency of nano treated and untreated samples were performed to evaluate the effect of nano finish. Sample of 18cm x 18cm was fastened securely in the 15.2 cm (Diameter) wooden hoop so that it presents a smooth wrinkle free surface. Test was performed on spray tester (figure 3.5) as per the AATCC Test Method 22-2005 under standard condition. Five tests were conducted for each sample. An average of five readings for each sample was calculated and reported here.

Figure 3.5 Spray tester

3.3.3.4 Evaluation of water permeability and permittivity

These test methods provide procedure for determining the hydraulic conductivity (water permeability) of textiles materials in terms of permittivity under standard testing conditions in uncompressed state. It shows flow of water perpendicular to plane of fabric which is very important to assess for filtration and drainage purpose. Permittivity is an indicator of the quantity of water that can pass through a textile material in an isolated condition, by using ASTM D 4491 water permeability test method.

There are two methods to assess water permeability of a textile material.

- Constant Head Method
- Falling Head Method

Constant head method has been selected for this test.

Constant Head Test

Assemble the apparatus with the specimen in place as shown in Figure 3.6 (Circle of red colour represent sample position). Open the bleed valve and backfill the system through the standpipe or discharge pipe with desired water. The water filled up to the bottom level of the specimen installed and backfilling of water such a way that no air trap inside the water. Close the bleed valve once water flows from it. With water flowing in to the system through the water inlet adjust the discharge pipe along with rater of water flowing into the apparatus to obtain 50 mm (2inch) head of water on the sample. This is the head (h) under which the test will be performed initially. Submerge the tube attached to a source of vacuum to the surface of the textile material moving the tube gently over the surface while applying a slight vacuum in order to remove any trapped air which may be in or on the specimen. If necessary, readjust the head 50 mm (2 inch) after removing the vacuum. Record the values of time (t), quantity of flow (Q) as collected from the discharge pipe and water temperature (T). Take the reading by holding water level at 50 mm (2 inch) and determine an average value of permittivity for the specimen.

Figure 3.6 Water permeability testing apparatus

- Calculate permittivity Ψ as follows

$$\Psi = QR_T/hAt \qquad \ldots\ldots 3$$

Where

Ψ = Permittivity (S^{-1})

Q = Quantity of flow (mm^3)

h = Head of water on the specimen (mm)

A = Cross sectional area of test area specimen (mm^2)

t = Time for flow Q (S)

R_T = Temperature correlation factor determined using Equation (c)

$$R_T = U_t/U_{20t} \qquad \ldots\ldots 4$$

Where: U_t = Water viscosity at test temperature millipoises.

U_{20t} = Water viscosity at 20 ^{0}C millipoises.

3.3.3.5 *Evaluation of air permeability*

The air permeability of treated and untreated fabric samples were measured on Metefem air permeability tester, show in figure 3.7. The testing was carried out as per ASTM D 737 test method. The result of the test measured in m^3/ m^2/ h to three significant digits.

Figure 3.7 Metefem air permeability tester

3.3.3.6 *Evaluation of antibacterial activity*

Soil Burial Test AATCC Test Method 30-2004. For the preparation of test soil, following materials were mixed thoroughly,

a) A layer of good and loam soil, 13 cm thick.

b) A layer of fresh cow-dung manure 7.5 cm thick and

c) A layer of finely chopped straw 15 cm thick.

The mixture was allowed to ferment for 2 months turning it once a week, maintaining the moisture content at approximately 22 to 25 % on the total weight of the mixture.

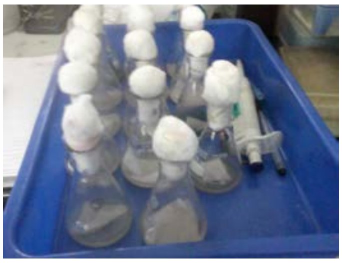
Assessment Methods

After preparing test soil, put it in five 500 ml beakers and buried one specimen in each beaker in such a way that the ends of the specimen are free (Except for the free end, the rest of the specimen should be surrounded by 2.5 cm thick soil). Incubate the specimens at 30±2°C and 98±2 % RH for 7 days, if the fabric under test is light in weight or for 28 days, if the fabric under test in heavy in weight. At the end of the period, remove the specimens, wash them free from soil, dry them in air and determine the breaking strength of each individual specimen. Find the average of all the values.

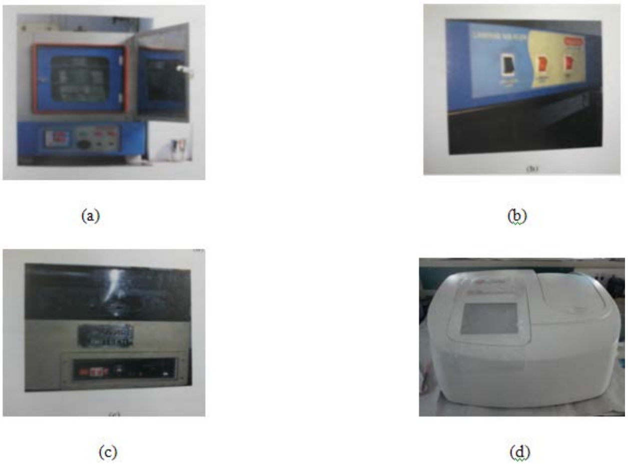
The samples exposed to the action of micro-organism in compost soil were tested for the change in tensile strength measured as per B.S. 2576:1959 test method on Instrument Model-Lloyd, LRX. Samples of 2 cm x 8 cm were tested at 100 mm/min traversing speed. Breaking load was determined and reported here.

Evaluation of anti-bacterial property

Antimicrobial activity was measured as per ASTM E-2149 test methods. Antimicrobial test of cotton, wool, jute and silk fabrics with and without nano Cu, Ag and Zn were carried out with gram-positive *Staphylococcus aureus* and gram-negative *Escherichia coli* bacterium. Samples with and without nano were kept separately into two 50ml conical flask containing 10 ml of liquid culture (Luria Broth) in which 0.1ml of microbial culture was inoculated in laminar flow. The closed flasks were stirred with shaker incubator for four hours at 200rpm. The inoculated test cultures with treated and untreated samples were tested for optical density at 600 nm wavelength. The instruments used for the test is shown in figure 3.8.



Testing sample



(a)

(b)

(c)

(d)

Figure 3.8 Apparatus used for antimicrobial testing a) Incubator cum oven, b) Laminar airflow, c) Orbit shaker incubator and d) UV spectrophotometer.

Optical density of the inoculated culture of treated sample was found very low as compared with inoculated test culture with untreated sample. Lower the optical density indicates low growth of bacterium.

In this way from the optical density readings, the percent reduction in growth of bacteria per ml of bacterial culture was calculated. The percentage reduction in bacterial growth was calculated using following equation

$$\text{Percent Reduction in bacterial growth} = \frac{(B - A)}{B} \times 100$$

Where,

A is the optical density of the inoculated test culture containing the treated sample.

B is the optical density of the inoculated test culture containing the untreated sample.

3.3.3.7 Evaluation of UV transmission property

The UV transmission properties of the nano treated and untreated fabric were investigated by absorption spectroscopy The fabric samples were evaluated on UV-VIS spectrophotometer at 200 to 400nm wavelength, the blank reference was conducted as air.

Figure 3.9 UV-VIS spectrophotometer

The whole set-up was programmed on the computer by the Thermo Electron vision pro software V4.10. The computer screen directly showed the graph between wavelength v/s % transmittance. The % transmissions were calculated using following equation.

$$\text{UV transmission}(\%) = \frac{\sum_{\lambda 1}^{\lambda 2} T(\lambda)}{\lambda 2 - \lambda 1}$$

Where,

T (λ): Spectral transmission of the specimen

λ1: Initial wavelength

λ2: Final wavelength

The UV profile of the untreated sample was compared with the spectra of fabric treated with nanoparticles.

3.3.3.8 Determination of electrical surface resistivity

The purpose of this test method was to determine the electrical surface resistivity of fabric. The test was carried out as per AATCC test method 76-2005. The specimen size of the treated and untreated cotton and polyester fabric samples were used as electrodes and the electrical surface resistivity of fabric samples were measured on KEITHLEY-614 electrometer as shown in figure 3.10. The instrument directly showed the electrical resistivity (R) value of the fabric samples.

Figure 3.10 KEITHLEY-614 electrometer

3.3.4 Dyeing of nano treated and untreated fabrics

3.3.4.1 Dyeing of untreated and treated cotton and jute with direct dyes

All dyeing were carried out in a laboratory dyeing machine at a liquor to material ratio of 20: 1, in the presence of 50 gpl of sodium chloride and 20 gpl of sodium bicarbonate using 2.0% dye on the weight of the sample. The sample was treated at 40°C for 10 min. The temperature was slowly raised to boil over 30 min (2 °C ⁄ min) and the dyeing was continued at boil for further 45 min. Finally the samples were washed and dried in air. For comparison purpose, untreated cotton and jute were also dyed under the same condition.

3.3.4.2 Dyeing of untreated and treated wool and silk with direct dyes

Dyeing of wool and silk were carried out in a laboratory dyeing machine at a liquor to material ratio of 20: 1, in the presence of 1 gpl of wetting agent, 2 % (owf) of dilute acetic acid and 20 gpl sodium chloride using 2.0% dye on the weight of the sample.

The sample was treated at 40°C for 10 min. The temperature was slowly raised to boil over 30 min (2 °C ⁄ min) and the dyeing was continued at boil for further 45 min. Finally the samples were washed and dried in air. For comparison purpose, untreated wool and silk were also dyed under the same condition.

3.3.4.3 Dyeing of untreated and treated wool and silk with acid dyes

The wool and silk fabric samples, before and after nano treatment, were dyed with 2% (owf) acid dye by exhaust technique in a shaking water bath at a material-to-liquor ratio of 1: 30, in the presence of 1 gpl of wetting agent and 2 % of dilute acetic acid.

The fabric sample was introduced in the bath at 40 °C and the material was run for 10 minutes, the temperature was then gradually (2 °C ⁄ min) raised to boil and dyeing was continued for 45 min more. Finally the samples were washed with 2 g/l non-ionic detergent (Lissapol N) at 60 °C for 15 min with the goods to liquor ratio 1:20 and air dried. For comparison purpose, untreated wool and silk were also dyed under the same condition.

3.3.4.4 Dyeing of wool and silk with natural colourants

Dyeing of silk fabric with these natural dyes namely, *Azadirachta indica, Lawsonia inermis* and *Ocimum sanctum* were performed using exhaust dyeing technique on a laboratory constant temperature dye bath. The dye bath liquors for individual dye containing methanolic extract-20 %(owf) and acetic acid ~2 % (owf) to maintain dye bath pH 4.5. Dyeing was started at room temperature, the temperature was then gradually raised to boil within 15 min. the sample worked at this temperature for another 30 min. Finally the samples were washed thoroughly and air-dried.

3.3.5 Evaluation of dyed samples

3.3.5.1 Measurement of colour strength value (K/S Value)

The colour strength values (*K/S* value) of the samples were measured using Spectra Scan 5100 (RT) spectrophotometer (Premium Colourscan Instruments, India).

3.3.5.2 Evaluation of fastness properties

All the dyed samples were evaluated for fastness to light and washing using standard methods.

Fastness to light

The dyed specimens were exposed to artificial light in a fad-o-meter, a carbon arc lamp in which the specimens rotate about the arc. The surrounding air being humidified (R.H. less than 50%) and maintained at a constant temperature (46°C or less). Each specimen was placed between opaque covers, shielding it from light except for an area about 15/8 by 2 inch. The specimens were exposed for 5 hours according to ISO 105-BO2 (1990). Light fastness was evaluated by comparison of exposed portion with the unexposed portion of the material. They were graded from 1 to 8.

Fastness to washing

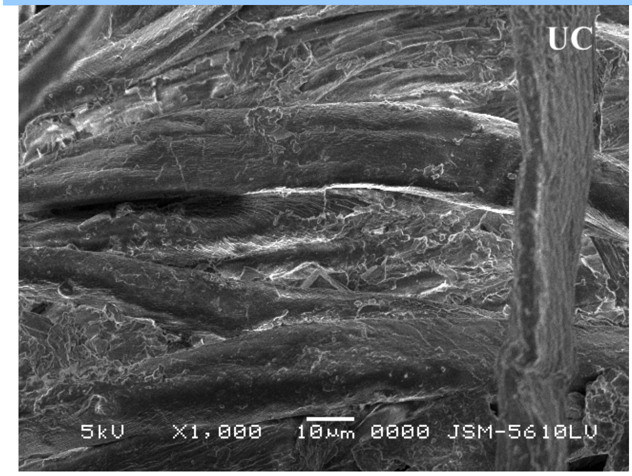
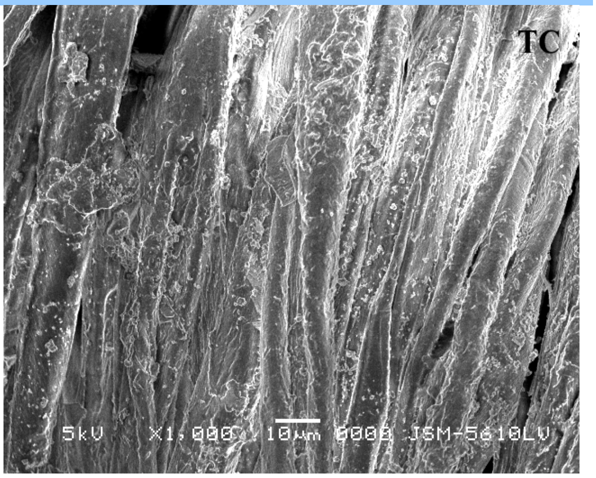
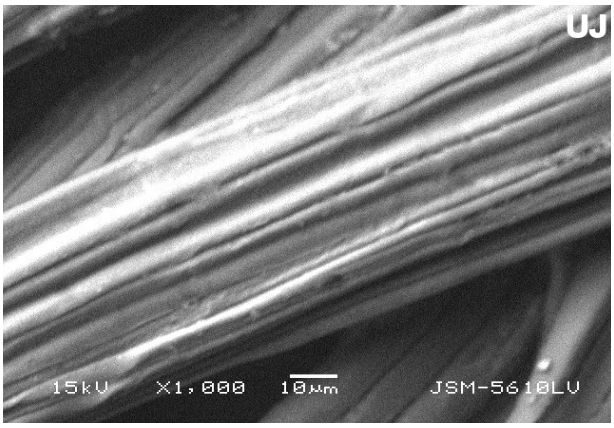
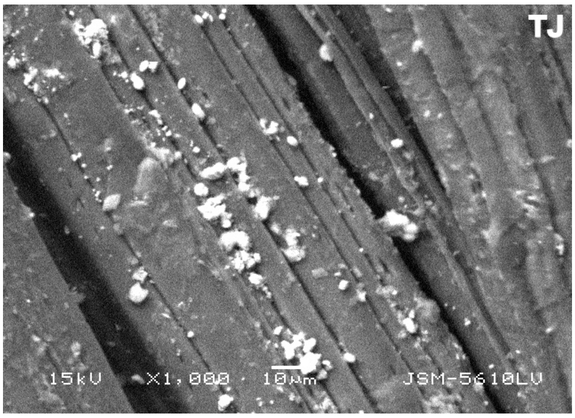
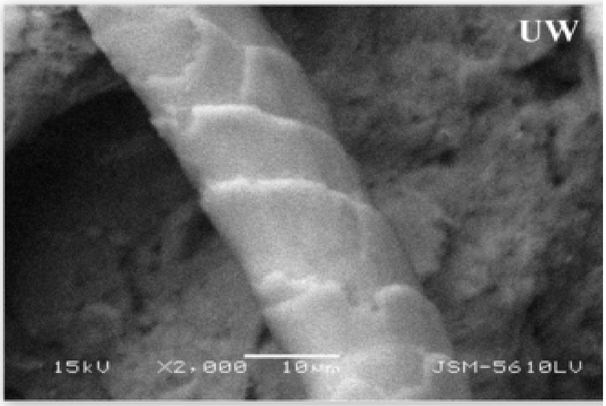
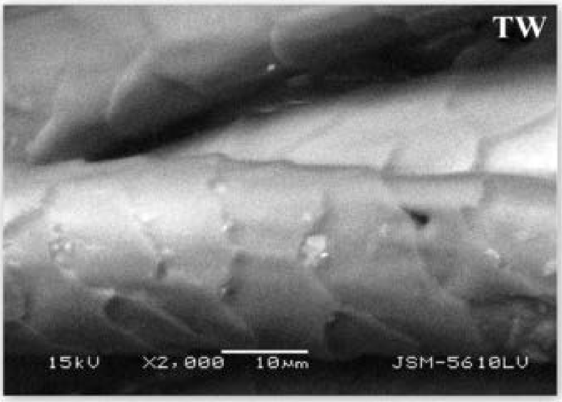
The test was carried out in launder-ometer (Digi.wash, Paramount Scientific Instruments., India). The Launder-o-meter consists of a water bath maintained at the desire constant temperature rotates at a standard speed of 42 rpm containing 20 standard pint jars of glass. The test specimen was made up by using standard methods (ISO 105-CO6 (C2S)). Each specimen was placed in a glass jar containing 100c.c. of 0.5% soap and 0.2% sodium carbonate solutions. The jar was closed and he machine was run at 80°C temperatures for 45 minutes. Then the samples were removed from the container rinsed twice with cold water and in cold running tap water for 10 minutes and squeezed. The stitching was removed and the test specimen was opened out and dried in air. The change in colour was evaluated from Grey-scale for alteration of colour consisting of grade 1 to 5.

3.4 RESULTS AND DISCUSSIONS

In the present investigation metallic nanoparticles were applied to various natural fibers by exhaust and pad-dry-cure techniques. In the first phase of research, the nanoparticles were applied by exhaust technique using constant temperature shaking water bath. In the second phase the treatment with nanoparticles were performed using pad-dry-cure technique. The distributions of nanoparticles on the surface of the fabric were observed using SEM and elementally analyzed using XRF technique.

3.4.1 Characterization of copper nano treated fabrics

The surface morphology of cotton, jute, wool and silk fabric samples were examined before and after nano copper treatment by pad-dry-cure technique (Figure 3.11). Some particles are noticed on the surface of the treated samples.

Untreated fabric	**Copper nano treated fabric**
	
	
	

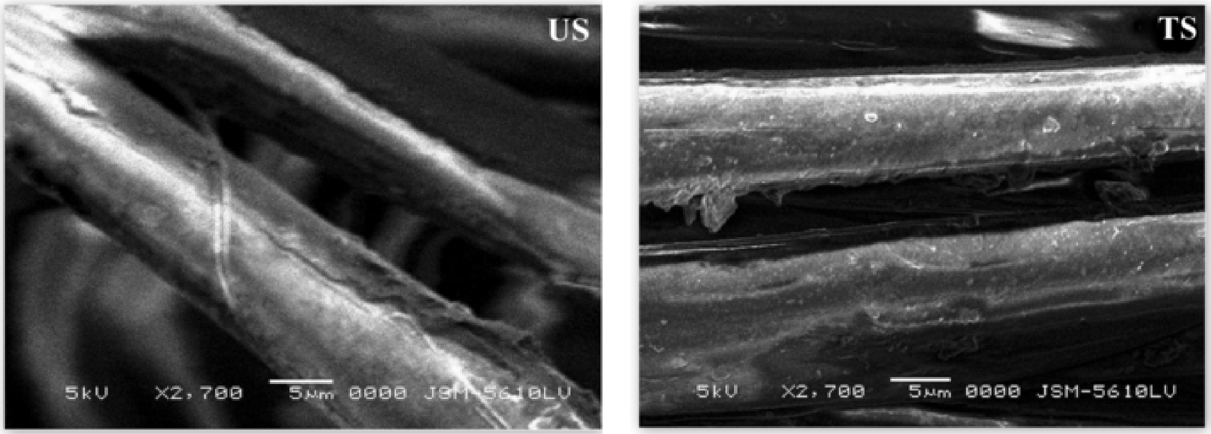


Figure 3.11 Scanning Electron Microscope (SEM) images of (UC) Untreated cotton and (TC) Treated cotton; (UJ) Untreated jute and (TJ) Treated jute: (UW) Untreated wool and (TW) Treated wool: (US) Untreated silk and (TS) Treated silk fabric.

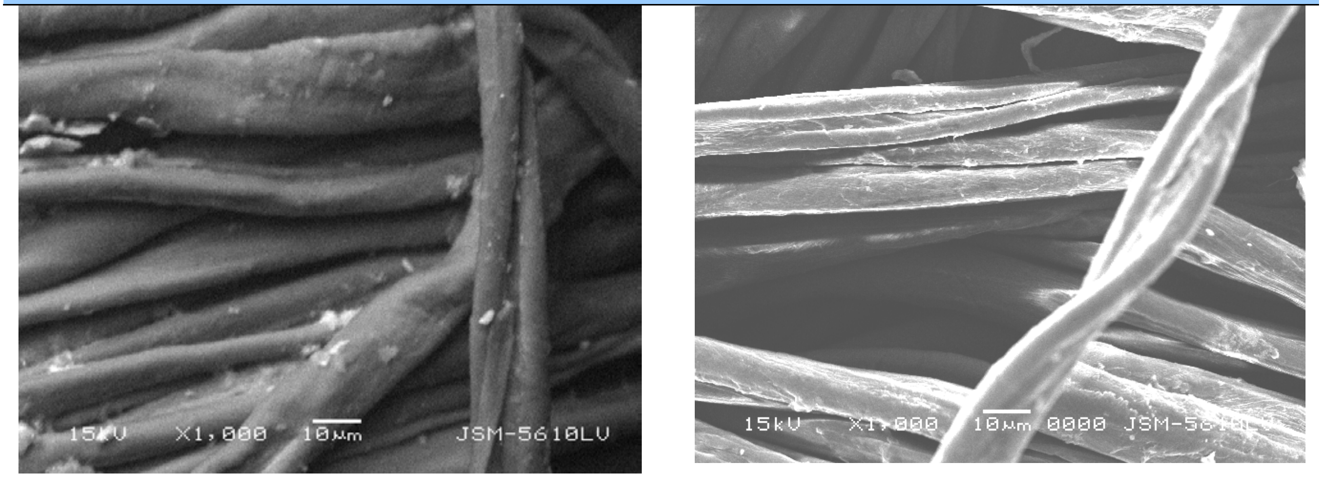
Both the treated and untreated cotton were elementally analyzed using X- ray fluorescence spectroscopy for the detection and measurement of elemental copper.

Table 3.2 Amount of copper detected with XRF

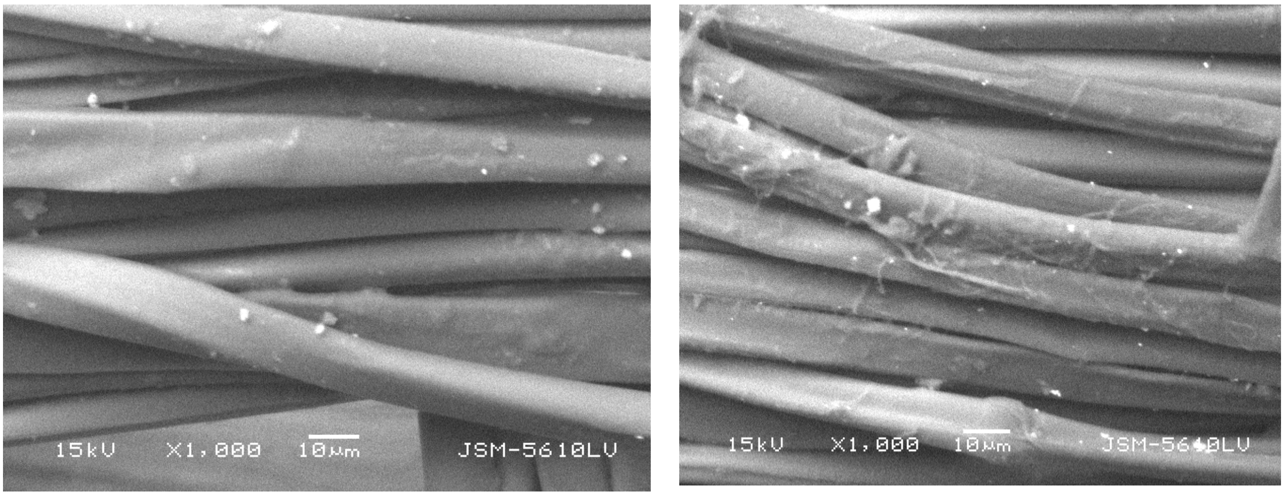
Sample	**Amount of copper, µg**
Cotton	Nil
Cu nano treated cotton fabric	0.31
Jute	Nil
Cu nano treated jute fabric	0.26
Wool	Nil
Cu nano treated wool fabric	0.38
Silk	Nil
Cu nano treated silk fabric	0.34

Deposition of copper nano was also done successfully using exhaust technique. Uniform deposition on the surface of cotton, jute and silk fabric is seen from the SEM microphotographs given in figure 3.12

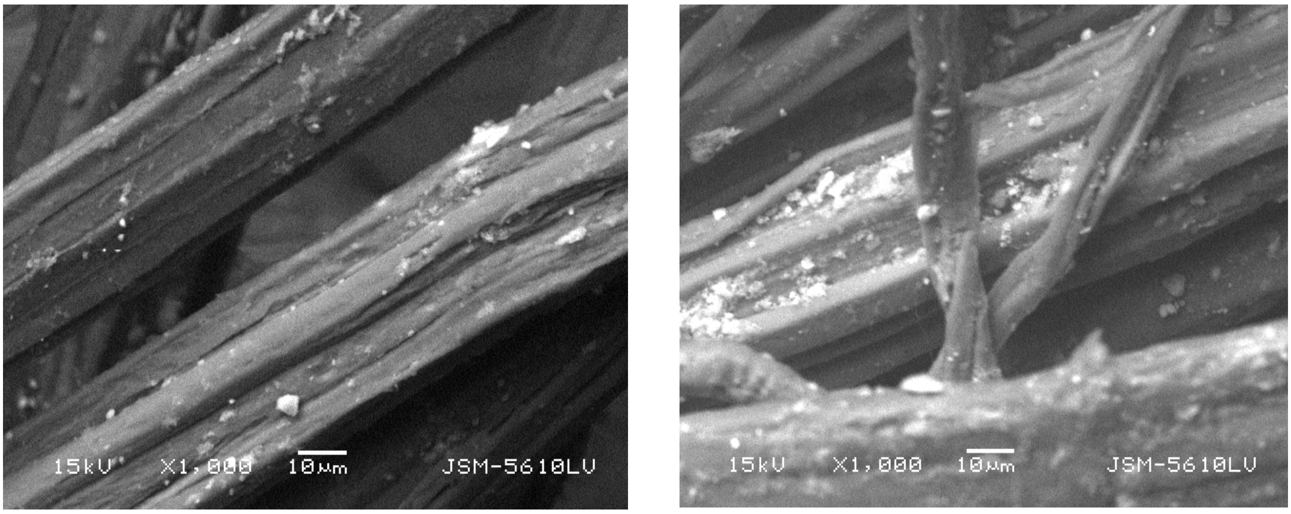
Treated by exhaust technique | **Treated by pad-dry-cure technique**



Cotton treated with nano copper | Cotton treated with nano copper



Silk treated with nano copper | Silk treated with nano copper



Jute treated with nano copper | Jute treated with nano copper

Figure 3.12 SEM microphotographs of cotton, silk and jute loaded with copper nano using exhaust and pad-dry-cure techniques.

On comparing the effect of two techniques adopted for the deposition of copper nanoparticles. It has been observed from the SEM microphotographs given in figure 3.12 that there is no significant change on fabric surface due to the techniques of application.

Table 3.3 Amount of copper detected on cotton, jute, wool and silk fabric

Fabric	Cotton	Jute	Wool	Silk
Amount of Cu nano by Exhaust technique	0.19 µg	0.16 µg	0.23 µg	0.21 µg

Further, among two techniques of application, it was observed by SEM and quantitatively analyzed on XRF (Table 3.2) that in most of the cases, pad-dry-cure technique performed better than the exhaust technique. The pad-dry-cure process was however expensive as it largely consumes the valuable thermal energy, where as in exhaust method, less thermal energy or steam is required. Keeping in mind the ease and continuous application of nanoparticles to textiles, the pad-dry-cure technique was utilized for the application of nanoparticles to textiles throughout this work.

3.4.2 Effect of copper nano treatment on physical properties

In order to investigate the effects of copper nano treatment on tensile strength, crease recovery and stiffness of cotton, jute, wool and silk, these properties of the treated samples were determined and compared with the untreated samples. It is seen from Figure 3.13 and Table 3.4 that the load bearing capacity of the nano treated textiles was improved. From Figure 3.13 it is clearly seen that the improvement in breaking load due to nano copper treatment is maximum for cotton followed by wool.

Table 3.4 Effect of copper nano treatment on physical properties of sample

Sample	**Breaking load (kgf)**	**Crease recovery angle °(deg)**	**Bending length (cm)**
Cotton (Control)	8.02	90	1.05
Cotton pre-treated with cu nano	10.66 (+32.91)	101 (+12.22)	1.45 (+38.09)
Jute (Control)	10.44	90	3.00
Jute treated with Cu nano	10.81 (+3.54)	100 (+11.11)	3.60 (+20.00)

Wool (Control)	6.43	139	3.10
Wool pre-treated with cu nano	7.66 (+19.12)	146 (+5.03)	3.70 (+19.35)
Silk (Control)	6.32	124	2.80
Silk pre-treated with cu nano	6.63 (+4.90)	133 (+7.26)	3.60 (+28.57)
Note: Values in the parenthesis indicate percentage change in physical properties.			

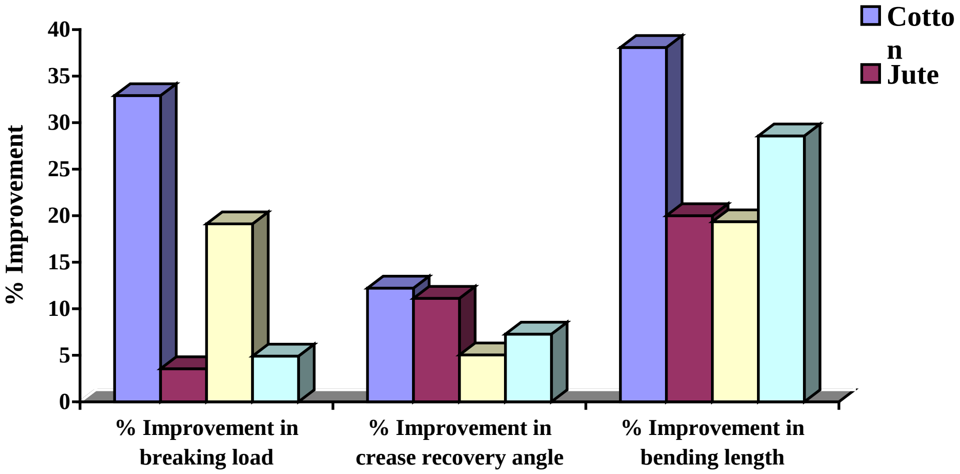


Figure 3.13 Improvement in breaking load, crease recovery angle and bending length due to copper nano treatment

Slight improvement in crease recovery angle of the copper nano treated textiles was also seen from the results shown in Table 3.4. Figure 3.13 revels that the maximum enhancement in crease recovery angle is seen in case of cotton due to the treatment. Similarly there is maximum improvement in bending length is observed in cotton sample when treated with copper nano. The nano copper particles because of their small size can enter in between the polymer molecules and perhaps act as fillers or cross linking agents which also contribute to the load sharing phenomenon during load application to the material. Unlike chemical cross linking which causes an improvement in crease recovery angle at the cost of imparting some rigidity in the material to an extent depending on the extent of cross linking, the incorporation of nano copper particles remained quite gentle in this regard. There was a little stiffening as indicated by the higher values of bending lengths. Therefore though the particles entered in between the polymer chain molecules did not interfere much to the polymer flexibility of the system, the treatment was thus devoid of harshness to the material.

3.4.3 Effect of copper nano treatment on absorbency

The Cu nano treated fabrics were tested for their absorbency, wicking behavior and water repellency using standard test methods. The results of Cu nano treated fabrics were compared with the untreated samples of cotton, jute, wool and silk fabric. The water absorbency of copper nano treated and untreated fabric samples were measured as per the standard AATCC test method. Results for the same are presented in Table 3.5 and Figure 3.14.

Table 3.5 Absorbency of copper nano treated and untreated fabrics

Fabric sample	**Time (sec)**	
	Untreated	**Treated with Cu nano**
Cotton	6	6.8
Jute	13	13.6
Wool	4	4.4
Silk	4	4.3

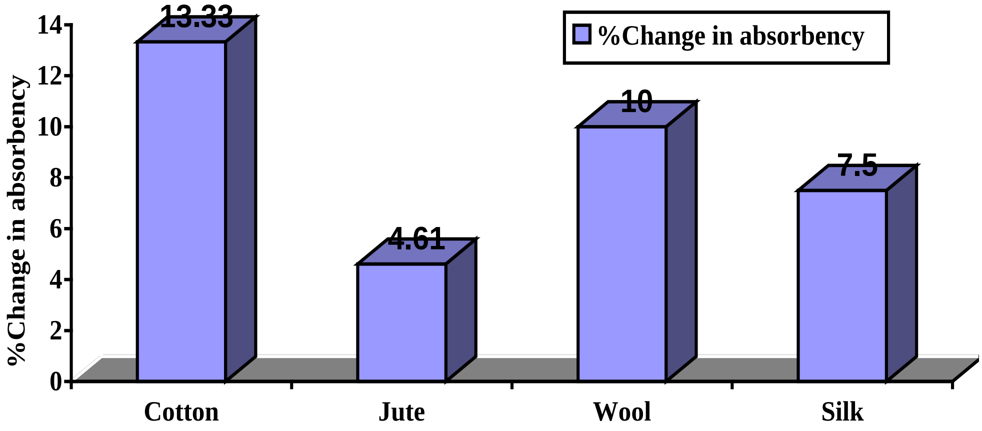


Figure 3.14 Drop in absorbency of fabrics due to nano Cu treatment

It is found from the results that nano copper treatment caused a drop in water absorbency of all the fabric samples. The nano metal particles act as whiskers and resists immediate penetration of water droplets, which increased the time to get water molecules absorbed, inside the fabric structure. The drop in absorbency was found to be maximum in case of cotton whereas jute was found to be last affected.

The height traveled by water when one end of the sample was dipped in water for a fixed time i.e. the wicking length of the untreated and treated samples were measured. The results (Table 3.6 and Figure 3.15) show that due to the application of nano copper wicking length was reduced, that is for a fixed time the length traveled by water was reduced in treated samples. But when the fabric sample was kept for a longer time the xtent of effect got diminished as seen in Figure 3.5

Table 3.6 Wicking height (mm) of copper nano treated fabrics

Fabric sample	Wicking height(mm)					
	Untreated			Treated with Cu nano		
	1 min	5 min	10 min	1min	5 min	10 min
Cotton	22	41	50	20	38	47
Jute	17	24	37	16	23	36
Wool	26	43	56	23	39	52
Silk	19	29	42	17	27	40

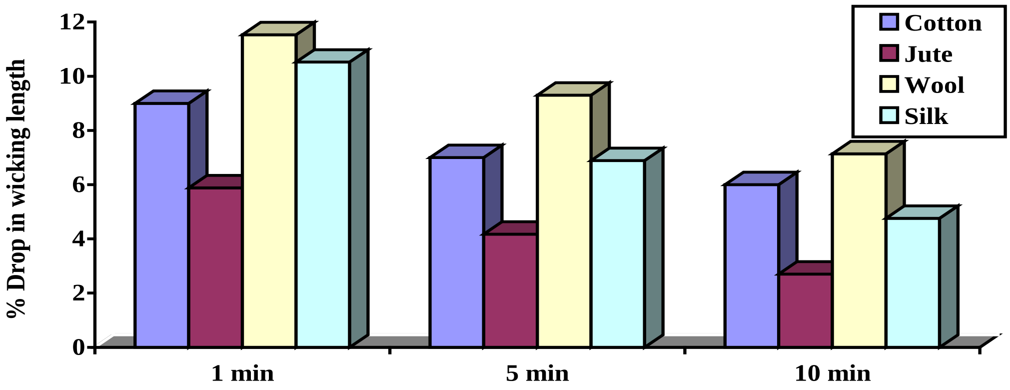


Figure 3.15 Drop in wicking behavior of copper nano treated fabric

3.4.4 Effect of nano copper on water permeability of fabric

The treated and untreated fabric samples were also tested for water permeability. The results show that the water permeability of all the treated samples was dropped after the copper nano treatment. As the nanoparticles present in polymer matrix resists the flow of water through the fabric.

Table 3.7 Water permeability of fabrics before and after the copper nano pretreatment

Sample	Ψ-**Water Permeability**(S^{-1})			
	Cotton	Jute	Wool	Silk
Untreated sample	0.3579	0.3726	0.3475	0.3286
Treated with Cu nano	0.3498	0.3682	0.3396	0.3256

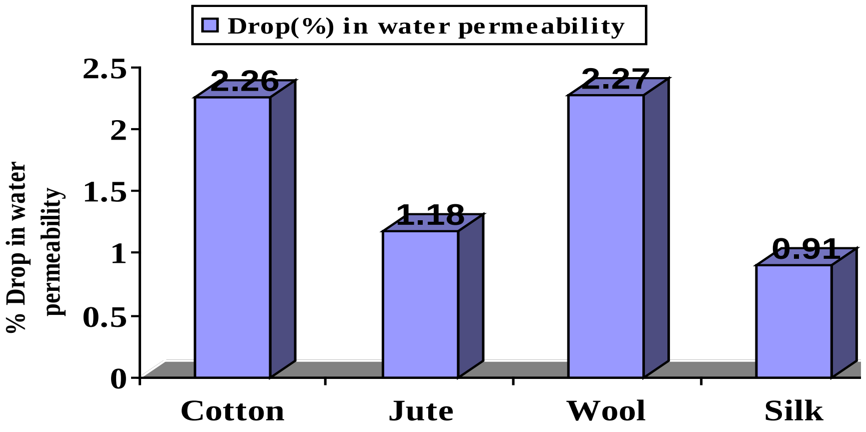


Figure 3.16 Reduction (%) in water permeability due to the copper nano treatment

3.4.5 Effect of copper nano on air permeability of fabric

The treated and untreated fabric samples were tested on Metefem Air Permeability Tester. The results are presented in Table 3.8 and Figure 3.17

Table 3.8 Air permeability of cotton & polyester fabric

Sample	**Air permeability (m^3/ m^2/ h)**			
	Cotton	Jute	Wool	Silk
Untreated sample	682.66	884.28	652.32	511.66
Treated with Cu nano	636.17	863.14	606.77	488.11

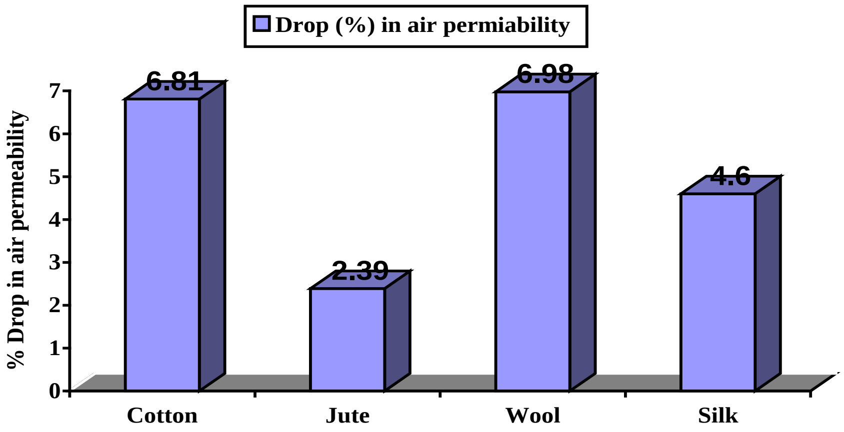


Figure 3.17 Reduction (%) in air permeability due to the nano Cu treatment

It shows that the air permeability through all treated samples was reduces compared to untreated sample. It is seen that the nanoparticle present in the fabric structure also affected the flow of air.

3.4.6 Effect of copper nano on resistance against microbes

Antimicrobial activity was measured by soil burial test and the results are shown in table 3.9. It is clear that the Cu-nano treatment was found to enhance the resistance of all the natural fibers, used in the study, towards microbial attack when measured in terms of loss in breaking load due to soil burial test. The breaking load of untreated control samples were reduced due to microbial damage during soil burial treatment test whereas copper nanoparticle treatment could not only protect the sample against bacterial attack but also improved its strength.

Table 3.9 Effect of Cu nanoparticles on resistance against microbial attack

Sample	**Breaking load, kgf**		**% Change**
	Before soil burial	After soil burial	
Untreated cotton sample	8.02	4.50	-43.89
Cotton pre-treated with Cu nanoparticles	10.66	9.71	-8.91
Untreated Jute sample	10.44	5.02	-51.92
Jute pretreated with Cu nanoparticles	10.81	9.47	-12.39
Untreated wool sample	6.43	4.09	-36.39
Wool pre-treated with Cu nanoparticles	7.66	6.86	-10.44
Untreated silk sample	6.32	4.12	-34.81
Silk pre-treated with Cu nanoparticles	6.63	6.21	-6.33
Note – change (%) values indicate percentage change in strength before and after the test			

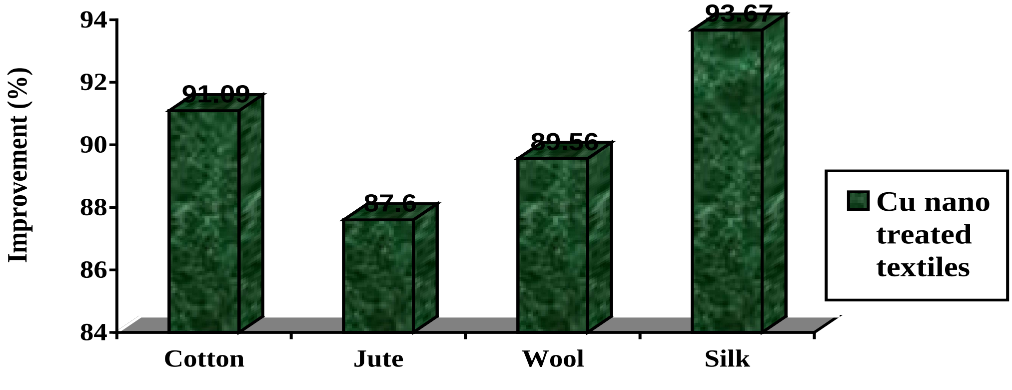


Figure 3.18 Improvement in resistance against microbial attack due to Cu nano treatment

Figure 3.18 shows the change in antimicrobial behavior of fabrics treated with copper nanoparticles. A clear improvement in the resistance of fabrics against microbial attack is seen in cotton, jute, wool and silk fabrics treated copper nano colloids. In case of cotton fabric 91.06 % improvement is observed with Cu nano colloidal treatment. The improvement in the resistance against microbial attract may be due to the fact that the metallic ions and metallic compounds display a certain degree of sterilizing effect. It is considered that part of the oxygen in the air or water is turned into active oxygen by means of catalysis with the metallic ion, thereby dissolving the organic substance to create a sterilizing effect [12]. With the use of nano-sized particles, the number of particles per unit area was increased, and thus antimicrobial effects can be maximized.

The antibacterial property of treated and untreated fabrics was also tested against S.aureus bacteria, the results in terms of % reduction in bacterial growth are given in the table 3.10. There is significant improvement in antibacterial property of all the four fabric samples treated with Cu nano colloids compared with the untreated counter part of the same fabrics. From the results it can also be seen that the maximum improvement in the anti-bacterial property was observed in case of cotton fabric. The enhancement in the resistance towards bacterial attack may be attributed to the certain degree of sterilizing effect of the metal atoms. It is possible that Cu nanoparticles may get attached to the surface of the microbe's cell membrane, enter inside the cell and destroy their metabolic function. Further, nano size of Cu particles, having larger available surface area for interaction, provides high bactericidal effect than the bulk.

Table 3.10 Anti-bacterial effect of copper nano treated fabrics

Fabric sample	**Reduction (%) bacterial growth**
Cotton (Control)	Nil
Copper nano treated cotton	88.28
Jute(Control)	Nil
Copper nano treated Jute	75.61
Wool(Control)	Nil
Copper nano treated Wool	85.63
Silk(Control)	Nil
Copper nano treated Silk	84.95

3.4.7 Effect of copper nano treatment on UV transmission property

The UV transmission rate (%T) of copper nano treated and untreated cotton, wool, jute and silk fabric were measured by UV-VIS spectrophotometer at different wavelength. The results are presented in table 3.11. The results show that the UV transmission for the control samples were comparatively higher than the fabrics treated with copper nanoparticles, i.e. better UV protection is obtained as compared to untreated fabric. In case of jute fabric there was no significant reduction in UV transmission recorded for copper nano treated fabric. This may be due to the construction of the fabrics which was not capable to restrict the UV transmission.

Table 3.11 UV transmission % of copper nano treated and untreated fabrics

Sample	**Control**		**Cu nano treated**	
	UV transmission (%)		**UV transmission (%)**	
	UV-A (330-400 nm)	UV-B (280-320 nm)	UV-A (330-400 nm)	UV-B (280-320 nm)
Cotton	17.39	17.07	9.95	9.20
Wool	23.09	22.51	13.31	12.81
Silk	33.59	33.57	28.13	25.90

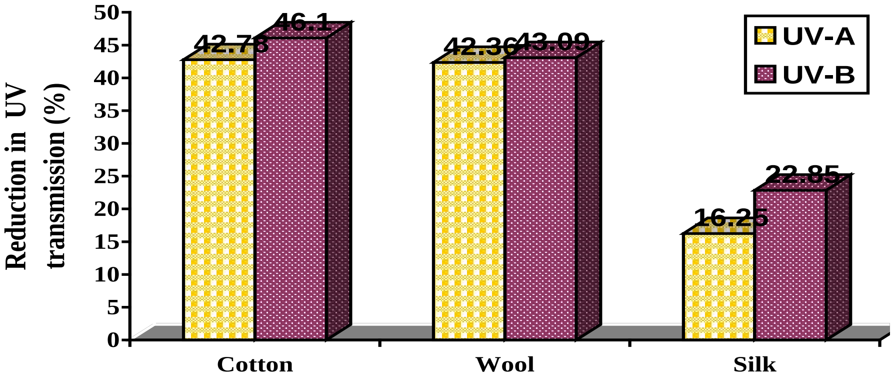


Figure 3.19 Reduction in UV transmission (%) in copper nano treated fabrics

It is found from the results that nano copper treatment restricts the UV transmission in the region between 300 nm and 400 nm in all the fabrics. The maximum reduction in UV transmission was found in case of cotton followed by wool due to the nano Cu treatment.

3.4.8 Effect of copper nano treatment on electrical surface resistivity

The Electrical surface resistivity of treated and untreated fabric samples was measured on KEITHLEY614-Electrometer and the results are given in table 3.12.

Table 3.12 Electrical surface resistivity of copper nano treated and untreated fabric samples

Fabric sample	Electrical surface resistivity (ohm Ω)			
	Cotton	Wool	Jute	Silk
Untreated sample	180 x 10^9	>200 x 10^9	>200 x 10^9	>200 x 10^9
Cu nano treated sample	35 x 10^9	180 x 10^9	186 x 10^9	176 x 10^9

The result shows that the electrical resistivity of treated fabrics is reduced irrespective of the class of fabric compared to the untreated fabric samples. The incorporation of copper nanoparticle in polymer matrix resulted in the higher surface resistivity of the fabrics. The reduction in the electrical resistivity of treated fabric may be due to the higher conductivity of copper deposited on the fabric surface.

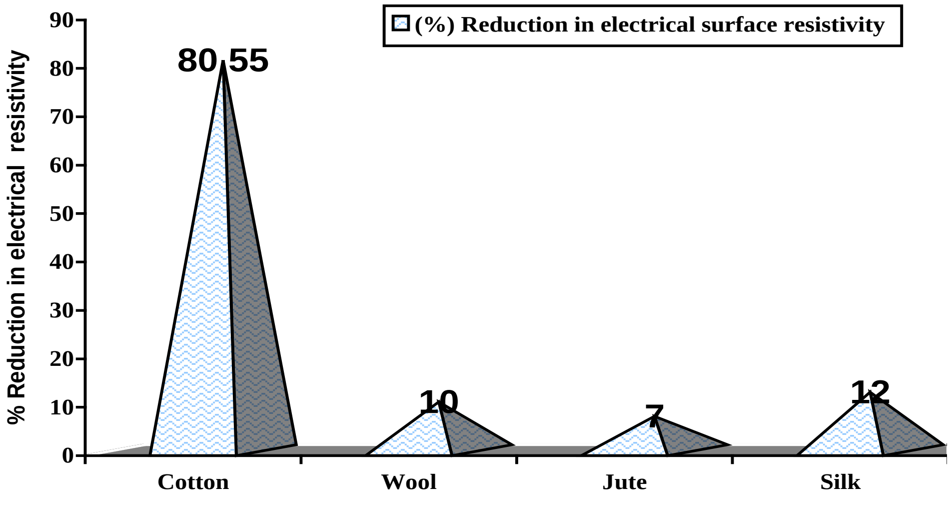


Figure 3.20 Reduction in electrical surface resistivity of fabric samples

3.4.9 Effect of copper nano treatment on dyeing behavior

Cu nanoparticle treated cotton, wool jute and silk fabric samples were dyed with three direct dyes. The results in terms of colour strength (*K/S*) values were compared with the colour strength of untreated dyed fabric samples.

Table 3.13 Effect of Cu nano-particles on colour strength of fabrics dyed with direct dyes

Sample	**Colour strength *(K/S)***					
	C.I. Direct Red 9		**C.I. Direct Blue 67**		**C.I. Direct Green 6**	
	Control	Cu nano treated	Control	Cu nano treated	Control	Cu nano treated
Cotton	5.32	7.36	8.22	11.35	8.06	13.17
Jute	14.15	15.90	16.43	16.92	17.26	18.12
Wool	10.12	11.26	12.31	13.66	11.52	13.24
Silk	4.64	5.87	6.89	7.83	7.56	9.77

The *K/S* values of the nano copper pre-treated samples were found to be higher (Table 3.13) than the corresponding untreated samples of cotton, wool, jute and silk. Figure 3.21 shows that the maximum improvement in colour strength was with direct green 6 dye except in case of jute sample where direct red 9 performed better than the direct green 6 in terms of *K/S* value. The higher *K/S* values of nano treated samples indicate that the presence of Cu nano metal particles increased the dye affinity towards the material. The copper nanoparticles in the fabric thus acted as mordant. The negatively charged dye anions got attracted towards the fiber probably due to the polarity developed in the metal particles by induction which resulted in better bonding between the dye and the fiber.

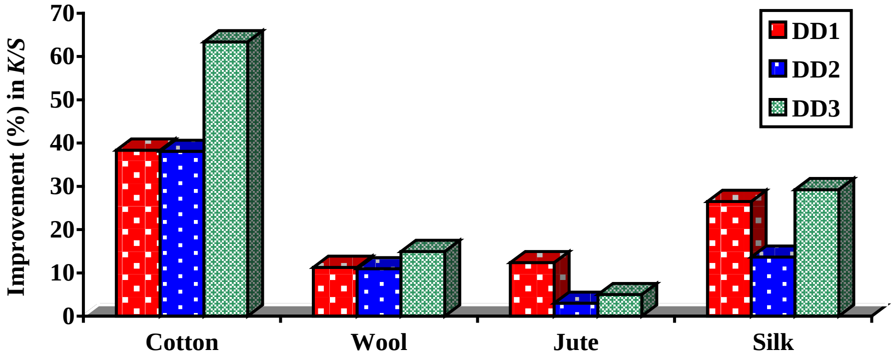


Figure 3.21 Improvement in colour strength values of fabric dyed with direct dye after Cu nano pretreatment

The fastness properties of Cu nano treated and untreated samples are reported in Table 3.14. The better coupling of the dye and fiber is also reflected in the improvement of the colour fastness properties. Where the Cu-nano treated / untreated and dyed fabrics after washing off using 2 gpl non-ionic detergent, the washing treatment caused little effect on the colour bleeding of the nano Cu treated and dyed samples. Thus copper nano pre-treatment not only improved the colour strength but also improved the colour fastness which is a major drawback for most direct dyes.

Table 3.14 Effect of Cu nano-particles on fastness properties of samples dyed with direct dyes

Sample	**Fastness to**											
	Light						**Washing**					
	DD1		DD2		DD3		DD1		DD2		DD3	
	C	T	C	T	C	T	C	T	C	T	C	T
Cotton	3	4	3	4	3	4-5	2-3	4	2-3	4	2-3	4-5
Jute	2-3	3-4	3	3	2-3	3-4	3	3-4	2-3	3-4	3	4
Wool	2-3	3-4	2-3	3	3	3-4	3	3-4	2-3	3-4	2-3	4
Silk	3	4	3	3-4	3	4	3	4	3	4	3	4

Note-DD1 – C.I. Direct Red 9, DD2 – C.I. Direct Blue 67 and DD3 –C.I. Direct Green 6, C – Control sample, T – Sample treated with Cu Nano-particles.

Natural protein fibers i.e. wool and silk are usually dyed with acid dyes. To investigate the effect of Cu nano treatment on the dyeing of wool and silk with acid dye, the study was further extended to dye Cu nano pretreated wool and silk fabrics with three acid dyes namely, Acid orange R (AD1), Acid navy blue (AD2) and Acid rose 6B (AD3) by conventional method and their dyeing performance is compared with conventionally dyed wool and silk fabric without copper nano pretreatment. Dyeing performance of Cu-nano treated and untreated samples, evaluated in terms of *K/S* values is presented in Table 3.15.

Table 3.15 Colour strength values, fastness ratings of wool and silk fabric dyed with acid dye

Dye	**Fabric samples**	**Colour strength (*K/S*) values**	**Fastness ratings**	
			LF	WF
AD1	Wool (Control)	9.05	5	4
	Cu nano treated wool	10.62	6-7	4
AD2	Wool (Control)	13.10	4-5	4
	Cu nano treated wool	14.15	6	4
AD3	Wool (Control)	10.33	6	4
	Cu nano treated wool	12.25	7	4-5
AD1	Silk (Control)	4.58	5-6	4
	Cu nano treated silk	5.02	6-7	4-5
AD2	Silk (Control)	7.62	4-5	4
	Cu nano treated silk	8.19	5-6	4
AD3	Silk (Control)	6.26	6	4
	Cu nano treated silk	7.11	6-7	4-5

Note: AD1- Acid orange R, AD2- Acid navy blue, AD3- Acid rose 6B, LF-Light Fastness, WF-Washing Fastness

It is seen from the Table 3.15 that both wool and silk fabric samples picked up more dyes after treatment with copper nanoparticles. The introduction of copper in nano form thus enhanced the affinity of the fiber towards acid dyes.

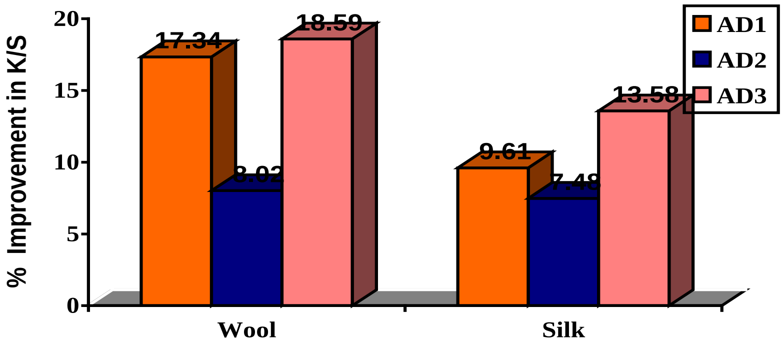


Figure 3.22 Enhancement on colour yield of wool and silk due to nano copper pretreatment

It is also seen from Figure 3.22 that improvement in colour strength values is higher in case of wool compared to silk fabric dyed with acid dye after Cu nano pretreatment. The light and washing fastness ratings for cu nano pretreated and dyed samples were found to be improved. The improvement in fastness ratings may be due to the formation of metal-dye complex.

The effect of nano Cu pre-treatment on the dyeability of wool and silk, using three natural dyes viz., *Azadirachta indica* (ND1), *Lawsonia inermis* (ND2) and *Ocimum sanctum* (ND3). Table 3.16 represents the results in terms of colour strength values (*K/S*) of dyed samples with and without Cu nano treatment.

Table 3.16 Colour strength values of wool and silk fabric dyed with natural colourants

Dye	Fabric sample	Colour strength (*K/S*) values	Fastness ratings	
			LF	WF
ND1	Wool (Control)	10.14	6-7	4
	Cu nano treated wool	13.66	6-7	4-5
ND2	Wool (Control)	14.24	6-7	4
	Cu nano treated wool	16.37	7	4-5
ND3	Wool (Control)	11.16	6	4
	Cu nano treated wool	13.55	6-7	4-5
ND1	Silk (Control)	7.62	6	4
	Cu nano treated silk	10.26	6-7	4
ND2	Silk (Control)	9.35	6-7	4
	Cu nano treated silk	12.39	7	4-5
ND3	Silk (Control)	10.23	6	4
	Cu nano treated silk	15.46	6-7	4-5

Note:ND1- Azadirachta indica,ND2- Lawsonia inermis, ND3- Ocimum sanctum , LF-Light Fastness, WF-Washing Fastness

From Table 3.16, it can be seen that nano treated as well as untreated wool and silk fabrics can be successfully dyed with all three natural colourants. For 20 % (owf) depth of shade using methanolic extract of *Azadirachta indica, Lawsonia inermis* and *Ocimum sanctum* as a natural colourant, a pale to medium green colour was obtained, while dark green colour shade was obtained in case of nano Cu pretreated sample.

The higher *K/S* values of nano-treated samples indicate that the presence of nano metal particles increased the dye affinity towards the fabric. The effect of Cu nano treatment of the fiber is also reflected in the improvement in the colour fastness properties. Thus, copper nano pre-treatment not only improves the colour strength but also enhanced the colour fastness of wool and silk fabric dyed with natural dyes.

3.4.10 Characterization of silver nano treated fabrics

Figure 3.23 represents SEM photographs of various fabrics, viz. cotton (SC), jute (SJ), wool (SW) and silk (SS) treated with silver nano particles with pad dry cure technique. Nano silver particles are clearly seen on all the fabric samples.

Silver nano treated fabric

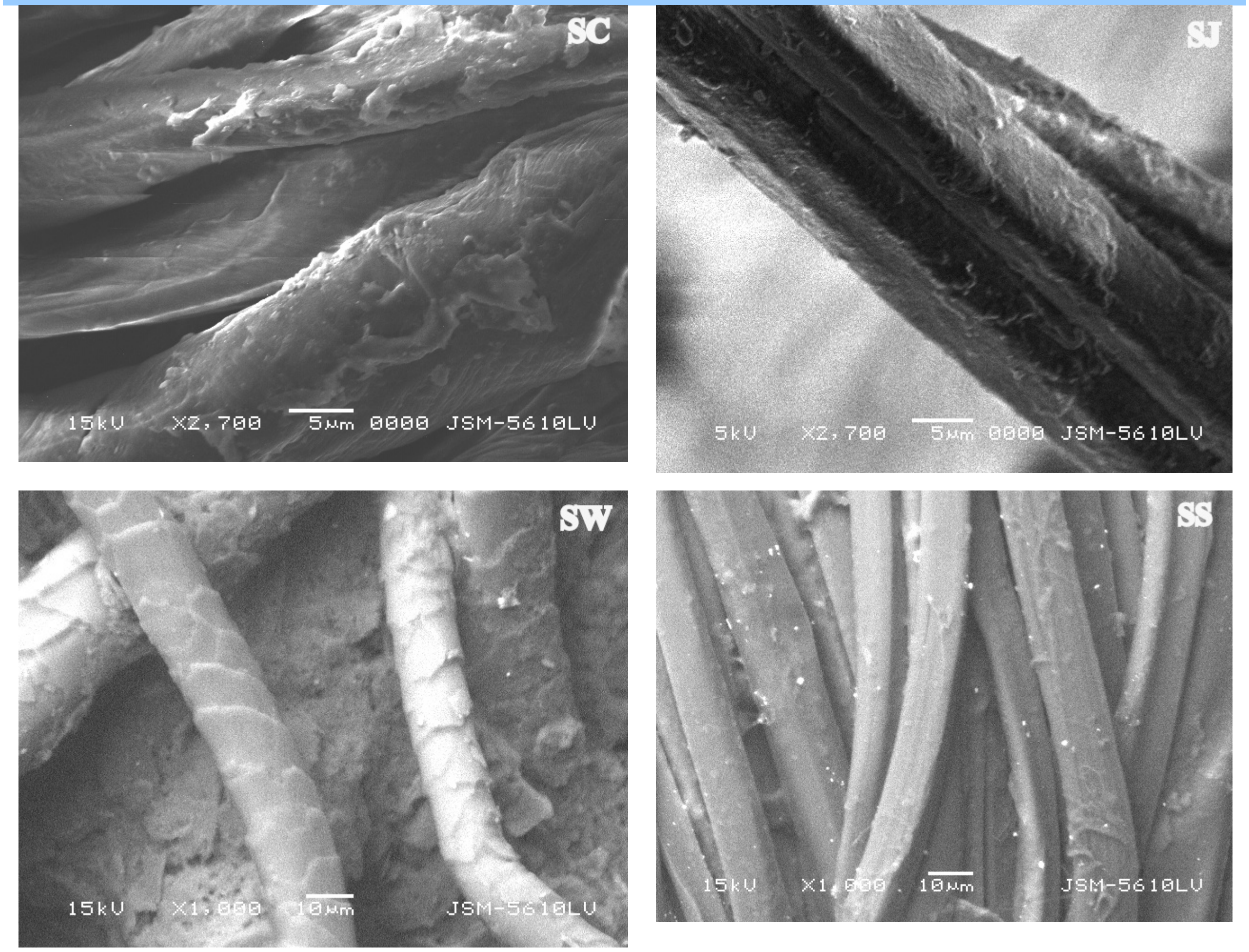


Figure 3.23 Scanning electron microscope (SEM) images of cotton (SC), Jute (SJ), wool (SW) and silk (SS) fabrics treated with silver nano.

All treated fabric samples were elementally analyzed using XRF.

Table 3.17 Amount of silver detected with XRF

Sample	**Amount of silver, µg**
Cotton	Nil
Ag nano treated cotton fabric	0.29
Jute	Nil
Ag nano treated jute fabric	0.18
Wool	Nil
Ag nano treated wool fabric	0.32
Silk	Nil
Ag nano treated silk fabric	0.30

Table 3.17 shows the quantitative and qualitative analyzed results for all the samples treated with nano silver. Deposition of silver nano was done successfully using P-D-C technique. Uniform deposition on the surface of cotton, jute and silk fabric is seen from the SEM microphotographs given in figure 3.17.

3.4.11 Effect of silver nano treatment on physical properties

In order to investigate the effects of silver nano treatment on tensile strength, crease recovery and stiffness of cotton, jute, wool and silk, these properties of the treated samples were determined and compared with the untreated samples. It is seen from Figure 3.24 and Table 3.18 that the load bearing capacity of the nano treated textiles was improved. From Figure 3.24 it is clearly seen that the improvement in breaking load due to nano silver treatment is maximum for cotton fabric.

Table 3.18 Effect of silver nano treatment on physical properties of cotton, wool and silk fabrics

Sample	**Breaking load Kgf**		**Crease recovery angle Deg**		**Bending length Cm**	
	Control	Nano Ag applied	Control	Nano Ag applied	Control	Nano Ag applied
Cotton	8.02	8.64 (+7.73)	90	95 (+5.55)	1.05	1.35 (+28.57)
Wool	6.36	6.49	142	153	2.10	2.20

		(+2.04)		(+7.74)		(+4.76)
Silk	6.24	6.36 (+2.00)	127	136 (+7.08)	2.50	2.65 (+6.00)
Jute	10.44	10.56 (+ 1.14)	90	94 (+4.44)	3.00	3.10 (+3.33)

Note- Values in parentheses indicate percentage change in physical properties.

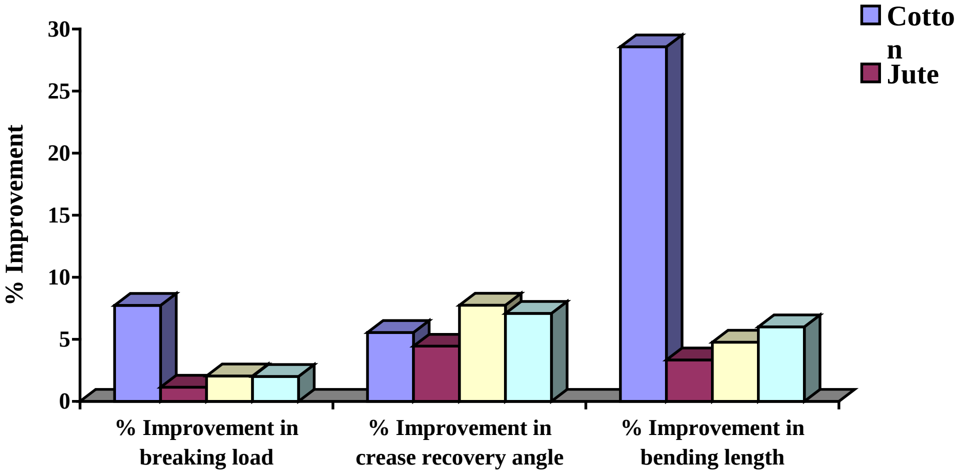


Figure 3.24 Improvement in breaking load, crease recovery angle and bending length due to silver nano treatment

Slight improvement in crease recovery angle of the silver nano treated textiles was also seen from the results shown in Table 3.18. Figure 3.24 revels that the maximum enhancement in crease recovery angle is seen in case of cotton due to the treatment. Similarly there is maximum improvement in bending length is observed in cotton sample when treated with silver nano. Figure 3.24 also indicate improvement in crease recovery angle as well as in bending lengths. These may be due to the size of nanoparticles as explain in section 3.1.

3.4.12 Effect of silver nano treatment on absorbency

The water absorbency of silver nano treated and untreated fabric samples were measured as per the standard AATCC test method. Results for the same are presented in Table 3.19 and Figure 3.25.

Table 3.19 Absorbency of silver nano treated and untreated fabrics

Fabric sample	**Time (sec)**	
	Untreated	**Treated with Ag nano**
Cotton	6	6.4
Jute	13	13.1
Wool	4	4.6
Silk	4	4.4

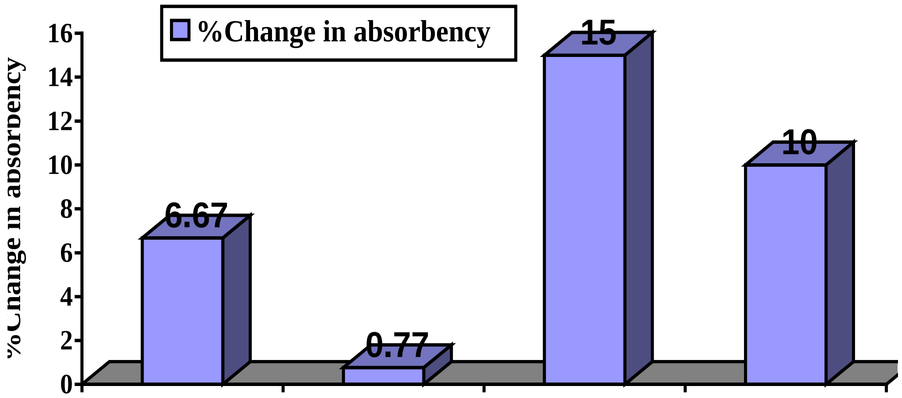


Figure 3.25 Drop in absorbency of fabrics due to nano Ag treatment

From the results it is found that nano silver treatment caused a drop in water absorbency of all the fabric samples. The nano metal particles act as whiskers and resists immediate penetration of water droplets, which increased the time to get water molecules absorbed, inside the fabric structure. The drop in absorbency was found to be maximum in case of cotton whereas jute was found to be last affected.

The results presented in Table 3.20 show that due to the application of nano silver wicking length was reduced, that is for a fixed time the length traveled by water was reduced in treated samples. But when the fabric sample was kept for a longer time the extent of effect got diminished as seen in Figure 3.26

Table 3.20 Wicking height (mm) of silver nano treated fabrics

Fabric sample	**Wicking height(mm)**					
	Untreated			**Treated with Ag nano**		
	1 min	**5 min**	**10 min**	**1min**	**5 min**	**10 min**
Cotton	22	41	50	21	40	49
Jute	17	24	37	16	22	35
Wool	26	43	56	24	41	53
Silk	19	29	42	18	29	41

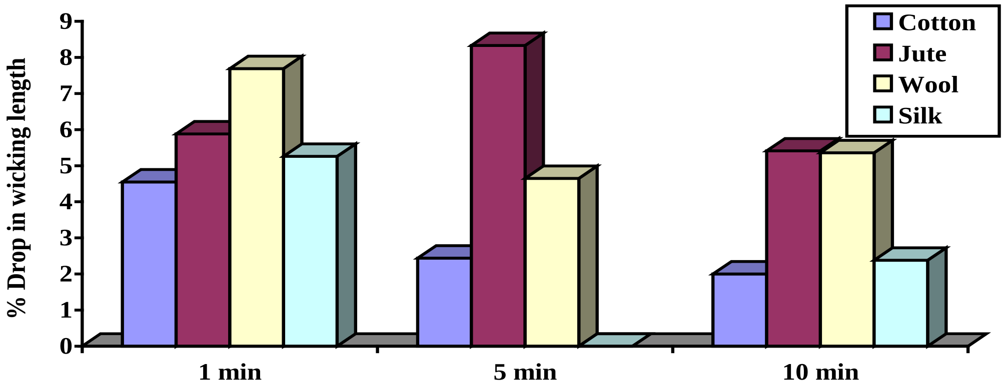


Figure 3.26 Drop in wicking behavior of silver nano treated fabric

3.4.13 Effect of silver nano on water permeability of fabric

The results presented in Table 3.21 show that the water permeability of all the treated samples was dropped after the silver nano treatment. As the nano particles present in polymer matrix resists the flow of water through the fabric.

Table 3.21 Water permeability of fabrics before and after the silver nano pretreatment

Sample	**Ψ-Water Permeability**(S^{-1})			
	Cotton	Jute	Wool	Silk
Untreated sample	0.3579	0.3726	0.3475	0.3286
Treated with Ag nano	0.3508	0.3693	0.3413	0.3268

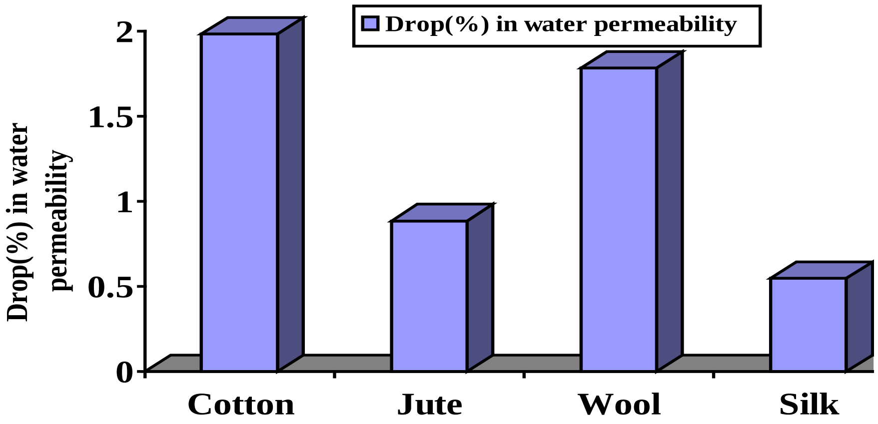


Figure 3.27 Reduction (%) in water permeability due to the silver nano treatment

3.4.14 Effect of silver nano on air permeability of fabric

The results presented in Table 3.22 were measured on Metefem for air permeability of silver nano treated and untreated fabric samples.

Table 3.22 Air permeability of silver nano treated and untreated fabric

Sample	Air permeability ($m^3/h/m^2$)			
	Cotton	Jute	Wool	Silk
Untreated sample	682.66	884.28	652.32	511.66
Treated with Ag nano	646.02	868.32	619.24	493.21

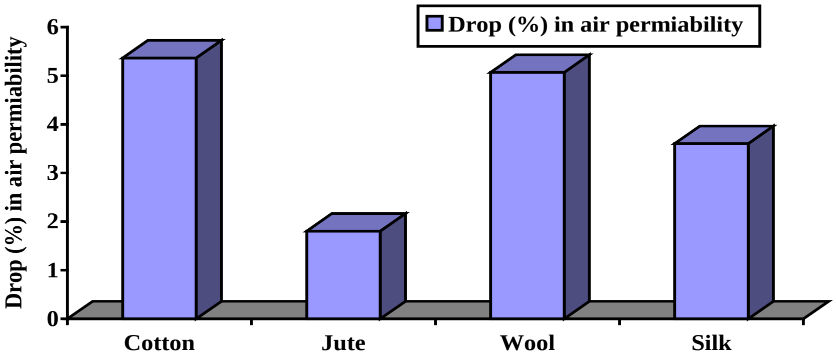


Figure 3.28 Reduction (%) in air permeability due to the nano Ag treatment

It shows that the air permeability through all treated samples was reduces compared to untreated sample. It is seen that the nano particle present in the fabric structure also affected the flow of air.

3.4.15 Effect of silver nano on resistance against microbes

Antimicrobial activity was measured by soil burial test and the results are shown in table 3.23. It is clear that the Ag-nano treatment was found to enhance the resistance of all the natural fibers, used in the study, towards microbial attack when measured in terms of loss in breaking load due to soil burial test. The breaking load of untreated control samples were reduced due to microbial damage during soil burial treatment test whereas silver nanoparticle treatment could not only protect the sample against bacterial attack but also improved its strength.

Table 3.23 Effect of Ag nanoparticles on resistance against microbial attack

Sample	Breaking load, kg			
	Before soil burial		After soil burial	
	Control	Nano Ag applied	Control	Nano Ag applied
Cotton	8.02	8.64	4.32 (-46.13)	7.32 (-15.27)
Wool	6.36	6.49	4.48 (-29.55)	5.68 (-12.48)
Silk	6.84	6.86	4.20 (-38.60)	6.24 (-09.03)
Jute	10.44	10.56	5.86 (- 43.87)	8.94 (-15.34)

Note-Values in parentheses indicate percentage change in load

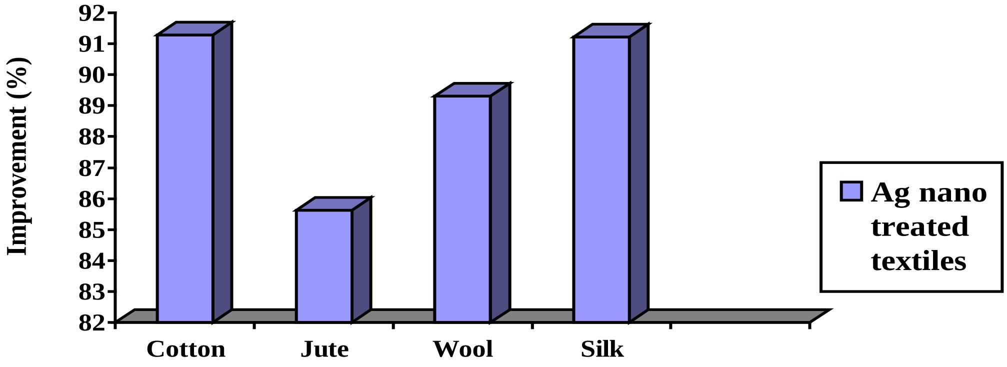


Figure 3.29 Improvement in resistance against microbial attack due to Ag nano treatment

The resistance against bacterial attack of untreated and treated samples of cotton, wool, jute and silk was determined by measuring the loss in breaking load due to soil burial test (Table 3.8). It is observed that after Ag nanoparticle application the loss is reduced in all the fibres, which shows that the Ag nano treatment enhances the resistance of cotton, wool, jute and silk towards bacterial attack. This may be due to the fact that metallic ions and metallic compounds display a certain degree of sterilizing effect. It is considered that part of the oxygen in the air or water is turned into active oxygen by means of catalysis with the metallic ion, thereby dissolving the organic substance to create a sterilizing effect [9]. Nano silver particles have an extremely large relative surface area, thus increasing their contact with bacteria or fungi, and vastly improving their bactericidal and fungicidal effectiveness. Nano silver is very reactive with proteins. When contacting bacteria and fungus, it adversely affects cellular metabolism and inhibits cell growth. It also suppresses respiration, the basal metabolism of the electron transfer system, and the transport of the substrate into the microbial cell membrane. Furthermore, it inhibits the multiplication and growth of those bacteria and fungi which cause infection, odour, itchiness and sores. Nano silver treatment thus improves the properties of cotton, wool, jute and silk in many ways.

The antibacterial property of silver nano treated and untreated fabrics was also tested against S.aureus bacteria, the results in terms of % reduction in bacterial growth are given in the Table 3.24. There is significant improvement in antibacterial property of all the four fabric samples treated with Ag nano colloids compared with the untreated counter part of the same fabrics. From the results it can also be seen that the maximum improvement in the anti-bacterial property was observed in case of cotton fabric. The enhancement in the resistance towards bacterial attack may be attributed to the certain degree of sterilizing effect of the metal atoms. It is possible that Ag nano particles may get attached to the surface of the microbe’s cell membrane, enter inside the cell and destroy their metabolic function. Further, nano size of Ag particles, having larger available surface area for interaction, provides high bactericidal effect than the bulk.

Table 3.24 Anti-bacterial effect of silver nano treated fabrics

Fabric sample	**Reduction of bacterial growth (%)**
Cotton (Control)	Nil
Silver nano treated cotton	84.73
Jute (Control)	Nil
Silver nano treated Jute	67.37
Wool (Control)	Nil
Silver nano treated Wool	83.54

Silk (Control)	Nil
Silver nano treated Silk	81.45

3.4.16 Effect of silver nano treatment on UV transmission property

The UV transmission rate (%T) of silver nano treated and untreated cotton, wool, jute and silk fabric were measured by UV-VIS spectrophotometer at different wavelength. The results are presented in table 3.25. The results show that the UV transmission for the control samples were comparatively higher than the fabrics treated with silver nano particles, i.e. better UV protection is obtained as compared to untreated fabric. In case of jute fabric there was no significant reduction in UV transmission recorded for silver nano treated fabric. This may be due to the construction of the fabrics which was not capable to restrict the UV transmission.

Table 3.25 UV transmission % of silver nano treated and untreated fabrics

Sample	Control		Ag nano treated	
	UV transmission (%)		UV transmission (%)	
	UV-A (330-400 nm)	UV-B (280-320 nm)	UV-A (330-400 nm)	UV-B (280-320 nm)
Cotton	17.39	17.07	6.73	5.39
Wool	23.09	22.51	9.35	8.44
Silk	33.59	33.57	15.34	14.34

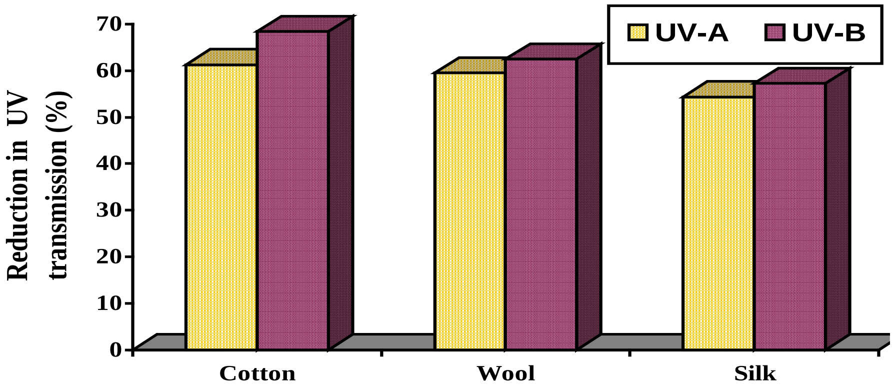


Figure 3.30 Reduction in UV transmission (%) in silver nano treated fabrics

It is found from the results that nano silver treatment restricts the UV transmission in the region between 300 nm and 400 nm in all the fabrics. The maximum reduction in UV transmission was found in case of cotton followed by wool due to the nano Ag treatment.

3.4.17 Effect of silver nano treatment on electrical surface resistivity

The Electrical surface resistivity of treated and untreated fabric samples was measured on KEITHLEY614-Electrometer and the results are given in table 3.16.

Table 3.26 Electrical surface resistivity of natural textile fabrics

Fabric sample	**Electrical surface resistivity (ohm Ω)**			
	Cotton	Wool	Jute	Silk
Untreated sample	180×10^9	$>200 \times 10^9$	$>200 \times 10^9$	$>200 \times 10^9$
Ag nano treated sample	144×10^9	125×10^9	$>200 \times 10^9$	110×10^9

The result shows that the electrical resistivity of treated fabrics is reduced irrespective of the class of fabric compared to the untreated fabric samples. The incorporation of silver nano particle in polymer matrix resulted in the higher surface resistivity of the fabrics. The reduction in the electrical resistivity of treated fabric may be due to the higher conductivity of silver deposited on the fabric surface.

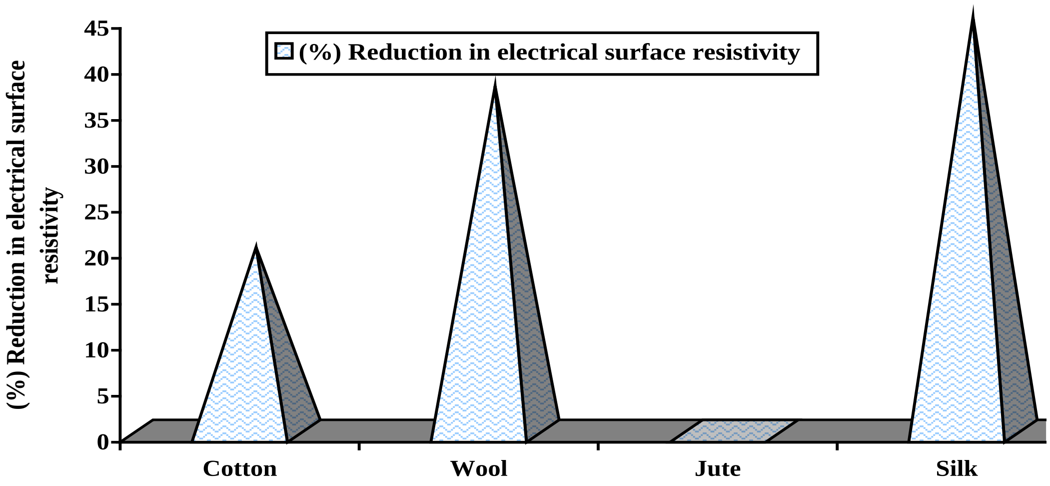


Figure 3.31 Reduction in electrical surface resistivity of fabric samples

3.4.18 Effect of silver nano treatment on dyeing behavior

Ag nanoparticle treated cotton, wool jute and silk fabric samples were dyed with three direct dyes. The results in terms of colour strength (*K/S*) values were compared with the colour strength of untreated dyed fabric samples.

Table 3.27 Effect of Ag nano-particles on colour strength of fabrics dyed with direct dyes

Sample	**Colour strength *(K/S)***					
	D1		**D2**		**D3**	
	Control	**Ag nano treated**	**Control**	**Ag nano treated**	**Control**	**Ag nano treated**
Cotton	5.32	6.50 (+22.18)	8.22	10.55 (+28.34)	8.06	11.22 (+39.20)
Wool	9.05	10.18 (+12.48)	11.85	13.21 (+11.47)	11.41	14.85 (+30.14)
Silk	4.75	6.11 (+28.63)	7.34	8.37 (+14.03)	7.39	9.09 (+23.00)
Jute	6.11	6.38 (+4.41)	8.73	9.06 (+3.78)	8.34	9.95 (+19.30)

Values in parentheses indicate percentage change in *K/S* values, D1 – C.I. Direct Red 9, D2 – C.I. Direct Blue 67 and D3 –C.I. Direct Green 6

The Ag nanoparticle treated cotton, wool, jutr and silk fabrics were dyed with three direct dyes and compared with the untreated samples. It is observed from Table 3.27 that the *K/S* values of the nano silver pretreated samples are higher than those of the corresponding untreated samples of cotton, wool, jute and silk fabrics. The maximum improvement in colour strength is observed with C.I. Direct Green 6 dye. The higher *K/S* values (Table 3.27) of nano-treated samples indicate that the presence of nano metal particles increases the dye affinity towards the material. The silver nanoparticles in the fabric thus act as mordant. The negatively charged dye anions get attracted towards the fibre probably due to the polarity developed in the metal particles by induction which results in better bonding between the dye and the fibre. The better coupling of the dye and the fibre is also reflected in the improvement in the colour fastness properties (Table 3.13). Thus, silver nano pre-treatment not only improves the colour strength but also improves the colour fastness.

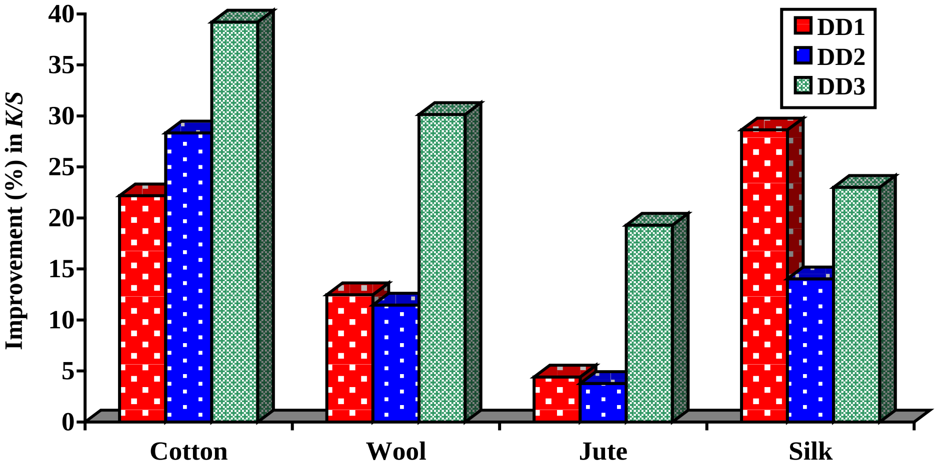


Figure 3.32 Improvement in colour strength values of fabric dyed with direct dye after Ag nano pretreatment

The fastness properties of Ag nano treated and untreated samples are reported in Table 3.28. The better coupling of the dye and fiber is also reflected in the improvement of the color fastness properties. Where the Ag-nano treated / untreated and dyed fabrics after washing off using 2 gpl non-ionic detergent, the washing treatment caused little effect on the colour bleeding of the nano Ag treated and dyed samples.

Table 3.28 Effect of Ag nano-particles on fastness properties of samples dyed with direct dyes

Sample	**Fastness to**											
	Light						Washing					
	D1		D2		D3		D1		D2		D3	
	C	T	C	T	C	T	C	T	C	T	C	T
Cotton	3	3-4	3	3-4	3	4	2-3	4	2-3	4	2-3	4-5
Wool	3	3-4	2-3	3	3	3-4	2-3	3-4	2-3	4	2-3	4
Silk	3	3-4	2-3	3-4	3	4	3	4	2-3	4-5	3	4-5
Jute	2-3	3	3	3	2-3	3-4	3	3-4	2-3	3-4	3	4

D1 – C.I. Direct Red 9, D2 – C.I. Direct Blue 67 and D3 –C.I. Direct Green 6,
C – Control sample, T – Sample treated with Ag Nanoparticles.

Natural protein fibers i.e. wool and silk are usually dyed with acid dyes. To investigate the effect of Ag nano treatment on the dyeing of wool and silk with acid dye, the study was further extended to dye Ag nano pretreated wool and silk fabrics with three acid dyes namely, Acid orange R (AD1), Acid navy blue (AD2) and Acid rose 6B (AD3) by conventional method and their dyeing performance is compared with conventionally dyed wool and silk fabric without silver nano pretreatment. Dyeing performance of Ag-nano treated and untreated samples, evaluated in terms of *K/S* values is presented in Table 3.29.

Table 3.29 Colour strength values, fastness ratings of wool and silk fabric dyed with acid dye

Dye	**Fabric samples**	**Colour strength (*K/S*) values**	**Fastness ratings**	
			LF	WF
AD1	Wool (Control)	9.05	5	4
	Ag nano treated wool	9.57	6	4
AD2	Wool (Control)	13.10	4-5	4
	Ag nano treated wool	13.68	5-6	4
AD3	Wool (Control)	10.33	6	4
	Ag nano treated wool	10.92	6-7	4-5
AD1	Silk (Control)	4.58	5-6	4
	Ag nano treated silk	4.96	6	4-5
AD2	Silk (Control)	7.62	4-5	4
	Ag nano treated silk	8.03	6	4-5
AD3	Silk (Control)	6.26	6	4
	Ag nano treated silk	6.84	6-7	4-5
Note: AD1- Acid orange R, AD2- Acid navy blue, AD3- Acid rose 6B, LF-Light Fastness, WF-Washing Fastness				

The colour strength values of samples dyed with acid dyes is represented in Table 3.29. It is seen from the results that wool and silk fabric samples picked up some more dyes after treatment with silver nano particles. The introduction of silver in nano form thus enhanced the affinity of the fibre towards acid dyes.

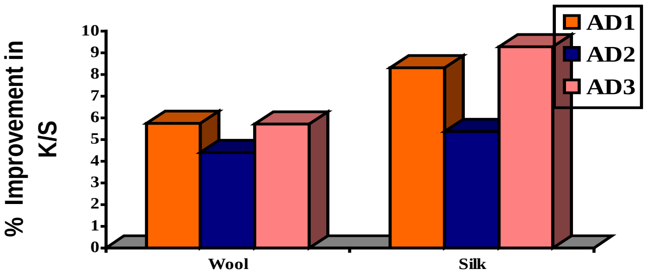


Figure 3.33 Enhancement on colour yield of wool & silk due to nano silver pretreatment

It is also seen from Figure 3.33 that improvement in colour strength values is higher in case of wool compared to silk fabric dyed with acid dye after Ag nano pretreatment. The light and washing fastness ratings for Ag nano pretreated and dyed samples were found to be improved. The improvement in fastness ratings may be due to the formation of metal-dye complex. The effect of nano Ag pre-treatment on the dyeability of wool and silk, using three natural dyes viz., *Azadirachta indica* (ND1), *Lawsonia inermis* (ND2) and *Ocimum sanctum* (ND3). Table 3.30 represents the results in terms of colour strength values (*K/S*) of dyed samples with and without Ag nano treatment.

Table 3.30 Colour strength values of wool and silk fabric dyed with natural colourants

Dye	**Fabric sample**	**Colour strength (*K/S*) values**	**Fastness ratings**	
			LF	WF
ND1	Wool (Control)	10.14	6-7	4
	Ag nano treated wool	11.75	7	4-5
ND2	Wool (Control)	14.24	6-7	4
	Ag nano treated wool	15.87	7	4-5
ND3	Wool (Control)	11.16	6	4
	Ag nano treated wool	12.39	6-7	4-5
ND1	Silk (Control)	7.62	6	4
	Ag nano treated silk	9.57	6-7	4
ND2	Silk (Control)	9.35	6-7	4
	Ag nano treated silk	11.55	7	4-5
ND3	Silk (Control)	10.23	6	4
	Ag nano treated silk	13.10	6-7	4-5

Note:ND1- Azadirachta indica,ND2- Lawsonia inermis, ND3- Ocimum sanctum , LF-Light Fastness, WF-Washing Fastness

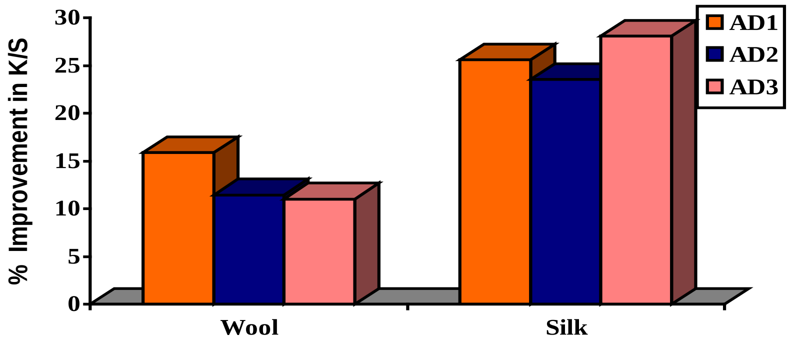


Figure 3.34 Enhancement on colour yield of wool and silk due to nano silver pretreatment

From Table 3.30 and figure 3.34, it can be seen that nano treated as well as untreated wool and silk fabrics can be successfully dyed with all three natural colourants. For 20 % (owf) depth of shade using methanolic extract of *Azadirachta indica, Lawsonia inermis* and *Ocimum sanctum* as a natural colourant, a pale to medium green colour was obtained, while dark green colour shade was obtained in case of nano Ag pretreated sample. The higher *K/S* values of nano-treated samples indicate that the presence of nano metal particles increased the dye affinity towards the fabric. The effect of Ag nano treatment of the fibre is also reflected in the improvement in the colour fastness properties. Thus, silver nano pre-treatment not only improves the colour strength but also enhanced the colour fastness of wool and silk fabric dyed with natural dyes.

3.4.19 Characterization of zinc nano treated fabrics

Zinc nanoparticles were deposited on cotton, jute, wool and silk fabrics using P-D-C method. The surface morphology of these fabrics were examined by SEM. From SEM images shown in figure 3.32, deposition of nanoparticles is clearly seen, uniformly dispersed on the surface of fabrics.

Zinc nano treated fabrics

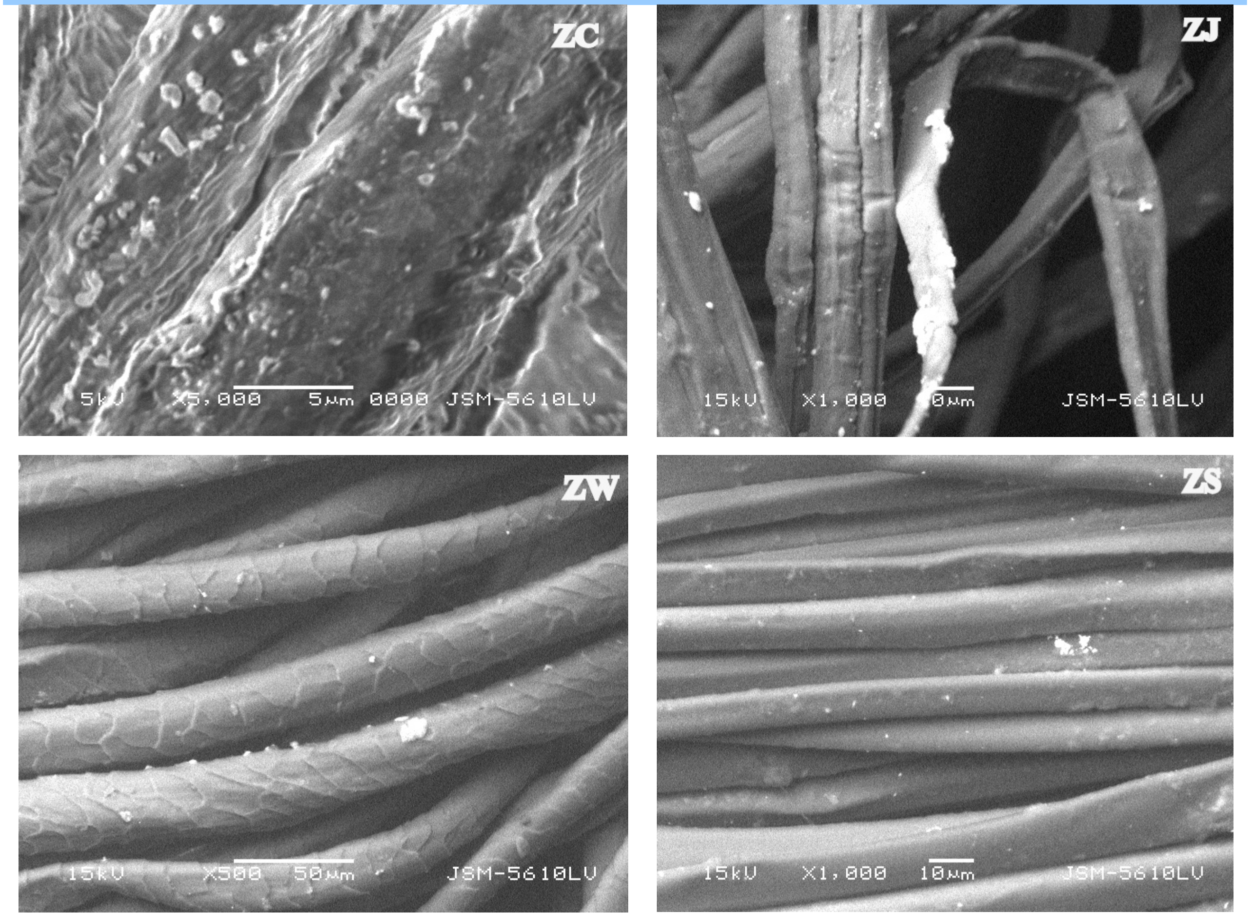


Figure 3.35 Scanning electron microscope (SEM) images of zinc nano treated cotton (ZC), jute (ZJ), wool (ZW) and silk (ZS) fabrics.

Figure 3.35 represents the amount of zinc detected on textile samples. Maximum 0.26 µg zinc nanoparticles were measured on wool substrate.

Table 3.31 Amount of zinc detected on cotton, jute, wool and silk fabrics using XRF.

Fabric	Cotton	Jute	Wool	Silk
Amount of zinc nano	0.23 µg	0.18 µg	0.26 µg	0.20 µg

3.4.20 Effect of zinc nano treatment on physical properties

The effects of nano Zn treatment on the physical properties of cotton, Jute, wool and silk were presented in Table 3.32. It is seen from the results that introduction of nano zinc particles into the structure of the fiber caused an improvement in the load bearing capacity of the fiber. Improvements in the bending length and crease recovery angle of treated fabrics are also observed. These may be due to the interference of zn nano-particles with polymer chain mobility. From the SEM microphotograph of nano zn treated samples shown in figure 3.35, it can be clearly seen that the Zn nano-particles are distributed on the surface of the treated samples, being distributed in polymer matrices, nano-particles can carry load and increase the toughness and abrasion resistance; nano-fillers can transfer stress away from polymer matrices and enhance tensile strength of treated fiber.

Table 3.32 Effect of zinc nano treatment on physical properties of sample

Sample	**Breaking load (kgf)**	**Crease recovery angle °(deg)**	**Bending length (cm)**
Cotton (Control)	8.02	90	1.05
Cotton pre-treated with Zn nano	8.83 (+10.09)	105 (+16.66)	1.17 (+11.42)
Jute (Control)	10.44	90	3.00
Jute treated with Zn nano	10.78 (+3.26)	101 (+12.22)	3.32 (+10.67)
Wool (Control)	6.43	139	3.10
Wool pre-treated with Zn nano	7.41 (+15.24)	152 (+9.35)	3.46 (+11.61)
Silk (Control)	6.32	124	2.80
Silk pre-treated with Zn nano	6.80 (+7.59)	141 (+13.71)	3.27 (+16.79)
Note: Values in the parenthesis indicate percentage change in physical properties.			

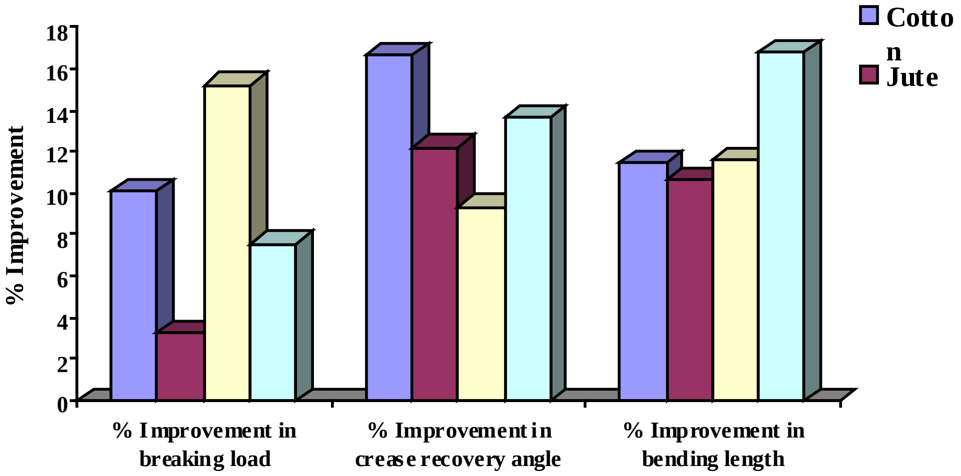


Figure 3.36 Improvement in breaking load, crease recovery angle and bending length due to zinc nano treatment

3.4.21 Effect of zinc nano treatment on absorbency

Effect of zinc nano treatment on water absorbency was measured by drop test. From the results given in Table 3.33 it was found that the drop in absorbency is higher for samples treated with zinc nano particles compared to the original fibers. The reduction in absorbency (Figure 3.36) has been noticed partial higher for cotton fiber.

Table 3.33 Absorbency of zinc nano treated and untreated fabrics

Fabric sample	**Time (sec)**	
	Untreated	**Treated with Zinc nano**
Cotton	6	7.1
Jute	13	13.6
Wool	4	5.1
Silk	4	4.8

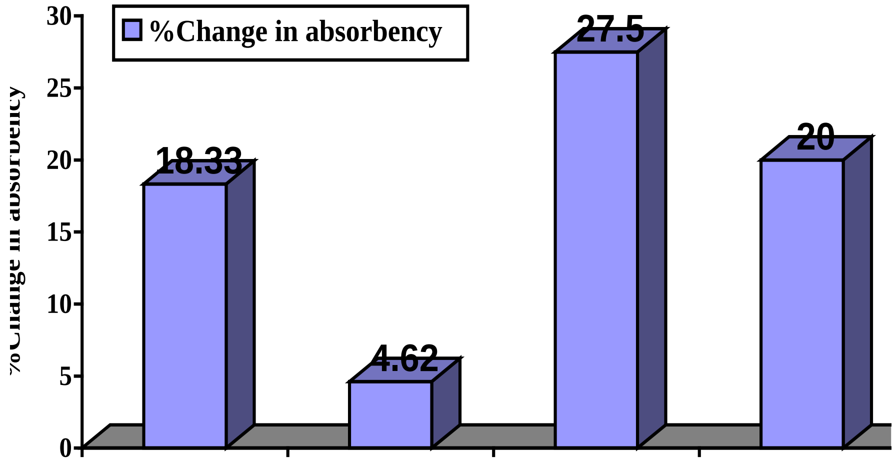


Figure 3.37 Drop in absorbency of fabrics due to nano zinc treatment

It has been observed from the results presented in Table 3.34 and corresponding Figure 3.37 that deposition of zinc nano particles reduced the wicking length of textile fiber. The small size of nano penetrates inside the fiber matrix. These particles may hindered the travel of water through capillary.

Table 3.34 Wicking height (mm) of zinc nano treated fabrics

Fabric sample	**Wicking height(mm)**					
	Untreated			**Treated with Zinc nano**		
	1 min	**5 min**	**10 min**	**1min**	**5 min**	**10 min**
Cotton	22	41	50	17	32	43
Jute	17	24	37	15	21	33
Wool	26	43	56	22	37	49
Silk	19	29	42	16	25	37

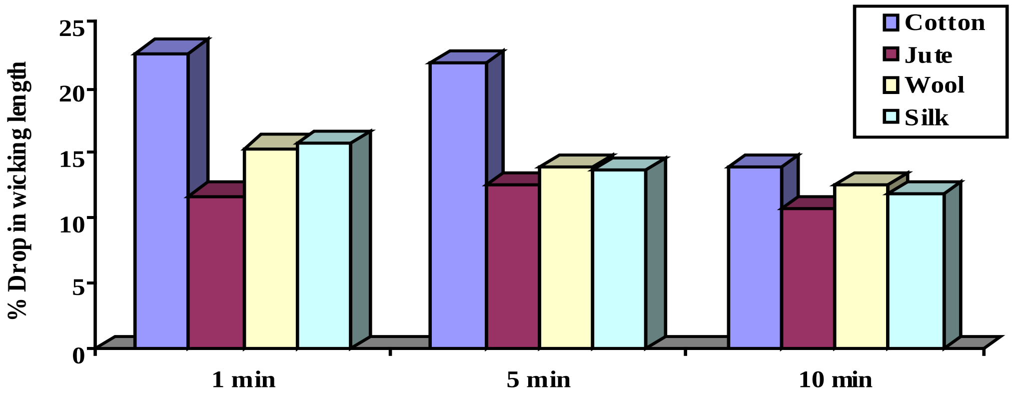


Figure 3.38 Drop in wicking behavior of zinc nano treated fabric

3.4.22 Effect of zinc nano on water permeability of fabric

Water permeability of zinc nano treated textiles was evaluated by constant head method. The results show that the water permeability of all the treated samples was dropped after the zinc nano treatment. As the nano particles present in polymer matrix resists the flow of water through the fabric.

Table 3.35 Water permeability of fabrics before and after the zinc nano pretreatment

Sample	**Ψ-Water Permeability**(S^{-1})			
	Cotton	Jute	Wool	Silk
Untreated sample	0.3579	0.3726	0.3475	0.3286
Treated with zinc nano	0.3438	0.3659	0.3368	0.3237

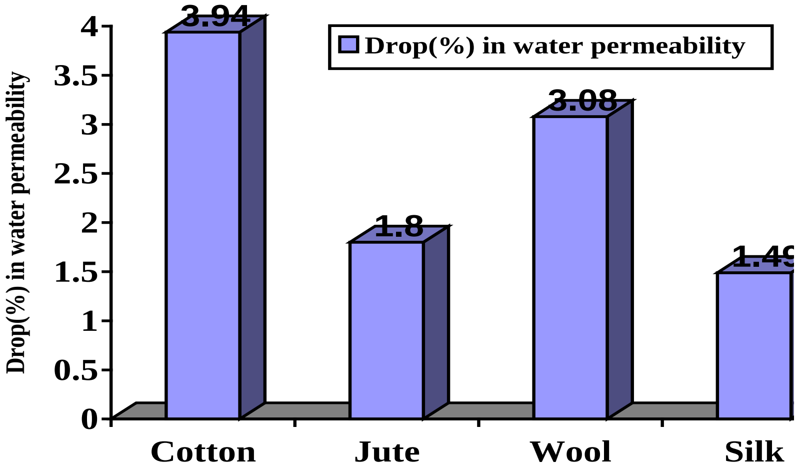


Figure 3.39 Reduction (%) in water permeability due to the zinc nano treatment

3.4.23 Effect of zinc nano on air permeability of fabric

Air permeability of nano treated samples was evaluated as per ASTM D 737 test method. The results are presented in Table 3.36 and Figure 3.39

Table 3.36 Air permeability of untreated and zinc nano treated textiles

Sample	**Air permeability ($m^3/h/m^2$)**			
	Cotton	Jute	Wool	Silk
Untreated sample	682.66	884.28	652.32	511.66
Treated with zinc nano	621.09	859.24	592.25	473.63

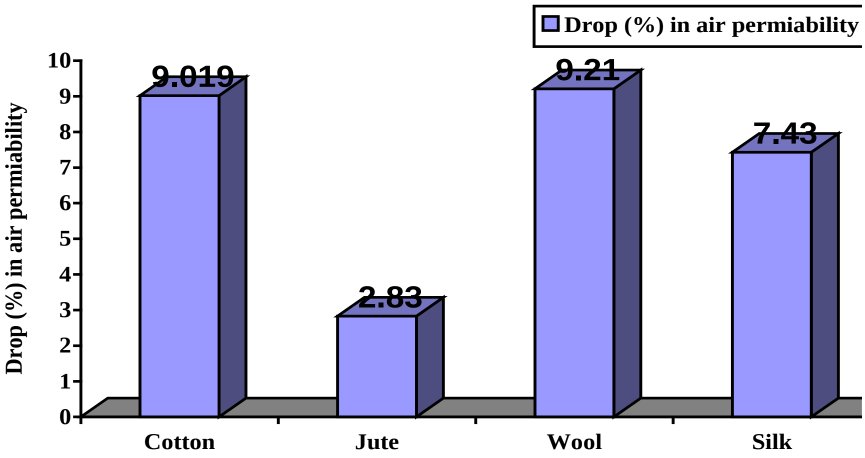


Figure 3.40 Reduction (%) in air permeability due to the nano zinc treatment

It shows that the air permeability through all treated samples was reduces compared to untreated sample. It is seen that the nano particle present in the fabric structure also affected the flow of air.

3.4.24 Effect of zinc nano on resistance against microbes

Antimicrobial activity was measured by soil burial test and the results are shown in Table 3.37 and Figure 3.40. It is clear that the Zn nano treatment was found to enhance the resistance of cotton, wool, silk and jute towards microbial attack when measured in terms of loss in breaking load due to soil burial test. The breaking load of untreated control samples were reduced due to bacterial damage during soil burial test whereas zinc nano-particle treated sample resist against the bacterial attack. This may be due to the sterilizing effect of metallic ions and metallic compounds.

Table 3.37 Effect of zinc nanoparticles on resistance against microbial attack

Sample	**Breaking load, kgf**	
	Before soil burial	After soil burial
Untreated cotton sample	8.02	4.32
Cotton pre-treated with zinc nano particles	8.83	7.44
Untreated jute sample	10.44	5.02
Jute pretreated with zinc nano particles	10.92	9.86
Untreated wool sample	6.43	4.09
Wool pretreated with zinc nano particles	7.73	7.09
Untreated silk sample	6.32	4.12
Silk pretreated with zinc nano particles	6.71	6.32

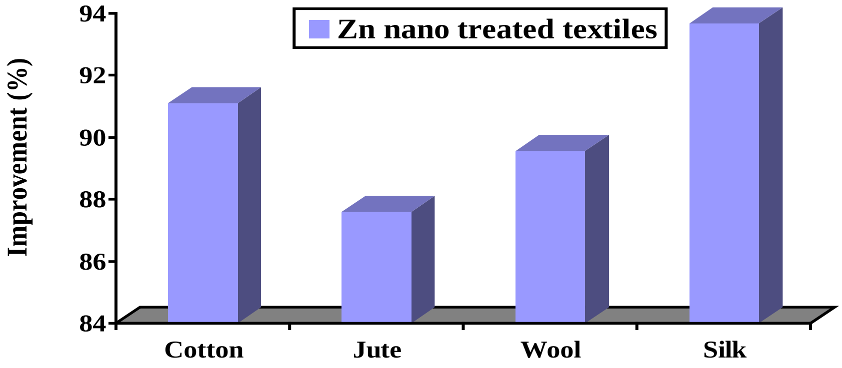


Figure 3.41 Improvement in resistance against microbial attack due to zinc nano treatment

The treated samples were also tested against gram-positive *Staphylococcus aureus* bacteria. Anti bacterial efficiency of zinc nano treated samples against the original fabric samples is reported in Table 3.38. It is found from the results that the zinc nano treated cotton sample have maximum resistance against bacterial growth followed by nano zinc treated wool sample.

Table 3.38 Anti-bacterial effect of zinc nano treated fabrics

Fabric sample	**Reduction of bacterial growth (%)**
Cotton (Control)	Nil
Zinc nano treated cotton	86.72
Jute (Control)	Nil
Zinc nano treated Jute	73.12
Wool (Control)	Nil
Zinc nano treated Wool	85.06
Silk (Control)	Nil
Zinc nano treated Silk	83.35

3.4.25 Effect of zinc nano treatment on UV transmission property

The UV transmission rate (%T) of zinc nano treated and untreated cotton, wool, jute and silk fabric were measured by UV-VIS spectrophotometer at different wavelength. The results are presented in Table 3.39. The results show that the UV transmission for the control samples were comparatively higher than the fabrics treated with zinc nano particles, i.e. better UV protection is obtained as compared to untreated fabric. In case of jute fabric there was no significant reduction in UV transmission recorded for zinc nano treated fabric. This may be due to the construction of the fabrics which was not capable to restrict the UV transmission.

Table 3.39 UV transmission % of zinc nano treated and untreated fabrics

Sample	**Control**		**Zinc nano treated**	
	UV transmission (%)		**UV transmission (%)**	
	UV-A (330-400 nm)	UV-B (280-320 nm)	UV-A (330-400 nm)	UV-B (280-320 nm)
Cotton	17.39	17.07	8.32	8.17
Wool	23.09	22.51	11.40	10.65
Silk	33.59	33.57	21.08	20.15

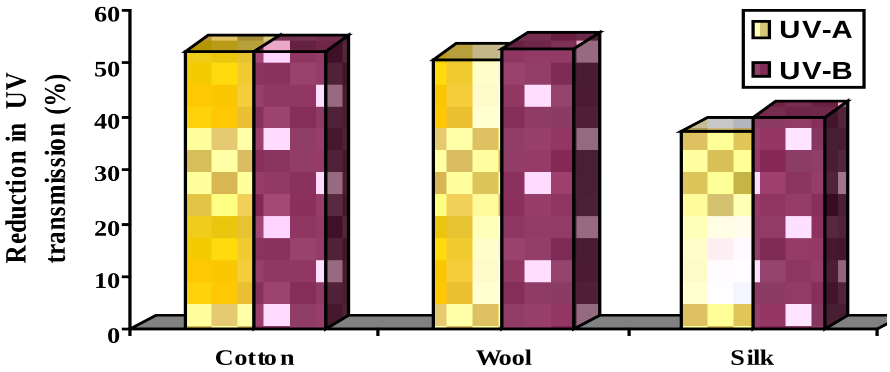


Figure 3.42 Reduction in UV transmission (%) in zinc nano treated fabrics

It is found from the results that nano zinc treatment restricts the UV transmission in the region between 300 nm and 400 nm in all the fabrics.

3.4.26 Effect of zinc nano treatment on electrical resistivity

The Electrical surface resistivity of treated and untreated fabric samples was measured as per AATCC test method 76-2005.and presented in Table 3.40.

Table 3.40 Electrical surface resistivity of textile treated with zinc nanoparticles

Fabric sample	**Electrical surface resistivity (ohm Ω)**			
	Cotton	Wool	Jute	Silk
Untreated sample	180 x 10^9	>200 x 10^9	>200 x 10^9	>200 x 10^9
Zinc nano treated sample	157 x 10^9	>200 x 10^9	>200 x 10^9	>200 x 10^9

The result shows that the electrical resistivity of zinc nano treated fabrics is reduced in case of cotton fabric, whereas in case of wool, jute and silk there was no significant change in surface resistivity of textiles.

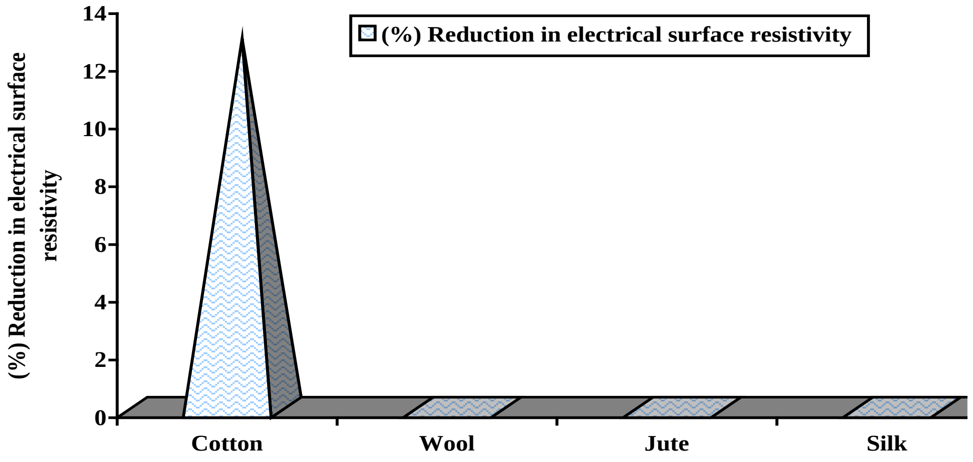


Figure 3.43 Reduction in electrical surface resistivity of fabric samples

3.4.27 Effect of zinc nano treatment on dyeing behavior

The Zn nanoparticle treated fabric samples were dyed with three direct dyes and compared with the untreated samples. The *K/S* values of the nano zinc pretreated samples were found to be higher (Table 3.41 and Figure 3.43) than the corresponding untreated samples.

Table 3.41 Effect of zinc nano-particles on colour strength of fabrics dyed with direct dyes

Sample	**Colour strength *(K/S)***					
	C.I. Direct Red 9		**C.I. Direct Blue 67**		**C.I. Direct Green 6**	
	Control	Zinc nano treated	Control	Zinc nano treated	Control	Zinc nano treated
Cotton	5.32	5.87	8.22	9.24	8.06	10.76
Jute	14.15	14.36	16.43	16.57	17.26	17.88
Wool	10.12	10.28	12.31	12.93	11.52	12.15
Silk	4.64	5.24	6.89	7.36	7.56	8.32

The maximum improvement in color strength was observed with direct green 6 dyes. The higher *K/S* values of nano-treated samples indicate that the presence of nano metal particles increased the dye affinity towards the material. The Zn nanoparticles in the fabric thus acted as mordant. The better coupling of the dye and fiber is also reflected in the improvement of the color fastness properties (Table 3.3.12), which is a major drawback of most direct dyes.

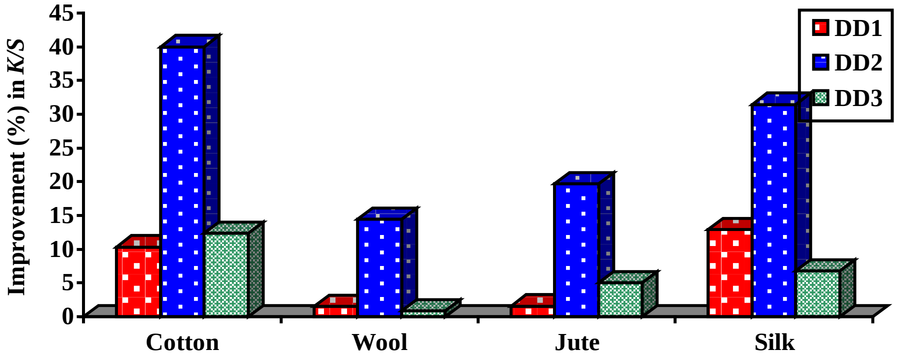


Figure 3.44 Improvement in colour strength values of fabric dyed with direct dye after Zinc nano pretreatment

Table 3.42 Effect of zinc nanoparticles on fastness properties of samples dyed with direct dyes

Sample	**Fastness to**											
	Light						**Washing**					
	DD1		DD2		DD3		DD1		DD2		DD3	
	C	T	C	T	C	T	C	T	C	T	C	T
Cotton	3	3-4	3	3-4	3	4	2-3	4	2-3	3-4	2-3	3-4
Jute	2-3	3	3-4	3-4	2-3	3	3	3-4	3	3-4	3	4
Wool	2-3	3-4	3	3-4	3	3-4	3-4	4	2-3	3	3	3-4
Silk	3	3-4	3	3-4	3	3-4	3	3-4	3	4	3	3-4
Note-DD1 – C.I. Direct Red 9, DD2 – C.I. Direct Blue 67 and DD3 –C.I. Direct Green 6, C – Control sample, T – Sample treated with Zinc Nano-particles.												

Natural protein fibers i.e. wool and silk are usually dyed with acid dyes. To investigate the effect of zinc nano treatment on the dyeing of wool and silk with acid dye, the study was further extended to dye zinc nano pretreated wool and silk fabrics with three acid dyes namely, Acid orange R (AD1), Acid navy blue (AD2) and Acid rose 6B (AD3) by conventional method and their dyeing performance is compared with conventionally dyed wool and silk fabric without zinc nano pretreatment. Dyeing performance of zinc-nano treated and untreated samples, evaluated in terms of *K/S* values is presented in Table 3.43.

Table 3.43 Colour strength values, fastness ratings of wool and silk fabric dyed with acid dye

Dye	**Fabric samples**	**Colour strength (*K/S*) values**	**Fastness ratings**	
			LF	WF
AD1	Wool (Control)	9.05	5	4
	Zinc nano treated wool	9.22	6	4
AD2	Wool (Control)	13.10	4-5	4
	Zinc nano treated wool	13.29	6	4-5
AD3	Wool (Control)	10.33	6	4
	Zinc nano treated wool	10.79	6-7	4-5
AD1	Silk (Control)	4.58	5-6	4
	Zinc nano treated silk	4.82	6	4-5
AD2	Silk (Control)	7.62	4-5	4
	Zinc nano treated silk	7.89	6	4-5
AD3	Silk (Control)	6.26	6	4
	Zinc nano treated silk	6.53	6-7	4-5
Note: AD1- Acid orange R, AD2- Acid navy blue, AD3- Acid rose 6B, LF-Light Fastness, WF-Washing Fastness				

It is seen from the Table 3.3.13 that both wool and silk fabric samples picked up more dyes after treatment with zinc nano particles. The introduction of zinc in nano form thus enhanced the affinity of the fibre towards acid dyes.

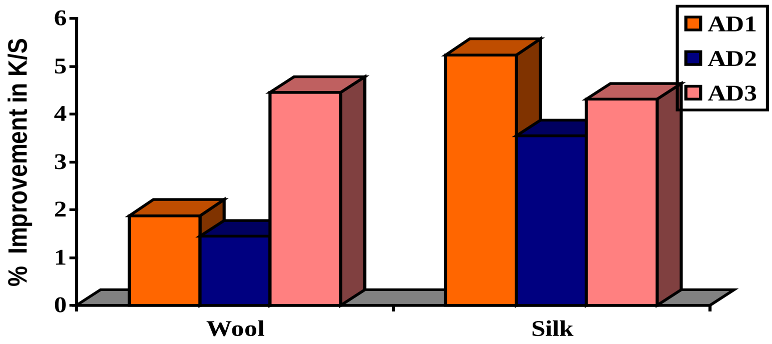


Figure 3.45 Enhancement on colour yield of wool and silk due to nano zinc pretreatment

It is also seen from Figure 3.45 that improvement in colour strength values is higher in case of wool compared to silk fabric dyed with acid dye after zinc nano pretreatment. The light and washing fastness ratings for zinc nano pretreated and dyed samples were found to be improved. The improvement in fastness ratings may be due to the formation of metal-dye complex.

The effect of nano zinc pre-treatment on the dyeability of wool and silk, using three natural dyes viz., *Azadirachta indica* (ND1), *Lawsonia inermis* (ND2) and *Ocimum sanctum* (ND3). Table 3.3.14 represents the results in terms of colour strength values (*K/S*) of dyed samples with and without Zinc nano treatment.

Table 3.44 Colour strength values of wool and silk fabric dyed with natural colourants

Dye	**Fabric sample**	**Colour strength (*K/S*) values**	**Fastness ratings**	
			LF	WF
ND1	Wool (Control)	10.14	6-7	4
	Zinc nano treated wool	11.23	6-7	4-5
ND2	Wool (Control)	14.24	6-7	4
	Zinc nano treated wool	15.19	7	4-5
ND3	Wool (Control)	11.16	6-7	4
	Zinc nano treated wool	12.08	6-7	4-5
ND1	Silk (Control)	7.62	6	4
	Zinc nano treated silk	8.75	6-7	4
ND2	Silk (Control)	9.35	6-7	4
	Zinc nano treated silk	10.38	7	4-5
ND3	Silk (Control)	10.23	6	4
	Zinc nano treated silk	12.41	6-7	4-5

Note:ND1- Azadirachta indica,ND2- Lawsonia inermis, ND3- Ocimum sanctum , LF-Light Fastness, WF-Washing Fastness

From Table 3.44, it can be seen that nano treated as well as untreated wool and silk fabrics can be successfully dyed with all three natural colourants. For 20 % (owf) depth of shade using methanolic extract of *Azadirachta indica*, *Lawsonia inermis* and *Ocimum sanctum* as a natural colourant, a pale to medium green colour was obtained, while dark green colour shade was obtained in case of nano Zinc pretreated sample.

The higher *K/S* values of nano-treated samples indicate that the presence of nano metal particles increased the dye affinity towards the fabric. The effect of zinc nano treatment of the fibre is also reflected in the improvement in the colour fastness properties. Thus, zinc nano pre-treatment not only improves the colour strength but also enhanced the colour fastness of wool and silk fabric dyed with natural dyes.

3.5 REFERENCES

1. Y.W.Wang, C.W.M.Yuen, M.Y.S.Leung, S.K.A.Kuand, H.L.I.Lam, Nanotechnologies in textiles, *Textile Asia*, 2004, **35**, 5, 27.
2. H. J. Lee and S. H. Jeong, Bacteriostasis of nanosized silver on polyester nonwovens, *Textile Research Journal*, 2004, **74**, 5, 442.
3. L. Qian, Applicaton of nanotechnology for high performance textiles, *Journal of Textile and Apparel, Technology and Management*, 2004, **4**, 1, 1-7.
4. L. Qian, Nanotechnology in Textiles: Recent Developments and Future Prospects, *AATCC Review*, 2004, **4**, 5, 14.
5. Hartley, M.Scott, A.Holly, The Next Generation of Chemical and Biological Protective Material Utilizing Reactive Nano-particles, Gentex corp., Carbondale, pa.
6. He, Junhui, T.Kunitake and A. Nakao, A.Facile in situ synthesis of noble metal nanoparticles in porous cellulose fibers, *Chemical Materials*, 2003, **15**, 23, 13.

CHAPTER 4

SYNTHESIS, CHARACTERIZATION AND APPLICATION OF CELLULOSE WHISKERS

4.1 INTRODUCTION

Textile materials made from natural fibers have played an important role in the life of human beings from time immemorial and still are widely used in the modern textiles industry for their unique properties as high quality textile materials. Due to the variation in staple length, the natural fibers with short staple length can’t be used to spin yarns. Consequently, natural fibers such as wool, silk, cotton or hemp are wasted during processing and final usages. A new way of reusing these fibers has large marketing potential because of their excellent intrinsic properties. Meanwhile, not only the textile industry, but many other industries like the bio-medical industries need such bio-compatible materials [1].

In this chapter, the preparation, characterization and application of nano cellulose are discussed. Nano scale cellulose polymers were synthesized from viscose by a simple technique developed. The nano polymers were then applied to polyester to improve its various properties. Nano-whiskers are wonder molecules, which can impart various functional properties not only to the textiles but also contribute significantly in the field of electronics and medicines. Recently several works has been reported, where nano-whiskers have been synthesis from variety of materials by using some new and improved techniques.

Some potential applications of nano cellulose in the field of paper and paperboard applications as dry strength agent, surface strength agent or nanocoatings/ nanobarriers, bio-nanocomposites, food applications, cosmetics/ skin creams, medical/pharmaceutical applications, hygiene/absorbent products, emulsion/ dispersion applications and oil recovery applications.

Many researchers [2] have tried to establish new application areas for natural fibers by developing from them new materials for use in bio-technological and bio-medical fields. US Patent 4,233,212 claimed a method to crush silk fibers into fine powders to obtain powders particularly useful as an additive for cosmetic preparations [3]. CN 94115873.X disclosed a method to prepare nano-scale cellulose powder with an average size of 2.5-10 nm from cotton or hemp fibers by chemical treatment together with low temperature drying and pulverization and filtration. These US and CN patents reported specific methods to prepare fine/super fine powder from protein or cellulose fiber and suggested some potential applications, but none of them reported the technique to prepare nano-scale fibrous materials and characterization of its morphology and functional properties.

Native cellulose (cellulose that is produced by plants is referred to as native cellulose, Figure 4.1) is composed of distinct number of glucan chains that are arranged in a manner to form nanostructure called microfibrils. These microfibrils are known to have regions of order (crystalline forms) along with regions of disorder (amorphous forms). The crystalline regions within these microfibrils constitute the nanocrystals, which can be effectively derivatized and used in various industrial applications including nanocomposites.

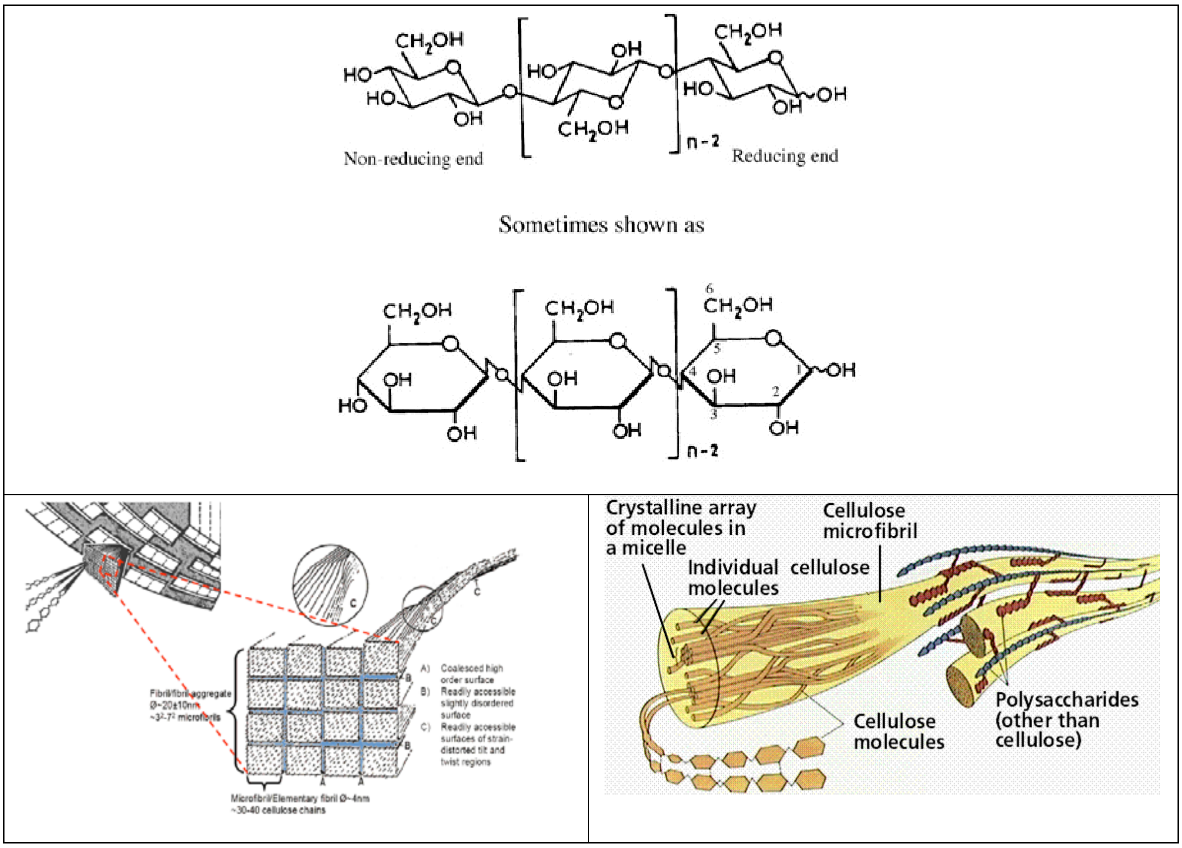


Figure 4.1 Chemical structure and organization of cellulose in fiber

A chemist by the name of Girard was the first to explain this effect as hydrolysis of cellulose fibers, which was initially recognized in the textile industry [4]. With structural analysis it was clear that cellulose microfibrils consisted regions of high order in combination with regions of less order. Cellulose nanocrystals originate from the highly ordered crystalline segment of cellulose whereas the amorphous (less ordered) regions constitute a random arrangement of cellulose chains. These randomly arranged chains are easily attacked by an acid where the hydronium ions cause a hydrolytic cleavage of glycosidic bonds by penetrating the low order regions. The breaking of glycosidic linkage results in the separation of highly ordered crystalline regions, which appear like individual rods. These rod-like nanoparticles essentially have the reducing end on side and the non reducing end on the other. This method of producing cellulose nanocrystals in an acidic environment, initially reported in 1951 by Ranby, is called as acid hydrolysis [5].

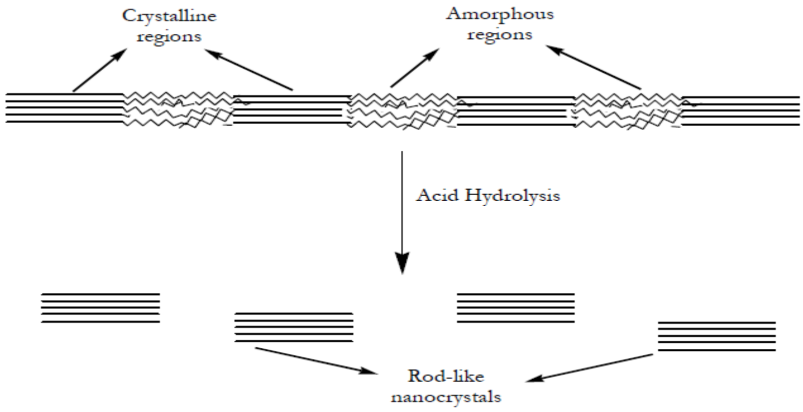


Figure 4.2 Formation of cellulose crystals from acid hydrolysis of cellulose fibers.

4.2 MATERIAL

Pure polyester woven fabric with specification as mentioned in Table 4.1 was used. The fabrics was cleaned with 2 % sodium carbonate and 5 % nonionic detergent at 70°C temperature for 15 minute then again washed and neutralized before used.

Table 4.1 Specifications of polyester fabric

Sample	Material Specification						
	Count/Denier						
	Warp	Weft	Ends/inch	Pick/inch	Type weave	Wt.gm/sq.m.	Thickness (mm)
100% polyester	128d	146d	90	72	Plain	109.7	0.21

4.3 EXPERIMENTAL METHODS

Nano-cellulose was prepared by treating waste viscose rayon fibers with freshly prepared solution of sodium zincate.

4.3.1 Preparation of sodium zincate solution

Sodium zincate was prepared by adding 180 gms of NaOH to 200 ml of water then 80 gms of ZnO was gradually added with constant stirring. The solution was kept for 24 hours in a container. Finally, the solution was filtered using Whatman No.1 filter paper to get sodium zincate solution.

4.3.2 Preparation of nano cellulose

In this study, suspensions of nanocrystals were prepared from waste viscose rayon fibers the scheme for the preparation of nano cellulose is illustrated in the following figure 4.3.

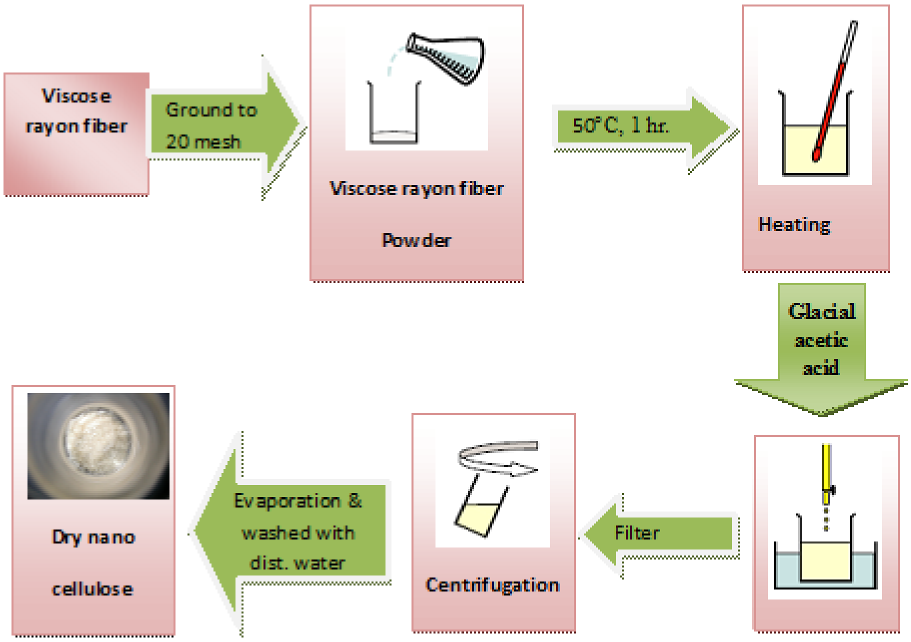


Figure 4.3 Scheme for preparation of cellulose nanocrystals

The waste viscose rayon fibers were ground to smaller than 20 mesh powder. Ground viscose rayon fiber powder was mixed with sodium zincate in a ratio of 1:9 (g/ml). A reaction temperature of 50°C was maintained for the diffusion of sodium zincate into the amorphous region of the fibers resulting in a subsequent cleavage of the glycosidic bonds. After 1 hour the particles were neutralized by glacial acetic acid solution. The suspension was washed and further filtered by Whatman No.1 filter paper.

The colloidal suspension was evaporated and converted in powder form. The powder was washed with distilled water and dried.

4.3.3 Characterization of nano cellulose particles through

4.3.3.1 Particle size analyzer

The particle size and size distribution of nano cellulose particles were measured using particle size analyzer. The instrument was based on the diffraction/scattering of laser beam by particle in stable suspension.

4.3.3.2 Image analyzer

The samples were observed on microscope at 100 X magnification. The images at selected places of the specimen were captured by digital camera attached to the microscope. These images were transferred to image analyzer in computer. Image analyses of these samples were carried out using Image-Pro$^{\text{® Plus}}$, Version 4.1 Software of Media Cybernetics, USA.

4.3.3.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopy was used to characterize the nano cellulose particles shape and size.

4.3.3.4 Fourier Transform Infrared Spectroscopy (FTIR)

The chemical composition of the synthesized nano cellulose material was evaluated using FTIR Spectroscopy Nicolet is10 FT-IR Spectrometer (Thermo Scientific).

4.3.4 Application of nano cellulose to polyester fabric

4.3.4.1 Exhaust method

1) Preparation of nano cellulose dispersion for open bath

The nano cellulose solutions were prepared using 1 gpl, 5 gpl, and 10 gpl concentrations.

For 1gpl solution, 0.1 gm of nanoparticle was added in 100 ml of total liquor, with 2 % (owf) citamol WS (dispersing agent) and 2% Carrier PP (swelling agent). The mixture was stirred at 250 rpm for 30 min at 50^{o}C temperature using magnetic stirrer. Likewise all concentration solution were prepared

2) Application of nano cellulose suspension to polyester fabrics

Polyester fabric samples (size 40cm X 30cm) were entered in the above suspension containing nanoparticles at room temperature in water bath. The temperature was gradually raised to boil at 2^{o}C/min, the treatment was continued at this temperature for 45 min. Finally, the samples were squeezed and dried in oven at 80^{o}C temperature.

4.3.4.2 Pad–dry–cure method

1) <u>Preparation of nano cellulose dispersion for padding</u>

Polyester fabric samples were padded with varying concentrations of nano cellulose suspension viz., 1 gpl, 5 gpl, and 10 gpl. For 1 gpl solution, 0.1 gm nanoparticle was added in 100 ml liquor with 5 gm lissapol L surfactant. The mixture was then stirred using magnetic stirrer at 250 rpm for 30 minutes at 50^{o}C temperature. Likewise all concentration solution was prepared.

2) <u>Application of nano cellulose suspension to polyester fabric</u>

Polyester fabric samples (size: 40cm X 30cm) were immerged in padding liquor at room temperature for 10 minutes and then passed through a two bowl laboratory padding mangle, which was running at a speed of 15 rpm with a pressure of 1.75 Kg/cm^2 using 2-dip-2-nip padding sequence at 70% expression for polyester fabric. The padded substrates were dried at 80 ^{o}C. The dried samples were cured in a preheated curing oven at 180 ^{o}C temperature for 60 seconds.

4.3.5 Testing and analysis

4.3.5.1 Fabric characterization

The treated and untreated samples were examined using scanning electron microscope and Fourier transform infrared spectroscopy (FTIR).

4.3.5.2 Physical testing

Before physical testing the samples were dried and conditioned at 65± 2 % RH and 27 ± 2°C temperature.

<u>Determination of Tensile Properties</u>

2 cm x 8 cm fabric samples were tested at 100 mm/min traversing speed for the determination of breaking load, breaking elongation, stress and strain. The test was performed as per B.S. 2576:1959

<u>Determination of crease recovery angle</u>

The test specimen was folded and compressed under controlled condition of defined force to create a folded angle, the specimen was suspended in an instrument for a controlled recovery and the recovery angle was measured. The test was performed as per AATCC test method 66-2003.

Determination of bending length

The stiffness in terms of bending length of nano treated and untreated samples were measured as per AATCC Test Method 115-2005 using Prolific stiffness tester (India).

4.3.5.3 Determination of absorbency

Drop test method

Absorbency of nano treated and untreated fabric sample were evaluated using AATCC Test Method 79-2000

Wicking test

Wicking behavior of the treated and untreated samples were evaluated as per T-PACC standard method.

4.3.5.4 Evaluation of water permeability and permittivity

These test methods provide procedure for determining the hydraulic conductivity (water permeability) of textiles materials in terms of permittivity under standard testing conditions in uncompressed state. The test was conducted using ASTM D 4491 (Constant Head Method) water permeability test method.

4.3.5.5 Evaluation of air permeability

The air permeability of treated and untreated polyester fabric samples were measured on Metefem air permeability tester as per ASTM D 737 test method. The result of the test measured reported in $m^3/h/m^2$ to three significant digits.

4.3.6 Dyeing of nano cellulose treated and untreated fabric samples

Mild scoured polyester fabric samples were dyed with commercial direct dye. Dyeings were performed on Laboratory constant temperature waterbath. The dyebaths were prepared at two concentration levels viz., 3 and 5 % (on weight of fiber) 1 gm of dye powder was pasted with (2ml) of acetic acid. 20 ml of hot water was added with constant stirring. The solution was heated slightly to dissolve the dye particles completely. Finally the required volume was adjusted with distilled water to get strength of the stock solution to 1:100.

4.3.6.1 Dyeing by exhaust technique

Dyebaths were prepared for 3 and 5% (owf) concentration levels, maintaining the liquor ratio of 50:1. 2% sodium carbonate and 10 % glauber's salt ($Na_2SO_4.10\ H_2O$) was added to the dyebath. The fabric samples were entered into the dyebath at 40^0C temperature. The dyebath temperature was gradually raised to boil within 25 minutes with a heating rate of 2.0^0C/minutes was continued for 45 minutes. After dyeing the temperature of dyebath was lowered to room temperature gradually. The sample was withdrawn from the dyebath, squeezed and washed in tap water. The dyed samples were soaped in the bath containing 5 gpl non-ionic detergent (Lissapol N) at 70^0C temperature for 15 minutes. Finally all samples were washed thoroughly in tap water, squeezed and dried under shade.

4.3.6.2 Dyeing by Pad-dry-cure technique

Polyester samples (size: 40cm x 30cm) were immerged in the padding liquor containing 3 gram and 5 gram cellulose nano, 2 gram sodium carbonate and 5 gram glauber's salt in 100 ml liquor. Polyester sample were entered in above liquor at room temperature for 10 minutes and then passed through a two bowl laboratory padding mangle, which was running at a speed of 15 rpm with a pressure of 1.75 Kg/cm^2 using 2-dip-2-nip padding sequence at 70% expression for polyester fabric. The padded substrates were dried at 80^oC. The dried samples were cured in a preheated curing oven at 180 ^oC temperature for 60 seconds.

4.3.7 Evaluation of dyed samples

4.3.7.1 Measurement of colour strength value (*K/S* Value)

The dyed samples were assessed for K/S values using computer colour matching system (illuminant D65/100 observer, Spectra scan 5100 RT, Spectrophotometer, Premier Colourscan Instrument, India).

4.3.7.2 Fastness Tests

The light fastness of the dyed samples was tested on Fad-o-meter (FDA-R, Atlas, U.S.A.) after partially exposing the samples to the xenon arc lamp for 16 h and graded for the colour change with the ratings. The wash fastness of the samples was performed as per ISO-2 tests using launder-o-meter (Digi.wash, Paramount Scientific Instruments., India). Samples were also evaluated for the rating in terms of colour change

4.4 RESULTS AND DISCUSSION

This section of the chapter discussed the results of preparation of nano cellulose particles and their application to polyester fabrics by exhaust and pad-dry-cure techniques. The prepared nanoparticles were characterized using particle size analyzer, the morphology of the particles were observed using SEM. The nano cellulose polymers were using FTIR. The functional properties of nano treated fabrics were tested as per the standard methods of testing.

The rod-like particles that were produced as a result of treatment were dried and again washed with distilled water and dried (Figure 4.4).

Figure 4.4 Images of dried nano cellulose powder

4.4.1 Characterization of prepared nano cellulose

The dried powder of nano cellulose prepared is in the photographs shown in figure 4.4. The analysis of the sample of cellulose powder dispersed in water by particle size analyzer showed a narrow and sharp peak at around 348 nm diameter.

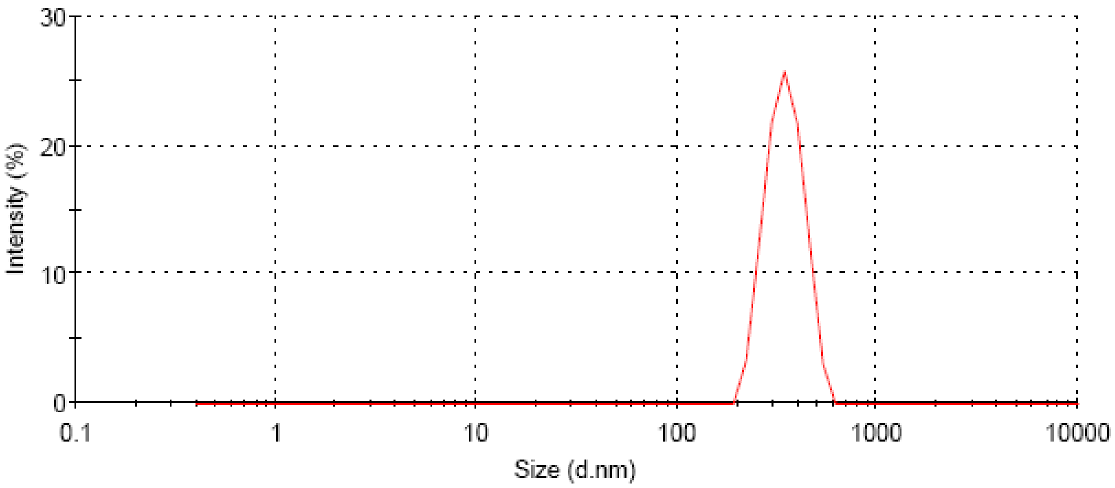


Figure 4.5 Particle size distribution of prepared nano cellulose

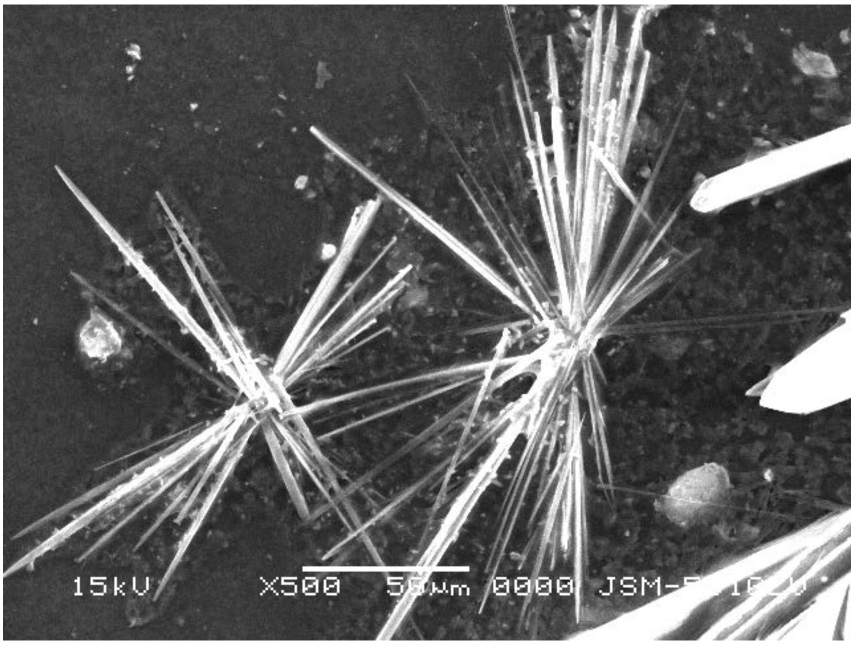


Figure 4.6 Scanning electron microphotographs of nano cellulose deposited on carbon coated aluminum sheet

Figure 4.6 shows the scanning electron micrographs of prepared nano cellulose particles deposited on carbon coated aluminum sheet. It can be seen from the figure that the shape of prepared nano cellulose particles was rod-like. The breaking of the cellulose chain, which contains high order crystalline regions, connected with low order amorphous regions, which appear like individual rods. These rod-like particles are commonly called as whiskers.

The FTIR spectrum of the nano cellulose powder is shown in figure 4.7.

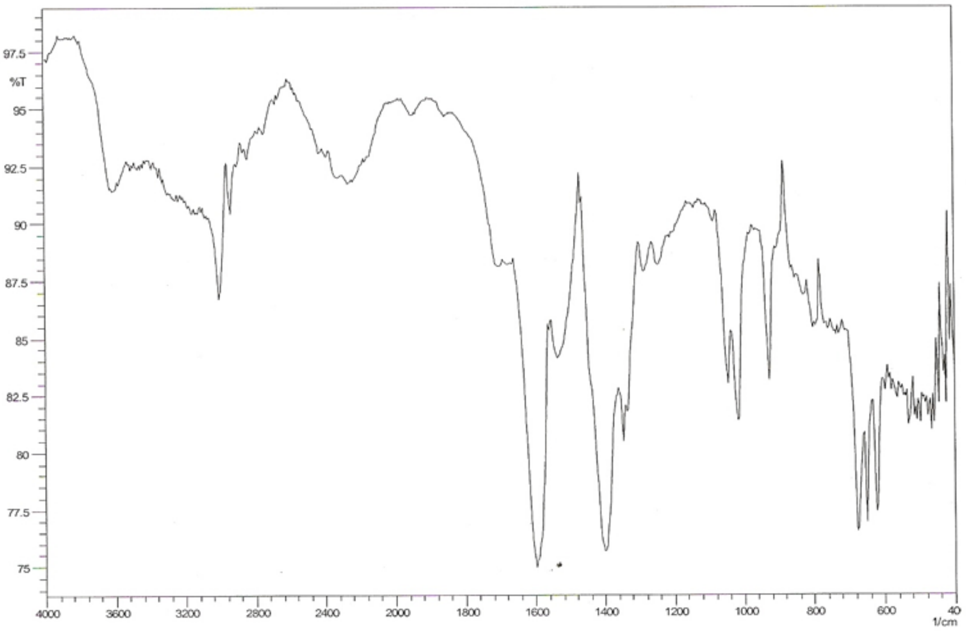


Figure 4.7 IR Characterization absorption peak of prepared nano cellulose powder

The absorption in the region of 3600-3100 cm^{-1} was due to the stretching of –OH group and at 3000 to 2800 cm^{-1} to the CH stretching. The band observed at 1642 cm^{-1} across from the H-O-H bending of the absorbed water. The symmetric C-H bending occurred at 1400 cm^{-1}; the FTIR absorption band at 1430 cm^{-1}, assigned to a symmetric CH_2 bending vibration, decreases. This band is also known as the “crystallinity band”, indicating that a decrease in its intensity reflects reduction in the degree of crystallinity of the samples. The main characteristic peaks were detected at absorption band 898 cm^{-1}, assigned to C–O–C stretching at β-(1→ 4)-glycosidic linkages, is designed as an “amorphous” absorption band. The IR spectra confirmed the presence of amorphous microcrystalline celluloses structure.

The dispersion of nanoparticles on the surface of the fiber and their penetration in the polymer matrix were examined by image analyzer (100 X). Cross sectional and longitudinal view of the sample were prepared in laboratory as per AATCC Test method 20-2005. (AATCC Technical manual, vol. 81, 2006, pp-40.). The prepared cross sectional and longitudinal sections were further stained with direct dye and examined under image analyzer. The images captured by image analyzer are shown in figure 4.8.

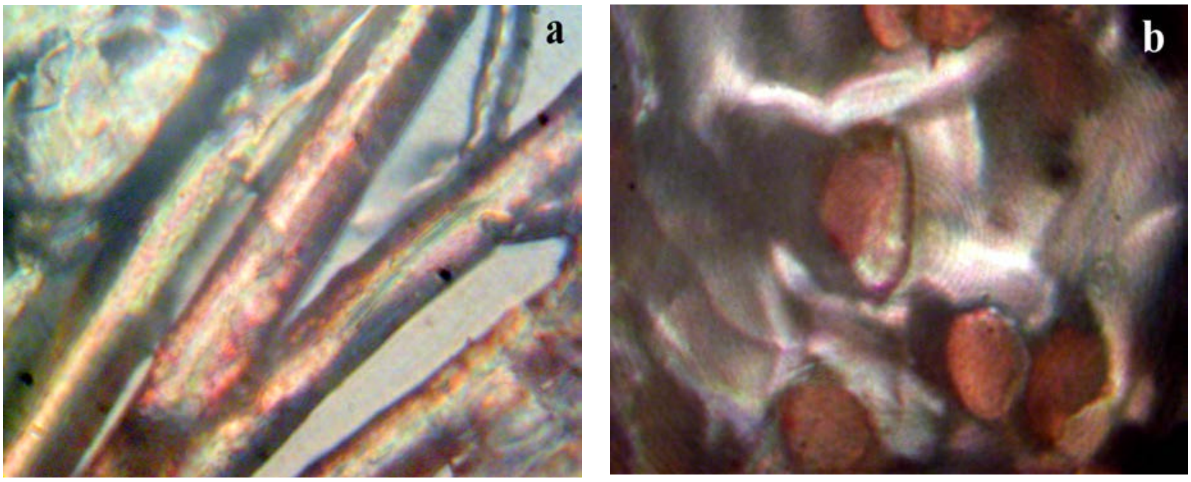


Figure 4.8 Images (100X) of polyester substrate treated with nano-cellulose and stained with congored direct dye (a) longitudinal and (b) cross sectional view

Cellulose particles applied on 100 % polyester fabric, the treated fabric was then stained with a direct dye (Congo Red BDC) to highlight the cellulose particles. Deposition of cellulose particles is seen on the surface of polyester fiber, from the longitudinal view of the polyester fiber presented in figure 4.8 (a). Dispersion of these particles in the polymer matrix is also observed from the figure 4.8 (b) which represents the cross sectional view of polyester fiber.

Figure 4.9 shows the SEM images of polyester fiber surfaces after the nano-cellulose treatment. The Micro photographs captured at different magnifications i.e 500 X, 1000 X, 1500 X and 2000 X show that the fiber surface is covered with nano-cellulose particles after treatment.

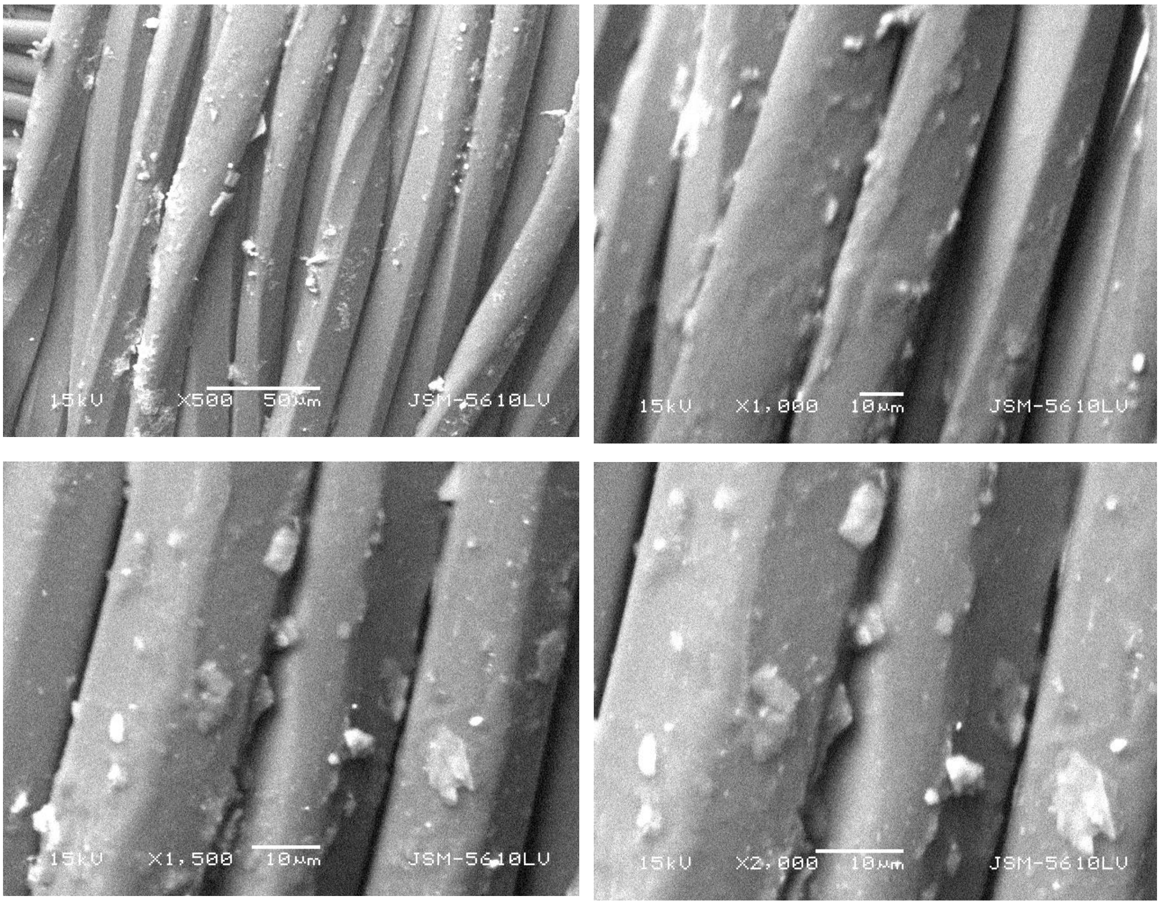


Figure 4.9 Polyester fiber surface morphology after treatment with the nano-cellulose treatment

The FTIR spectra of the polyester fabric before and after nano cellulose treatment are illustrated in IR spectra figure 4.10(a) and 4.10(b) respectively. The peaks in the IR spectra of the polyester loaded with nano cellulose and untreated fabric appeared in the range of 600-4000 cm^{-1}. The waves were assigned as follows: 1715 cm^{-1} (C=O), 1409 cm^{-1} (aromatic ring), 1331 cm^{-1}and 1021 cm^{-1} (carboxylic ester or anhydride), and 1021 cm^{-1} (O=C–O–C or secondary alcohol), 967 cm^{-1} (C=C), 869 cm^{-1} (five substituted H in benzene). The peak at 1409 cm^{-1} corresponded to the aromatic ring. It was the characteristic absorption peak of PET. The peak at 1715 cm^{-1} was assigned to the ester group.

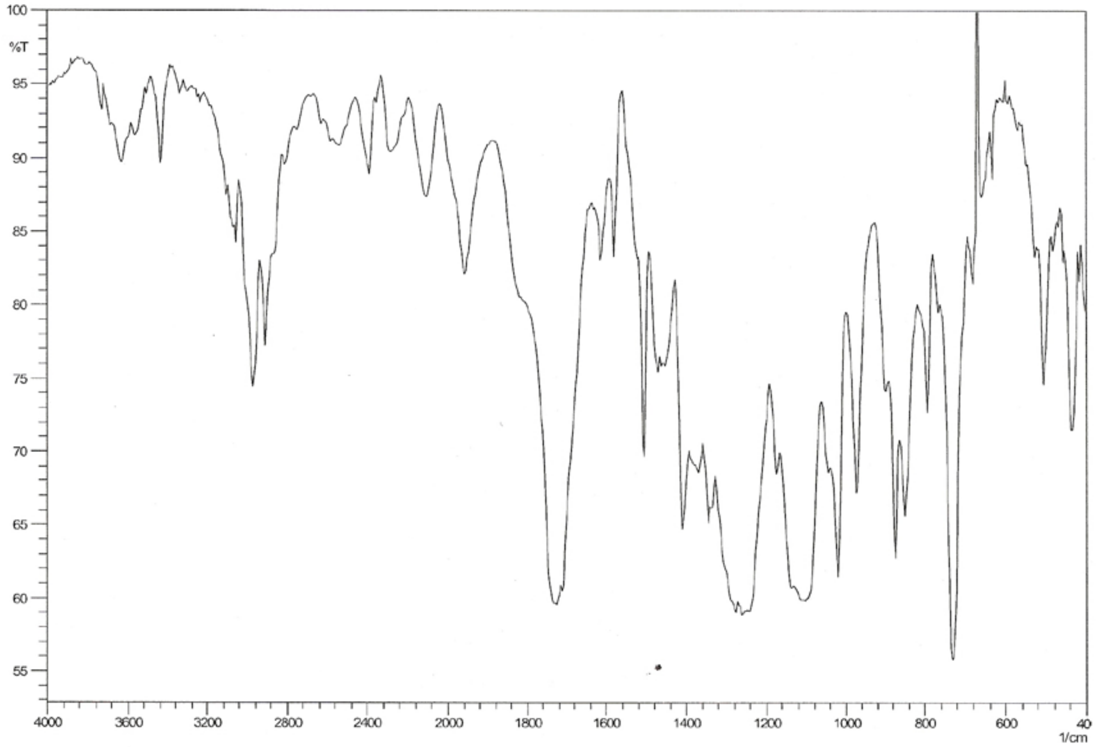


Figure 4.10 (a) FTIR spectra of 100 % polyester fabric

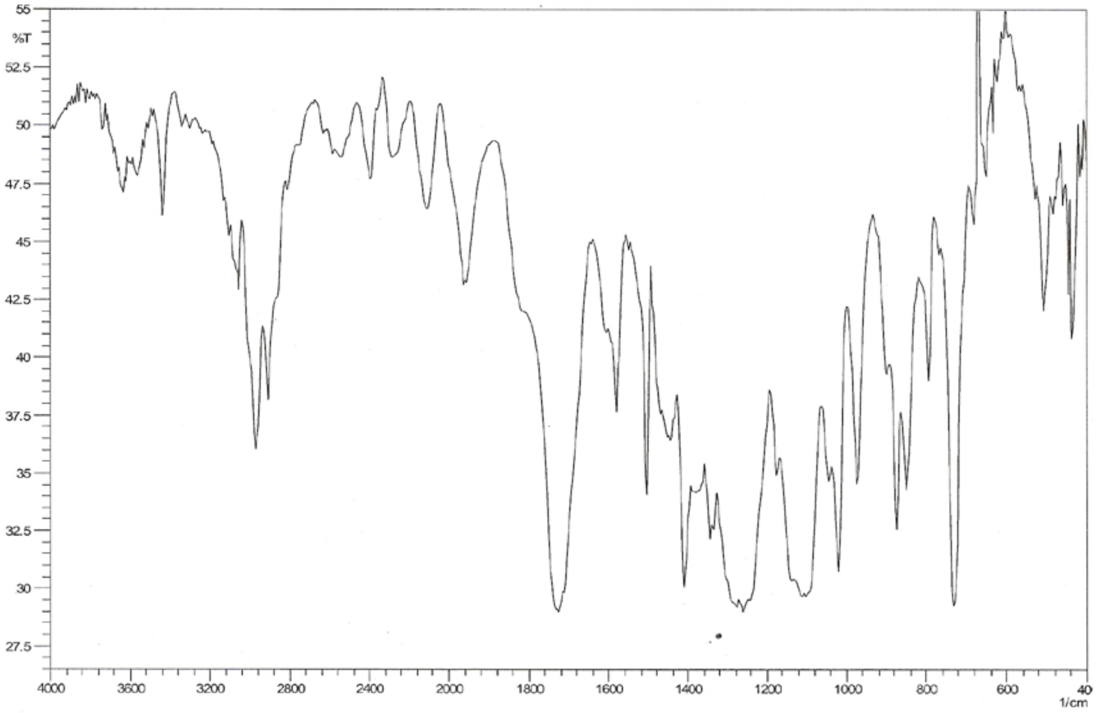


Figure 4.10 (b) FTIR spectra of polyester fabric treated with nano-cellulose

No significant changes in the spectra were observed after nano cellulose treatment for polyester portion appears over the course. But the spectra also confirmed the presence of cellulose from the absorption peaks in the region of 3600-3100 cm^{-1} due to the stretching of –OH group; at 3000 to 2800 cm^{-1} to the CH stretching; 1642 cm^{-1}

across from the H-O-H bending of the absorbed water; symmetric C-H bending occurred at 1430 cm^{-1}; at absorption band 898 cm^{-1}, assigned to C– O–C stretching.

4.4.2 Effect of nano cellulose on physical properties of polyester fabric

Treated and untreated polyester fabrics were evaluated for the change in physical properties in terms of breaking load and crease recovery angle.

4.4.2.1 Effect on tensile strength

The treated and untreated polyester samples were tested to evaluate change in tensile strength; the results are shown in Table 4.2 and Figure 4.11. The results show that the application of nano cellulose particles to polyester fiber causes an improvement in the load bearing capacity of the fiber. With the increase in concentration of nanoparticles, better results were obtained in exhaust method compared to pad-dry- cure method. It may be due to the more amount of nano cellulose diffused in the polymer matrix in case of exhaust method of application.

Table 4.2 Effect of nano cellulose treatment on tensile strength of sample

Sample	**Tensile Strength (kgf)**			
	Exhaust method		**Pad –dry –cure method**	
	Bre.load(kgf)	Extension(mm)	Bre.load(kgf)	Extention(mm)
Control Polyester	105.6	63.07	105.6	63.07
Polyester treated with 1 g/L nano cellulose	107.3	63.80	106.7	63.03
Polyester treated with 5 g/L nano cellulose	109.6	64.73	108.3	64.77
Polyester treated with 10 g/L nano cellulose	111.7	67.21	110.5	66.05

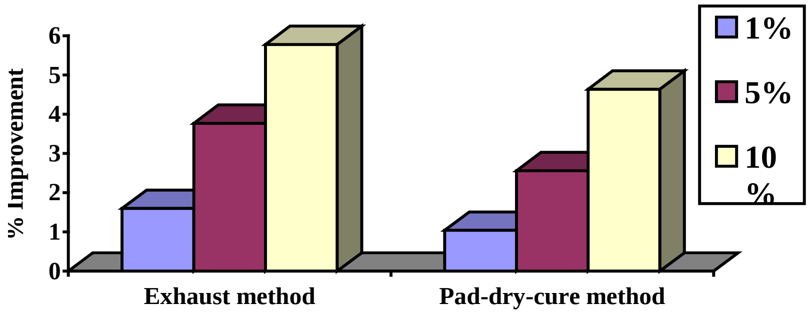


Figure 4.11 Improvement in breaking load of polyester fabric after nano cellulose treatment

4.4.2.2 Effect on crease recovery

The result presented in Table 4.3 and Figure 4.12 shows minor improvement in crease recovery angle of the treated samples. The nano cellulose particles because of their small size can enter in between the polymer molecules and perhaps act as filler or cross linking agent. The crease recover angle of fabric was improved with increase in the concentration of nanoparticle. The crease recovery angle was found to be better in samples prepared using exhaust method compared to the samples prepared using pad-dry -cure method.

The improvement in physical properties is due to the mechanical interlocking caused by the mechanical anchoring of the nano cellulose in the intermolecular pores.

Table: 4.3 Crease recovery angle of nano cellulose treated polyester fabric

Sample	**Crease recovery angle (^{0})**	
	Exhaust method	**Pad –dry –cure method**
Control Polyester	148	148
Polyester treated with 1 g/L nano cellulose	158	157
Polyester treated with 5 g/L nano cellulose	162	158
Polyester treated with 10 g/L nano cellulose	166	162

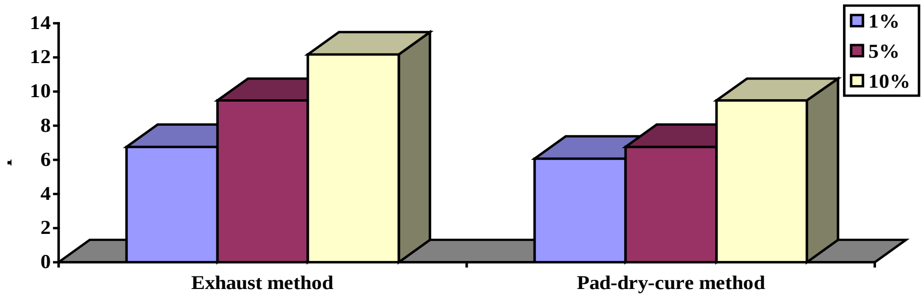


Figure 4.12 Improvement in crease recovery angle of polyester fabric due to nano cellulose treatment

4.4.3 Effect of nano cellulose on water absorbency of polyester fabric

The absorbency of polyester fabric treated with nano cellulose was measured by drop test and wicking behavior test. Table 4.4 and figure 4.13 show results of absorbency of the fabric using drop test.

Table 4.4 Effect on absorbency of polyester fabric due to the nano cellulose treatment

Polyester fabric treated with nano cellulose (grams/liter)	**Time (sec)**	
	Exhaust method	P –D –C method
Untreated sample	20.10	20.10
1	14.0	12.0
5	67.0	76.0
10	98.0	110

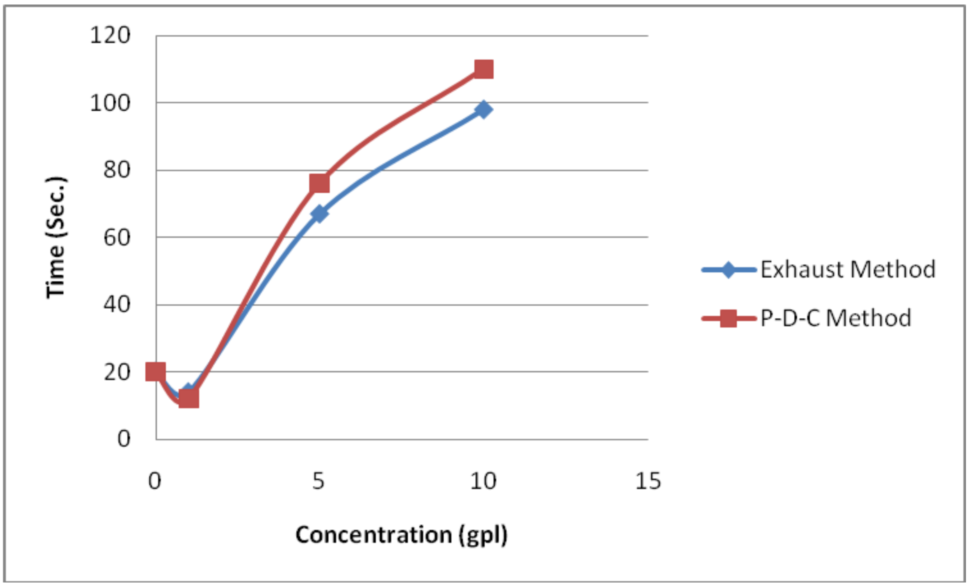


Figure 4.13 Effect on absorbency of polyester fabric due to the nano cellulose treatment

It is found from the results shown in Table 4.4 that the water absorbency of polyester fabric treated with 1 gpl concentration of nano cellulose take less time for the absorption of water indicates improvement in absorbency. But as the concentration of nano cellulose was increased to 5 gpl and 10 gpl, the water droplet took more time to absorb water drop indicating reduction in absorbency of nano treated material.

Table 4.5 Effect of nano cellulose treatment on wicking height (mm) of polyester fabric

Polyester fabric treated with nano cellulose (grams/liter)	**Wicking height(mm)**					
	Exhaust method			**Pad –dry –cure method**		
	1 min	**5 min**	**10 min**	**1min**	**5 min**	**10 min**
Untreated sample	20	40	55	20	40	55
1	24	46	61	22	44	57
5	16	30	43	15	29	41
10	12	24	36	11	22	31

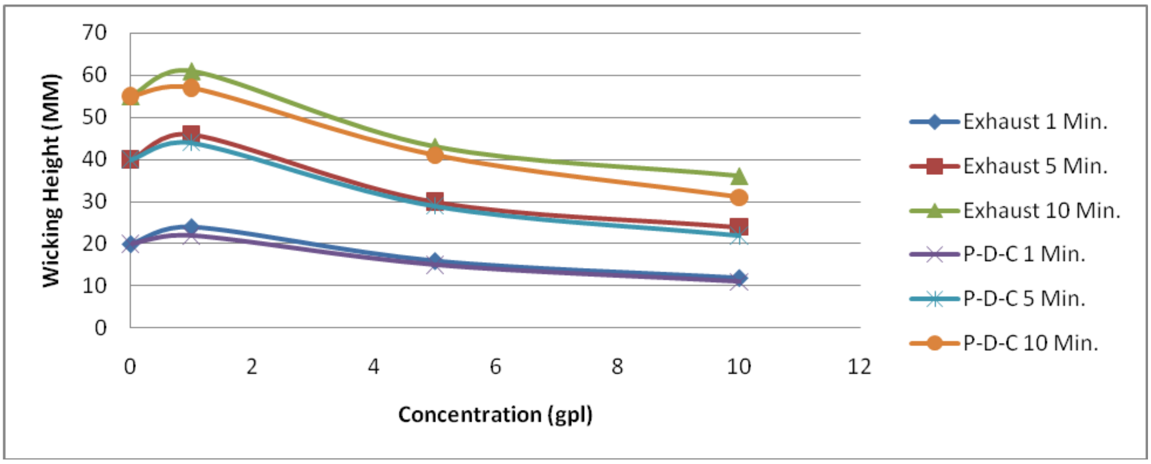


Figure 4.14 Effect of nano cellulose treatment on wicking height (mm) of polyester fabric

The improvement in hydrophilicity of polyester treatment due to low dosage of nano cellulose treatment is because of the inherent hydrophilicity of cellulose. But interestingly as the concentration of nano cellulose was increased it started hindering the penetration of the water molecules as they start acting as nano whiskers and do not allow the water drop to be accommodated within the interpolymeric spaces.

4.4.4 Effect of nano cellulose on water permeability of polyester fabric

Table 4.6 and corresponding Figure 4.15 shows reduction in water permeability through the polyester fabric sample treated with nano cellulose compared to untreated sample, it may be attributed due to the resistance offered by the nanoparticle present in the polymer matrix towards the flow of water through the fabric. It can also be seen that as the concentration of nanoparticle in fabric was increased, the permeability of water was reduced. The extent of reduction in water permeability was found to be more in case of exhaust application compared with pad-dry-cure treatment of application.

Table 4.6 Effect of nano cellulose on water permeability of polyester fabric

Polyester fabric treated with nano cellulose (grams/liter)	**Ψ-Water Permeability** (S^{-1})	
	Exh. Method	P –D – C method
Untreated sample	0.3253	0.3253
1	0.3191	0.3223
5	0.3020	0.3087
10	0.2892	0.2965

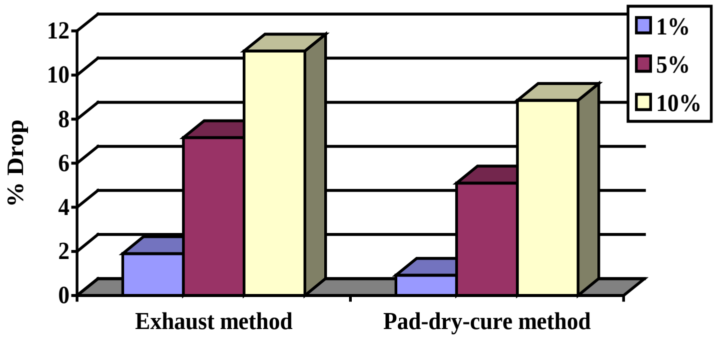


Figure 4.15 Drop (%) in water permeability of polyester fabric due to nano cellulose treatment

4.4.5 Effect of nano cellulose on air permeability of polyester fabric

The treated polyester fabric were tested for air permeability and compared with air permeability of untreated polyester sample. The results presented in Table 4.7 and figure 4.16 show that the air permeability of polyester fabric treated with nano cellulose was reduced compared with the untreated sample. It may be due to the resistance of the nanoparticles present in the polymer matrix towards the flow of air through the fabric sample.

Table 4.7 Effect of nano cellulose treatment on air permeability of polyester fabric

Polyester fabric treated with nano cellulose (grams/liter)	**Air permeability ($m^3/m^2/h$)**	
	Exhaust Method	P –D – C method
Untreated sample	223.14	223.14
1	212.98	215.33
5	208.17	211.47
10	172.34	195.21

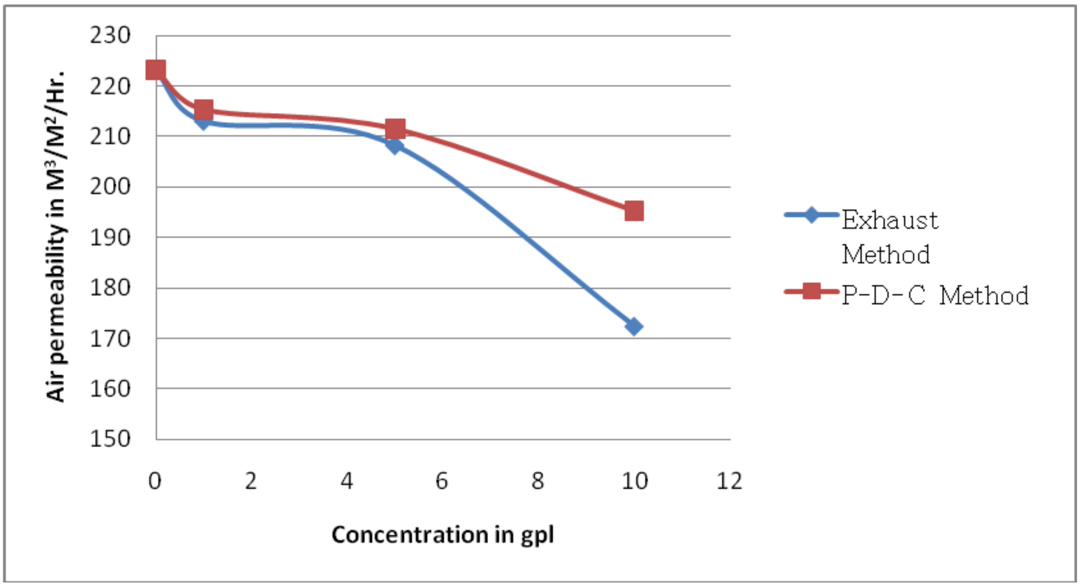


Figure 4.16 Effect of nano cellulose treatment on air permeability of polyester fabric

4.4.6 Effect of nano cellulose on dyeing of treated fabric with direct dye

The dyeing of polyester fabric treated with 5 gpl nano cellulose using pad-dry-cure method and subsequently dyed with direct dye (Congo red BDC) using exhaust and pad-dry-cure method. The results in terms of colour strength and colour coordinate values are reported in Table 4.8. From the table it can be seen that the polyester fabric dyed without nano cellulose treatment is stained only, in both the cases of dyeing i.e. exhaust and pad-dry-cure methods. It can be observe from the table that as the concentration of dye in the dye bath increases the *K/S* value of the sample also increases in case of treated polyester fabric subsequently dyed with direct dye. The treated and dyed samples were further soaped with 5 % (v/v) non ionic detergent at 70 ^{0}C temperature for 15 minutes. The results shows that the loss in *K/S* values of these samples still remain higher than the samples dyed without the nano treatment. Further when comparing exhaust method with pad-dry-cure method interms of *K/S* values it was found that the pad-dry-cure method exhibits better colour strength value. The dyeing of nano cellulose treated polyester fabric with direct dye may be attributed due to the presence of cellulose particles in the polyester structure.

Table 4.8 Colour strength and co-ordinate values of polyester fabric pretreated and dyed with direct dye (Congo red BDC)

Exhaust method							***Pad-dry-cure method***						
Concentration of dye (% owf)	***sample***	***K/S***	**Sample**	***L****	***a****	***b****	***Concentration of dye (gpl)***	***sample***	***K/S***	**sample**	***L****	***a****	***b****
5	*Treated with 5 gpl nano cellulose*	*11.14*	🟥	*66.55*	*25.90*	7.65	50	*Treated with 5 gpl nano cellulose*	23.84	🟥	66.81	29.66	7.51
	Soaped	*6.27*	🟥	*65.78*	*17.55*	5.93		*Soaped*	14.44	🟥	66.51	27.97	6.84
	Without nano cellulose treatment	*5.34*	🟥	*66.45*	*18.47*	9.86		*Without nano cellulose treatment*	6.05	🟥	66.06	20.15	6.80
3	*Treated with 5 gpl nano cellulose*	*10.56*	🟥	*66.07*	*26.84*	7.83	30	*Treated with 5 gpl nano cellulose*	21.71	🟥	66.83	29.48	7.65
	Soaped	*6.28*	🟥	*66.77*	*22.70*	*9.06*		*Soaped*	5.15	🟥	65.94	23.78	5.74
	Without nano cellulose treatment	*5.19*	🟥	*66.63*	*22.83*	8.52		*Without nano cellulose treatment*	2.29	🟥	66.34	14.05	7.77

4.5 REFERENCES

1. L.Havancsak, Nanotechnology at present and its promises in the future, *Mat. Sci., Forum*, 2003, 414, 85.
2. H. Mark, K. H. Meyer, *Phys. Chem.*, 1929, *B2*, 115.
3. Gardner, Douglas, Adhesion and Surface Issues in Cellulose and Nanocellulose, *Journal of Adhesion Science and Technology*, 2008, 22, 545–56.
4. R.H. Atalla, The Structures of Cellulose; *ACS Symposium Series*, 1987, 340.
5. M.Plunguian, Cellulose Chemistry, *Chemical Publishing Co.*, Inc: New York, 1943.
6. G.Ranby, The colloidal properties of cellulose micelles. *Discussions Faraday Society*, 1951, 11, 158.

CHAPTER 5

ENVIRONMENTAL ASPECTS

5.1 INTRODUCTION

Nanotechnology has brought a new area of finishing applications to the textile industry. Coating the surface of textiles and clothing with nanoparticles has become a common approach for the production of highly active surfaces to have UV blocking, antimicrobial, flame retardant, water repellant or self-cleaning properties. While antimicrobial properties are exerted by nanosilver, UV blocking, self-cleaning and flame-retardant properties are imparted by coatings containing zinc oxide or titanium oxide nanoparticles. For centuries, silver has been used to prevent and treat a variety of diseases. Silver is known as one of the oldest antimicrobial agents and it has been used effectively against different bacteria, fungi and viruses [1]. Further nanoparticle polymer result from the combination of inorganic and organic elements (DNA, colour pigments). As there are now textile products treated with nanoparticles and bearing the “nano” designation already on the market, the issues of environmental safety arise for the processing textile industry.

In recent times the nano particles used in textile industry is chemically well characterized inorganic nanoparticles, such as silicone, titanium, zinc or iron oxide. Before they are applied, they are protected against aggregation so that stable, i.e. individual, nanoparticles can be applied to textile surfaces by means of binder systems, for example conventional foularding processes. At present, no use is made of particles known to be toxic or carcinogenic (for example particles with a quartz or asbestos content or what are termed carbon nanotubes) [2].

The end user of textiles modified on the nano-scale is primarily interested in consumer safety in accordance with the GPSG legislation on technical equipment and product safety, as arising out of the exposure resulting from day-to-day use of the clothing. Here, the primary question is that of particles being rubbed off as the textiles are worn. For this reason, a comprehensive test involving scrubbing of nano-treated textiles forms a component part of the Hohenstein “Nanotechnology” quality label criteria. Furthermore, apart from including a test of the product for its suitability in particle use, the Hohenstein Nanolabel is also the only label to offer as options other valid safety studies for consumers and employees in the textile industry [1].

There are two basic ways in which nanoparticles can penetrate into the human body once rubbed off: through the skin or inhaled along with the air breathed.

Investigation is currently taking place at the Hohenstein Institutes into the extent of nanoparticle abrasion from fibers when textiles are in partical use. In the process, it is becoming clear that emission into the air does not necessarily take place. Nanoparitcles are also prone to adhering to larger particles of dust, liquids, or the surfaces of bodies. It is suspected that it is not possible for nanoparticles rubbed off from textile fibers to penetrate through the body's surface skin. This has been investigated in numerous scientific studies by research groups within the "Nanoderm" project.

Researchers in Switzerland have now examined what happens to silver nanoparticle-treated textiles during washing. The scientists studied release of nanoparticles in laundry water from nine different textiles, including different brands of commercially available anti-odor socks. They found that the total released varied considerably from less than 1 to 45 percent of the total nanosilver in the fabric and that most came out during the first wash. These results have important implications for the risk assessment of silver textiles and also for environmental fate studies of nanosilver, because they show that under certain conditions relevant to washing, primarily coarse silver-containing particles are released (greater than 450 nm). There are ways that manufacturers and consumers can minimize the release of these particles to the environment, where they potentially could harm fish and other wildlife. The release of the nanoparticles depends on the way the silver is incorporated into the textile fiber. It is reported that little dissolution of silver nanoparticles occurs under conditions relevant to washing (pH 10) with dissolved concentrations 10 times lower than at pH 7. However, bleaching agents such as hydrogen peroxide or peracetic acid can greatly accelerate the dissolution of silver. However, the amount and form of silver released from the fabrics as ionic and particulate silver to a large degree depends on how the silver particles are incorporated into the textile. There are ways to apply only small amounts of silver that show hardly any release. The trick for manufacturers is to use a nanofinishing process that binds silver to the fiber so that some release of dissolved silver occurs – for the antimicrobial effect – but that the nanoparticles are efficiently immobilized and don't get released during washing. This means that textile companies have options to optimize the use and release of silver nanoparticles, i.e. it is possible to have a nanosilver-treated textile that releases only small amounts of nanoparticles. Keeping this in mind washing effluent parameters like BOD, COD and TDS for nano treated textiles are studied and reported in this chapter.

5.2 EXPERIMENTAL METHODS

5.2.1 Determination of BOD

BOD is a measure of the polluting efficiency of water. Oxygen is required in the effluent for the oxidation of inorganic and organic matter. The demand of oxygen by the organic matter is known as BOD which is defined as the amount of oxygen required to carry out the biological decomposition of dissolved solids under aerobic conditions at a standard temperature. In a 500 ml BOD bottle, a 5 ml sample, 1 ml each of four standard buffers (magnesium sulphate buffer, calcium chloride buffer, phosphate buffer and ferric chloride buffer) and 1 ml of waste effluent were taken and diluted with distilled water. The dissolved oxygen was found immediately (blank, A) by iodimetric titration. Another sample was prepared as above and incubated at 27 °C for 3 days and then the dissolved oxygen was found (sample value, B). The BOD (in mg) was then determined according to Eqn 1.

$$\text{BOD} = (A - B) \text{ X dilution factor} \qquad (1)$$

5.2.2 Determination of COD

COD is the measure of oxygen required to oxidize unstable materials in a sample by means of a dichromate in an acid solution. In a 250 ml conical flask, 50 ml of the sample was added; 1 g of mercury (II) sulphate was added, followed by 180 ml of silver sulphate ⁄ sulphuric acid solution. Then, 10 ml of 0.00833 M standard potassium dichromate solution was added and the resulting mixture was boiled for 15 min. After cooling, the inner side of the condenser was rinsed with 50 ml of water. Either a diphenylamine indicator (1 ml) or a ferroin indicator (1 ml) was added and titrated with 0.025 M ammonium iron(II) sulphate solution. Diphenylamine gives a colour change from blue to green at the endpoint, whilst for ferroin that is blue–green to red–brown. This titration is called A ml; the back-titration is repeated for the blank (B ml). The difference between the two values is the amount of potassium dichromate used up in the oxidation. COD (in mg) was then determined according to Eqn 2.

$$\text{COD} = (A - B) \text{ X } 0.2 \text{ X } 20 \text{ mg l}^{-1} \qquad (2)$$

5.2.3 Determination of TDS

TDS is an expression for the combined content of all inorganic and organic substances contained in a liquid which are present in a molecular, ionised or microgranular (colloidal sol) suspended form. The TDS of the effluent was determined by a portable conductivity ⁄ TDS meter.

5.3 RESULTS AND DISCUSSION

Washing effluent parameters like BOD, COD and TDS for treated and control samples are evaluated by standard methods and reported in Table 5.1.

Table 5.1 BOD, COD and TDS of washing effluent with and without metallic and cellulose nano treatment

Sample	**Washing effluent**	**BOD (mg/l)**	**COD (mg/l)**	**TDS(mg/l)**
Control	Soap solution (ISO-3)	10	14	132
Cotton	Without Cu nano	Nil	22	264
	With Cu nano	5.0	38	276
Jute	Without Cu nano	Nil	25	232
	With Cu nano	5.0	47	248
Wool	Without Cu nano	Nil	20	288
	With Cu nano	5.0	60	296
Silk	Without Cu nano	Nil	22	196
	With Cu nano	5.0	40	204
Cotton	Without Ag nano	Nil	22	353
	With Ag nano	5.0	48	365
Jute	Without Ag nano	Nil	25	321
	With Ag nano	5.0	57	327
Wool	Without Ag nano	Nil	20	376
	With Ag nano	5.0	63	384
Silk	Without Ag nano	Nil	22	285
	With Ag nano	5.0	49	303
Cotton	Without Zn nano	Nil	22	466
	With Zn nano	5.0	58	471
Jute	Without Zn nano	Nil	25	433
	With Zn nano	5.0	67	439
Wool	Without Zn nano	Nil	20	482
	With Zn nano	5.0	61	487
Silk	Without Zn nano	Nil	22	372
	With Zn nano	5.0	58	380
Polyester	Without nano cellulose	Nil	16	236
	With nano cellulose	Nil	23	249

Note: National environment quality standard for municipal and liquid industrial effluent: BOD, 80 mg/l; COD, 400 mg/l; TDS, 3500 mg/l

Today, nano-particles are used worldwide, with much research being carried out into developing new synthetic procedures to improve their application characteristics. However, because of their high surface energy, nano-particles can cause great effluent problems for environment. It is clear from Table 5.1 that the washing effluent with metallic nano treatment as well as nano cellulose treatment does not increases the BOD, COD and the TDS when compared with the conventional washing effluent of sample without the nano treatment. From the lower values of TDS it may be safely interpreted that nano-particles can provide high durability of the desired textile functions. By virtue of its small size and high surface energy, nano-particles are bound to the fabric surface may be by Vander walls forces which give a reasonable wash fastness

5.4 REFERENCES

1. Dr. D P Chattopadhyay and B H Patel, Introduction to nanotechnology in textiles and effect on environment & human health, U G C Sponsored National Conference on Environmental Sustainability of Textile Industry, 8-9 January 2009, International College for Girls, Jaipur, India.
2. Dirk HÖfer, Safety in dealing with nanoparticles in the textiles industry: opportunities and risks, *Melliand English*, September 2006, 87, 9, E 145- E 147.

SUMMARY AND CONCLUSIONS

The textile wet processing industry, normally seen as a traditional industry, needs now-a-days to fight against increased competition from global market. There is a general recognition that traditional processing techniques may be no longer sufficient to sustain a viable business and the textile industries have to move towards more innovative and high quality products. New materials and technologies promote development of high-tech textiles, characterized by unprecedented functions and effects.

In this study, nanoscaled copper, silver and zinc (10-100 nm) were synthesized in water by borohydride reduction method under atmospheric conditions. These nano particles were applied to textiles by exhaust and pad-dry–cure methods to enhance their functional properties. This can be a promising alternative for conventional textile wet processing at an industrial level, since it is an effective way of improving physical & functional properties and can be a cost effective option to the conventional processing treatments. This process needs to be further investigation for its complete understanding and optimization.

In first phase of the research, nano copper colloids were prepared, by reducing Cu^{+2} ions using chemical bath deposition technique. The absorbance spectrum of the solution was observed at different stages of the synthesis process. The plasmon resonance absorbance of yellow coloured nano colloids was noticed at 580 nm. These particles were elementally detected by SEM-Inca software. The particle size and their distribution, of freshly prepared system and after storing for 24 hours in atmospheric condition, were examined by particle size analyzer shows that the maximum size of the particle was increased from 70 nm to 400 nm during storage for 24 hours. Similar trend was observed in AFM study. The stability of the particles was improved by the introduction of citrate anions in the colloidal system. In this system the particles were found to be quite stable even up to 4 weeks. These particles were observed by SEM technique. It reveals that with the adopted method of synthesis and stabilization it is possible to keep the prepared copper nano below 100nm size, a qualifying limit to be called as nanoparticles.

The prepared nanosized copper colloidal solution was successfully applied to cotton, wool, jute and silk fabric, the results has been discussed in second phase of the study. The average particle size was found to be about 60-90 nm. Copper nano treatment has shown improvement in tensile strength, crease recovery angle and bending length of fabric made from natural fibres viz. cotton, wool, jute and silk. The results indicate improvement in surface electrical resistivity of all the treated substrates. The copper nano treatment was also found to enhance the dyeability of cotton, wool, jute and silk fiber with direct dyes; wool and silk with acid dye; wool and silk with three natural dyes i.e. *Azadirachta indica, Lawsonia inermis* and *Ocimum sanctum*. Both the wash and light fastnesses of direct dyed substrates were upgraded due to copper nano particle pre-treatment. Copper nano treatment also increased the resistance to microbial attack. Copper nano treatment thus increased the effective life span of the treated fabric.

The formation of silver nanoparticles was confirmed by uv-vis absorption and elemental analysis results discussed in chapter 2. Study on ageing of synthesized silver nano was carried out by uv-vis measurements confirmed that the size of the nanoparticles in colloid did not changed, but with time the concentration slowly increased within few weeks. The z-average size of the synthesized silver nano particle was found to be 62.06 nm. The SEM images have indicated that silver nanoparticles produced were of spherical in shape. It was also found that the treatment with silver nanoparticles improves the breaking load and crease recovery angle with almost no effect on rigidity of the material. Nano silver treatment has enhanced the colour strength of cotton, wool, jute and silk fabrics dyed with direct dyes, wool and silk with acid dyes and few natural dyes. The silver nano treatment has also improved the fastness towards light and washing. The results in chapter 3 have proved that Ag nano treatment to cotton, wool, jute and silk also improves the resistance to microbial attack.

The nano-structural zinc particles were prepared successfully and applied to cotton, wool, jute and silk fabric; the average particle size was approximately ~ 80 nm. The treatment with zinc nano particles on these substrates was found to improve the tensile strength of fibers with some improvement in crease recovery angle and bending length. The treatment also enhanced the dyeability of treated fabrics with improved fastness properties for direct dyes, acid dyes and selected natural colourants viz. *Azadirachta indica, Lawsonia inermis* and *Ocimum sanctum*. The resistance of cotton, wool, jute and silk to microbial attack was also improved by the treatment.

Rod-like cellulose crystals were successfully separated from the waste viscose rayon fiber by treatment with sodium zincate and characterized by FTIR spectral analysis. Prepared cellulose nano whiskers having particle size of 348 nm were applied to polyester fabric. The treatment was altered the absorbency and dyeability of polyester fabric. It was found that at lower concentration absorbency of treated fabric was increased but as the concentration of cellulose nano particles in fabric increased the absorbency of the fabric dropped.

The determination of COD, BOD and TDS values of the effluent collected from the washing drain water of the fabric treated with nanoparticles proved that such tratement did not increase the eco load in the waste water system.

SCOPE FOR FURTHER STUDY:

These results encourage further investigation on incorporation of nano particles during filament preparation stage their analysis by X-Ray differection and other advanced techniques to evaluate their effect on functional properties through the changes in polymer matrix, promoting the interest on potential applications of such nanocomposite fibers in technical textile field.

ABBREVIATIONS

$CuSO_4$	-	**C**opper **S**ulphate
$AgSO_4$	-	**S**ilver **S**ulphate
$Zn\ (NO_3)_2$	-	**Z**inc **N**itrate
$NaBH_4$	-	**S**odium **B**orohydride
SiO_2	-	**S**ilicon dioxide or **S**ilica
NNI	-	**N**ational **N**anotechnology **I**nitiative
DNA	-	**D**eoxyribonucleic acid
Fe_3O_4	-	**F**errous ferric oxide
FeO	-	**F**errous oxide
CNTs	-	**C**arbon **N**ano-**T**ubes
C60	-	**C**obalt **60**
RAM	-	**R**andom **A**ccess **M**emory
CVD	-	**C**hemical **V**apor **D**eposition
LASiS	-	**L**aser **A**blation **S**ynthesis
PECVD	-	**P**lasma-**E**nhanced **C**hemical **V**apor **D**eposition
SP	-	**S**pray **P**yrolysis
ODOP	-	**O**ne **D**roplet- to-**O**ne-**P**roduct particle
CdSe	-	**C**admium **S**elenide
TEM	-	**T**ransmission **E**lectronic **M**icroscopy
SEM	-	**S**canning **E**lectron **M**icroscopy
CCD	-	**C**harge-**C**oupled **D**evice
AFM	-	**A**tomic **F**orce **M**icroscopy
DLS	-	**D**ynamic **L**ight **S**cattering
XPS	-	**X**-ray **P**hotoelectron **S**pectroscopy
XRD	-	**X**-ray **D**iffraction
FTIR	-	**F**ourier **T**ransform **I**nfrared **S**pectroscopy
MALDI-TOF	-	**M**atrix-**A**ssisted **L**aser **D**esorption/**I**onization **T**ime-**O**f-**F**light
MS	-	**M**ass **S**pectrometry
NMR	-	**N**uclear **M**agnetic **R**esonance
MRI	-	**M**agnetic **R**esonance **I**mage
TGA	-	**T**hermo **G**ravimetric **A**nalysis
DSC	-	**D**ifferential **S**canning **C**alorimetric

DTA - **D**ifferential **T**hermal **A**nalysis
CTE - **C**oefficients of **T**hermal **E**xpansion
ATO - **A**ntimony-Doped **t**in **O**xide
Tg - **G**lass **T**ransition **T**emperature
HF - **H**ydrofluoric acid
HCL - **H**ydrochloric acid
SFB - **S**tobe–**F**ink–**B**ohn method
EDX - **E**nergy **D**ispersive **X**-Ray **A**nalyzer
ASTM - **A**merican **S**ociety for **T**esting and **M**aterials
AATCC - **A**merican **A**ssociation of **T**extile **C**hemists and **C**olorists.
B.S - **B**ritish **S**tandards
ISO - **I**nternational **O**rganization for **S**tandardization
BOD - **B**iochemical **O**xygen **D**emand
COD - **C**hemical **O**xygen **D**emand
TDS - **T**otal **D**issolved **S**olids
WL - **W**avelength of UV rays
gpl - **G**ram **P**er **L**iter
S.Aureus - **S**taphylococcus **A**ureus
P-D-C - **P**ad- **D**ry-**C**ure method
P-D-S - **P**ad- **D**ry-**S**team method
Exh. - **E**xhaust method
NP - **N**ano **P**article
CB - **C**arbon **B**lack
PET - **P**oly**E**thyline**T**erpthalete
CCM - **C**omuter **C**olour **M**atching
TSC - **T**ri-**S**odium **C**itrate
SLS - **S**odium **L**auryl **S**ulphate

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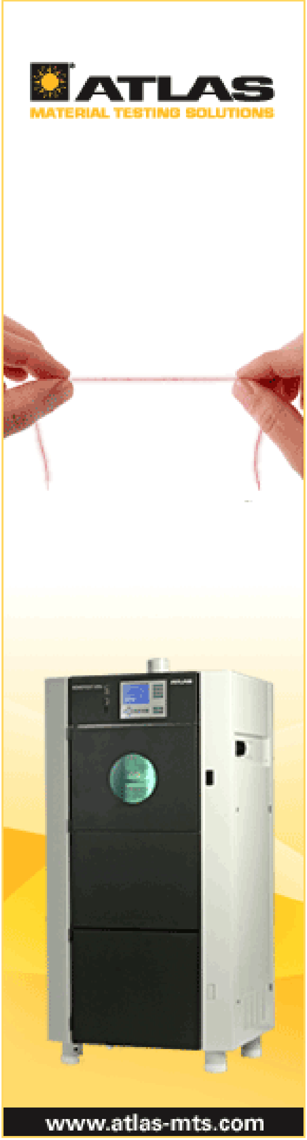
Processing, Dyeing & Finishing

Nano-particles & their uses in textiles

Nano-particles can help enhance the physical properties of conventional textiles in areas such as anti-microbial properties, water-repellency, soil-resistance, anti-static, anti-infrared and flame retardant properties, dyeability, and strength of textile materials, aver ***B H Patel*** *and* ***Dr D P Chattopadhyay.***



These days, the word "nano" seems to be popping up everywhere. Wall Street, Hollywood, and major universities around the globe have all endeavored to associate their diverse enterprises with this word. "Nano" is a metric unit that means one billionth of a unit; as of late, it has been used most frequently in reference to nanotechnology. The term "nanotechnology" has never been used so broadly.

K Eric Drexler coined it in his 1986 book, Engines of Creation to refer to his theories for molecular manufacturing, following up on visionary ideas presented 27 years earlier by famed physicist, Richard Feynman. As the possibilities of molecular nanotechnology grew and excitement built in the scientific community many researchers began using the term for their own endeavors at the nanoscale, unrelated to molecular manufacturing.

Nanotechnology seeks to provide and apply knowledge of the behaviour of objects in the nanometre (nm) size range to the assembly of complex structures for use in a variety of practical applications. The tiniest substances promise to transform industry and create a huge market. In chemicals, cosmetics, pharmaceuticals, technology and textiles, businesses are researching and manufacturing products based on nanotechnology, which uses bits of matter measured in billionths of a metre.

The technology, utilising materials a thousand times smaller than the width of a human hair, is showing up in everything from auto parts to sunscreens and clothing (1,2). However, nanotechnology has been used to improve products that most of us use everyday. These include laundry detergent, 6-pack rings, and surgical tools. One of the most widespread applications of nanotechnology is in clothing. Nanotechnology is also called a "bottom up" technology owing to using such small-scale building units, in contrast to bulky material engineering that is considered a "top down" approach (3). Many textile industries and research organisation has already developed fabrics with distinguishing properties. Scratch-and-sniff clothing is one example. Pleasantly scented, tiny polymer beads are added to clothing, such as within a strawberry applied on a shirt. Then there are menthol pajamas, scented to open the nasal passages of people suffering from colds, ensuring a good night's sleep.

Some other type of clothing niche being explored on many fronts, with perhaps more staying power than scratch-and-sniff shirts, involves the nanoscale improvement of fabrics and fibres. Nanotechnology is adding its labels to popular clothing brands with various products: Resists Spills, Resists Static, Coolest Comfort, and Repels and Releases Stains. Researchers all around the world are looking at all sorts of metal additives and polymer additives, inorganic, organic materials to take them at nanoscale to impart lots of interesting properties to textiles.

Preparation of nano-sized materials

There are several physico-chemical methods for preparation of nano-sized material mentioned as below (4) :

- Vapour phase reaction.
- Chemical vapour deposition.
- Inert gas condensation.
- Laser ablation.
- Plasma spraying.
- Spray conversion.
- Sputtering.

Some commercially available nano-particles

Nano-particles may consist of various elements and compounds. The size of the molecules is the sole criterion for inclusion in the category of nano-particles. Nano-particles have a length of 1 to 100 nm. Conventional materials have grain sizes ranging from microns to several millimeters and contain several billions atoms each, nanometre sized grains contain only about 900 atoms, exhibit new and improved properties compared to the corresponding bulk material (Table1). Some nano-particles currently available are as follows (5-7):

1. Metals: Pd/Pt, Ag, Fe, etc.
2. Compounds: - Organic: Vitamins, DNA, Hydroxylapatite, Colour pigments.
   - Inorganic: TiO2, ZnO, Fe2O3, MgO, SiO2 etc.
3. Polymer: - cellulose nano-whiskers
   - carbon nano-whiskers.

Sr.No	Nano-Particles	Properties
1	Silver Nano-Particles	Anti-bacterial finishing
2	Fe Nano-Particles	Conductive magnetic properties, remote heating.
3	ZnO and TiO_2	UV protection, fiber protection, oxidative catalysis
4	TiO_2 and MgO	Chemical and biological protective performance, provide self-sterilizing function.
5	SiO_2 or Al_2O_3 Nano-particles with PP or PE coating	Super water repellent finishing.
6	Indium-tin oxide Nano-Particles	EM / IR protective clothing.
7	Ceramic Nano-Particles	Increasing resistance to abrasion.
8	Carbon black Nano-Particles	Increasing resistance to abrasion, chemical resistance and impart electrical conductivity, colouration of some textiles.
9	Clay nano-particles	High electrical, heat and chemical resistance.
10	Cellulose Nano-whiskers	Wrinkle resistance, stain resistance, and water repellency.

Table 1 Nano-particles and potential textile applications

Metals and metal oxides nano-particles

Nano-size particles of Pd/Pt, Ag and Fe can be applied on textiles to impart antibacterial, conductive magnetic properties and remote heating properties. Silver has been used for the treatment of medical ailments for over 100 years due to its natural anti-bacterial and anti-fungal properties. Nano-silver particles are widely applied in socks to prohibit the growth of bacterial. In addition, nano-silver can be applied to a range of other healthcare products such as dressings for burns, scald, and skin donor and recipient sites.

Nano-silver particles can be applied on textiles by padding method with good laundering durability (8). Hoon Joo Lee and Song Hoon Jeong (9) have reported that nano-sized silver colloids and nano-silver treated polyester nonwovens have good bacteriostasis. Water based and ethanol based nano-silver colloids with spherical nano-particals of diameter 2-5 nm can be applied to polyester nonwoven fabric. It has been reported that the growth of bacteria colonies is absolutely inhibited with only 10 ppm colloidal silver nano-particles.

Nano-size particles of TiO_2, ZnO, Al_2O_3, and MgO are a group of metal oxide that possesses photo catalytic ability, electrical conductivity, UV absorption, and photo-oxidising capacity against chemical and biological species. Intensive research involving the nono-particles of metal oxides have been focusing on antimicrobial, self decontaminating, and UV blocking functions for both military protection gears and civilian health products. Nylon fibre filled with ZnO nano-particles can provide UV shielding function and reducing static electricity of nylon fibre. A composite fibre with nano-particles of TiO_2/MgO can provide self-sterilising function (10).

TiO_2 and MgO nano-particles can be entrapped into a textile fibres during the spinning process or incorporated into a textile material via normal textile finishing methods with a resultant material having chemical and biological protective performance (11).Cellulose fibre filled with nano-particles of metal oxides (such as TiO_2) from in situ synthesis can be used as a catalyst in fuel cells (12).

Polymer and polymer nano-composites

It has been established in recent years that polymer-based composites reinforced with a small percentage of strong fillers can significantly improve the mechanical, thermal and barrier properties of the pure polymer matrix. Moreover, these improvements are achieved through conventional processing techniques without any detrimental effects on processability, appearance, density and aging performance of the matrix. Now-a-day's hybrid polymers (such as Organoallcoxy silanes), which are the hybrid structure of inorganic-organic nano-composite materials are being used to impart the combination of scatch resistance with dirt-repellent effect, high transparency, special barrier properties or antimicrobial function to the material (13).

Clay nano-particles: Clay basically consists of hydrous aluminosilicate and is low in density. Nanosize clay particles or flaks can impart excellent flame retardant functionality to the textile due to the heat resistant behaviour of the nanoclay (14). UV blocking power and outstanding barrier functionality are due to the internees of nanoclay to corrosive chemicals and its neatly layers configuration inside fibre (15,16). In terms of mechanical attributes, nylon6 clay composite with a clay mask fraction of 5% shows 40% higher tensile strength, 68% greater tensile modulus, 60% higher flexural strength, and 126% greater flexural modulus.

Such a significant improvements in composite strength even leads to application of nano clay filler as a protective insert in infantry helmets (15,16). Nano clay fillers modified with quaternary ammonium salt have been introduced into polypropylene fibre, the resultant fibre can be coloured by acid and disperse dyes to 1-4% colour shades for incorporation of less than 5% nano-dry fillers. The modified nano clay introduces dye attaching sites to the polypropylene fibre generates void space inside the fibre to entrap dyes without degrading the beneficial properties of polypropylene (17).

Carbon nano particles: Carbon nano black particles are extremely effective reinforcing material for composite fibres (10). With their high aspect ratio, carbon black nano particles can improve abrasion resistance and hence increase the durability of composite fibres. Carbon black nano particles can also result in high chemical resistance and electric conductivity after they are mixed with fibre polymer matrix. Polyester, nylon and polypropylene have been used as polymer matrix with weight percentage of nano size filler range from 5% to 20% (18,19).

Dapeng Li and Gang Sun (20) have reported that carbon black nano-particles can directly be used in traditional dyeing processes to dye polyester and acrylic fabrics. Polyester and acrylic fabric were dyed with nano carbon black particles using a dip-pad, dry and cure technique. Effective colouration of these fabrics has been reported with 8 nm particles, using cationic dispersing agent, at 180^{0}C treatment temperature.

Polymer nano-whiskers: Nano-whiskers, each of which is just 10 nanometres long (a grain of sand is 1 lakh nanometres in comparison). Basically, nano whiskers, 1/1000 the size of a typical cotton fibre are attached to the individual, constituent fibres of the fabric. The whiskers are hydrocarbons added by dipping in an aqueous solution 8. The whiskers modify water-resistance of fabric due to surface tension that causes water to form into drops or spheres. The spaces between the whiskers on the fabric are smaller than a typical drop of water while the whiskers are hydrophobic and do not absorb water. As a result, water remains on top of the whiskers and above the surface of the fabric.

Another similar product is nanosphere that makes fabric water and soil-resistant. In his work Soane (2) immersed the cotton fabric in a pool containing a mixture of water and billions of these nanowhiskers, then heated the pool in order to evaporate the water and cause the nanowhiskers to chemically bond to the cotton's cylindrical fibres, coating each thread entirely.

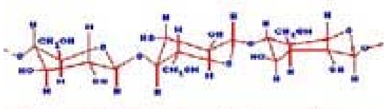


Figure1: Molecular structure of cellulose.

Cotton fibres, primarily composed of cellulose (Figure 1), owe their high degree of absorbency to the many The stain-repellent fabrics from Nano-Tex, incorporate billions of tiny fibres, each about to nanometres (that's 0.0000004 inches) long, that are embedded within traditional cotton or linen. The waterproof fibres, which Nano-Tex calls "nanowhiskers," make the fabric dense, increasing the surface tension so drops of liquid can't soak through-just like raindrops on a freshly waxed car.

The company says this Nano-Care treatment will withstand 50 home launderings before its effectiveness is lost. These may be due to the negatively charged, hydrophilic hydroxyl groups that lie along the naturally occurring polymer's carbohydrate structure. The outer-shell electrons of the carbon atoms from which the whiskers are constructed form nonpolar covalent bonds and therefore do not readily bind to polar water molecules.

Thus, the attachment of the carbon whiskers to the cotton fibres permanently alters the physical properties of the cotton by changing the fibres from hydrophilic to hydrophobic. Because the nanowhiskers are so small, they are able to permeate the cotton fabric and attach to each thread without modifying the appearance or feel of the pants. The ability to engineer effective nanostructures such as these owes its many promising applications to the enduring maturation of nanoscience.

In another study the cotton nanocomposites, fibre modified with organo clays, have been developed to improve the thermal properties of cotton with minimal impact on other desirable properties (21). A method of laboratory scale wet spinning and nonwoven production has been developed; regenerated cellulose nanocomposite fibres have been produced by a wet spinning technique that is a modification of the Lyocell method for producing regenerated cellulose commercially. The nanocomposite fibres were processed into nonwoven substrates using small-scale paper production equipment. Thermal analysis revealed that the nonwoven production process does not hinder the improvements in thermal behaviour seen in earlier tests on fibres. Moisture regains analysis showed that the water uptake of these materials is comparable to that of unprocessed cotton.

In another work, carbon nanowhiskers and carbon nanotubes were doped with two types of polymer precursors were used; linear low density polyethylene and nylon-6. The fillers in each case were carbon nanowhiskers and multi-walled carbon nanotubes. It has been reported that the improvement with carbon nanowhiskers was around 17% while it increased to 34% with MWCNT.

Out of the four systems (two fillers and two polymers) investigated, the system with Nylon-6 infused with MWCNT yielded the most promising results. Tension tests on individual filament of this system showed about 150-300% improvement in strength and stiffness with 1% MWCNT loading. TEM studies revealed that extrusion technique caused sufficient alignment of MWCNT along the length of the filament, which may have caused the gain in mechanical properties.

The former involves separation of nano-whiskers from cellulose fibres, proper treatment and embedment into polymers. It has been found that these nano-whiskers have twice the strength of conventional glass fibres. The embedment of graphene layers into polymers has its own advantages. Apart from high modulus, electrically conductive graphene layers enable proper orientation (by applying known voltage) of the graphene layers in the polymer during manufacturing thereby increasing the reinforcement effect and hence the enhancement of many properties.

Nano-whiskers are wonder molecules, which can impart various functional properties not only to the textiles but also contribute significantly in the field of electronics and medicine. Recently several works has been reported, where nano-whiskers have been synthesised from a variety of materials by using some new and improved techniques.

Nano-particles in functional textile finishing

In some typical textile finishing applications nano-particles can substantially alter surface properties and also confer different functions to the textile materials (22,23). The nano size particles offer a larger surface area compared to bigger particles. Being in the nanometre range, the particles are transparent, so they do not blur colour or alter brightness of textile substrates.

Nano-particles can be applied on textiles by two-stage process. Initially, there is the manufacture of new, stable nano-material, which must in the first instance be protected against properties defined by the size of the particles. The second step sees the creation of the foils, emulsions and dispersions that can be applied to the final textile product, in the most favourable case, by means of conventional finishing processes.

Nano particles are most commonly applied to textiles by coating using a composition of nano particles, a surfactant, ingredients and a carrier medium. Coating techniques, which modify the surface of the textile, include:

- Spraying: the coating composition is sprayed on to textiles, with control of the depth and targeting to specific areas.
- Dipping and soaking in an immersion container followed by a drying step.
- Transfer printing such as rotary, flexography and inkjet printing.
- Washing, accomplished by using a washing solution containing nano particles during wash or rinse cycles in a washing machine.
- Padding, where nano particles are attached to the fabrics with the use of padder applied under pressure.

Nano particles have large surface area to volume ratio, which makes it easy for them to attach to fibre or fabrics, and increase the durability of the functions imparted by the particles. In addition, the coating of nano particles does not affect the breathability, and hand feel of the textile. The commonest functions are wrinkle resistance, stain, soil and water repellency and anti static, anti bacterial and anti ultraviolet protection (8).

Wrinkle resistance: Wrinkling occurs when the fibre is severally creased. When fibre or fabric is bent, hydrogen bonds between the molecular chains in the amorphous regions break and allow the chains to slip past one another. The bonds, reform in new places and fibre or fabric is held in the creased configurations. The disadvantages of conventional resin applications include decrease in the strength of fibre and in abrasion resistance, water absorbency and dyeability, as well as in as in breathability.

Stain resistance: Staining of fabrics occurs from re-deposition of soil during laundering or dry cleaning, deposition of dry soil from the air or contact with foreign matter. Silicon chemicals and fluorochemical finishes can be used to confirm resistance to soil, water and even oily stains. The stain-repellent fabrics from Nano-Tex (Figure 2), incorporate billions of tiny fibres, each about to nanometres (that's 0.0000004 inches) long, that are embedded within traditional cotton or linen. The waterproof fibres, which Nano-Tex calls "nanowhiskers," make the fabric dense, increasing the surface tension so drops of liquid can't soak through-just like raindrops on a freshly waxed car. The company says this Nano-Care treatment will withstand 50 home launderings before its effectiveness is lost.

The most developed nanotechnology application for textiles is currently in the areas of stain, oil, and water repellency;

stain release and wrinkle resistance. Stain resistance, stain repellent, and dual action repel and release finishes all can be applied by using nanotechnology.

Repellent products lower the critical surface tension of the fabric so the fabric does not attract stains or soil. Oil and water bead up and roll off the fabric. When a repellent finish is applied to fabrics, the invisible repellent finish provides superior water/oil repellency and protection against spills and stains.

Stain release products allow for stains and spills to soak into the fabric; oil and water may bead slightly and stains are applied, the fabric will be slightly oil/water repellent, but the invisible stain release finish allows for ground in stains to be easily removed during laundering. This finish with the addition of a water-loving component allows absorbed stains to wash out and easily removed with home laundering. When a stain release finish is Dual-action repel and release is the newest finish in the industry. The finish combines advantages of both stain release and repellent finishes into one. This twofold protection offers a unique balance of repellency that works in tandem with an advanced stain release, which helps to liberate the toughest stains including tough ground-in stains. With dual-action repel and release finishes, consumers get twice the stain protection in one easy-to-care-for fabric.

Figure 3: Nanocare water resistant fabric.

Water repellency: Water repellant finishes modify the surface of fibre and do not block the interstices. Hence fabric permits air and water vapour to pass through. Early water repellant coatings were easily removed dry cleaning or laundering. Nowadays, wax emulsions, pyridinium compounds, N-methylol compounds, silicons and fluoro chemicals are used to impart water repellency to various natural and synthetic fibres.

To improve the properties of wrinkle resistance, stain resistance and water repellency recently several products have been introduced. Nano Whisker introduced by Nano-tex is one of the best options. They are attached to the fabric permanently, unlike the topical coatings or bulky laminated fabrics that have traditionally been used for this purpose. The whiskers are hydrocarbons added to the fibres in an aqueous solution. The changes to the fibres do not affect the natural hand feel and breathability of the fabric. The fabric shows very good wrinkle resistance, the processing is undetectable and a " peach fuzz" effect has been reported. The finish can be applied onto textiles through a nanoscale emulsification process in a more thorough, even, and precise manner than traditional methods.

In the case of fabric, rolls of woven cotton fabric from textile mills are immersed in liquids containing trillions of nanowhiskers they are waterproof and increase the density of the fabric. Then this treated cotton, is dried in ovens binding the tiny fibres to the comparatively much larger cotton threads. This increases the surface tension on the outer layer of the fabric so liquid cannot soak through.

Though the final product looks unchanged, it provides a nearly solid barrier to liquid or wrinkles, for instance. Nanowhiskers provides an even application and does not change the surface properties unlike traditional finishes. Nano-particles are extremely tiny and therefore the addition of these particles on fabric is not detectable by hand.

Fig 3

Nano-particles added on textile materials cannot be detected by the naked eye; therefore the original colour of the products will not be altered. Nano-particles form a protective layer on the face of textile materials instead of changing their chemical properties; therefore they give no hazardous substances and have no side effects. Textile products, which have been processed with nano-particles, are more durable than the traditional finishes with repeated washing.

Nano-finishes can add additional functionality to fabrics such combination of wrinkle and stain repellency in one application. But on the other hand, Nano-tech garments could under perform if proper care is not taken. Proper care for these garments includes the use of delicate machine washes and drip dying, no dry-cleaning and avoiding the use of chlorine bleach and wringing of the clothes.

Anti static performance: Static usually builds up in synthetic fibres such as in nylon and polyester because they absorb little water. Conventionally surfactants are used to spread the small amount of moisture on the surface of fibre so as to pose the charge to leak away. One of the best electrically conductive nano particles is silver. Silver nano particle helps to dissipate the static charge effectively.

Anti bacterial effect: The commonly used anti bacterial agent was quaternary ammonium compounds. Many chlorinated organic compounds and organo metallic compounds containing copper, silver, iron, manganese or zinc also make fabrics resist growth of bacteria. The use of nano silver particle offers durable anti-bacterial finishing to the textile.

Ultra violet protection: To impart UV protection, several nano compounds or nano particles can be applied on textile material. The commonest nano compounds used are titanium dioxide and zinc oxide of nano size. They provide a protective benefit by reflecting, scattering or absorbing harmful UV.

At present several research organisations and industries are offering nanotechology and its application techniques for textiles. Some of them are as follows:

1. Nano-Tex, LLC, Greensbara, NC, USA.
2. Texcote Technology (International) Ltd, Sweden.
3. Schoeller Textiles AG, Switzerland.
4. Beiging Zhong-Shong Century Nanotechnology Co Ltd, China.

Testing and analysis of nano-materials The morphological features of nano material and structures need to be determined in various stages of production such as size distribution, porosity, pore size distribution, surface structure and composition, which are critical to ensure the materials and structures are in nano scale to archive special properties (24-26). Such structural feature can be characterised by a rang of techniques and instruments such as Particle Analyser, Atomic Force Microscopy (AFM), Scanning Tunneling Microscopy (STM), Scanning Electron Microscopy (SEM), High Resolution Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES), Near Field Scanning Optical Microscopy (NSOM or SNOM), X-ray and Neutron Diffraction or other spectroscopic techniques.

The properties of nano materials and structures/composites also need to be measured to test whether specific and unique properties can be derived due to the nano scale structures. Properties characterisation should be carried out in various aspects in relation to specific functions to be achieved such as in physics, mechanical, electrochemical, optical and thermal properties. Examples of propertie's characterisation techniques: property to be characterised techniques; Dynamic Time Resolved Techniques; Magnetic Scanning Electron Microscopy with Polarisation Analysis (SEMPA); Surface Magnet - Optic Kert Effect (SMOKE) Spectroscopy; Spin-Polarised Low -Energy Electron Microscopy (SPLEEM); Magnetic Force Microscopy (MFM); Electrochemical Impedance Spectroscopy; Potential Sweep Method; Electrochemical Quartz Crystal Microbalance, Mechanical Electricity Method; Vibrating Reed Method; Thermal Diffractional Scanning Colorimeter(DSC).

Finally, functional performances of final products need to be characterised to test the roles and impact of nano materials and nano scale structures. Only when new and/or significantly enhanced properties are introduced, due to the nano scale sizes or structures, can nano-products be claimed, based on the definition of nanotechnolgy.

Economical and environmental aspects

The unique properties of nanomaterials have attracted not only scientists and research workers but also businesses, because of their huge economic potential. The national science foundation reports that nano-related goods and services will increase to a US$ 1 trillion market by 2015. This amount is larger than the combined businesses of the telecommunications and information technology industries. Several hundred billion Euros are forecast to be created by nanotechnology in the next decade (24). The nano materials markets could expand to US$ 4 billion by 2007. It was believed that 2 million new employment opportunities would be created in order to meet the worldwide annual production demand of US$ 1 trillion in 10-15 years.

Nanotechnology may impart favourably on the environment as well. By using less resource without sacrificing performance, nanotechnology may save raw materials and also upgrade quality of life.

Conclusion

The development in the applications of nano-particles, nano-composites and nano-sphere has been very rapid in past years, particularly in the field of textile finishing. These nano-size materials are able to enhance the physical properties of conventional textiles in areas such as anti-microbial properties, water-repellency, soil-resistance, anti-static, anti-infrared and flam retardant properties, dyeability, and strength of textile materials. In future the application of these wonder nano-particles can be extended to produce textiles with health-care and wound healing functions as well as self-cleaning and repairing functions.

References

1. Information from http://www.dictionary.com
2. Information from http://www.nano-tex.com
3. E Menezes, K Singh: Colourage, LI, 8, 2004, 55.
4. P B Jhala, The Indian Textile Journal, CXIV, 8, 2004,13.
5. J Beringer, D Hofor: Melliand Textileberichte, 85,9, 2004,698.
6. L Zhu, and K H Narh: Journal of Polymer Science: B: 42, 2003, 2391.
7. Information from http://www.egr.msu.edu/cmsc/biomaterials/research.html
8. Y W Wang, C W M Yuen, M Y S Leung, S K A Kuand, H L I Lam: Textile Asia, XXXV, 5,2004,27.
9. H J Lee and S H Jeong: Textile Research Journal, 74,5,2004,442.
10. L Qian: AATCC Review, 4,5,2004,14.
11. Hartley, M Scott, A Holly: The Next Generation of Chemical and Biological Protective Material Utilising Reactive Nano-particles, Gentex corp, Carbondale, pa.
12. He, Junhui, T Kunitake and A Nakao: Chemical Materials, 15,23,2003,13.
13. Dr S Amberg-schwab, D Ulrikeweber: International Textile Bulletin, 50, 1, 2004,
14. Information from- http://www.egr.msu.edu/-tomanek/phy905/w-1-2-6.html
15. J W Gilman, et al: In Chemistry and Technology of Polymer additives, Edited by A K Malaika, S A Golovoy and C A Wilkie: Blackwell Science Inc, Malden, Mass., 1999, 249.
16. Information from- http;//www.ccmr.cornell.edu/-gianellis/research/silicates.html
17. F Qinguo, et al: AATCC Review, 3, 6, 2003,25.
18. Information from- http;//www.nanophase.com/applications/, 2002.
19. J Chen, and N Tsubokawa: Polymer Journal, 32,9, 2000, 729.
20. D Li and G Sun: AATCC Review, 3, 12, 2003.19.
21. Information from- http://www.egr.msu.edu/cmsc/biomaterials/index.html
22. Soane S David: US Patent, No.6, 607,994,2003.
23. A V Shivaprakash and M Mohankumar: Man-made Textiles in India, XLVII, 2,2005,75.
24. Li L Lokyuen and H Junyan: Textile Asia, XXXIV, 11,2003,26.
25. Information from- http://www.egr.msu.edu/cmsc/esem/index.html.
26. Information from- http://www.egr.msu.edu/cmsc/nano/index.html.

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Improvement in physical and dyeing properties of natural fibres through pre-treatment with silver nanoparticles

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Silver nano colloids have been synthesised by chemical reduction of silver salt solution, characterised by its surface plasmon resonance peak in absorption spectra at 450 nm and by SEM images of nanoparticles. The size and size distribution of these nanoparticles have also been examined using particle size analyzer; the average size of the particles is found to lie between 80 nm and 90 nm. The findings support the size and shape of the synthesised nano silver particles. These nanoparticles have been applied to cotton, silk and wool fabrics by usual padding technique and manifested the improved microbial resistance as measured through soil burial test. The dyeing behaviour of the treated fabrics with three direct dyes has also been studied and the build-up of dyes, measured as colour strength in terms of *K/S* values, reported. The higher *K/S* values are obtained when the Ag nano is anchored in the fibre matrix, i.e. when the fibre is pre-treated and dyed with direct dyes. Improved colour strength with good wash and light fastness is also obtained after treatment of fabrics with nano colloids.

Keywords: Absorption spectrum, Bacterial resistance, Cotton, Dyeing, Nanoparticles, Silk, Silver nano colloids, Wool

1 Introduction

During the past two decades, the small-particle research has become quite popular in various fields of chemistry and physics. The small-particles now we call nano structured materials are having interesting properties. Metallic nanoparticles represent a class of materials that are increasingly receiving attention as important starting points for the generation of micro and nanostructures. These particles are under active research because they posses interesting physical properties differing considerably from that of the bulk phase. It has small sizes and high surface/volume ratio[1]. Silver nanoparticles have received considerable attention due to their attractive physical and chemical properties.

Metallic silver colloids were first prepared more than a century ago. Ag nanoparticles can be synthesized using various methods, such as chemical, electrochemical, γ-radiation, photochemical, laser ablation, etc[2]. The most popular preparation of Ag colloids is chemical reduction of silver salts by sodium borohydride or sodium citrate. This preparation is simple, but the great care must be exercised to make stable and reproducible colloid. The purity of water and reagents and cleanliness of the glassware are critical parameters. Solution temperature, concentrations of the metal salt and reducing agent, and reaction time influence particle size. Controlling size and shape of metal nanoparticles remains a challenge. The size-induced properties of nanoparticles enable the development of new applications or the addition of flexibility to existing systems in many areas, such as catalysis, optics, microelectronics and textiles.

Silver nano is a trademark name of an antibacterial technology which uses silver nanoparticles in washing machines, refrigerators, air conditioners, air purifiers and vacuum cleaners. Antimicrobial effect of silver nanoparticles on textiles has already been shown by various researchers[3-6]. But the effect of Ag nano treatment on other physical and chemical properties of textiles is hardly found in the literatures. In the present work, Ag nanoparticles have been synthesized by the reduction of silver salt ($AgSO_4$) with sodium borohydride in the presence of tri-sodium citrate and characterized by particle size analyzer, scanning electron microscope (SEM) and atomic force microscope. Prepared silver nano collides have been applied to textiles and the effect on various properties,

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like tensile, creasing, stiffness, dyeing and bacterial resistance, are examined by standard methods.

2 Materials and Methods

2.1 Materials

2.1.1 Fabric

Mill scoured and bleached cotton, wool and silk fabrics with specification as given in Table 1 were procured from local market and used for the study. The procured fabric was further thoroughly washed, neutralised and air dried.

2.1.2 Dyes and Chemicals

Three commercial direct dyes, namely C.I. Direct Red 9 (D1), C.I. Direct Blue 67 (D2) and C.I. Direct Green 6 (D3), were used for this study without further purification. Silver sulphate ($AgSO_4.5H_2O$, MW 249.68), sodium borohydride ($NaBH_4$, MW 37.83) and tri-sodium citrate ($C_6H_5Na_3O_7.2H_2O$, MW 294.10) of analytical grade purity were procured from Sd Fine Chemicals.

2.2 Methods

2.2.1 Preparation of Nano Ag Colloid

The 100 mL solution of $1{\times}10^{-3}$ M $AgSO_4$, kept in the specially designed reaction chamber, was slowly reduced by drop-wise addition of very dilute chilled solution of sodium borohydride in a nitrogen atmosphere. During the process of reaction the solution mixture was stirred vigorously. When the colour of the solution turned to light yellow, 5 mL of 1 % trisodium citrate was added drop by drop with vigorous stirring. Distilled water was used for preparing the solutions of all the chemicals. Mechanism of reaction could be expressed as shown below:

$$4Ag^{+2} + NaBH_4 + 2H_2O \rightarrow 4Ag + BH_4 + Na^+ + 4H^+ + O_2$$

2.2.2 Characterization Techniques

The absorbance of colloidal solutions was recorded at different stages of synthesis on UV-visible spectrophotometer (Shimadzu UV-2450, Japan). The particle size and size distribution of the Ag colloid were analyzed on the particle size analyser (Malvern Instrument, MAL501131, DTS version 5.03, U.K.). For elemental analysis, the synthesized nanoparticles were deposited on carbon coated aluminium sheet and further coated with gold, which were then observed on scanning electron microscope (SEM) (Model JSM5610LV, version 1.0, Jeol, Japan) using Oxford-Inca software (U.K.). The morphology of silver nanoparticles was examined after depositing the nanoparticles on carbon-coated aluminium sheet.

Table 1 – Specification of cotton, wool and silk fabrics

Fabric	Weave	Ends/ inch	Picks/ inch	Weight, g/m^2
Cotton	Plain	112	72	118
Wool	Plain	80	60	65
Silk	Plain	84	62	29

2.2.3 Treatment of Textiles with Silver Nanoparticles

Silver nanoparticles were applied to the cotton, wool and silk fabric samples by dipping them in the dispersion for 10 min and then padded on an automatic padding mangle machine using 2-dip-2-nip padding sequence at 70% expression. The padded substrates were air dried and finally cured at 120°C for 20 min in a preheated curing oven.

2.2.4 Determination of Fabric Properties

Cotton, wool and silk fabrics were tested for the tensile properties before and after nano colloid treatment. The breaking load of the samples was determined on tensile tester instrument (LRY Model, Lloyd, U K).

The crease recovery angle of the samples was determined as per AATCC Test Method 66-2003 using Sasmira crease recovery tester (India).

The stiffness in terms of bending length of nano-treated and untreated samples was measured as per AATCC test method 115-2005 using Prolific stiffness tester (India) for the measurement of bending length.

2.2.5 Dyeing of Untreated and Treated Samples

Dyeing of well prepared fabric samples was carried out in laboratory constant temperature water bath (Paramount, India), using standard dyeing method for individual fabrics, 2% (owf) direct dye and a liquor–to–material ratio of 40:1. After dyeing, all the dyed samples were rinsed, washed thoroughly and dried at ambient temperature.

The dyed samples were assessed for *K/S* values using computer colour matching system (Spectra scan 5100 RT Spectrophotometer, Premier Colorscan Instrument, India).

The light fastness of the dyed samples was tested on fad-o-meter (FDA-R, Atlas, U.S.A.) after partially exposing the samples to the xenon arc lamp for 16 h and graded for the colour change with the ratings.

The wash fastness test of the samples was performed as per ISO – 2 test methods in lounder-o-meter (Digi.wash, Paramount Scientific Instruments., India). The samples were evaluated for the rating in terms of colour change.

2.2.6 Evaluation of Antimicrobial Activity

The untreated and treated samples were subjected to soil burial test as per AATCC test method 30-2004. After the stipulated period the samples were removed, washed with water and dried in air. The samples were than tested for breaking load on tensile tester.

3 Results and Discussion

3.1 Optical Properties of Ag Nano Colloid

The absorption spectrum of the prepared colloidal solution was taken at different time intervals after synthesis (Fig. 1). It is found that the yellow colour solution after synthesis gives an absorbance peak at 445nm due to plasmon resonance of the nanoparticles (Fig. 1a). The absorption band in visible light region (350 – 550 nm, plasmon peak at 445 nm) is typical for silver nanoparticles. Similar observation was also reported by Šileikaitė *et al*[7]. The plasmon peak and the full-width of half-maximum (fwhm) depend on the extent of colloid aggregation[8]. To monitor the stability of the silver colloid, the absorption spectra of the colloid was examined after 2 weeks (Fig. 1b) and 4 weeks (Fig. 1c) intervals. There is no change in the peak position even after storing for 4 weeks. The inset photograph (Fig. 1) shows that there is no reasonable change in the colour of the colloidal solutions except little darkening of colour when stored for 4 weeks. The stable position of the absorbance peak (λ_{max}) indicates that the particles do not aggregate. The increase in absorbance value after storing for 4 weeks is indicative of increase in concentration of the nanoparticles through the generation of new particles. The aggregation of the particles could be avoided with the help of citrate anions. The Ag colloidal particles form a negative screen due to the adsorbed citrate ions. The repulsive force of these negatively charged spheres prevents further aggregation.

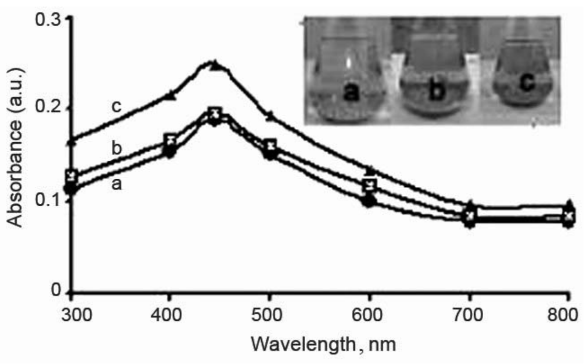

Fig. 1—UV-VIS spectra of Ag colloids [time after synthesis: (a) 1 h, (b) 2 weeks and (c) 4 weeks]

3.2 Characterization of Ag Colloid

The particle size and size distribution of the prepared and stabilized Ag colloid were analyzed on Malvern instrument. Figure 2a shows the intensity size distribution of Ag nanoparticles dispersed in water. The first peak at around 110 nm arises from the dispersion. The peak positioned at 4 microns arises from stabilised Ag nanoparticles. The presence of the second peak has resulted in the z-average diameter for this sample increasing to 62.06 nm. The statistical graph by intensity is given in Fig. 2b. It is also evident from the statistical graph that the average size of the stabilized nanoparticles was ranging from 60 nm to 120 nm.

Figure 3a shows the scanning electron micrographs of stabilized Ag nanoparticles deposited on carbon coated aluminium sheet. The average size as seen from the scale of the photograph is about 90-100 nm which is found in good agreement with the size determined by the particle size analyser. Figure 3b represents the SEM image of gold coated Ag nanoparticles. It can be seen from the figure that the shape of synthesised particles is spherical and the size of nanoparticles is increased by 500 – 800 nm due to the gold coating.

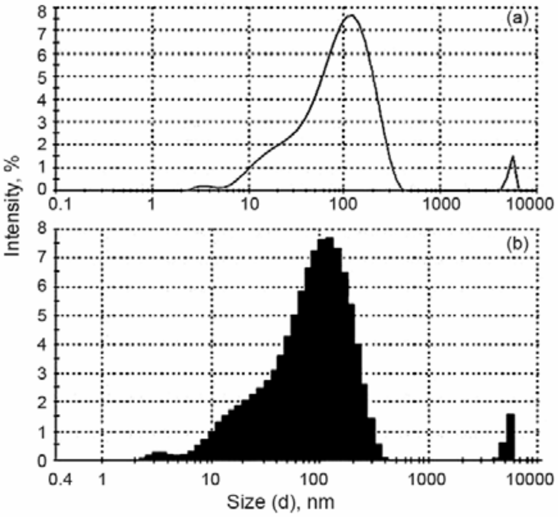

Fig. 2—Particle size distribution stabilized Ag nanoparticles [(a) size distribution by intensity and (b) statistical graph by intensity]

Elemental analyses of gold coated nanoparticles were performed in the scanning electron microscope using Oxford-Inca software. The result observed in this test is shown in Fig. 4. Presence of silver is confirmed by the elemental analysis curve.

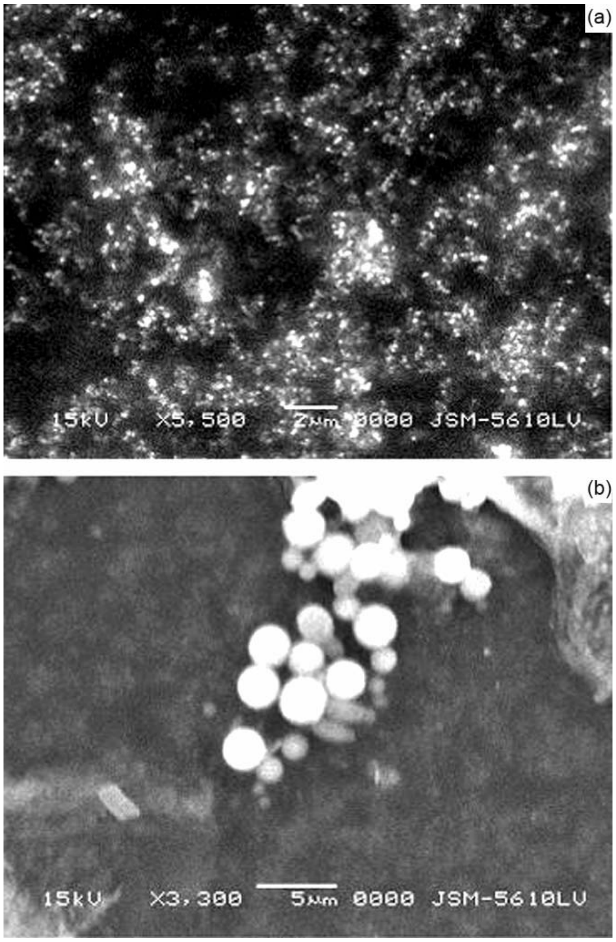

Fig. 3—Scanning electron microphotographs of silver nano particles [(a) deposited on carbon coated aluminium sheet and (b) coated with gold and deposited on carbon coated aluminium sheet]

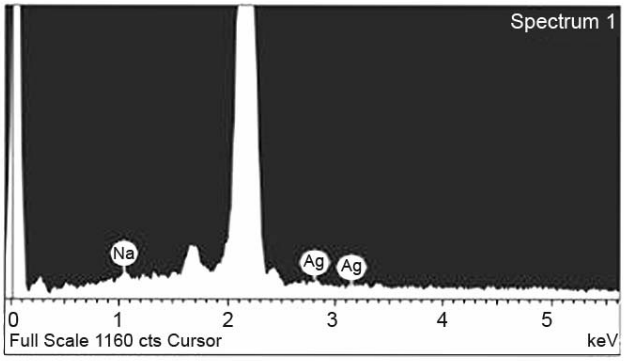

Fig. 4—Elemental analysis result of silver nanoparticles deposited on carbon coated aluminium sheet and further coated with gold

3.3 Effect of Ag Nano Treatment on Physical Properties

The effect of silver nano treatment on tensile strength, crease recovery and bending length has been studied. It is observed from Table 2 that the introduction of nano silver particles into the structure of the fibre causes an improvement in the load bearing capacity of the fibre. The treatment increases the breaking load of cotton by about 8%.

The nano silver particles because of their small size can enter in between the polymer molecules and perhaps act as filler or crosslinking agent which also contribute to the load sharing phenomenon during load application to the material. Unlike chemical crosslinking which causes an improvement in crease recovery angle at the cost of imparting some rigidity in the material to an extent depending on the extent of cross linking, the incorporation of nano silver particles remains quite gentle in this regard. There is little improvement in crease recovery angle of all the fibres with a little increase in bending length. This observation proves that the particles penetrated in between the polymer chain molecules do not interfere much to the polymer flexibility of the system. The treatment is thus devoid of harshness to the material.

3.4 Effect of Ag Nano Treatment on Dyeing

The Ag nanoparticle treated cotton, wool and silk fabrics were dyed with three direct dyes and compared with the untreated samples. It is observed from Table 3 that the *K/S* values of the nano silver pretreated samples are higher than those of the corresponding untreated samples of cotton, wool and silk fabrics. The maximum improvement in colour strength is observed with C.I. Direct Green 6 dye. The higher *K/S* values (Table 3) of nano-treated samples indicate that the presence of nano metal particles increases the dye affinity towards the material. The silver nanoparticles in the fabric thus act as mordant. The negatively charged dye anions get attracted towards the fibre probably due to the polarity developed in the metal particles by induction which results in better bonding between the dye and the fibre. The better coupling of the dye and the fibre is also reflected in the improvement in the colour fastness properties (Table 4). Thus, silver nano pretreatment not only improves the colour strength but also improves the colour fastness which is a major drawback of most direct dyes.

3.5 Effect of Ag Nano Treatment on Resistance against Microbes

The resistance against bacterial attack of untreated and treated samples of cotton, wool and silk was

Table 2—Effect of silver nano treatment on physical properties of cotton, wool and silk fabrics

Sample	Breaking load, kg		Crease recovery angle, deg		Bending length, cm	
	Control	Nano Ag applied	Control	Nano Ag applied	Control	Nano Ag applied
Cotton	8.02	8.64 (+7.73)	90	95 (+5.55)	1.05	1.35 (+28.57)
Wool	6.36	6.49 (+2.04)	142	153 (+7.74)	2.10	2.20 (+4.76)
Silk	6.24	6.36 (+2.00)	127	136 (+7.08)	2.50	2.65 (+6.00)

Values in parentheses indicate percentage change in physical properties.

Table 3—Effect of Ag nanoparticles on colour strength of fabrics dyed with direct dyes

Sample	Colour strength *(K/S)*					
	D1		D2		D3	
	Control	Ag nano treated	Control	Ag nano treated	Control	Ag nano treated
Cotton	5.32	6.50(+22.18)	8.22	10.55 (+28.34)	8.06	11.22 (+39.20)
Wool	9.05	10.18(+12.48)	11.85	13.21 (+11.47)	11.41	14.85 (+30.14)
Silk	4.75	6.11 (+28.63)	7.34	8.37 (+14.03)	7.39	9.09 (+23.00)

Values in parentheses indicate percentage change in *K/S* values. D1 – C.I. Direct Red 9, D2 – C.I. Direct Blue 67 and D3 –C.I. Direct Green 6.

Table 4—Effect of Ag nanoparticles on fastness properties of samples dyed with direct dyes

Sample	Fastness to											
	Light						Washing					
	D1		D2		D3		D1		D2		D3	
	C	T	C	T	C	T	C	T	C	T	C	T
Cotton	3	3-4	2	3-4	3	4	2-3	4	2-3	4	2-3	4-5
Wool	3	3-4	2-3	3	3	3-4	2-3	3-4	2-3	4	2-3	4
Silk	3	3-4	2-3	3-4	3	4	3	4	2-3	4-5	3	4-5

D1 – C.I. Direct Red 9, D2 – C.I. Direct Blue 67 and D3 –C.I. Direct Green 6, C– Control sample, T – Sample treated with Ag Nanoparticles.

determined by measuring the loss in breaking load due to soil burial test (Table 5). It is observed that after Ag nanoparticle application the loss is reduced in all the fibres, which shows that the Ag nano treatment enhances the resistance of cotton, wool and silk towards bacterial attack. This may be due to the fact that metallic ions and metallic compounds display a certain degree of sterilizing effect. It is considered that part of the oxygen in the air or water is turned into active oxygen by means of catalysis with the metallic ion, thereby dissolving the organic substance to create a sterilizing effect[9]. Nano silver particles have an extremely large relative surface area, thus increasing their contact with bacteria or fungi, and vastly improving their bactericidal and fungicidal effectiveness. Nano silver is very reactive with proteins. When contacting bacteria and fungus, it adversely affects cellular metabolism and inhibits cell growth. It also suppresses respiration, the basal metabolism of the electron transfer system, and the transport of the substrate into the microbial cell membrane. Furthermore, it inhibits the multiplication and growth of those bacteria and fungi which cause infection, odour, itchiness and sores. Nano silver treatment thus improves the properties of cotton, wool and silk in many ways.

Table 5—Effect of Ag nanoparticles on resistance towards bacterial attack

Sample	Breaking load, kg			
	Before soil burial		After soil burial	
	Control	Nano Ag applied	Control	Nano Ag applied
Cotton	8.02	8.64	4.32 (-46.13)	7.32 (-15.27)
Wool	6.36	6.49	4.48 (-29.55)	5.68 (-12.48)
Silk	6.84	6.86	4.20 (-38.60)	6.24 (-09.03)

Values in parentheses indicate percentage change in load.

4 Conclusions

4.1 UV-Vis absorption and elemental analysis results confirm the formation of silver nanoparticles.

4.2 UV-Vis measurements have shown that the size of the nanoparticles in colloid does not change, but with time the concentration slowly increases within few weeks.

4.3 The z-average size of the synthesized Ag nano particle is found to be 62.06 nm. The SEM images indicate that silver nanoparticles produced are of spherical shape.

4.4 The treatment with silver nanoparticles improves the breaking load and crease recovery angle with almost no effect on rigidity of the material.

4.5 Nano Ag treatment enhances the colour strength of cotton, wool and silk fabrics dyed with direct dyes and also improves the fastness towards light and washing.

4.6 Ag nano treatment to cotton, wool and silk also improves the resistance to microbial attack.

References

1 Chattopadhyay D P, *Textiles,* 33(1) (2006) 21-24.

2 Yakutik I M, Shevchenko G P & Rakhmanov S K, *Colloids Surfaces A: Physicochem Eng Aspects,* 242 (2004) 175 – 179.

3 Patel K, Kapoor S, Dave D P & Mukherjee T J, *Chem Sci,* 117 (1) (2005) 3 – 60.

4 Razafimahefa L, Chlebicki S, Vroman I & Devaux E, *Color Technol*, 124(2) (2008) 86-91.

5 Radetić M, Ilić V, Vodnik V , Dimitrijević S, Jovančić P, Šaponjić Z & Nedeljković J M , *Polym Advanced Technol*, 19(12) (2008) 1816-1821.

6 Lala N L, Ramaseshan R , Bojun L, Sundarrajan S , Barhate R S, Ying-jun L & Ramakrishna S, *Biotechnol Bioeng*, 97(6) (2007) 1357-1365.

7 Šileikaitė A, Prosyčevas I, Puišo J, Juraitis A & Guobienė A, *Mater Sci (Medžiagotyra),* 12(4) (2006) 287-291.

8 Yamamoto S, Fujiwara K & Watari H, *Anal Sci,* 20 (2004) 1347 – 1352.

9 Saito M, *Coated Fabrics*, 23 (1993) 150-164.

Effect of Nanosized Colloidal Copper on Cotton Fabric

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ABSTRACT

This research deals with the synthesis of nanosized copper as colloidal solution and its application to cotton fabric. Copper nano colloids were prepared by chemical reduction of copper salt using sodium borohydride as reducing agent in presence of tri-sodium citrate. The size and size distribution of the particles were examined by particle size analyzer and the morphology of the synthesized particles was examined by SEM and AFM techniques. X-ray fluorescence spectroscopy detected the presence of copper in the treated fabric. The results of particle size analysis showed that the average particle size varied from 60 nm to 100 nm. The nano copper treated cotton was subjected to soil burial test for the assessment of its resistance towards microbial attack. SEM images of treated fabric indicate copper nano particles are well dispersed on the surface of the specimens. The treatments of nano copper colloidal solution on cotton not only improve its antimicrobial efficiency but also influenced the tensile strength of the fabric sample positively. The treatment was found to enhance the color depth and fastness properties of direct dyed cotton fabric samples.

Keywords: Absorption spectrum, Bacterial resistance, Copper, Cotton, Dyeing, Nanoparticles

INTRODUCTION

The fundamentals of nanotechnology lie in the fact that properties of substrates dramatically change when their size is reduced to the nanometer range. Moreover, a small amount of nanosize species can interfere with matrix polymer that is usually in similar size range, bringing up the performance of resultant system to an unprecedented level.

The textile industry, among other leading industries, is also an area in which nanotechnology is being implemented with full enthusiasm [1]. Nanotech-textiles are on the way of becoming the most popular textiles with their protective, functional and electronic features. One of the most important advantageous features of nanotech-textiles is their protective properties.

The unique properties of metal nano particles are well known. Nano metals like Au, Ag, Pd, Pt, Zn etc were synthesised by many workers [2-3]. Applications of some of these particles on textiles were also reported in the literature [4-6]. Beside well known antimicrobial property of Ag nano particle, Chattopadhyay and Patel showed that silver nano particle treatment could improve the tensile strength and color depth on cotton, wool and silk fabric [7]. Information on synthesis cum application of Cu nano particles on textile material is hardly found in the literature. The present study was, therefore, aimed at synthesizing nano copper particles by a suitable method and investigating its effect on the properties of cotton fabric.

EXPERIMENTAL

Fabric

Mill scoured and bleached 100 % cotton fabric with following specifications was used in this study; Plain weave with a weight of 238g ⁄m² and a density of 44 threads ⁄cm in the warp and 28 threads ⁄cm in weft directions.

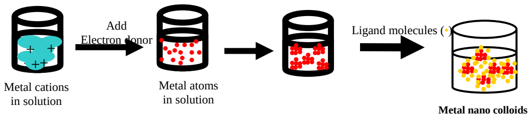
Dyes and Chemicals

Three commercial direct dyes namely, C.I. Direct red 9 (X), C.I. Direct blue 67 (Y) and C.I. Direct Green 6 (Z) were selected for this study without any purification. Silver sulphate Copper sulphate ($CuSO_4.5H_2O$, M.W.249.68), sodium borohydride ($NaBH_4$, M.W.37.83) and tri-sodium citrate ($C_6H_5Na_3O_7.2H_2O$, M.W.294.10) of analytical grade purity were procured from Sd Fine Chemicals, (India).

Equipment

Copper nano were synthesized in specially designed reaction chamber with N_2 gas supply. The particle size and size distribution was analyzed on particle size analyzer (Malvern instrument, MAL501131, DTS version 5.03, U.K.) Atomic Force Microscope (easy Scan 2 Nanosurf AG, Switzerland.) operating in a contact mode (cantilever force constant 3 N/m) was employed for visual observation of the particles. The particles were also imaged through Scanning Electron Microscope (SEM), (model JSM5610LV, version 1.0. Jeol, Japan). The amount of copper as element in the polymer structure was detected and measured using an X-ray fluorescence spectrometer (EDX 800 Simadzu, Japan). The operating X-ray source voltage and current were 35 kV and 26 mA respectively. Registration time was 30 s and the investigated area was 78.5 mm^2.

Application of synthesized nano on cotton and dyeing of nano treated fabric was carried on a constant temperature shaking water bath (Alliance enterprise, India). After dyeing the color strength in terms of *K/S* values were recorded on Spectra scan 5100 (RT) spectrophotometer, (Premium Colorscan Instruments, India). The washing fastness of the fabric was performed on launder-ometer (Digi.wash, Paramount Scientific Instruments., India). Light fastness was carried out on Xenon arc Fad-ometer, (FDA-R, Atlas, U.S.A.).



Scheme 1

SCHEME 1 Schematic process diagram of copper nano colloid synthesis

The 100 ml solution of copper sulphate ($CuSO_4.5H_2O$, 0.3 gm, 4.17 mmol in 100ml water) kept in the specially designed reaction chamber, was slowly reduced by drop wise addition of very dilute chilled solution of sodium borohydride ($NaBH_4$,, 0.1gm, 3.83 mmol in 50ml water) in a nitrogen atmosphere. During the process of reaction the solution mixture was stirred vigorously. As the color of the solution turned to light yellow 5 ml of trisodium citrate ($C_6H_5Na_3O_7.2H_2O$, 0.1gm, 29.41mmol in 100ml water), were added drop by drop with vigorous stirring. Distilled water was used for preparing the solutions of all the chemicals. *Scheme 1* gives schematic picture of Cu nano particle formation and their stabilization by citrate anions.

Nano Cu Treatment on the Cotton Fabric

The synthesized nano cu dispersion was applied to cotton fabric using exhaust method at 40°C and liquor to material ratio of 50:1. After 1 h, the temperature was increased to 80°C over 30 min. the treated fabric samples were thoroughly washed, neutralized and dried in air.

Determination of Tensile Properties

Cotton fabrics were tested for the change in their tensile properties before and after nano treatment. The breaking load of the samples was determined on tensile tester instrument (LRY model, Lloyd, U K)

Determination of Crease Recovery Angle

The crease recovery angle of the samples was determined as per AATCC Test Method 66-2003 using Sasmira crease recovery tester (India).

Determination of Bending Length

The stiffness in terms of bending length of nano treated and untreated samples were measured as per AATCC Test Method 115-2005 using Prolific stiffness tester (India) for the measurement of bending length.

Dyeing of Untreated and Treated Cotton

All dyeing were carried out in a laboratory dyeing machine at liquor to material ratio of 20: 1, in the presence of 10–50 g ⁄ l of sodium chloride and 20 g ⁄ l of sodium bicarbonate using 2.0% dye on the weight of the sample. The sample was treated at 50°C for 10 min. The temperature was slowly raised to boil over 30 min and the dyeing was continued at boil for further 45 min. After samples were wash in cold running water for 30 minutes.

Evaluation of Dyed Samples

The effect of nano Cu treatment on the dyeability of cotton in terms of *K/S* was measured on computer color matching system Spectra Scan 5100 (RT) spectrophotometer interphased with computer color matching system.

Fastness Testing

The dyed sample was tested according to ISO standard methods. The specific tests used were: ISO 105-CO6 (C2S) for color fastness to washing; ISO 105-BO2 (1990) for color fastness to light.

Evaluation of Antimicrobial Activity

The untreated and treated samples were subjected to soil burial test as per AATCC Test Method 30-2004 [8]. After the stipulated period the samples were removed from soil, washed thoroughly with water and dried in air. The samples were then tested for breaking load on tensile tester.

RESULTS AND DISCUSSIONS

Copper nano particles were prepared by reduction of copper salt and stabilized with citrate anions. The nano cu particles in the solution were analyzed by particle size analyzer. The particles were also observed using SEM and AFM instruments .The presence of Cu was detected and measured by X-ray fluorescence spectrometer.

The formation of synthesized nano Cu was noticed by the change in the optical properties of the reaction solution. The optical properties of metal nanoparticles depend strongly upon the particle size and shape [9]. The blues-green color of $CuSO_4$ solution gradually changes to intense yellow when the particle size of copper reduced to nano level [10]. These effects are the result of the changes in the so-called surface plasmon resonance [11], the frequency at which conduction electrons oscillate in response to the alternating electric field of incident electromagnetic radiation. However, only metals with free electrons (essentially Au, Ag, Cu, and the alkali metals) possess plasmon resonances in the visible spectrum, which give rise to such intense colors. The aggregation of the particles was controlled with the help of citrate anions. The copper nano colloidal particles formed a negative surface charge due to the adsorbed citrate ions. Each sphere of Cu nano particles surrounded by citrate ions therefore repelled each other and prevented further aggregation.

The particle size and size distribution of the prepared and stabilized Cu colloid were analyzed on Malvern instrument. *Figure 1* shows the intensity size distribution of Cu nano particles dispersed in water.

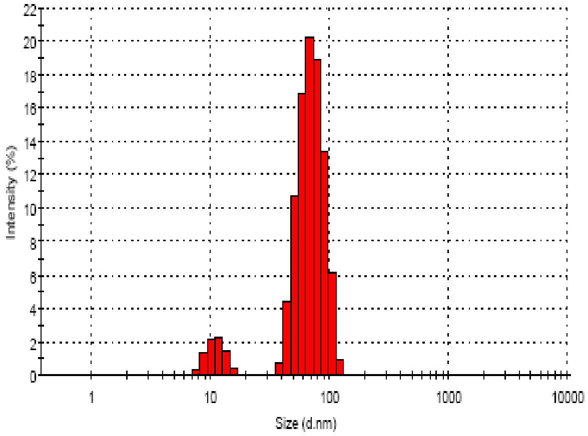


FIGURE 1. Particles Size and their distribution for synthesized Cu nano colloids

Figure 2 shows the scanning electron micrographs of stabilized Cu nano particles deposited on carbon coated aluminum sheet.

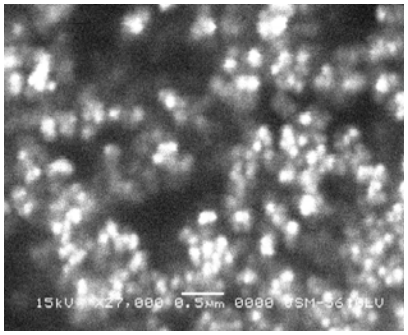


FIGURE 2. Scanning Electron Microscope (SEM) images of synthesised copper nano particles

The average size as seen from the scale of the photograph is about 60-100 nm which is also in agreement with the size distribution found using particle size analyzer. It can also be seen from the picture that the shape of synthesized particles is spherical.

The copper nano particles were deposited on glass plate for observation under atomic force microscopy (AFM). The size of nano Cu particles as seen from the scale on the AFM image (*Figure 3*) and topography lies below 100 nm, which also supports the results, obtained using particle size analyzer.

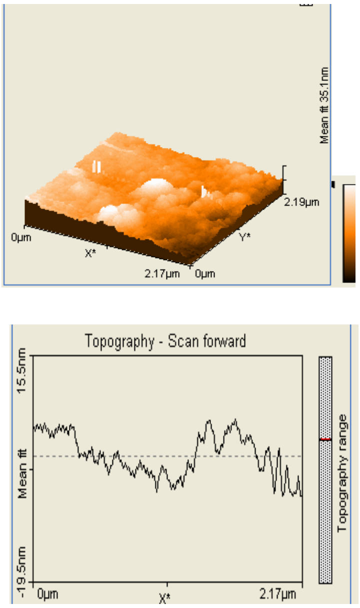


FIGURE 3. Atomic Force Microscopic image and topography of synthesized Cu nano colloids

Both the treated and untreated cotton were elementally analyzed using X- ray fluorescence spectroscopy for the detection and measurement of elemental copper.

TABLE I. Amount of copper detected with XRF

Structure	**Amount of copper, μg**
Cotton	Nil
Cu/Cotton fabric	0.19

The results given in *Table I* show that the amount of copper found on treated cotton was about 0.19 μg against nil for untreated one.

The effects of nano Cu treatment on the physical properties of cotton were examined and presented in *Table II*. It is seen from the results that introduction of nano copper particles into the structure of the fiber caused an improvement in the load bearing capacity of the fiber. The treatment could raise the breaking load of cotton by about 71%.

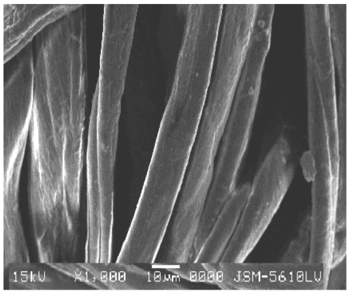
The nano copper particles because of their small size can enter in between the polymer molecules and perhaps act as fillers or cross linking agents which also contribute to the load sharing phenomenon during load application to the material. Unlike chemical cross linking which causes an improvement

TABLE II. Effect of cupper nano treatment on physical properties of cotton sample.

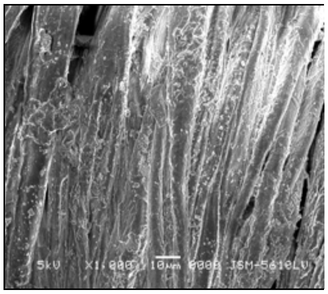
Sr. No.	**Sample**	**Breaking load (kg)**	**Crease recovery angle °(deg)**	**Bending length (cm)**
1.	Untreated cotton sample	8.02	90	1.05
2.	Cotton pre-treated with cu nano particles	13.75 (+71.44)	99 (+10.00)	1.50 (+42.86)

Note: Values in the parenthesis indicate percentage change in physical properties.

in crease recovery angle at the cost of imparting some rigidity in the material to an extent depending on the extent of cross linking, the incorporation of nano copper particles remained quite gentle in this regard. There was little improvement in crease recovery angle of the fiber with a little increase in bending length. Therefore though the particles entered in between the polymer chain molecules did not interfere much to the polymer flexibility of the system, the treatment was thus devoid of harshness to the material.



a) Untreated cotton fabric



b) Copper nano treated cotton fabric

FIGURE 4 Scanning Electron Microscope (SEM) images of (a) Untreated and (b) Treated cotton fabric.

From the SEM microphotograph of nano Cu treated cotton sample (*Figure 4b*), it can be clearly seen that the Cu nanoparticles are distributed on the surface of the treated cotton sample.

The Cu nanoparticle treated cotton fabric sample was dyed with three direct dyes and compared with the untreated samples. The *K/S* values of the nano copper pre-treated samples were found to be higher (*Table III*) than the corresponding untreated samples of cotton. The maximum improvement in color strength was observed with direct green 6 dye.

TABLE III. Effect of Cu nanoparticles on dyeing of cotton fabric with direct dyes

Sample	**Dye**	***K/S***
Untreated cotton sample	X	5.32
	Y	8.22
	Z	8.06
Cotton pre-treated with cu nano particles	X	7.36 (+38.34)
	Y	11.35 (+38.08)
	Z	13.17 (+63.39)

Note – Values in the parenthesis indicate percentage change in *K/S*, X – C.I. Direct Red 9, Y – C.I. Direct Blue 67 and Z –C.I. Direct Green 6

TABLE IV. Effect of Cu nanoparticles on the fastness properties of cotton fabric dyed with direct dyes.

Sample	**Fastness rating**								
	Light			**Washing**					
	X	**Y**	**Z**	**X**		**Y**		**Z**	
				A	**S**	**A**	**S**	**A**	**S**
Untreated cotton	3	3	3	2-3	2	2-3	2-3	2-3	2
Cu-nano treated cotton	4	4	4-5	4	4	4	4	4-5	4-5

Note X; Direct Fast Pink BD, Y; Direct Blue B, and Z; Direct Green 6, A; Change in depth, S: stain on cotton

The higher *K/S* values of nano treated samples indicate that the presence of nano metal particles increased the dye affinity towards the material. The copper nanoparticles in the fabric thus acted as mordant. The negatively charged dye anions got attracted towards the fiber probably due to the polarity developed in the metal particles by induction which resulted in better bonding between the dye and the fiber. The better coupling of the dye and fiber is also reflected in the improvement of the color fastness properties (*Table IV*). Where the Cu-nano treated / untreated and dyed fabrics after washing off using 2 g/l non-ionic detergent, the Cu-nano treated and dyed sample was almost remaining unaffected by the wash-off procedure. Thus copper nano pre-treatment not only improved the color strength but also improved the color fastness which is a major drawback of most direct dyes.

TABLE V. Effect of Cu nanoparticles on resistance of cotton bacterial attack

Sample	Breaking load		
	Before soil burial	After soil burial	% Change
Untreated cotton sample	8.02	6.50	-18.93
Cotton pre-treated with Cu nano particles	13.75	11.71	-14.80

Note – Values in the parenthesis indicate percentage change in *breaking load.*

Antimicrobial activity was measured by soil burial test and the results are shown in *Table V*. It is clear that the Cu-nano treatment was found to enhance the resistance of cotton towards microbial attack when measured in terms of loss in breaking load due to soil burial test. The breaking load of untreated control samples were reduced due to bacterial damage during soil burial test whereas copper nanoparticle treated sample could not only protect the sample against bacterial attack but also improved its strength. Metallic ions and metallic compounds display a certain degree of sterilizing effect. It is considered that part of the oxygen in the air or water is turned into active oxygen by means of catalysis with the metallic ion, thereby dissolving the organic substance to create a sterilizing effect [12]. With the use of nano-sized particles, the number of particles per unit area is increased, and thus antibacterial effects can be maximized.

CONCLUSIONS

The nanosized copper colloidal solution were prepared successfully and applied to cotton fabric; The average particle size was found to be about 60 nm. Cu nano treatment on cotton has been shown to improve the tensile strength of cotton fiber with little improvement in crease recovery angle and bending length. The Cu nano treatment was also found to enhance the dyeability of cotton with direct dyes. Both the wash and light fastness of direct dyed cotton were upgraded due to Cu nano pre-treatment. Cu-nano treatment also increased the resistance to microbial attack. Copper nano treatment thus increased the effective life span of the treated fabric.

REFERENCES

1. D P Chattopadhyay, *Textiles (The Textile Institute),* **1** (2006)21-24.
2. L Qian and J P Hinestroza, *Journal of Textile and Apparel, Technology and Management,* **4**(2004)1-7.
3. L Qian, *AATCC Review*, **4(**2004)14-16.
4. B F Smith and I Block, Textiles in Perspective, Prentice-Hall, Inc., NJ, (1982)326.
5. E R Trotman, Dyeing and Chemical Technology of Textile Fibers, John Wiley & Sons Inc., NY, (1984) 252-253.
6. L Lokyuen Li and H Junyan, *Textile Asia*, **114**(2003) 26.
7. D P Chattopadhyay and B H Patel, *Indian Journal of Fiber & Textile Research*, (2009) (In press).
8. AATCC TM 30-2004, Test-II, *AATCC Technical manual,* **81**(2006) 81.
9. X Gao, G Gu, Z Hu, Y Guo, X Fu & J Song, *Colloids and Surfaces A: Physico chemical Engineering Aspects,* **254** (2005)57 – 61.
10. Y Xia and N J Halas, *MRS Bulletin*, **30** (2005)338 – 343.
11. P V Kazakevich et al, *Quantum Electron*, **34** (2004) 951-956.
12. M Satio, *Journal of Coated Fabrics*, **23** (1993)150-164.

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Modification of Cotton Textiles with Nanostructural Zinc Particles

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Modification of Cotton Textiles with Nanostructural Zinc Particles

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In this work, zinc nanoparticles were prepared by wet chemical method. The particles were examined by particle size analyzer, their morphology and micro structure were observed and elementally detected through scanning electron microphotography. Antimicrobial properties were evaluated using soil burial test. The effect of zinc nanoparticle treatment on physical properties and dyeing performance of cotton was evaluated. The work opened up a new avenue of manufacturing a new generation cotton nanocomposites with barrier properties against microbe with improved physical as well as dyeing performances.

KEYWORDS *anti-microbial, zinc nanoparticles, cotton, particle size, synthesized*

INTRODUCTION

It is well known that cotton fabrics provide desirable properties such as absorbency, breathability, and softness. However, their applications are often limited due to their inferior strength, crease resistance, and resistance toward microbes. With recent advancement in nanotechnology, it has been now possible to develop next-generation cotton fabrics with improved performance by introducing nanostructural elements. In recent years nanosize particles of Pd/Pt, Ag and Fe can be applied on textiles to impart antibacterial, conductive, magnetic, and remote heating properties. Silver has been used for the treatment of medical ailments for over 100 years because of

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Address correspondence to D. P. Chattopadhyay, Department of Textile Chemistry, Faculty of Technology & Engineering, The M S University of Baroda, Baroda, Gujarat, India. E-mail: dpchat6@gmail.com its natural antibacterial and antifungal properties. Nanosilver particles are widely applied in socks to prohibit the growth of bacteria. In addition, nanosilver can be applied to a range of other healthcare products such as dressings for burns, scald, and skin donor and recipient sites. Nanosilver particles can be applied on textiles by padding method with good laundering durability. Chattopadhyay (2006) has reported that the nanosized silver colloids and nanosilver-treated polyester nonwovens have good bacteriostasis. Water- and ethanol-based nanosilver colloids with spherical nanoparticles of diameter 2–5 nm can be applied to polyester nonwoven fabric. It has been reported that the growth of bacteria colonies is absolutely inhibited with only 10-ppm colloidal silver nanoparticles.

Nanosize particles of TiO_2, ZnO, Al_2O_3, and MgO are a group of metal oxides that possess photocatalytic ability, electrical conductivity, UV absorption, and photo-oxidizing capacity against chemical and biological species (Patel and Chattopadhyay 2007). Intensive research involving the nonoparticles of metal oxides has been focusing on antimicrobial, self-decontaminating, and UV-blocking functions for both military protection gears and civilian health products. A composite fiber with nanoparticles of TiO_2/MgO can provide self-sterilizing function. TiO_2 and MgO nanoparticles can be entrapped into textile fibers during the spinning process or incorporated into a textile material via normal textile finishing methods with a resultant material having chemical and biological protective performance (Qian and Hinestroza 2004). Many studies are reported (Banerjee et al. 2002; Sójka-Ledakowicz et al. 2008; Yadav et al. 2006) on the synthesis and application of ZnO nanomaterials to textiles. However, the application of Zn nano-treatment on other physical and chemical properties of textiles is hardly found in the literature. Earlier we have reported the effect of Ag and Cu nanoparticles on physical properties of textiles (AATCC Test Method 30-2004 2006; Chattopadhyay and Patel 2009; Patel and Chattopadhyay 2008). In this study, we have synthesized Zn nanoparticles, characterized and applied to cotton textiles. The effects of such treatment on physical, chemical, and microbial properties of cotton fabric were studied.

EXPERIMENTAL

Materials

FABRIC

Mill-scoured and bleached cotton fabric (plain weave with a weight of 238 g/m^2 and a density of 44 threads/cm in the warp and 28 threads/cm in weft directions) was procured from local market and was used in the present investigation. The fabric was thoroughly washed, neutralized, and air-dried.

DYES AND CHEMICALS

Three commercial direct dyes, namely Direct Fast Pink BD [X], Direct Blue B [Y], and Direct Green B [Z] were selected for this study without any further purification. Zinc nitrate ($Zn (NO_3)_2.6H_2O$, M.W. 297.47), sodium borohydride ($NaBH_4$, M.W. 37.83), and tri-sodium citrate ($C_6H_5Na_3O_7.2H_2O$, M.W. 294.10) of analytical grade purity were procured from Sd Fine Chemicals, India.

Methods

PREPARATION OF ZN NANOCOLLOIDS

Zinc nanoparticles were prepared by wet chemical method using zinc nitrate and sodium borohydride as reducing agents and tri-sodium citrate as stabilizing agent. A 100-ml solution of (1×10^{-3} M) $ZnNO_2$, kept in a specially designed reaction chamber, was slowly reduced by dropwise addition of 5-ml solution of sodium borohydride (2×10^{-3} M). During the process of reaction the solution mixture was stirred vigorously. As the dropwise addition of sodium borohydride solution was completed, 5 ml of 1% tri-sodium citrate was added drop-by-drop with vigorous stirring. The reaction was allowed to proceed for 2 h after complete addition of tri-sodium citrate. Distilled water was used for preparing the solutions of all the chemicals.

CHARACTERIZATION TECHNIQUES

The particle size and size distribution of the Zn colloid were analyzed on the particle size analyzer (Malvern Instrument, DTS version 4.20, U.K.). For Energy Dispersive X-ray (EDX) analysis of the synthesized nanoparticles, the particles were deposited on carbon-coated aluminum sheet and further coated with gold and were observed on Scanning Electron Microscope (SEM) (model JSM5610LV, version 1.0, Jeol, Japan) using Oxford-Inca software (U.K.). The morphology of Zn nanoparticles deposited on carbon-coated aluminum sheet was observed in SEM. The amount of Cu as element in the polymer structure was detected and measured using an X-ray fluorescence spectrometer (EDX 800 Simadzu, Japan). The operating X-ray source voltage and current were 35 kV and 26 mA, respectively. Registration time was 30 s and the investigated area was 78.5 mm^2.

DEPOSITION OF ZINC NANOPARTICLES ON TEXTILES

Zinc nanoparticles were applied to the cotton fabric by dipping in the dispersion for 10 min and then padded using an automatic padding mangle applying 2-dip, 2-nip padding sequence at 70% expression. The padded substrates were air-dried for 2 h and finally cured at 120°C for 20 min in a preheated curing oven.

EVALUATION OF ANTIMICROBIAL ACTIVITY

The untreated and treated samples were subjected to soil burial test for 7 days as per the standard method (AATCC Test Method 30-2004 2006). After the stipulated period the samples were removed, washed with water, and dried in air. The samples were then tested for breaking load, crease recovery angle, and bending length (AATCC Test Method 66-2003 & AATCC Test Method 115-2005 2006).

DYEING PROCEDURE

Dyeing of well-prepared fabric samples was carried out on laboratory constant temperature water bath (Paramount, India), using conventional dyeing method for individual fabrics with 2% (owf) direct dye (Trotman 1994), using liquor ratio of 40:1. After dyeing, all the dyed samples were rinsed, washed thoroughly, and dried at ambient temperature.

MEASUREMENT OF COLOR VALUES

The dyed samples were assessed for K/S values using computer color matching system (illuminant D65/10° observer, Spectra scan 5100 RT, Spectrophotometer, Premier Colorscan Instrument, India).

FASTNESS TESTS

The light fastness of the dyed samples was tested on Fad-o-meter (FDA-R, Atlas, U.S.A.) after partial exposing of samples to the xenon arc lamp for 16 h and graded for color change with the ratings. The wash fastness of the samples was performed as per ISO-2 tests using launder-o-meter (Digi.wash, Paramount Scientific Instruments, India). Samples were evaluated for rating in terms of color change.

RESULTS AND DISCUSSIONS

Characterization of Zn Nanoparticles

The particle size and size distribution of the prepared and stabilized Zn colloid were analyzed on Malvern instrument. Figure 1 shows the intensity size distribution of Zn nanoparticles dispersed in water. Figure 2 shows the scanning electron micrographs of Zn nanoparticles. The average size as seen from the scale of the photograph is below 100 nm, which is in agreement with the size distribution found using particle size analyzer. Figure 3 shows the elemental analysis result, which confirms the presence of zinc. Both the treated and untreated cotton were observed by SEM (Figure 4) and analyzed

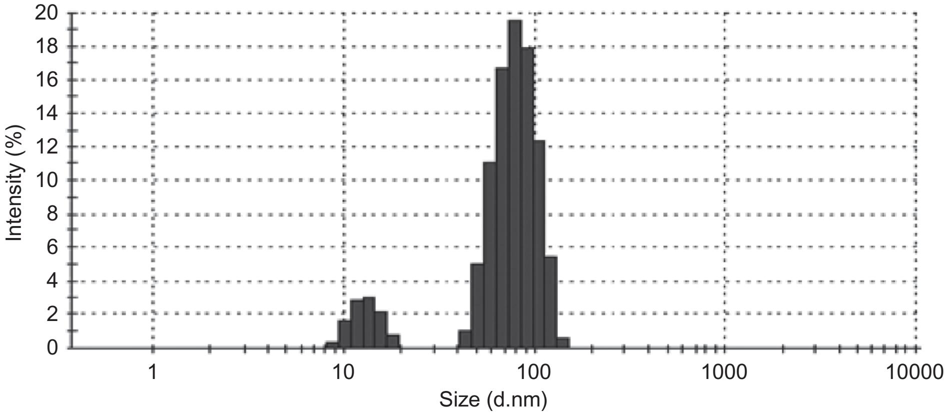

FIGURE 1 Particles size distribution of Zinc nano particles.

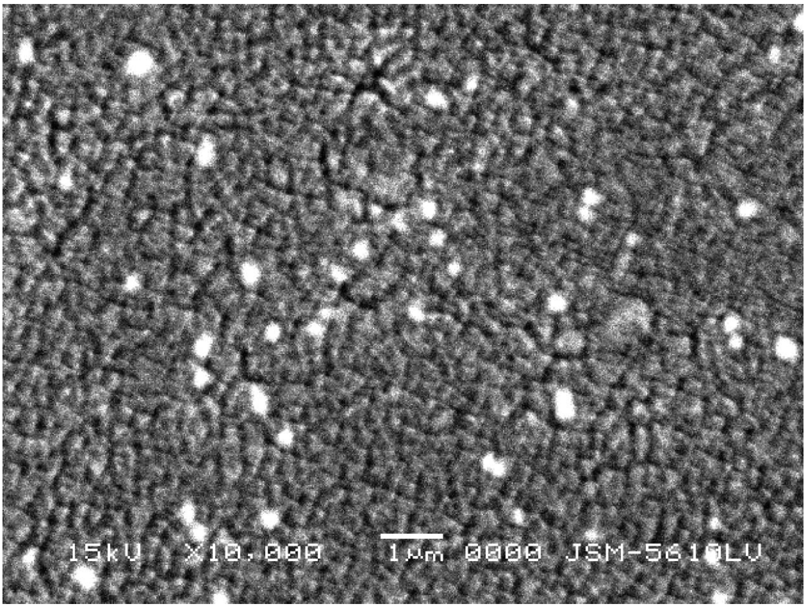

FIGURE 2 Scanning electron microscopic image of synthesised zinc nano-particles.

elementally by X-ray fluorescence spectroscopy for the detection and measurement of elemental zinc. The amount of zinc found on the treated cotton was about 1.16% against no zinc on untreated cotton.

Effect of Zn Nanoparticles on Physical Properties

The effects of nano-Zn treatment on the physical properties of cotton were presented in Table 1.

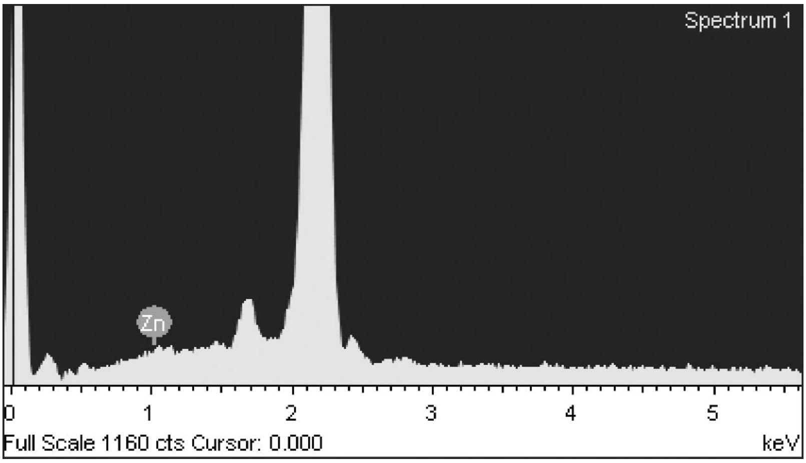

FIGURE 3 Elemental analysis of nano-particles using Oxford-Inca software in SEM.

TABLE 1 Effect of Zinc Nano-Treatment on Physical Properties of Cotton

Sample	Breaking load (kg)	Bending length (cm)	Crease recovery angle (°)
Before Zn nano-treatment	8.02	1.05	90
After Zn nano-treatment	8.83 (+10.09)	1.85 (+76.19)	105 (+16.66)

Note: Values in parentheses indicate percentage change in physical properties.

It is seen from the results that introduction of nano-Zn particles into the structure of fiber caused an improvement in the load bearing capacity of the fiber. Improvements in the bending length and crease recovery angle of the treated cotton are also observed. These may be due to the interference of Zn nanoparticles with polymer chain mobility. From the SEM microphotograph of nano-Zn-treated cotton sample (Figure 4b), it is clearly seen that the Zn nanoparticles are distributed on the surface of the treated cotton sample; being distributed in polymer matrices, nanoparticles can carry load and increase the toughness and abrasion resistance; and nano-fillers can transfer away stress from polymer matrices and enhance tensile strength of the treated fiber.

Effect of Zn Nanoparticle Treatment on Dyeing

The Zn nanoparticle-treated cotton fabric sample was dyed with three direct dyes and compared with the untreated samples. The K/S values of the nano-zinc pretreated samples were found to be higher (Table 2) than the corresponding untreated samples of cotton. The maximum improvement in

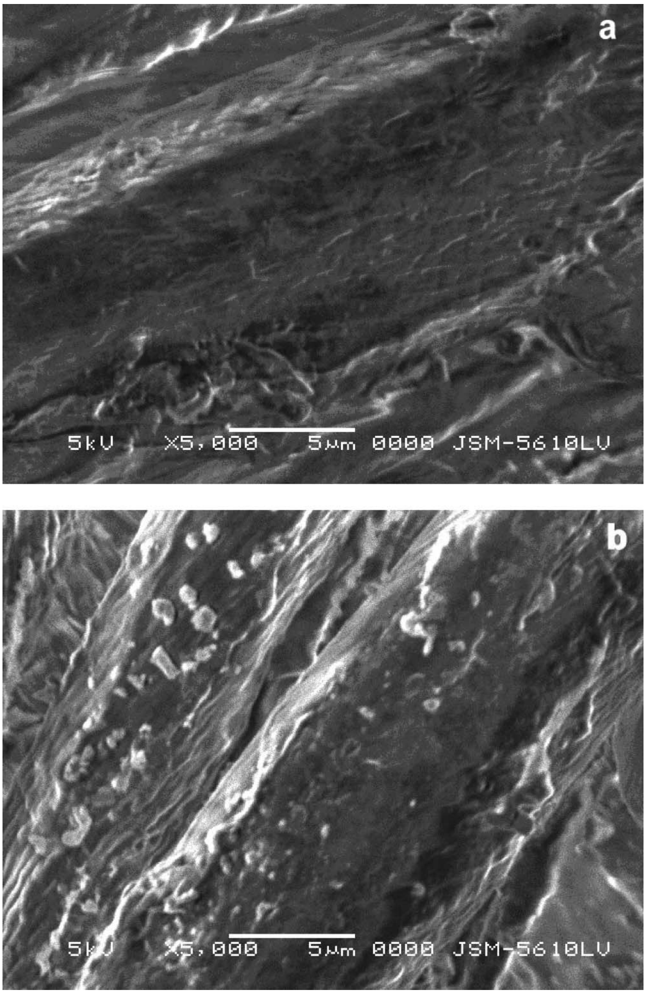

FIGURE 4 Scanning Electron Microphotographs of (a) untreated and (b) treated cotton fabric.

color strength was observed with direct Green 6 dye. The higher K/S values of nano-Zn-treated samples indicate that the presence of nano-metal particles increased the dye affinity toward the material. The Zn nanoparticles in the fabric thus acted as mordant. The better coupling of the dye and fiber is also reflected in improvement of the color fastness properties (Table 3), which is a major drawback of most direct dyes.

Effect of Zn Nanoparticles on Resistance Against Microbes

The antimicrobial activity was measured by the soil burial test and the results are shown in Table 4. It is clear that the Zn nano-treatment was found to

TABLE 2 Effect of Pretreatment with Zn Nanoparticles on Dyeability of Cotton Fabric with Direct Dyes

	Color strength (K/S)		
Sample	X	Y	Z
Control	5.32	8.22	8.06
Nano-treated	5.87 (22.18)	9.24 (28.34)	10.76 (39.20)

Note: Values in parentheses indicate percentage change in K/S, X = C.I. Direct Red 9, Y = C.I. Direct Blue 67, and Z = C.I. Direct Green 6.

TABLE 3 Effect of Zn Nanoparticles on the Fastness Properties of Cotton Fabric Dyed with Direct Dyes

	Fastness to					
	Light			Washing (color change)		
Sample	X	Y	Z	X	Y	Z
Untreated cotton	3	3	3	2–3	2–3	2–3
Nano-treated cotton	3–4	3–4	4	4	3–4	3–4

Note: Values in parentheses indicate percentage change in K/S, X = C.I. Direct Red 9, Y = C.I. Direct Blue 67, and Z = C.I. Direct Green 6.

TABLE 4 Effect of Zn Nanoparticles on Resistance Towards Bacterial Attack

	Breaking strength (kg)		
Sample	Before soil burial	After soil burial	Change (%)
Untreated cotton	8.02	4.32	−46.13
Zn nano-treated	8.83	7.44	−15.74

enhance the resistance of cotton toward microbial attack when measured in terms of loss in breaking load because of the soil burial test. The breaking load of untreated control samples was reduced due to bacterial damage during the soil burial test, whereas zinc nanoparticle-treated sample resisted against the bacterial attack. This might be due to the sterilizing effect of metallic ions and metallic compounds (Saito 1993).

CONCLUSIONS

The nano-structural zinc particles were prepared successfully and applied to cotton fabric; the average particle size was found to be about ~ 80 nm. Zn nano-treatment on cotton has been found to improve the tensile strength of cotton fiber with little improvement in crease recovery angle and bending length. The Zn nano-treatment enhanced the dyeability of cotton with improved fastness properties for direct dyes. The resistance of cotton to microbial attack was also improved by Zn treatment.

REFERENCES

AATCC Test Method 30-2004. 2006. *AATCC Technical Manual*, 81.

AATCC Test Method 66-2003 & AATCC Test Method 115-2005. 2006. *AATCC Technical Manual*, 81, 97, and 183.

Banerjee, S., A. Dan, and D. Chakravorty. 2002. Review synthesis of conducting nanowires. *Journal of Materials Science* 37: 4261–4271.

Chattopadhyay, D. P. 2006. Nanotechnology—the emerging trends. *Textiles* 33: 21–24.

Chattopadhyay, D. P., and B. H. Patel. 2009. Improvement in physical and dyeing properties of natural fibres through pre-treatment with silver nanoparticles. *Indian Journal of Fibre & Textile Research* 34: 368–373.

Patel, B. H., and D. P. Chattopadhyay. 2007. Nano-particles & their uses in textiles. *The Indian Textile Journal* 118: 23–31.

Patel, B. H., and D. P. Chattopadhyay. 2008. Improvement in the properties of cotton textiles through the application of synthesized Cu nano-particles. Paper presented at the Workshop on Synthesis and Characterisation of Nano-structured Materials (SCNM-08), March 30, at the M S University of Baroda, Vadodara in Gujarat, India.

Qian, L, and J. P. Hinestroza. 2004. Application of nanotechnology for high performance textiles. *Journal of Textiles and Apparel, Technology and Management* 4: 1–7.

Saito, M. 1993. Coated fabrics. *Journal of Coated Fabrics* 23: 150–164.

Sójka-Ledakowicz, J., J. Lewartowska, M. Kudzin, T. Jesionowski, K. Siwińska-Stefańska, and A. Krysztafkiewicz. 2008. Modification of textile materials with micro- and nano-structural metal oxides. *Fibres & Textiles in Eastern Europe* 16: 112–116.

Trotman, E. R. 1994. *Dyeing and chemical technology of textile fibres*, 6th ed. Delhi, India: BI Publishers.

Yadav, A., V. Prasad, A. A. Kathe, S. Rraj, D. Yadav, C. Sundaramoorthy, and N. Vigneshwaran. 2006. Functional finishing in cotton fabrics using zinc oxide nanoparticles. *Bulletin of Materials Science* 29: 641–645.

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Research Paper

Preparation, Characterization and Stabilization of Nano-sized Copper Particles

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Abstract: *Cu nanoparticles dispersed in water were prepared by the reduction of Cu^{+2} originated from the copper salt solution. The stability of the Cu nanoparticles in dispersion was monitored through the analysis of the absorbance spectra at different stages during the process of synthesis. The stability of the Cu nanoparticles dispersed in aqueous medium was investigated after different time intervals. Cu colloid was found to be stable up to 18 hours without major aggregation under atmospheric condition. The size and size distribution of the particles were examined by particle size analyzer. The morphology of the particle synthesised was examined by SEM and AFM. After 24 hours of storage in open air there was some agglomeration of nanoparticles as observed by particle size analyzer and AFM studies. But found stable with the use of 1 % trisodium citrate as stabilizer.*

Keywords*:* Absorbance, Copper, Nanoparticles, Particle size, Plasmon resonance.

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1. Introduction

In recent decades, nanotechnology has attracted scientists from many different areas. The fundamentals of nanotechnology lie in the fact that properties of substances dramatically change when their size is reduced to the nanometre range [1, 2]. When a bulk material is divided into small size particles with one or more dimensions (length, width, or thickness) in the nanometre range or even smaller, the individual particles exhibit unexpected properties which are different from those of the bulk material. It is known that atoms and molecules possess totally different behaviour than those of bulk materials; while the properties of the former are described by quantum mechanics, the properties of the latter are governed by classic mechanics. The behaviour of a material changes between these two distinct domains and the nanometre range is considered as the threshold for the transition of a material's behaviour.

Metal nanoparticles, due to their special properties and also small dimensions, find important applications in optical, magnetic, thermal, sensoric devices, catalysis, etc. Many metal nano particles are under active research because they posses interesting physical properties differing considerably from that of the bulk phase [3]. It comes from the small sizes and high surface/volume ratio. The most common method employed for the synthesis of metal nanoparticles is the reduction of metal ions in solution [4, 5, 6]. However, the control of size and shape at the nanometer level is a real problem, as the mechanism of size/shape control is still left largely unresolved.

In this work, an attempt has been made to analyse formation of Cu nanoparticles from copper salt at different stages of synthesis as well as after storing for variable time in atmospheric condition. The effect of time after synthesis on the shape and size of these particles was investigated using Particle size analyzer, SEM and AFM systems. Further, the effect of trisodium citrate as stabilizer for the nano particles was also investigated.

2. Experimental

2.1 Preparation of Cu Colloid

Copper sulphate $CuSO_4$, sodium borohydride $NaBH_4$ and tri-sodium citrate $C_6H_5O_7Na_3$ of analytical grade purity were used without further purification as starting materials.

The copper colloid was prepared using chemical reduction method. The solutions of all the reacting materials were prepared in distilled water. 100 ml of $1 \cdot 10^{-3}$ M $CuSO_4$ solution kept in a specially designed reaction chamber was reduced by drop wise addition of highly dilute and chilled solution of sodium borohydride in a nitrogen atmosphere. During the process of reaction, the solution was stirred vigorously. As the colour of the solution turned to light yellow 5 ml of 1 % trisodium citrate was added drop by drop as stabilizer.

2.2 Analysis Techniques

The absorbance of colloidal solution was recorded at different stages of synthesis using UV-visible spectrophotometer (Shimadzu UV-2450, Japan) in the wavelength range: 300 nm to 700 nm. Particle size and size distribution of the Cu colloid were analyzed using particle size analyzer (Malvern instrument, DTS version 4.20. U.K.), Copper nanoparticles were deposited on carbon coated aluminium sheet and on glass plate for examination in scanning electron microscope (SEM) and atomic force microscope (AFM) respectively. Morphology of Cu nanoparicles deposited on glass plate was examined with an Atomic Force Microscope (easy Scan 2, Nanosurf AG, Switzerland) operating in a contact mode (cantilever force constant 3 N/m). Image processing and analysis of the Scanning Electron Microscopy data was performed on SEM instrument (model JSM5610LV, version 1.0, Jeol, Japan). The synthesized nano particles were also elementally detected on SEM using oxford –Inca software (Oxford, U.K.).

3. Results and Discussion

3.1 Optical Properties of Cu Colloid

Figure 1 (a, b and c) represent the absorption spectra of different stages during the formation of Cu nanoparticle colloid from copper sulphate solution. It is seen from the adjacent photographs of the absorbance curves that a blue green solution of copper sulphate gradually turned to yellow indicating the formation of Cu nanoparticles. The shifting of colour is due to the surface plasmon resonance, with a significant contribution from the interband transition which produces yellow colour hydrosol having maximum absorption at 580 nm (Figure 1 c & d) indicating nano Cu particles generation. The plasmon resonance of Cu nano particles was also observed at near 580 nm by Kazakevich et al [7]. Metals with free electrons possess plasmon resonances in the visible spectrum, which give rise to such intense colours. These properties are mainly observed in Au, Ag, and Cu because of the presence of free conduction electrons. The electric field of the incoming radiation induces the formation of a dipole in the nanoparticle. A restoring force in the nanoparticle tries to compensate for this, resulting in a unique resonance wavelength [8]. The oscillation wavelength depends on a number of factors, among which particle size and shape, as well as the nature of the surrounding medium, are the most important factors [9]. For elemental analysis, the synthesized nanoparticles were deposited on carbon coated aluminium sheet and the particles on the sheet were further coated with gold which was then observed on SEM-Inca instrument. Fig.4 (a) shows the image of this observation and the elemental analysis results presented in Fig. 4(b) confirms the presence of copper particles.

To monitor the stability of the Cu colloid in air, we have measured the absorption of the colloid after different periods of time. The UV-VIS spectrums recorded after different time intervals are shown in Figure 2 (a, b and c). There was no change in peak position for 12 hrs and 18 hrs (Figure 2a and 2b) except for the increase of absorbance. As the particles gain in size, the absorption peak usually shifts towards redder side as we find in Figure 2c. Increase in absorption indicates that the quantity of Cu nanoparticles increased. The stable position of absorbance peak in Figure 2a and 2b indicates that new particles do not aggregate. During the initial trial experiments when Cu nanoparticles were synthesized without the addition of trisodium citrate, the yellow colour of the solution was persisted for few hours only in atmospheric condition. Therefore, trisodium citrate was introduced into the system as a stabilizer. Since the Cu colloidal particles possessed a negative charge due to the adsorbed citrate ions, a repulsive force worked along the particles and prevented further aggregation. But after storing for 24 hrs or more in atmospheric condition the wavelength for maximum absorbance was found to be slightly shifted towards redder side which indicates aggregation of the particles even after the addition of citrate anions. However the scanning electron micrographs (SEM) of Cu nanoparticles (Fig. 5) evident that the average size of the synthesized and citrate anions stabilized nano particles was below 100nm even after 4 weeks.

The particle size distributions of the freshly prepared nano Cu colloid and after storing for 24 hours (Fig 3a & Fig 3b) in atmospheric condition were analyzed on Malvern instrument. It is seen that the size of the majority of the nanoparticles when prepared fresh was about 70 nm but after storage for 24 hours the same was increased to about 400 nm. This is due to the aggregation of nanoparticles which resulted a broadening of peak in Fig.3b.

Stability of the nano Cu particles synthesised in absence of tri-sodium citrate was not satisfactory as observed from the rapid change in colour of the yellow coloured solution. AFM pictures of freshly prepared Cu nano particles and after storing for 24 hours in air are represented in Fig. 6. From the AFM pictures we can see that the size of nanoparticles is slightly increased, after 24 hours. However, when tri-sodium citrate was used, the particle size was controlled up to 4 weeks, which is also supported by the scanning electron micrographs of Cu nanoparticles (Fig. 5 a & b). Cu nanoparticles because of their high reactivity tend to form aggregates. The tendency of getting aggregated was controlled by the citrate anions.

4. Conclusions

Nano Cu colloids were successfully prepared, by reducing Cu^{+2}, using chemical bath deposition technique. The absorbance spectrum of the solution was determined at different stages of the synthesis process. The plasmon resonance absorbance of yellow coloured nano colloids was noticed at 580 nm. These particles were elementally detected by SEM-inca software. The particle size and their distribution, of freshly prepared system and after storing for 24 hours in atmospheric condition, were examined by particle size analyzer shows that the maximum size of the particle was increased from 70 nm to 400 nm during storage for 24 hours. The stability of the particles was improved by the introduction of citrate anions in the colloidal system. Addition of citrate anions resists major agglomeration of particles.

Figures

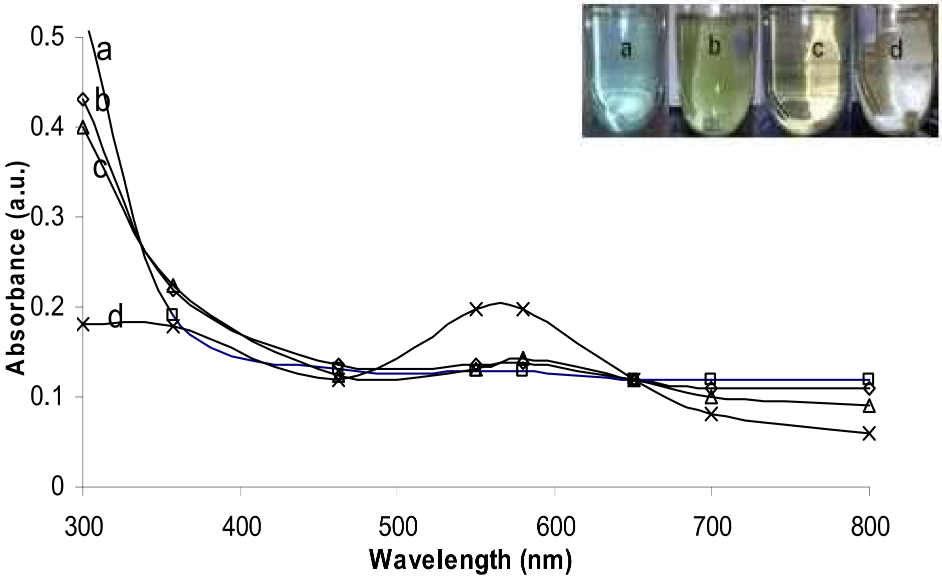

Fig. 1 The UV-VIS spectrums of Cu nano colloids at different stages of synthesis [(a) Stage 1: Cu salt solution, (b) Stage 2: After the addition of reducing agent, (c) Stage 3: formation of Cu nano colloids and (d) Stage4: stabilized Cu nano colloids.]

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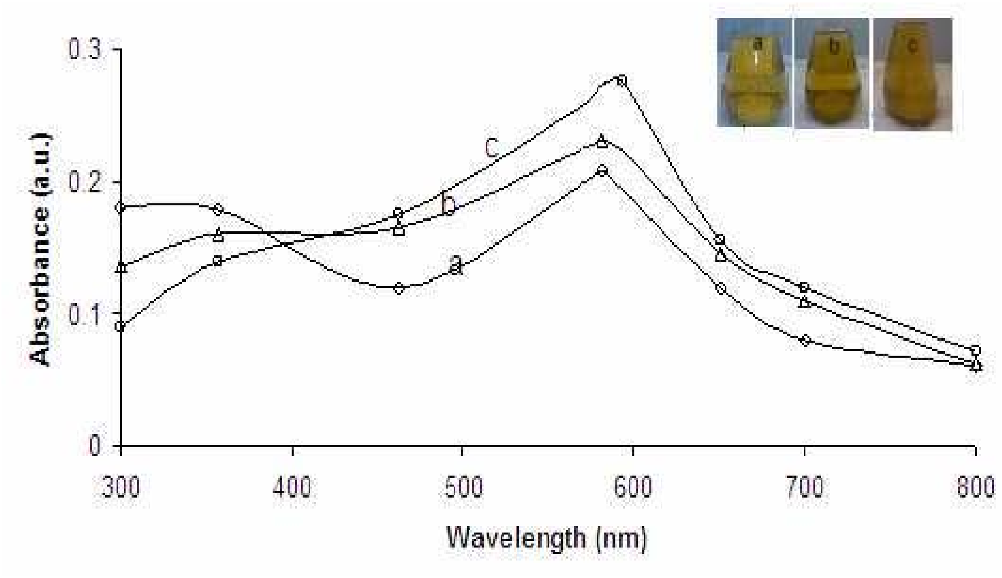


Fig. 2 UV-VIS spectra of Cu nano colloids [Time after synthesis: (a) 12 hours, (b) 18 hours and (c) 24 hours]

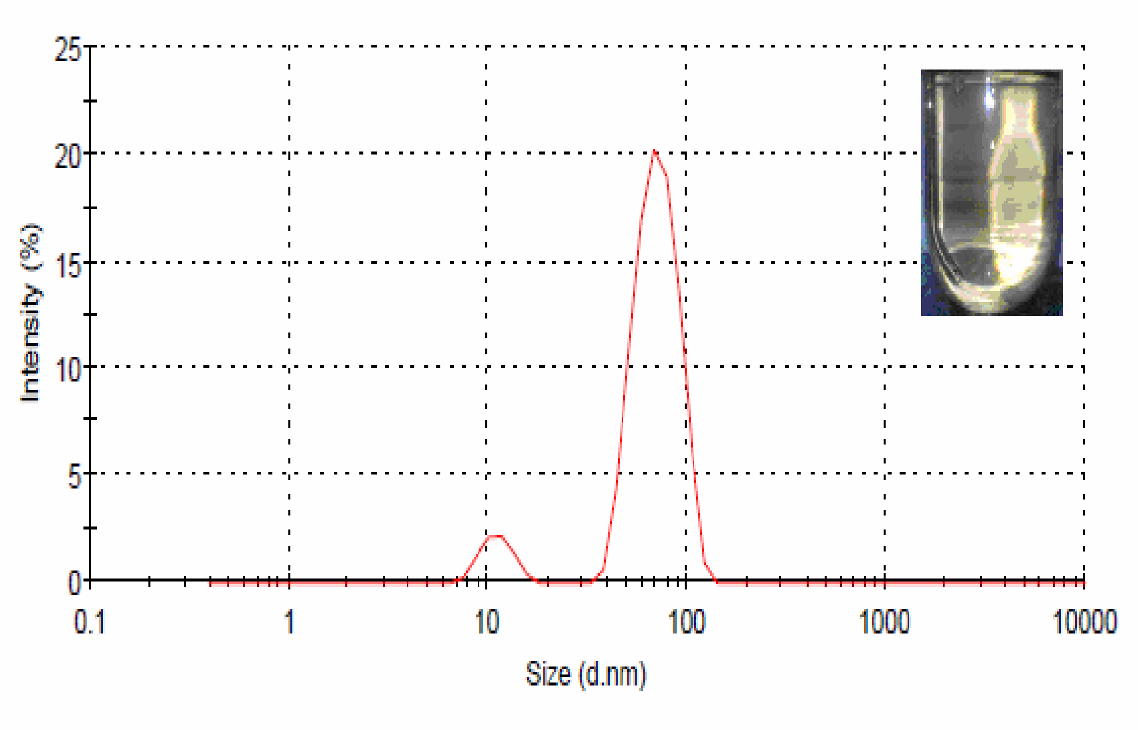


Fig. 3 (a) Particles Size and their distribution for freshly prepared Cu nano colloids

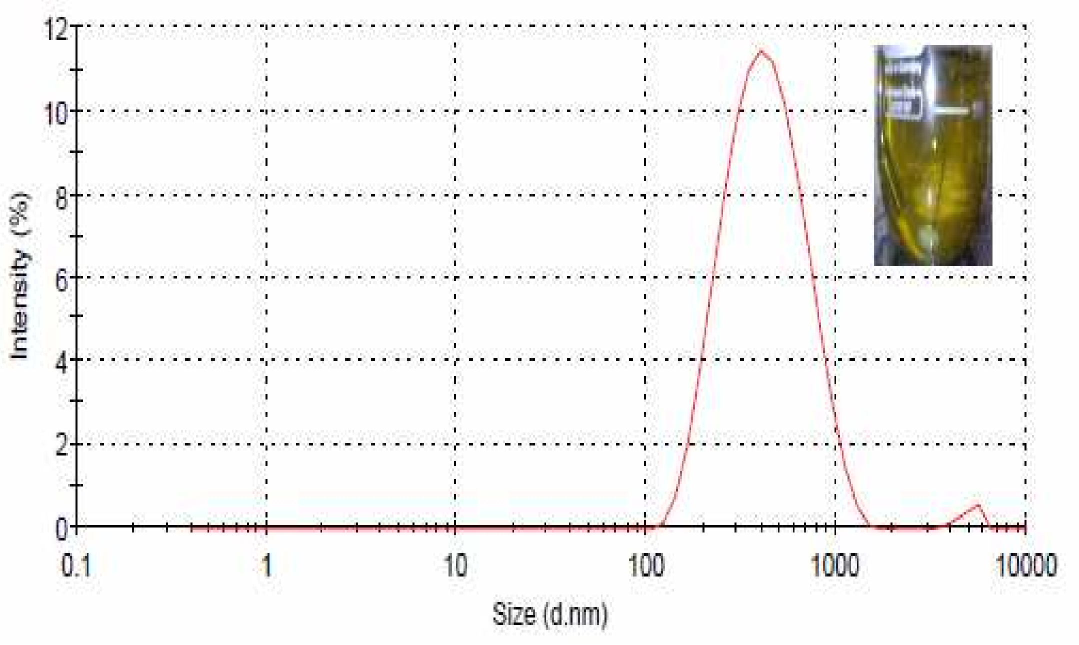


Fig. 3 (b) Particles Size and their distribution after storing for 24 hours

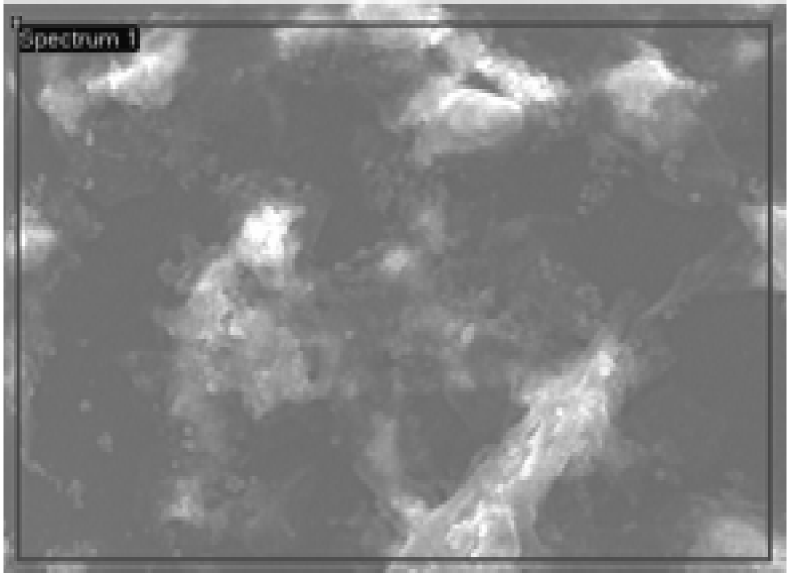


Fig. 4 (a) Selected area of gold coated Cu nano particles for SEM – Inca elemental analysis

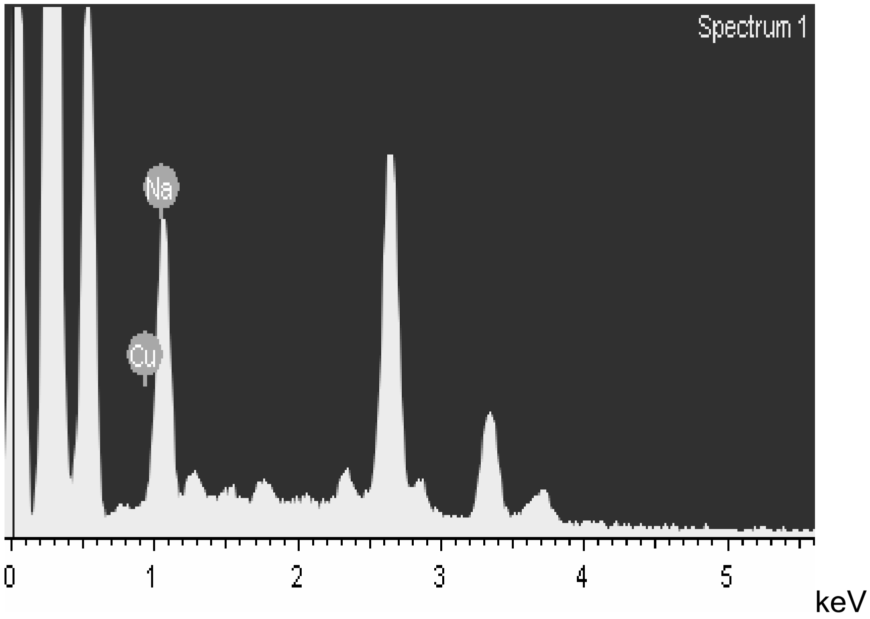
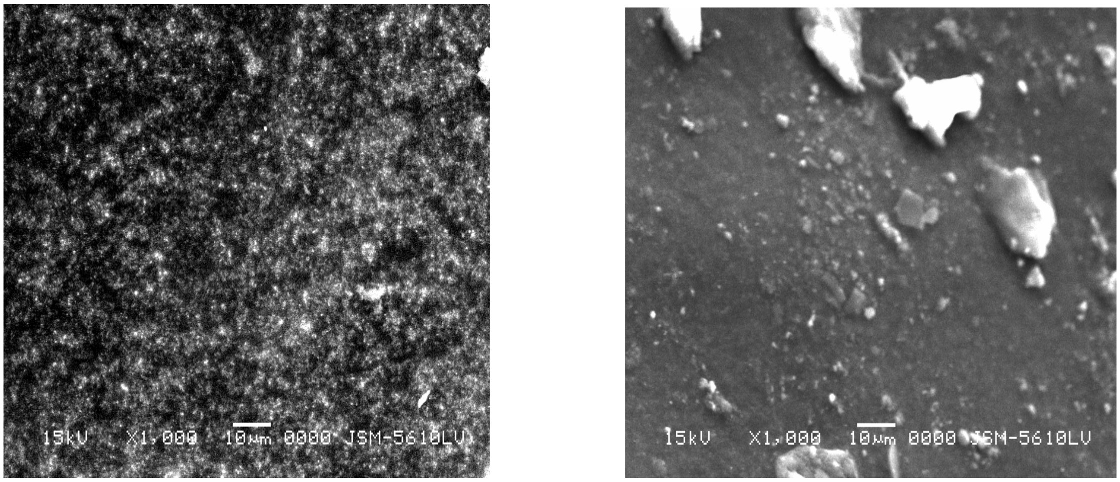
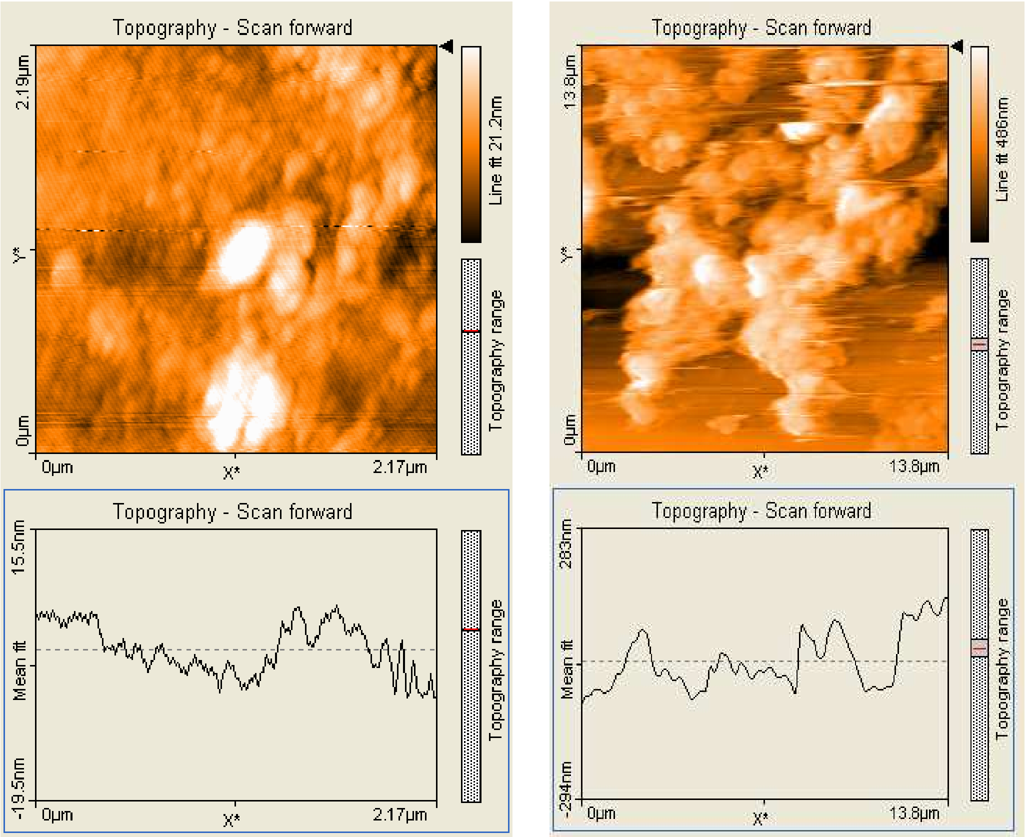


Fig. 4 (b) Elemental analysis of the synthesised particles using Inca software



(a) **(b)**

Fig.5 Scanning Electron Microscope (SEM) images of synthesised copper nano particles [(a) freshly prepared ; (b) after 4 weeks of synthesis]



(a) (b)

Fig. 6 (a) Atomic force microscopic image of freshly prepared Cu nano colloids and (b) After storing over 24 hrs

References

[1] D.P. Chattopadhyay, Nanotechnology-the emerging trends, *Textiles*, 33 (2006), 21-24.

[2] B.H. Patel and D.P. Chattopadhyay, Nano-particles and their uses in textiles, *The Indian Textile Journal*, 118 (2007), 23-31.

[3] D.P. Chattopadhyay and B.H. Patel, Improvement in physical and dyeing properties of natural fibres through pre-treatment with silver nano particles, *Indian Journal of Fibre & Textile Research*, 34 (2009), 368-373.

[4] D.P. Chattopadhyay and B.H. Patel, Modification of cotton textiles with nano structural zinc particles, *Journal of Natural Fibers*, 8 (2011), 39-47.

[5] D.P. Chattopadhyay and B.H. Patel, Effect of nano sized colloidal copper on cotton fabric, *Journal of Engineered Fiber Fabrics*, 5 (2010), 1-6.

[6] N.R. Jana, Z.L. Wang, T.K. Sau and T. Pal, Seed-mediated growth method to prepare cubic copper nano particles, *Current Science*, 79 (2000), 1367-1370.

[7] P.V. Kazakevich, V.V. Voronov, A.V. Simakin and G.A. Shafeev, Production of copper and brass nano particles upon laser ablation in liquids, *Quantum Electron*, 34 (2004), 951-956.

[8] A. Henglein, Physicochemical properties of small metal particles in solution: microelectrode reactions, chemisorptions, composite metal particles and the atom-to-metal transition, *J. Phys. Chem.*, 97 (1993), 5457–5471.

[9] P. Mulvaney, Surface plasmon spectroscopy of nanosized metal particles, *Langmuir*, 12 (1996), 788-800.

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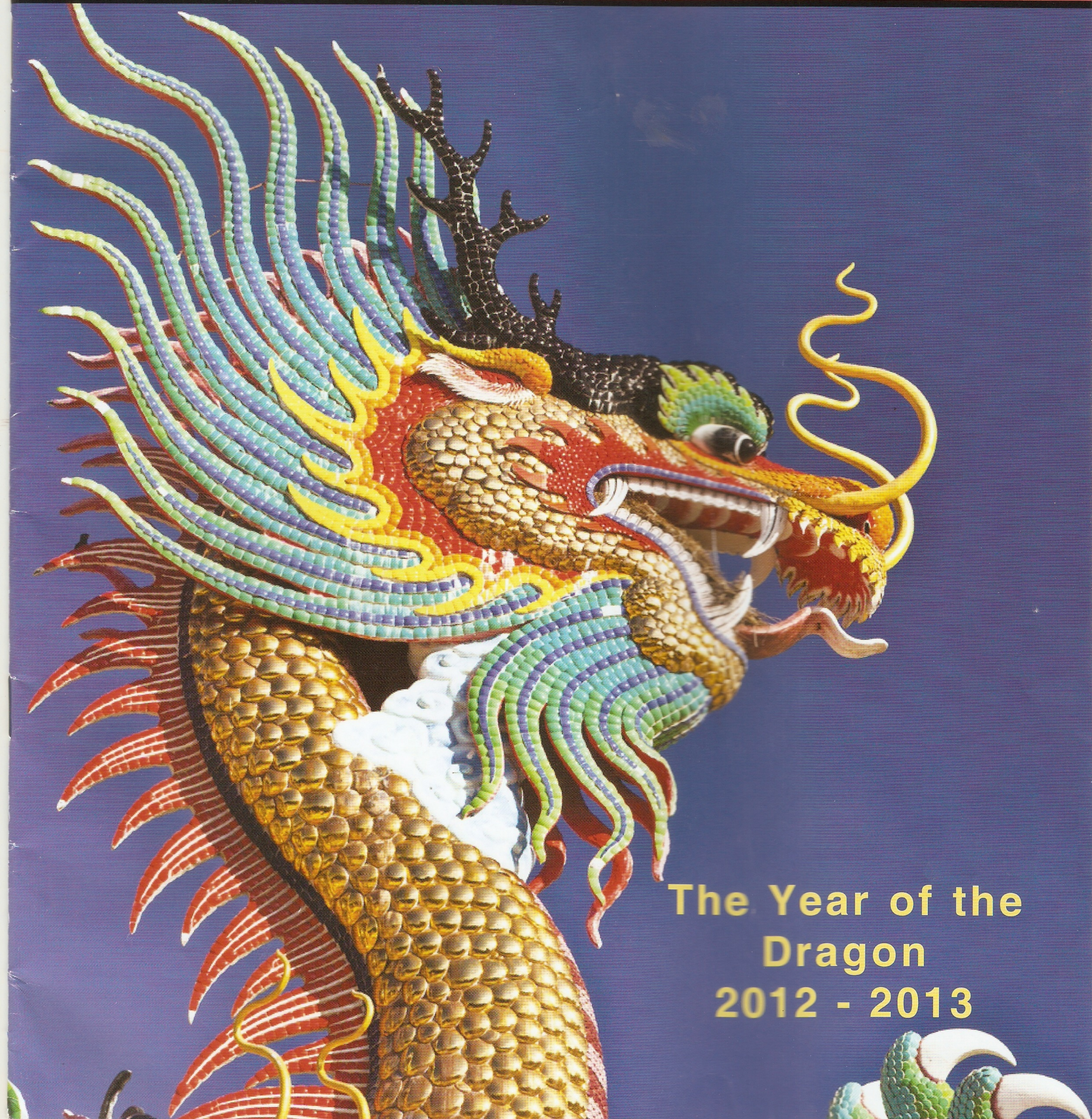

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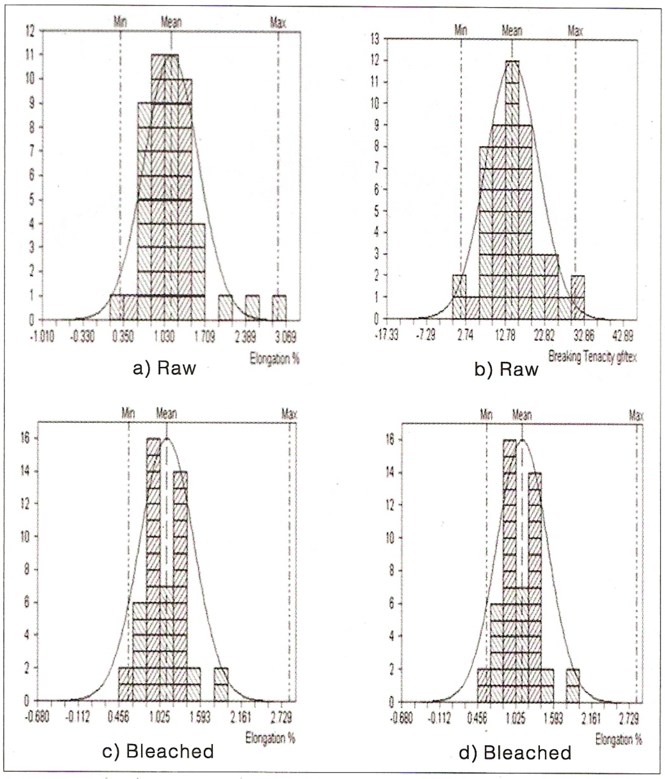

a) Raw b) Raw

c) Bleached d) Bleached

Figure 9 The Histograms of elongation and breaking tenacity of raw and bleached fibre

The histograms presented in Figure 9 provide information for the number of fibres having maximum, minimum and the mean value for the elongation and the tenacity of raw and bleached fibre. Each histogram summarises the tensile behaviour of fibres in different ranges.

Conclusions: The Physico-chemical studies have indicated that Sida Rhombifolia fibre can be scoured and bleached. The whiteness index and the ISO brightness are good as determined by spectrophotometer, which is an indication that the fibre is easily dyeable and can undergo further finishing processes. The % of weight loss is a bit high, but enzymatic scouring can correct it without degrading the polymer structure of the fibre. The raw fibre contains less moisture and absorbs less at the room temperature compared with cotton fibre. It is noticed that the moisture content and the moisture regain of the fibre increases after bleaching.

The longitudinal view of a single strand of the raw and bleached fibre showed that the structure of the bleached fibre is rough and opened up unlike the structure of the fibre in its raw state.

Results from mechanical studies revealed that the fibre has breaking tenacity and the elongation is slightly lower compared with some bast fibres like flax, hemp, ramie and jute which indicate brittleness of the fibre. It is also noticed that the effect of bleaching does not have any significant adverse effect on the strength of the fibre as indicated by the tensile behaviour of raw and bleached fibres.

Future studies will focus on the enzymatic scouring of the fibre, softening with silicon softener and it is assumed that these will go a long way to improve the harshness and the elongation of the fibre.

References:

1. Parrotta, J.A. Healing plants of Peninsular,India, CABI Publishing, Wallingford, UK and New York 917 P. 2001.
2. Hannelor Eberle, Clothing Technology from fibre to fashion, foith edition, November 1997.
3. M. Hartzeil, Y.L. Hsieh, Enzymatic Scouring to improve cotton fabric Wettability textile, 2003.
4. Dr. Claudio Puebla, Whiteness Assessment, Axiphos GMH Germany, September 2006.
5. L.Y. Mwaikambo and M.P. Ansell, The effect of chemical treatment on the properties of hemp, sisal,jute and kapok fibres for composite reinforcement, University of Bath, Bath BA27AY, Uk, 1998.
6. Murkhejee, A. Ganguly. PK ana Sur.D, Structural mechanics of jute, the effect of hemicelluloses or lignin removal, Journal of Textile Institute Vol 84 (3),348 – 353. (1993).
7. Hearle J.W.S, Moisture relations in textiles. Textile Institute, London, 1975.
8. Pinkie E. Zwane and Rinn M. Cloud, Development of fabric using chemically treated sisal fibres, AUTEX Research Journal, Vol. 6, No 2, June 2006.
9. W. E. Morton, MSc., Sc. Tech., F.T.I and J.W.S. Hearle, M.A., Sc. D. PhD., C. Text F.T.I (Hon), F. InSt.P. Physical properties of Textile fibres. University of Manchester Institute of Science and Technology,published by Textile Institute 1993.
10. Franck, Lewin and Pearce Mechanical properties of some bast fibres like flax, hemp, ramie, jute, kenaf and cotton (fruit), 1985.
11. H.P. Stout, Fibre and Yarn Quality in Jute Spinning, the Textile Institute, Manchester. U.K. 1988.
12. http://www.shamanaustralis.com/website/sidarhombifolia.htm.
13. http://www.rt66.com/hrbmoore/constituents/sida_rhombifolia.txt.
14. http://en.wikipedia.orghuiki/bast-fibre

Influence of copper nanocolloids on jute fibre

This study reports that copper nanotreated jute fabric can be used as high performance textiles, particularly in medical and healthcare services.

By D P Chattopadhyay and B H Patel*

Among the many metals like gold, silver, palladium, platinum, zinc, etc., towards which research is directed copper and copper based compounds are the most important[1-6]. Due to its excellent electrical conductivity and low cost nanoparticles, copper (Cu) has long been playing a significant role in transporting electrical energy; more so in modern electronics circuits. The nanocrystalline metal oxides typically have a mean particle size less than 100 nm. They are non-porous single crystals with well defined surface chemistry and are chemically pure. Further modification of these materials often involves vapour-phase coating to prepare a surface-modified dry powder, or liquid phase processing to prepare a dispersion that is compatible with the application. Nanophase's family of integrated technologies economically

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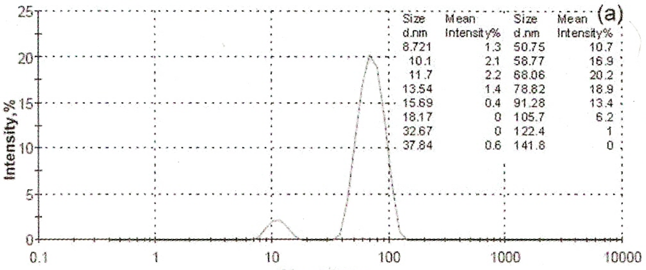
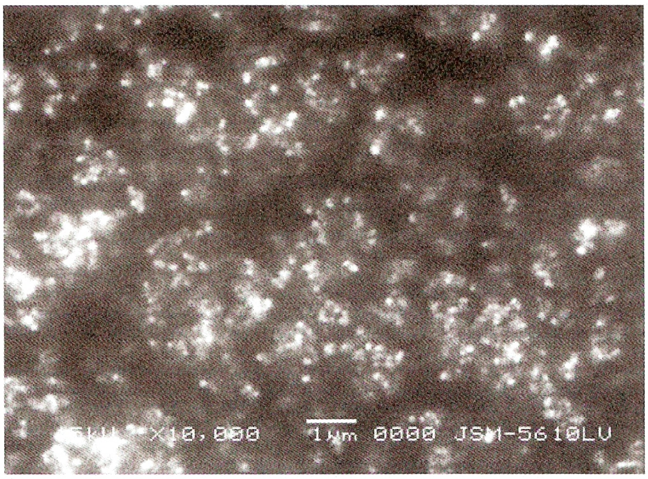
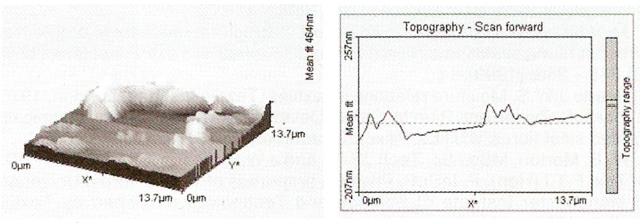


Size d.nm	Mean Intensity%	Size d.nm	Mean Intensity%
8.721	1.3	50.75	10.7
10.1	2.1	58.77	16.9
11.7	2.2	68.06	20.2
13.54	1.4	78.82	18.9
15.69	0.4	91.28	13.4
18.17	0	105.7	6.2
32.67	0	122.4	1
37.84	0.6	141.8	0

A. Particle size



B. SEM images



C. AFM images

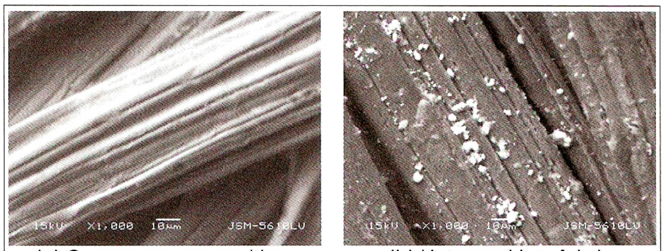
Fig1 Characterisation of tri sodiumcitrate capped copper nanoparticles by particle size (A), SEM images (B) and AFM images (C)

produces nanocrystalline materials and then nanoengineers those materials to fit customer's needs. These particles can be applied in the field of wood preservation, marine antifouling, permanent coatings, and thermoplastics and in textile fibers[3,7].

In the case of textile fibre, the nanoparticles have been incorporated into products such as nylon, polypropylene and other polymers to provide long-term antimicrobial character even in harsh environments and after extensive thermal cycling. The need for minimising or eliminating microbial growth on a variety of textile-based substrates has become a major topic of discussion in numerous industries, including healthcare, home furnishings, filtration and apparel[8-9]. However, most research in textiles is restricted to silver nanoparticles[10], copper nano is not even touched. This study, therefore, investigates the effect of synthesised copper nano to jute fabrics.

Materials and Methods: Fabric sample - Plan weave jute fabric ends/ inch-13, picks/inch-10 and weight-465.11 gm/m^2; Chemmicals — copper sulphate, sodium borohydride and trisodium citrate — were procured from Sd's fine chemicals.

Test Study: Copper nanoparticles were synthesised by various methods and studied in order to develop nano that would last for several washing and longer exposure to sunlight. Copper nanoparticles were synthesised by a simple novel technique i.e. chemical reduction method, stabilised and characterised scientifically using particle size analyser, scanning electron microscopy and atomic force microscopy. These particles were applied onto jute textiles by padding technique. Their functionalised abilities were compared with treated and untreated fabrics.



(a) Copper nanotreated jute fabric

(b) Untreated jute fabric

Fig 2 SEM images of treated and untreated Jute fabric

Table 1: Effect of cupper nano treatment on physical properties of Jute sample

Sr. No.	Sample	Breaking load (kg)	Crease recovery angle °(deg)	Bending length (cm)
1.	Untreated Jute sample	10.44	90	3.00
2.	Jute pre-treated with cu nano particles	10.81(+3.54)	100 (+11.11)	3.60 (+20.00)

Note: Values in the parenthesis indicate percentage change in physical properties.

Application of copper nano dispersion: After the preliminary treatments, the jute substrates were treated individually with the nano dispersion. The cleaned substrates were dipped in the dispersion for 10 min and then padded with an automatic padding mangle using 2-dip, 2-nip padding technique at 70% padding expression. The padded substrates were air dried for two hours and cured at 120 ^{0}C for 20 min in a preheated curing oven.

Results and Discussion: The nano particles were characterised using various techniques. The particle size analyser, the Scanning Electron Microscopic (SEM) image, and the Atomic Force Microscopic (AFM) image of copper nanoparticles are presented in Fig.1A, B and C respectively.

Particles with size ranging from 40 nm to 80 nm, which suggested a narrow range of size distribution, were observed. Similar observations were made through SEM and AFM studies.

The treated nanosubstrates were analysed using SEM studies. The Scanning Electron Microscopic images of both treated and untreated jute fabric are presented in Fig. 2(a) and 2(b) respectively. An excellent dispersion of nanoparticles on the fabric is observed.

Nanotreated samples were analysed for the change in physical properties and compared with untreated samples. The crease recovery angle of the samples was determined as per AATCC Test Method 66-2003 using Sasmira crease recovery tester (India). The stiffness in terms of bending length of nanotreated and untreated samples were measured as per AATCC Test Method 115-2005 using Prolific stiffness tester (India) for the measurement of bending length. The results are given in Table 1.

The antimicrobial activity was measured by soil burial test[11], subjecting untreated and treated samples to the test according to standard method for seven days. At the end of the

Table 3: Effect of Cu nanoparticles on dyeing of cotton and jute fabric with direct dyes

Sample	Colour strength (*K/S*)			*K/S* values After 48 hrs sunlight exposer			*K/S* values After soap at 80°C for 15 min.		
	Dye 1	Dye 2	Dye 3	Dye 1	Dye 2	Dye 3	Dye 1	Dye 2	Dye 3
Untreated jute	14.15	16.43	17.26	9.32	11.06	12.33	10.27	11.17	11.65
Jute pretreated with cu nanoparticles	15.90(+12.36)	16.92(+02.98)	18.12(+04.98)	14.53(+55.80)	14.06(+27.12)	16.21(+31.47)	14.33(+39.53)	14.93(+33.66)	16.78(+44.03)

Note –Data in the parenthesis indicate percentage change in *K/S value*, Direct Fast Pink BD [Dye 1], Direct Blue B [Dye 2], and Direct Green B [Dye 3].

Table 2: Effect of Cu Nanoparticles on resistance of jute towards bacterial attack

sample	strength		
	Before soil burial	After soil burial	% Change
Untreated Jute sample	10.44	5.02	-51.92
Jute pre-treated with cu nanoparticles	10.81	09.47	-12.39(+88.64)

Note: Data in the parenthesis indicate percentage change in tensile strength

period, samples were removed, washed and dried in air. The breaking load of the samples was determined on tensile tester instrument (LRY model, Lloyd, UK)

Table 2 shows the change in breaking strength of the substrates. Cu nanoparticles were found to enhance the resistance of jute towards bacterial attack when measured in terms of effect on tensile strength. The tensile strength of untreated control samples were reduced due to bacterial damage during soil burial test whereas Cu nanoparticles treated sample not only protected the sample against bacterial attack but also improved its strength.

Dyeing of well prepared jute fabric samples were carried out on laboratory constant temperature water bath (**Paramount Pvt Ltd**), with three direct dyes, namely, Direct fast pink BD [Dye 1], Direct blue B [Dye 2], Direct green B [Dye 3] using conventional method of dyeing. The dyed samples were assessed for colour strength K/S values (illuminant D65/100 observer) on Spectra scan 5100 (RT) spectrophotometer (premier colourscan instrument).

The results in Table 3 shows that K/S value of copper nanotreated substrate is higher then that of untreated and dyed samples, also the fastness properties of nano treated samples is better then that of the untreated samples. Copper nanoparticles have undergone intense absorption due to the increased surface area Cu nanoparticles pre-treatment could improve the colour strength and colour fastness to UV light.

Conclusions: The Cu nanoparticles were synthesised successfully and applied to jute fabric; the particle size ranged from 40nm to 80nm. The treatment with Cu nanoparticle not only improves the strength of the fibre, but also increases the resistance towards bacterial attack and dyeability compared with control even after sun light exposer. So, the copper nanotreated fabric of jute can be used to produce health care textiles and the copper nanotreated jute can also be utilised as high performance textiles.

References

1. Xu. C., Agari Y. and Matsuo M., *Polymer Journal*, Vol. 30, No.5, 1998, p372.
2.Chen. J. and Tsubokawa N., *Polymer Journal*, Vol. 32, No. 9, 2000, p729.
3. Lee H. J. and Jeong S. H., *Textile Research Journal*, Vol 74, No 5, 2004, p 442.
4. Chattopadhyay, D.P., & Patel, B.H., *Journal of Engineered Fiber Fabrics*, Vol 5, No.3, 2010, p.1-6.
5. Chattopadhyay, D.P.,& Patel, B.H., *Journal of Natural Fibers*, Vol 8, No 1, 2011, p.39-47.
6. Chattopadhyay, D.P.,& Patel, B.H., International Journal of Pure Sciences and Technology, vol 9, No 1, 2012,p- 1-8.
7. He, Junhui, Kunitake T. and Nakao A., *Chemical Materials*, Vol 15, No 23,2003, p 13.
8. Dr. Amberg-schwab S., Ulrikeweber D., *International Textile Bulletin*, Vol 50, No 1, 2004.
9. Li D. and Sun G., *AATCC Review*, Vol 3, No 12, 2003. p 19.
10. Chattopadhyay D. P. and Patel B.H., *The Indian Journal of fiber and Textile research*, Dec.2009, Vol. 34. p368.
11. SP; 1981 (Source: IS: 1389 – 1959) p. 405-409.

DRF yarns can cut knitwear cost by 40%

Making knitwear out of conventional yarns is expensive. This study finds better quality knitted fabric goods can be produced by using DRF yarn at up to 40% lower production cost in comparison with conventional yarn.

By Lokesh Shukla and Anita Nishkam*

Knitting, a labour intensive industry that in the beginning was centred only on the production of inner wears like vests, brief etc., has now expanded to making a wide variety of apparel. In developed economies it accounts for half of the total fabric production or more than 15% of the global fabric output.

Yarns of almost all common fibres and their blends are used for knitwear. However, making knitwear out of conventional yarns is expensive; therefore blends of polyester and wool have become one of the most popular options. They are usually knitted double yarns.

Considerable efforts have been made in the past for developing a process for the production of low-cost double yarns. They aimed largely at eliminating two-folding (plying) of yarn and produce a fine double yarn on conventional frame without resorting to either two-plying or sizing. The path followed was mainly Double Roving Feed (DRF) spinning and compact spinning[1].

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Effect of Cu-nano colloid treatment on the properties of wool and Silk

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Abstract

In this study synthesized copper nano colloids were applied to wool and silk fabric by exhaust technique. The presence of Cu- nano on wool and silk fabrics were observed by SEM and elementally confirmed using XRF. The treatment was found to enhance the physical properties and dyeing behaviour of both the fabrics without increasing effluent load. It was also observed that the treatment improved the bacterial resistance of wool and silk fabrics.

Keywords: Antimicrobial, Cu-nano colloids, Dyeing, Effluent, Silk, Wool

1. INTRODUCTION

Nanotechnology is an emerging interdisciplinary technology that has been booming in many areas during the recent decade. It is estimated that nanotechnology in textiles will be billion dollar business in the next few years. Finishing of textiles is an area where nanotechnology has great potential for application.[1-3] Particularly the micro and nano-structure particles of metal oxides have become topic of active research because they posses interesting physical properties differing considerably from that of the bulk phase. It comes from small sizes and high surface/volume ratio. Various reports are available on the synthesis and application of metal nano-particles to textiles.[2-6] But very few literatures available on application of nano material by exhaust technique.

Nanoparticles of Ag, CuO and ZnO have been used industrially for several purposes including amendments to textiles, cosmetics, sprays, plastics and paints.[7] Extensive use and increasing demand for nanoparticles will lead to their accumulation in the environment, especially in landfills and their water effluents. The aim of this study was to evaluate certain pollution parameters; for example, chemical oxygen demand (COD), biochemical oxygen demand (BOD) and total dissolved solids (TDS) of the effluent after application of Cu nano on wool and silk fabric.

Earlier we have reported the effect of Ag, Zn and Cu-nano particles on the properties of cotton.[8-11] As Cu properties are quite similar to those of silver; besides, Cu is much cheaper. In this work the effect of application of Cu nano solution on the physical properties of wool and silk fabrics is reported. An attempt has also been made to investigate whether the dyeability of direct dyes could be improved by treating fabrics with the Cu nano solution. The functionality and reactivity of the Cu nano treated and dyed fabrics were compared with untreated and conventionally dyed fabrics.

2. EXPERIMENTAL DETAILS

2.1. Materials and Equipments

Mill scoured and bleached wool and silk fabrics with specification as given in Table I, purchased from local market, were used in the present investigation.

Three commercial direct dyes, namely C.I. Direct Red 9 (D1), C.I. Direct Blue 67 (D2) and C.I. Direct Green 6 (D3) were used for this study without further purification. Copper sulphate ($CuSO_4.5H_2O$, MW 249.68), sodium borohydride ($NaBH_4$, MW 37.83) and tri-sodium citrate ($C_6H_5Na_3O_7.2H_2O$, MW 294.10) of analytical grade were collected from Sd's Fine Chemicals, India.

Table1. Specification of wool and silk fabrics

Fabric	Weave	Ends/ inch	Picks/ inch	Weight ,[g/m^2]
Wool	Plain	80	60	65
Silk	Plain	84	62	29

Copper nano colloid was synthesised through chemical reduction of copper sulphate in N_2 atmosphere. The detailed method of synthesis with characterization is reported in our earlier study.[12]

The particles were observed through Scanning Electron Microscope (SEM), (model JSM5610LV, version 1.0. Jeol, Japan). The elemental analysis of the nano copper treated wool and silk was done on X-ray fluorescence spectrometer (XRF) (EDX 800 Simadzu, Japan).

Application of nano-colloidal solution and dyeing of treated/untreated fabrics were carried out on constant temperature shaking water bath (Alliance enterprise, India). Colour yield in terms of *K/S* values was evaluated using Spectra

Scan 5100 (RT) spectrophotometer, (Premium Colorscan Instruments, India). The washing fastness of the fabric was performed on launder-o-meter (Digi.wash, Paramount Scientific Instruments., India). Light fastness was evaluated using Fad-o-meter, (FDA-R, Atlas, U.S.A.).

2.2. Treatment of wool and silk with copper nano colloids

The synthesized nano Cu-colloidal solution was applied to wool and silk fabrics by exhaust technique using a constant temperature shaking water bath. The fabric samples were initially treated at 40°C for 1h with a material-to-liquor ratio of 1:50. The temperature was then gradually raised to 70°C and the treatment continued for 20 min. All treated fabrics was then washed with 2 g/l soda ash and 5 g/l non-ionic detergent (Lissapol N) at 60 °C for 30 min with the goods to liquor ratio 1:20. For comparison, untreated samples were treated under the same condition but in the absence of Cu nano particles. The washing liquor was collected and further analysed for pollution parameters; COD, BOD and TDS.

2.2.1. Determination of BOD

BOD is a measure of the polluting efficiency of water. Oxygen is required in the effluent for the oxidation of inorganic and organic matter. The demand of oxygen by the organic matter is known as BOD which is defined as the amount of oxygen required to carry out the biological decomposition of dissolved solids under aerobic conditions at a standard temperature. In a 500 ml BOD bottle, a 5 ml sample, 1 ml each of four standard buffers (magnesium sulphate buffer, calcium chloride buffer, phosphate buffer and ferric chloride buffer) and 1 ml of waste effluent were taken and diluted with distilled water. The dissolved oxygen was found immediately (blank, A) by iodimetric titration. Another sample was prepared as above and incubated at 27 °C for 3 days and then the dissolved oxygen was found (sample value, B). The BOD (in mg) was then determined according to Eqn 1.

$$\text{BOD} = (A - B) \text{ X dilution factor} \qquad (1)$$

2.2.2. Determination of COD

COD is the measure of oxygen required to oxidize unstable materials in a sample by means of a dichromate in an acid solution. In a 250 ml conical flask, 50 ml of the sample was added; 1 g of mercury (II) sulphate was added, followed by 180 ml of silver sulphate ⁄ sulphuric acid solution. Then, 10 ml of 0.00833 M standard potassium dichromate solution was added and the resulting mixture was boiled for

15 min. After cooling, the inner side of the condenser was rinsed with 50 ml of water. Either a diphenylamine indicator (1 ml) or a ferroin indicator (1 ml) was added and titrated with 0.025 M ammonium iron (II) sulphate solution. Diphenylamine gives a colour change from blue to green at the endpoint, whilst for ferroin that is blue–green to red–brown. This titration is called A ml; the back-titration is repeated for the blank (B ml). The difference between the two values is the amount of potassium dichromate used up in the oxidation. COD (in mg) was then determined according to Eqn 2.

$$\text{COD} = (A - B) \times 0.2 \times 20 \text{ mg l}^{-1} \qquad (2)$$

2.2.3. Determination of TDS

TDS is an expression for the combined content of all inorganic and organic substances contained in a liquid which are present in a molecular, ionised or microgranular (colloidal sol) suspended form. The TDS of the effluent was determined by a portable conductivity ⁄ TDS meter.

2.3. Characterization of Cu nano-treated wool and silk fabrics

The depositions of particles on textiles were observed through Scanning Electron Microscope. The amount of copper as element in the polymer structure was detected and measured using an X-ray fluorescence spectrometer. The operating X-ray source voltage and current were 35 kV and 26 mA respectively. Registration time was 30 s and the investigated area was 78.5 mm^2.

The specimens were conditioned at 65± 2 % relative humidity and 27 ± 2°C before physical testing. The breaking load of fabrics was measured before and after nano-treatment on tensile tester (LRY model, Lloyd, U K). The crease recovery angle of the samples was determined as per AATCC Test Method 66-2003 using SASMIRA crease recovery tester (India). The bending length was measured as per AATCC Test Method 115-2005 using Prolific stiffness tester (India).

2.4. Dyeing of untreated and treated wool and silk

The wool and silk fabric samples, with and without nano copper treatment, were dyed with 2% (owf) direct dye by exhaust technique in a shaking water bath at a material-to-liquor ratio of 1: 30. The systematic presentation of this process is given in the flow chart (Fig.1). Finally the samples were washed with 5 g/l non-ionic detergent (Lissapol N) at 60 °C for 15 min with the goods to liquor ratio 1:20 and air dried. For comparison, untreated wool and silk were dyed under the same condition.

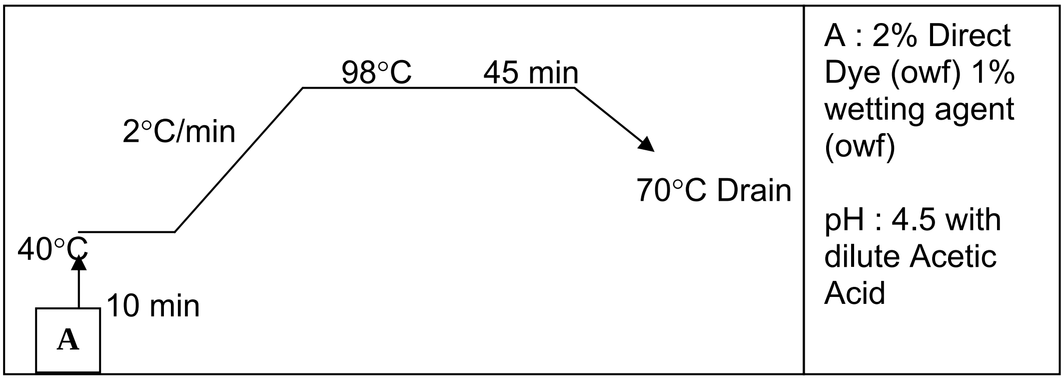

Fig.1. The flow chart of dyeing process.

2.4.1. Evaluation of dyed samples

The effect of nano Cu treatment on the dyeability of wool and silk fabrics in terms of *K/S* was measured on computer colour matching system Spectra Scan 5100 (RT) spectrophotometer interphased with computer colour matching system at particular λ_{max}.

The wash and light fastness of dyed samples were determined as per ISO105-CO6 (C2S) and ISO105-BO2 (1990) test methods respectively.

2.5. Evaluation of antimicrobial activity

The untreated and treated samples were subjected to soil burial test as per AATCC Test Method 30-2004. After the stipulated period the samples were removed from soil, washed thoroughly and dried in air. The samples were then tested for breaking load.

3. RESULTS AND DISCUSSION

The synthesis of copper nano colloid was confirmed as the blue green solution of copper sulphate gradually turned to yellow due to the surface plasmon resonance of copper nano-particles. The detailed discussion is given in our earlier study.[10]

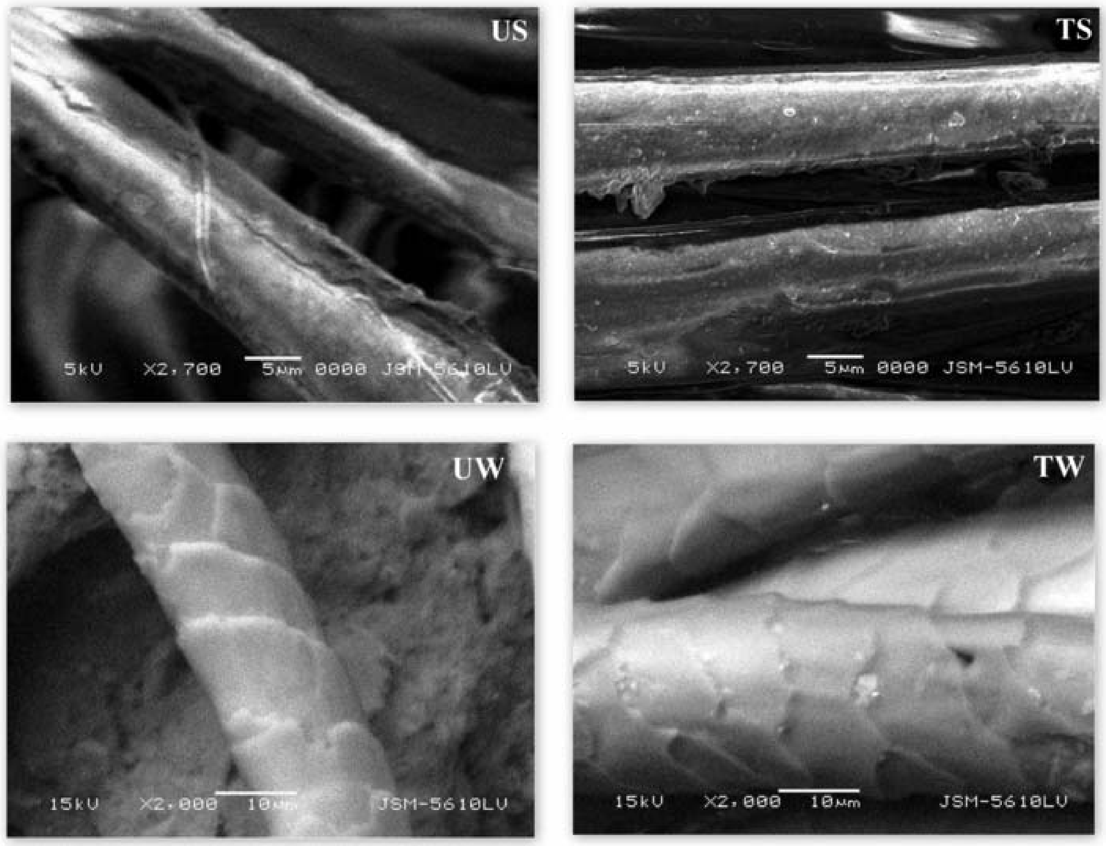

Fig.2. Scanning Electron Microscope (SEM) images of (US) Untreated silk, (TS) Treated silk, (UW) Untreated wool and (TW) Treated wool fabric.

The surface morphology of both wool and silk were examined before and after nano copper treatment (Fig.2). Some of the particles are noticed in the scanning electron microphotographs of the treated samples. The particles were detected and measured quantitatively using XRF technique. The elemental copper was found on treated wool and silk samples. Table II show the amount of copper detected within investigated area 78.5 mm^2 against nil for untreated one.

Table 2. Amount of copper detected with XRF

Structure	**Amount of copper, [µg]**
Wool	Nil
Cu/Wool fabric	0.38
Silk	Nil
Cu/Silk fabric	0.34

Today, nano-particles are used worldwide, with much research being carried out into developing new synthetic procedures to improve their application characteristics. However, because of their high surface energy, nano-particles can cause great effluent problems for environment. It is clear from Table III that the washing effluent with Cu- nano treatment does not increases the BOD, COD and the TDS when compared with the conventional washing effluent of sample without Cu nano treatment. From the lower values of TDS it may be safely interpreted that nano-particles can provide high durability of the desired textile functions. By virtue of its small size and high surface energy, nano-particles are bound to the fabric surface may be by Vander walls forces which give a reasonable wash fastness

Table 3. BOD, COD and TDS of washing effluent with and without Cu nano treatment

Sample	Washing effluent	BOD [mg/l]	COD [mg/l]	TDS [mg/l]
Wool	Without Cu nano	Nil	20	288
	With Cu nano	5.0	60	236
Silk	Without Cu nano	Nil	08	196
	With Cu nano	5.0	40	204

Note: National environment quality standard for municipal and liquid industrial effluent: BOD, 80 mg/l; COD, 400 mg/l; TDS, 3500 mg/l

Table 4. Effect of copper nano-treatment on physical properties of wool and silk

Sample	Breaking load [Kg]		Crease recovery angle [Deg]		Bending length [Cm]	
	Control	Nano Cu applied	Control	Nano Cu applied	Control	Nano Cu applied
Wool	6.43	7.66 (+19.12)	139	146 (+5.03)	3.10	3.70 (+19.35)
Silk	6.32	6.63 (+4.90)	124	133 (+7.26)	2.80	3.60 (+28.57)

Note-Values in the parenthesis indicate percentage change in physical properties.

In order to investigate the effects of copper nano treatment on tensile strength, crease recovery and stiffness of wool and silk, these properties of the treated samples were determined and compared with the untreated samples .It is clear from the results shown in Table IV that all these properties are improved to some extent due to the application of Cu nano colloids. The nano copper particles because of their small size can enter in between the polymer molecules and perhaps act as fillers or cross links which in turn improve the load bearing capacity of the fibres. It seems that they also help the fibres to recover from creasing without imparting significant harshness to the materials. Table V and Table VI show that copper nano treatment on both wool and silk raised the colour depth and fastness of the dyed samples. The nano copper particles increase the colour strength value *(K/S)* perhaps due to the polarity developed in the metal particles when dye anions come near the fibre surface. Their attachment with the metal nano particles could enhance the fastness property also. Similar effect was also noticed with cotton materials treated with copper nano colloids.[9]

Table 5. Effect of Cu nano-particles on fastness properties of samples dyed with direct dyes

Sample	**Fastness to**											
	Light						**Washing**					
	D1		D2		D3		D1		D2		D3	
	C	T	C	T	C	T	C	T	C	T	C	T
Wool	2-3	3-4	2-3	3	3	3-4	3	3-4	2-3	3-4	2-3	4
Silk	3	4	3	3-4	3	4	3	4	3	4	3	4

Note-D1 – C.I. Direct Red 9, D2 – C.I. Direct Blue 67 and D3 –C.I. Direct Green 6, C – Control sample, T – Sample treated with Cu Nano-particles.

Table 6. Effect of Cu nano-particles on colour strength of fabrics dyed with direct dyes

Sample	**Colour strength (K/S)**					
	D1		D2		D3	
	Control	Cu nano treated	Control	Cu nano treated	Control	Cu nano treated
Wool	10.12	11.26 (11.26)	12.31	13.66 (10.96)	11.52	13.24 (14.93)
Silk	4.64	5.87 (26.50)	6.89	7.83 (13.64)	7.56	9.77 (29.23)

Note-Values in the parenthesis indicate percentage change in K/S values, D1 – C.I. Direct Red 9, D2 – C.I. Direct Blue 67 and D3 –C.I. Direct Green 6

The wool and silk fibres when pretreated with nano-sized copper colloids showed improved antimicrobial activity (Table VII). The antimicrobial efficiency was determined by measuring the loss in breaking load due to soil burial test. The treated wool showed approximately 10% loss due to soil burial test which is much less compared with the loss experienced by the untreated sample which was about 36%. The treatment of Cu nano colloids has raised the bacterial resistance of silk remarkably. The enhancement in the resistance towards bacterial attack may be attributed to the fact that the metallic ions and metallic compounds display a certain degree of sterilizing effect. Copper is known for its antimicrobial properties and has been used for years in the medical field. It is possible that copper particles may get attach to the surface of the microbes cell membrane, enter inside the cell and destroy their metabolic function. Smaller copper particles having larger available surface area for interaction provides high bactericidal effect than larger particles.

Table 7. Effect of Cu nano-particles on resistance towards bacterial attack

Sample	**Breaking load, kg**			
	Before soil burial		**After soil burial**	
	Control	Nano Cu applied	Control	Nano Cu applied
Wool	6.43	7.66	4.09 (-36.39)	6.86 (-10.44)
Silk	6.32	6.63	4.12 (-34.81)	6.21 (-06.33)

Note-Values in the parenthesis indicate percentage change in load

4. CONCLUSIONS

Application of copper nano-colloids to wool and silk is found to improve their load bearing capacity, recovery from creasing and dyeability. The treatment enhanced their bacterial resistance also and the improvement is found to be remarkable with silk in this regard. From the literature it has been found that cu-nano particles in free form it is toxic but here it has been bound with textile material so it can be safely utilized for the modification of wool and silk textiles.

References

1. D P Chattopadhyay, *Textiles*, 33, 21**(2006)**.
2. B.H.Patel and Dr D.P.Chattopadhyay, *The Indian Textile Journal*, 118, 23 **(2007)**.
3. N R Jana, Z L Wang, T K Sau and T Pal, *Current Science* 79,1367**(2000**).
4. P V Kazakevich, V V Voronov, A V Simakin and G A Shafeev, *Quantum Electron* 34, 951 **(2004)**.
5. A Yadav, V Prasad, A A Kathe, S Rraj, D Yadav, C Sundaramoorthy and N Vigneshwaran, *Bull. Mater. Sci.* 29, 641 **(2006)**.

6. J Sójka-Ledakowicz, J Lewartowska, M Kudzin, T Jesionowski, K Siwińska-Stefańska, A Krysztafkiewicz, *Fibres & Textiles in Eastern Europe* 16, 112 **(2008)**.
7. N C Mueller, B Nowack, *Environ Sci Technol.* 42, 4447**(**2008).
8. D P Chattopadhyay and B H Patel, *Indian Journal of Fibre & Textile Researc*h. 34,368 **(2009)**.
9. D P Chattopadhyay and B H Patel, *Journal of Natural Fibers*., 08, 39 **(2011)**.
10. D P Chattopadhyay and B H Patel, *Journal of Engineered Fibre & Fabrics*., 05**,** 1 **(2010)**.
11. D P Chattopadhyay and B H Patel, *Textile Asia*, 43, 11 **(2012)**.
12. D P Chattopadhyay and B H Patel, *International Journal of Pure Sciences and Technology*, 9, 1 **(2012)**.

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Novel padding technique to prepare Ag-nano/silk nano composite fabric

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Abstract

In the present investigation generation of Ag nanoparticles as an integral part of silk is reported. The silk / Ag-nano composite fabric was characterized by X-ray fluorescence spectrometer and observed by Scanning Electron Micrograph (SEM). From SEM the size of the nano silver particles on silk was found to lie below 100 nm. The silk fabric with Ag- nano was tested for antimicrobial property by ASTM E-2149 test. Fabric samples with silver nanoparticles were found to enhance its antimicrobial activity. In addition, the methanolic extract of *Azadirachta indica*, *Lawsonia inermis* and *Ocimum sanctum* were prepared and applied on silk fabric to study the effect of in situ formation of Ag-nano on dyeing performance of samples manifested improved dyeing performance not only in terms of colour strength values (*K/S*) but also in terms of washing and light fastness properties.

Key words: Ag-nano, Antimicrobial, Dyeing, Natural dyes, Silk.

1. Introduction

Nano-particles can be applied on textiles by two-stage process. Initially, there is the manufacture of new, stable nano-material, which must in the first instance be protected against properties defined by the size of the particles [1-3]. The second step sees the creation of the foils, emulsions and dispersions that can be applied to the final textile product, in the most favorable case, by means of conventional finishing processes

[4-12]. Nano-particles are most commonly applied to textiles by coating using a composition of nano particles, a surfactant, ingredients and a carrier medium.

In view of the above limitations we have attempted the synthesis of silver nanoparticles through a single stage, economical technique. The aim of this study was to establish a continuous method for the synthesis of Ag nano particles in side the silk fiber matrix and also to investigate whether the dyeing performance of natural dyes could be improved by in-situ formation of Ag-nano particles on silk fabric. The functionality and reactivity of the silk fabric with Ag-nano and dyed were compared with untreated and dyed silk fabric.

Hee et.al, [12] reported that the wool textiles treated with a small quantity of sulfur nano-silver colloidal solution imparts antibacterial property. They have also investigated that the finished wool fabrics with sulfur nano-silver colloid had various functionalities, such as mothproofing, antibiotic, and antistatic property. In this study they have not investigated the effect of Ag-nano particles on physical and chemical properties of textiles.

In our earlier work [11] we have proposed chemical reduction technique for the synthesis of silver-nano particles and the particles were applied to wool, silk and cotton fabric by padding technique. Positive change in various properties viz, tensile, antimicrobial and dyeing behavior were reported. However the study was concentrated to study the dyeing behavior of Ag-nano treated fabric with direct dyes.

From the above literature survey it has been observed that most of the studies were focused on the antibacterial effect of Ag-nano particles evaluated by agar agar or bacterial count method. Only few literatures available where dyeing behavior of nano-treated fibers with direct dyes were reported [13, 14]. Information on in-situ formation of Ag-nano particles on silk fabric and subsequently dyed with natural dyes is hardly found in the literature. The present study was, therefore, aimed at generation of nano silver particles by a simple and economical method and investigating its effect on the antimicrobial property and dyeing performance of silk fabric using three natural dyes namely, *Azadirachta indica, Lawsonia inermis* and *Ocimum sanctum.*

3. Materials and Experimental methods

3.1 Materials

3.1.1 Fabric

Plain weave Silk fabric with 84 Ends/ inch, 62 Picks/ inch and 29 gm/m^2 Weight was purchased from Khadi Gramodhyog, Vadodara. The fabric was further scoured in 0.5 percent non-ionic soap solution in Digi. Wash Launder-o-meter at 90°C for thirty minutes to remove impurities from manufacturing.

3.1.2 Dyes and Chemicals

The following natural extracts were selected for present study. Methanolic extract of *Azadirachta indica, Lawsonia inermis* and *Ocimum sanctum* were used. Chemicals used throughout the work are Silver sulphate $AgSO_4$ (Sd's Fine Chemicals Ltd., Mumbai/India) and sodium borohydride $NaBH_4$ (Sd's Fine Chemicals) of analytical grade purity.

3.2 Experimental methods

3.2.1 In-situ formation of Ag-nano particles

The cleaned silk fabric samples were impregnated with very dilute chilled solution of sodium borohydride ($NaBH_{4,}$ 0.1gm, in 50ml water) for 10 min and then padded with an automatic padding mangle using 2-dip, 2-nip padding technique at 70% padding expression on laboratory two bowl padding mangle (EEC Pvt. Ltd., Mumbai). The samples further passed through the solution of $1{\cdot}10^{-3}$ M $AgSO_4$ and again padded by 2-dip, 2-nip padding technique. The padded substrates were air dried and finally cured at 120 ˚C for 2 min in a preheated curing oven.

3.2.2 Characterization of Silver nano/Silk composite

The amount of silver as element in the polymer structure was measured using an X-ray fluorescence spectrometer (EDX 800 Simadzu, Japan). The operating X-ray source voltage and current were 35 kV and 26 mA respectively. Registration time was 30 s and the investigated area was 78.5 mm^2 and the morphology of fabrics with and without silver nano was examined using scanning electron microscope (SEM) instrument (JSM5610LV, version 1.0, Jeol Ltd., Tokyo/Japan).

3.2.3 Dyeing of Silk with Natural colourants

The silk fabrics with Ag-nano were studied, in order to change in their functionalized abilities i.e. dyeing performance to methanolic extract of three natural dyes namely, *Azadirachta indica*, *Lawsonia inermis* and *Ocimum sanctum*. Dyeing of silk fabric with these natural dyes were performed using exhaust dyeing technique on a laboratory constant temperature dye bath (Peramount instruments Pvt. Ltd, India). The dye bath liquors for individual dye containing methanolic extract-20 %(owf) and acetic acid ~2 % (owf) to maintain dye bath pH 4.5. Dyeings were started at room temperature and gradually raised to boil within 15 min. the dyeing was continued at this temperature for 30 min. Finally the samples were washed thoroughly and air-dried.

The dyed samples were assessed for *K/S* values using computer color matching system (Spectra scan 5100 RT Spectrophotometer, Premier Color scan Instrument Pvt. Ltd., Mumbai/India). The light fastness of the dyed samples was tested on Fad-o-meter (FDA-R, Atlas Material Testing Technology LLC, Chicago, Ill/USA) and the wash fastness test of the samples was performed as per ISO – 2 test methods in launder-o-meter (Digi.wash, Paramount Scientific Instruments Pvt Ltd., New Delhi/India). The samples were evaluated for the rating in terms of color change.

3.2.4 Evaluation of Antimicrobial activity

Antimicrobial activity was measured by ASTM E-2149 test methods. Antimicrobial test of silk fabric with and without Ag-nano were carried out with gram-positive Staphylococcus aureus and gram-negative Escherichia coli bacterium. Samples with and without nano were kept separately into two 50ml conical flask containing 10 ml of liquid culture (Luria Broth) in which 0.1ml of microbial culture is inoculated in laminar flow. All the closed flasks stirred with shaker incubator for four hours at 200rpm.

The inoculated test cultures with treated and untreated samples were tested by UV spectrophotometer for optical density measurement. Optical density of inoculated culture of treated sample was found very low as compare to inoculated test culture with untreated sample. Lower the optical density means lower is the growth or very low growth of bacterium and vice versa.

In this way from the optical density readings, the percent reduction in growth of bacteria per ml of bacterial culture was calculated.

The percentage reduction in bacterial growth was calculated using the following equation

$$– \quad \text{Percent Reduction of bacterial growth} = \frac{(B - A)}{B} \times 100$$

Where,

A is the optical density for the inoculated test culture of containing the treated sample.

B is the optical density for the inoculated test culture of containing the untreated sample.

4. Experimental results and Discussion

The in-situ formed Ag-nano particles were observed and characterized to confirmed their chemical composition, size and dispersion on silk fabric.

4.1 Characterization of Ag-nano

The silk samples with the formation of Ag-nano and without the nano were elementally analyzed using X- ray fluorescence spectroscopy for the detection of elemental silver. The results given in Table 1 show that the amount of silver found on modified silk was about 2 % against nil for untreated one.

The Scanning Electron Microscopic images of silk fabrics without nano and the fabric with the formation of Ag-nano are presented in Figure 1 a) and b) respectively. Ag-nano particles, dispersed on the surface of the substrate are clearly observed.

4.2 Dyeing Performance of Natural extracts on Silk fabric

Table 2 represents the results in terms of colour strength values (*K/S*) of dyed samples with and without Ag-nano generation.

From Table 2, it can be seen that nano treated as well as untreated silk fabrics can be successfully dyed with all three natural colourants. For 20 % (owf) depth of shade using methanolic extract of *Azadirachta indica*, *Lawsonia inermis* and *Ocimum sanctum* as a natural colourant, a pale to medium green colour is obtained, while bright green colour shade is obtained in case of treatment with Ag-nano.

In case of samples treated and subsequently dyed with natural colourants, the colour strength (in terms of *K/S* Value) is higher than the samples dyed without the treatment, irrespective of the natural extract used. The higher *K/S* values of nano-treated samples indicate that the presence of nano metal particles increases the dye affinity towards the material. The silver nanoparticles in the fabric thus act as mordant. With the use of nano-sized particles, the number of particles per unit area is increased, and thus it results in better bonding between the dye and the fiber. The better coupling of the dye and the fiber is also reflected in the improvement in the colour fastness properties. Thus, silver nano pre-treatment not only improves the colour strength but also improves the colour fastness of silk dyed with natural dyes.

4.3 Antimicrobial activity of Treated Samples

The growth of microorganism on silk fabric was measured by ASTM E-2149 test methods. There is no antimicrobial reaction with E.coli bacteria with silk fabrics. Table 3 shows the Optical density of samples with S.aureus bacteria and reduction in bacterial growth.

It can be clearly seen from Table 3 that the silk sample with Ag-nano gives good resistance to microorganism, compared to the untreated sample where very poor resistance to microorganism was observed. Furthermore the samples treated with Ag-nano, subsequently dyed with methanolic extract of *Azadirachta indica* shows very good resistance to microorganism.

In case of Ag–nano treated samples dyed with *Lawsonia inermis* and *Ocimum sanctum* extracts the resistivity to microorganism is lower than the samples dyed with *Azadirachta indica* but still higher than the untreated sample. It has been also observed from the table that the sample with Ag-nano can increase the microbial resistivity of silk compared to untreated silk. The antimicrobial property imparted in silk fiber may be due to the fact that the presence of metallic ions and metallic compounds, which display a certain degree of sterilizing effect. It is considered that part of the oxygen in the air or water is turned into active oxygen by means of catalysis with the metallic ion, thereby dissolving the organic substance to create a sterilizing effect [10]. With the use of nano-sized particles, the number of particles per unit area is increased, and thus anti-bacterial effects can be maximized.

Nano-silver particles have an extremely large relative surface area, thus increasing their contact with bacteria or fungi, and vastly improving their bactericidal and fungicidal effectiveness. Nano-silver is very reactive with proteins. When contacting bacteria and fungus, it will adversely affect cellular metabolism and inhibit cell growth. It also suppresses respiration, the basal metabolism of the electron transfer system, and the transport of the substrate into the microbial cell membrane. Furthermore, it inhibits the multiplication and growth of those bacteria and fungi which cause infection, odor, itchiness and sores. Hence, nano-silver particles are widely applied to socks in order to prohibit the growth of bacteria. In addition, nano-silver can be applied to a range of other healthcare products such as dressings for burns, scald, skin donor and recipient sites.

5. Conclusions

Silver nano particles can successfully be prepared by a novel in-situ techniqu**e** on silk fabric. Particle distributed on silk fabric measurements shown that the average size of aggregates remains below 100 nm. The as prepared Ag-nano particles also increases the resistance to microbial attack

All three natural extracts namely; *Azadirachta indica*, *Lawsonia inermis* and *Ocimum sanctum* selected for the study can be successfully used as natural colourants to produce pale to dark green colours on silk/Ag-nano composite fabric as well as virgin silk fabric. The dyeing properties, such as the colour strength is influenced to some extent by the presence of Ag-nano in the fiber matrix. Also the fastness to light and washing of all dyes examined was improved by in case of silk/Ag-nano composite fabric. Dyeing with all three natural extract enhances the microbial resistance of silk fabric. Which can helps to increase the life of the fabric and provide more fresh and hygienic atmosphere.

Preparation of silk/Ag-nano composite fabric by a continuous padding technique and dyeing with all three natural extracts appears as an effective eco-option and may be commercialized.

References

1. J. E. Herrera, J. H. Kwak, J. Z.Hu, Y. Wang, and C. H. F. Peden. Synthesis of nanodispersed oxides of vanadium, titanium, molybdenum, and tungsten on mesoporous silica using atomic layer deposition. *Topics in Catalysis*, 245-255, 2006.
2. S. Iijima, A. Nomura, F. Mizukami, S. Shin, and F. Mizutani. Superparamagnetic behavior of iron oxides supported on porous silica gels. *Journal of Radioanalytical and Nuclear Chemistry*, 297-302, 1999.
3. F. E. Kruis, and H. Fissan. Nanoparticle charging in a twin Hewitt charger. *Journal of Nanoparticle Research*, 3:39-50, 2001.
4. Anonymous. Small-scale technology with the promise of big rewards, *Technical Textiles International*, 3:13-15, 2003.
5. S. Y. Yeo, H.J. Lee and S. H. Jeong. Preparation of nanocomposite fibers for permanent antibacterial effect, *Journal of Materials Science*, 38: 2143-2147, 2003.
6. Anonymous. Nanotechnologies keep feet healthy, *Advance in Textiles Technology*, 3:10-11. 2003.
7. H. J. Lee, S. Y. Yeo and S. H. Jeong. Antibacterial effect of nanosized silver colloidal solution on textile fabrics, *Journal of Materials Science*, 38:2199-2204, 2003.
8. S. Y. Yeo and S. H. Jeong. Preparation and characterization of polypropylene/silver nanocomposite fibers, *Polymer International*, 52:1053-1057, 2003.
9. W. A. Daoud and J. H. Xin. Nucleation and growth of anatase crystallites on cotton fabrics at low temperatures, *Journal of the American Ceramic Society*, 87:953-955, 2004.
10. M. Saito. Antibacterial, Deodorizing, and UV Absorbing Materials Obtained with Zinc Oxide (ZnO) Coated Fabrics, *Journal of Coated Fabrics*, 23:150-164,1993.
11. D P Chattopadhyay and B H Patel. Improvement in physical and dyeing properties of natural fibres through pre-treatment with silver nanoparticles, *Indian Journal of Fibre & Textile Research*, 34:368-373, December 2009.
12. Y. K. Hee, H. K. Jong, C. K. Soon and H. J. Sung. A study on multifunctional wool textiles treated with nano-sized silver. *J Mater Sci*, 42: 8020-8024, 2007.

13. D P Chattopadhyay and B H Patel, Effect of nanosized colloidal copper on cotton fabric, *Journal of Engineered Fibre & Fabrics.*, 05: 1-6, 2010.
14. D P Chattopadhyay and B H Patel, Modification of Cotton Textiles with Nanostructural Zinc Particles, *Journal of Natural Fibers*., 08: 39-47, 2011.

Table 1 Amount of silver detected with XRF

Structure	Amount of Silver in %
Ag/Silk	1.98
Silk	Nil

Table 2 Colour strength values of dyed sample.

Natural colour	Sample	Colour strength (*K/S*) values	Fastness ratings	
			LF	WF
Azadirachta indica	Without Ag-nano	7.62	6	4
	With Ag-nano	9.57 (+25.59)	6-7	4
Lawsonia inermis	Without Ag-nano	9.35	6-7	4
	With Ag-nano	11.55 (+23.53)	7	4-5
Ocimum sanctum	Without Ag-nano	10.23	6	4
	With Ag-nano	13.10 (+28.05)	6-7	4-5

Note-Data in the parenthesis indicates percentage increase in *K/S* values, LF=Light Fastness, WF=Washing Fastness

Table 3 Antimicrobial activity of the Silver nano/ Silk composite fabric

Natural Extract	Samples	Optical density of samples with S.aureus bacteria	Reduction of bacterial growth (%)
-	Without Ag-nano	0.966	No reaction
	With Ag-nano	0.528	45
Azadirachta indica	Without Ag-nano	0.679	29.7
	With Ag-nano	0.153	84.2
Lawsonia inermis	Without Ag-nano	0.925	4.3
	With Ag-nano	0.518	46.4
Ocimum sanctum	Without Ag-nano	0.697	27.8
	With Ag-nano	0.179	81.5

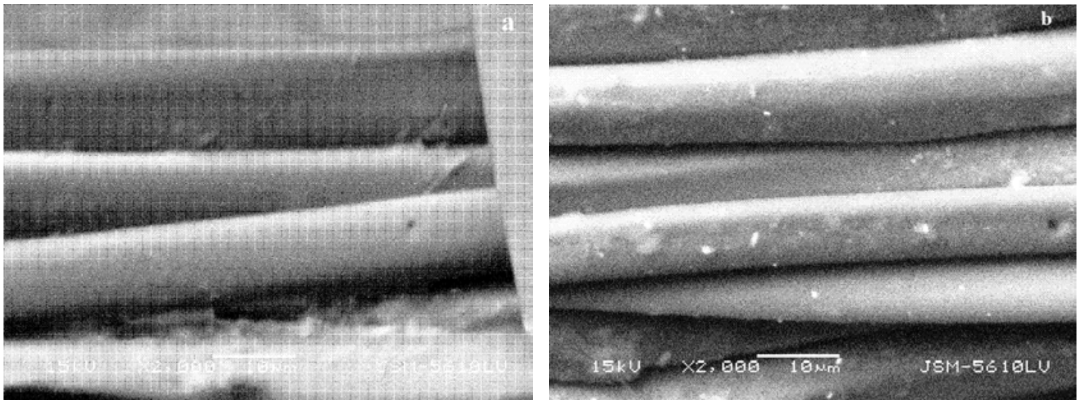

Figure 1 SEM microphotographs of a) Normal silk fabric and b) Silk fabric loaded with silver nano