Chapter 1: Introduction

1.1. Nanoparticles

Nanoparticles have received a lot of attention because of their comparatively high chemical activity and selectivity. Particles between 1 and 100 nanometres in size are called nanoparticles while materials with at least one dimension that measures 100 nanometres (nm) or less are called nanomaterials. Many researchers call nanoparticles in the range 1-3 nm as nanoclusters (Jin et al., 2016). Nanoparticles are referred to as iso-dimensional when all of their dimensions fall inside the nanometer range (G. Sharma et al., 2019).

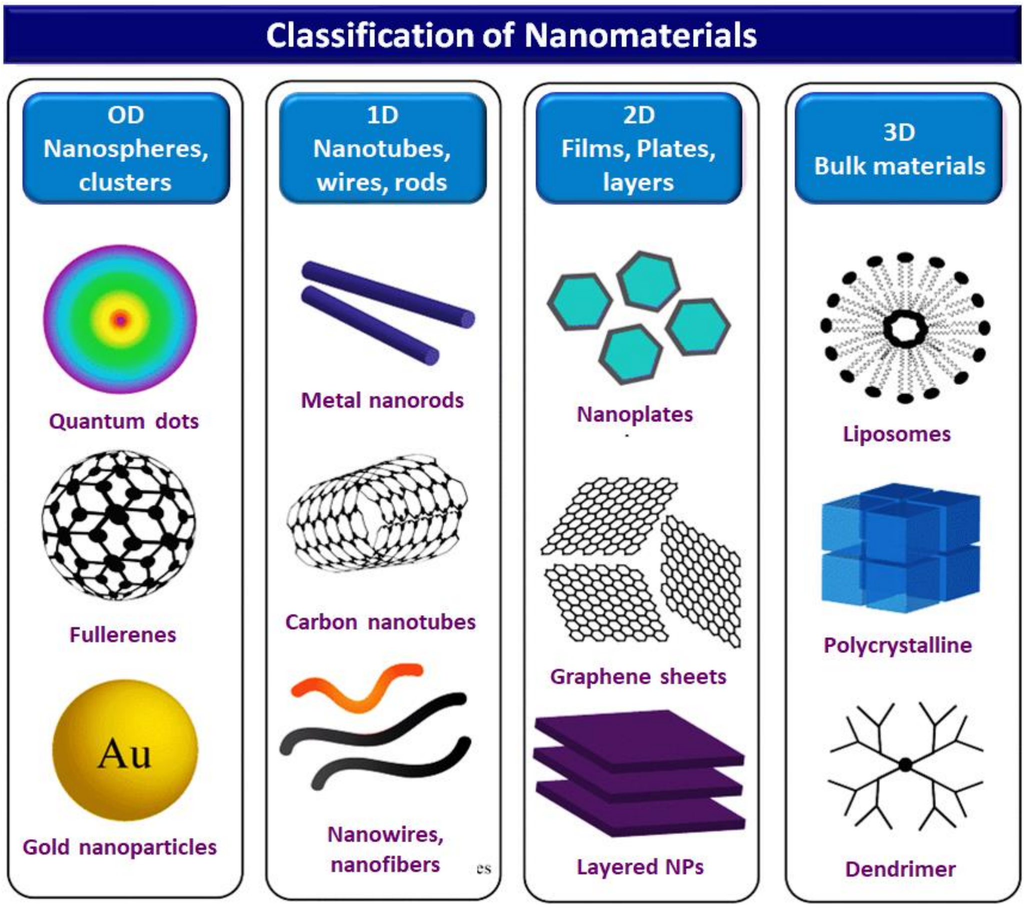

Figure 1.1: *Classification of nanomaterials based on dimensions* (Poh et al., 2018)

Based on the dimensions nanomaterials are classified as (Figure 1.1) (Kolahalam et al., 2019): 1) Zero-dimensional (0-D): Materials with all the 3 dimensions in nanometre range (e.g., quantum dots); 2) One dimensional (1-D): Materials with at least one dimension in nanometre range (e.g., Nanorods, nanotubes, nanowires); 3) Two-dimensional (2-D): Materials with any two dimensions in nanometre range (e.g., Nanofilms, nanolayers); 4) Three dimensional or bulk material (3-D): These nanomaterials are not in nanoscale range.

The compact size of these materials confers new properties and creates opportunities for novel applications. In comparison to conventional bulk materials, nanoparticles and nanomaterials exhibit either novel or unique physicochemical features, such as shape, size, composition, solubility, molecular weight, and surface charge(Kolahalam et al., 2019). Metallic nanoparticles are desirable candidates for catalytic applications because they have a higher surface to volume ratio than their bulk equivalents. The transition between the molecular and metallic states is one of the main characteristics (providing a local density of states (LDOS)), a short-range ordering and increasing number of kinks, corners and edges (Campelo et al., 2009)

Over the years the nanoparticles have evolved into diverse types with novel properties and architectures-

a) Monometallic nanoparticles: They comprise of single metal.
b) Bimetallic nanoparticles: They comprise of a noble metal (in particular, a platinum group metal) and a non-noble metal (in general, a first-row transition metal). Bi-metallization enhances properties of the original single-metal catalysts and adds a new property due to synergistic effect. The properties of bimetallics depend on their constituting metals and their size giving them unique optical, electronic, thermal and catalytic properties(Cruz et al., 2021).

The bimetallics may be synthesized by the combination of two metal nanoparticles with different architectures and may result in a variety of distinct structures. There are 2 main category of bimetallic nanoparticles 1) Alloys and 2) Hetero structure (Ramos & Regulacio, 2021).

Alloy nanoparticles may be furthered classified into 2 groups,

- Homogeneous alloys: Uniform distribution of atoms of 2 metals either in ordered (Intermetallic) or random manner
- Gradient alloys: Atoms of one metal grow more dominant in the core, while atoms of the other metal become more concentrated toward the surface.

In heterostructure bimetallic nanoparticles, the two metal components are clearly separated from one another. e.g., Core shell nanostructure and Heterodimer.

- Core shell nanostructure: It has a metal core and a shell made completely of a different kind of metal.
- Hetero dimer: Two metal components that are placed next to one another. (Figure 1.2)

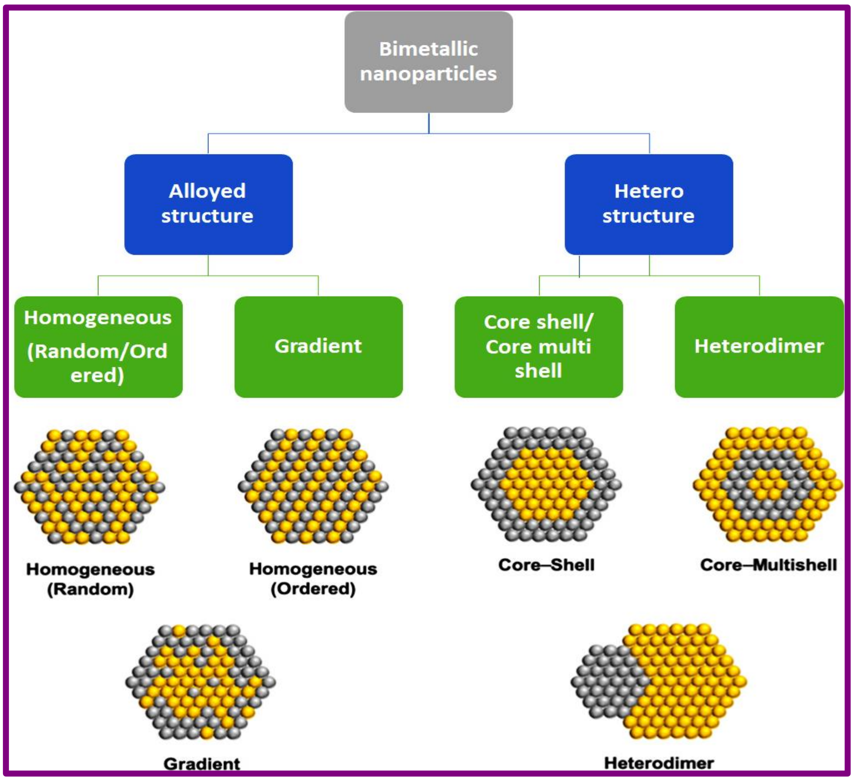

Figure 1.2: *Schematic of different configurations of bimetallic nanoparticles*

Metal oxide nanoparticles are another class of nanoparticles that have found extensive applications. For instance, TiO_2, ZnO have been used as photocatalysts and solar cells. Iron oxide nanoparticles have unique magnetic and superparamagnetic properties making them very useful in diagnostic and therapeutic applications, Fenton catalysts as well as supports for other metallic, bimetallic and metal oxide nano particles. Metal-metal oxide nanostructures and bimetallic oxides have also been extensively studied.

The metallic nano particles, bimetallic as well as oxide nanoparticles can form **Nanocomposites** which are a mixture of two or more materials with at least one dimension in the nanometre range with properties intermediate of the constituent materials. They possess enhanced thermal and mechanical properties making them promising candidates as catalysts and adsorbents.

These versatile classes of nanostructures have their unique morphology, photophysical properties and quantum confinement. The physicochemical characteristics of these nanosystems can be determined using a variety of characterisation techniques such as High-resolution transmission electron microscopy (HRTEM), Scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray Photoelectron spectroscopy (XPS), UV-Vis spectroscopy, Vibrating sample magnetometer (VSM), Thermogravimetric analysis (TGA), Inductively coupled plasma-mass spectrometer (ICP-MS), Dynamic light scattering (DLS), zeta potential (ZP), Raman spectroscopy (RS), and infrared spectroscopy (IR) (Mourdikoudis et al., 2018).

Various techniques have been proposed for the fabrication of nanoparticles that are generally classified as top-down and bottom-up approaches. Top-down methods like grinding, etching, milling and machining involve breaking down of bulk material while bottom-up approach such as; thermal and photochemical decomposition, electrochemical and chemical reduction, sputtering, sol-gel method, chemical precipitation method, micro-emulsion method and hydrothermal method involve formation of a larger structure by the assembly of smaller building blocks- known as growing of nanoparticles (Bolade et al., 2019; G. Sharma et al., 2019).

Usually, the nanoparticles are produced in large quantities on a commercial scale that are uncapped and when released as big aggregates, these nanoparticles become environmentally hazardous (Javed et al., 2020). Reducing agents such as sodium borohydride ($NaBH_4$) and hydrazine hydrate (N_2H_4) are necessary for the physical and chemical synthesis of nanoparticles. These are mostly poisonous substances with hazardous effects on humans and the environment (Bolade et al., 2019). This has necessitated the development of facile, greener and eco-friendly method for synthesising nanoparticles to protect the human health and environment.

It is important to utilise an effective and environmentally friendly stabilising or capping agent to increase the stability and effectiveness of metallic nanoparticles (Anjum et al., 2020). The choice of capping agent for nanoparticles is critical, since it affects various properties of the nanoparticles, such as size, shape and interactions with surrounding solvent. The bonding between the chains of capping ligands and the nanoparticle surface leads to steric hindrance providing ultimate stability and thus reducing the agglomeration of nanoparticles for a longer period of time. Apart from their primary role in stabilizing nanoparticles, some capping agents have the ability to reduce metal ions into metal nanoparticles as well (Heuer-jungemann et al., 2019; Javed et al., 2020)

Numerous capping agents such as surfactants, ligands, polymers, dendrimers, cyclodextrins and polysaccharides have been successfully used to immobilize nanoparticles on a support or wrap them in an organic ligand (Franconetti et al., 2019) of which biopolymers and Aminopolycarboxylic acids are attractive due to their unique binding capacities and green nature of biopolymers.

1.2. Biomaterials as capping ligands

Researchers have started using biomolecules and bioorganisms, such as bacteria, fungus, proteins, biopolymers, DNA and plant extracts, to manufacture metal nanoparticles in an environmentally friendly and sustainable manner. Biopolymers such as starch, cellulose, chitosan, pectin, guar gum etc. (Figure 1.3) have been widely employed in the synthesis of metal nanostructures. They contain abundant -NH_2 and -OH groups that can chelate strongly with metal ions by electrostatic interaction and act as a reducing agent to produce metal nanoparticles that are stabilised on the support (Ahmeda et al., 2014; Javed et al., 2020).

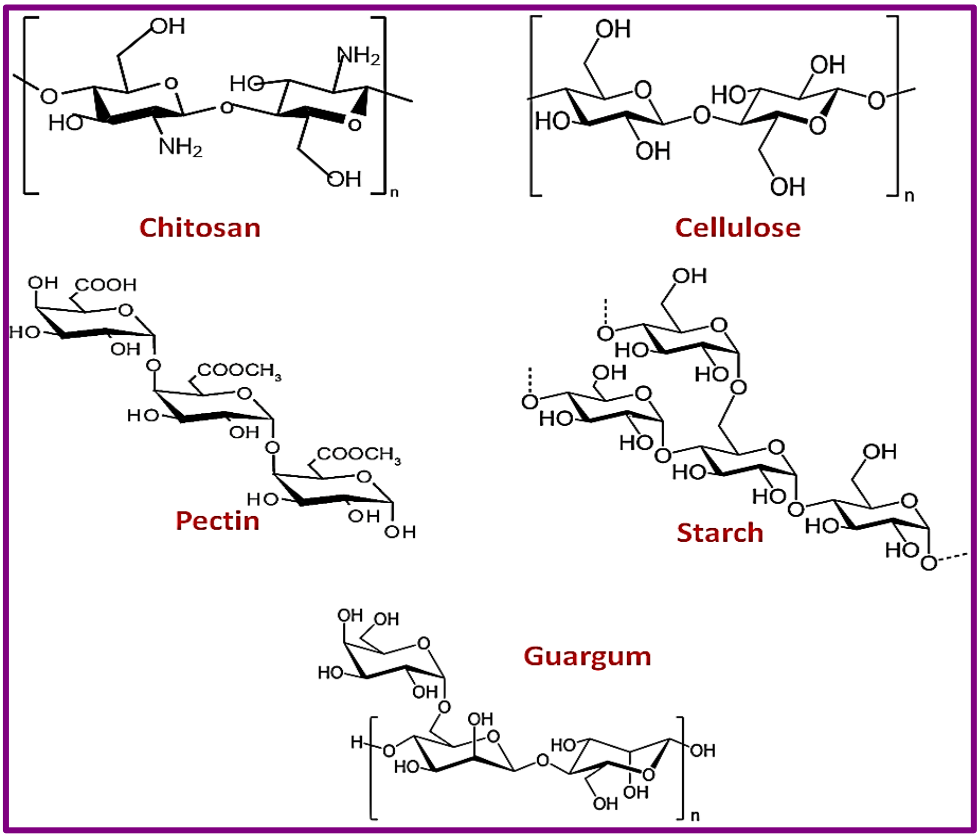

Figure 1.3: *Chemical structures of Biopolymers*

Chitosan is a naturally occurring biopolymer produced from the alkaline deacetylated derivative of chitin (copolymer of d-glucosamine and N-acetyl-d-glucosamine) and is derived from the exoskeleton of crustaceans (Franconetti et al., 2019). It is safe for industrial and biomedical applications (Gupta & Jabrail, 2006). Chitosan has many beneficial properties, including a flexible polymer chain structure, excellent chelation behaviour, chemical stability, biological compatibility, mechanical stability, ease of accessibility, high reactivity, high pollutant affinity, cost effectiveness, and environmental friendliness (Chang et al., 2008).

Chitosan is a good choice for stabilizing nanoparticles due to its polycationic nature and its conformation in the solution (Collado-Gonzalez et al., 2017).

Numerous applications have been reported for chitosan capped/supported nanoparticles. Mohan, et al prepared chitosan stabilized gold nanoparticles with potential application as a temperature abuse indicator in frozen products (Bhatt et al., 2018). Thana Thanayutsiri et. al., synthesised chitosan stabilized gold nanoparticles by microwave assisted method and used it as a colorimetric sensor for the quantitative determination of anionic ethylenediaminetetraacetic acid disodium salt (Na_2EDTA) (Thanayutsiri et al., 2020). Shanmugaraj et al. fabricated chitosan capped silver nanoparticles for the colorimetric determination of sulphide in water samples (Shanmugaraj & Ilanchelian, 2016). Mohamed Mahmoud Fathy reported the preparation of chitosan capped gold nanoparticles which were further loaded with an anticancer agent, Doxorubicin. This nano-formulation was utilized as a radiosensitizer and nanocarrier for cancer chemo-radiotherapy(Fathyb et al., 2018). Sharma et al. synthesized thiol terminated chitosan capped silver nanoparticles for the detection of mercury(II) in water (P. Sharma et al., 2018). Dickstein et al. prepared magnetically recoverable Ag and Ru nanoparticles capped with chitosan, and further used it for the reduction of nitrophenols in presence of sodium borohydride (Dickstein et al., 2021). Puente et al. have developed silver-chitosan and gold-chitosan SERS substrates for p-aminothiophenol as probe molecule (Puente et al., 2021).

DNA with its unique chiral structure (Figure 1.4) has been used as a support for metal nanoparticles such as palladium with applications in catalysis including synthesis of chiral molecules (Mart et al., 2018)

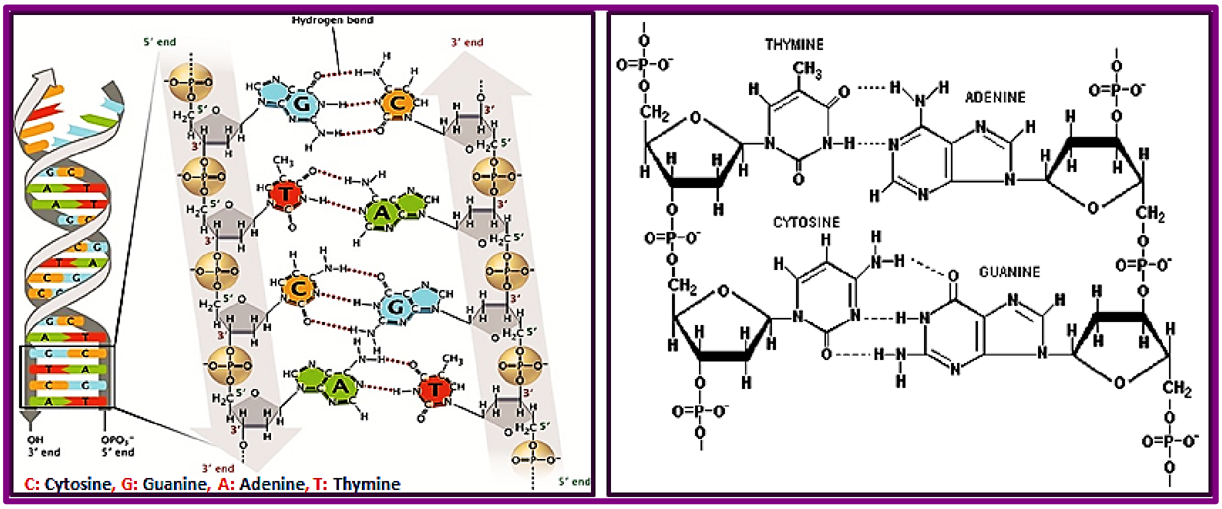

Figure 1.4: *Chemical structure of DNA(Kortaberria et al., 2009)*

1.3. Amino polycarboxylic acids as capping ligands

Amino polycarboxylic acids (APCAs) such as Ethylenediamine tetraacetic acid (EDTA), Diethylenetriamine pentaacetic acid (DTPA), Meso-Oxybis(butanedioic acid) (ODS), Iminodiacetic acid, Ethylenediiminodibutanedioic acid (EDDS), Ethylenediaminedi-(o-hydroxyphenylacetic) acid (EDDHA) and N,N'-Bis(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid (HBED) etc. are well-known and efficient chelators for metal ions and have good reducing and complexing properties.(Figure 1.5)

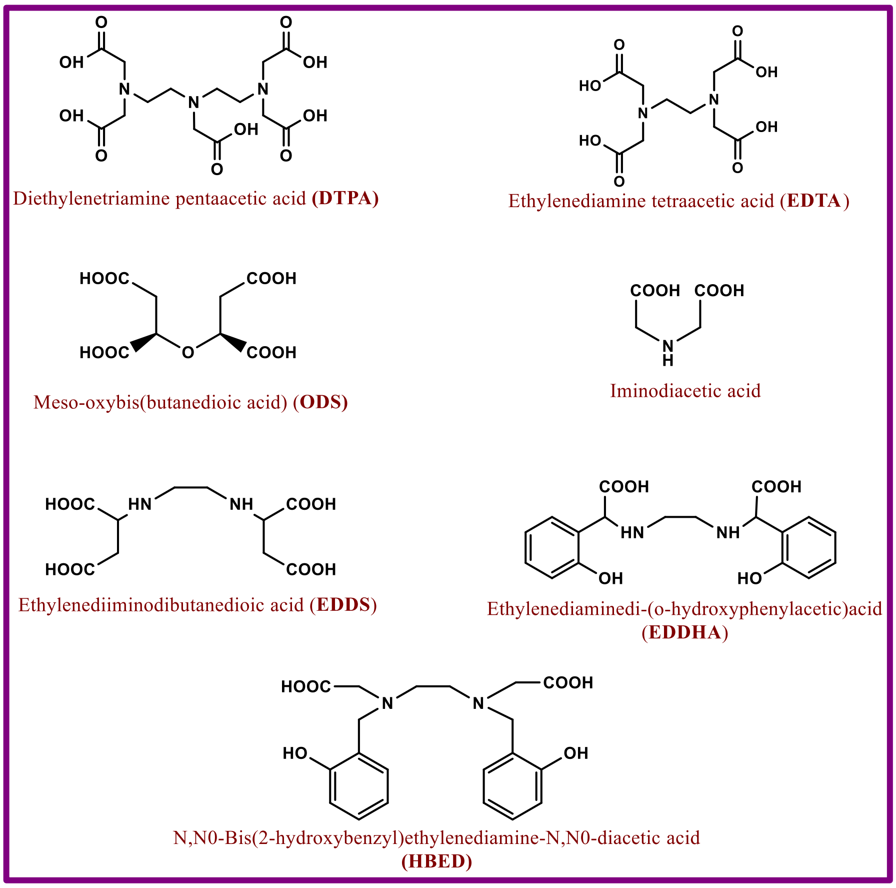

Figure 1.5*: Chemical structures of Amino polycarboxylic acids (APCAs)*

DTPA contain five carboxyl groups, with which it can act as an effective capping ligand. DTPA can bind to the surface of the nanoparticle due to the interaction between carboxyl group of DTPA and metal surface. DTPA has the ability to serve as both reducing agent and capping agent for stabilization (Bhatt et al., 2018) .

There are a number of reports in the literature wherein the metal nanoparticles have been synthesized using complexes of APCAs. Aghazadeh et al prepared EDTA capped superparamagnetic iron oxide (Fe_3O_4) (Aghazadeh et al., 2017) nanoparticles. Zhao et al fabricated magnetic material by binding EDTA onto Fe_3O_4/graphene oxide and used it for the removal of Uranium from aqueous solution. (D. Zhao et al., 2017). Bhatt et al synthesized Diethylenetriaminepentaacetic acid (DTPA) capped gold and silver nanofluids and applied it for chromium sensing. (Bhatt et al., 2018)

1.4. Application of Nanoparticles

The applications of nanoparticles are spreading in almost all the areas of science and technology. (Figure 1.6)

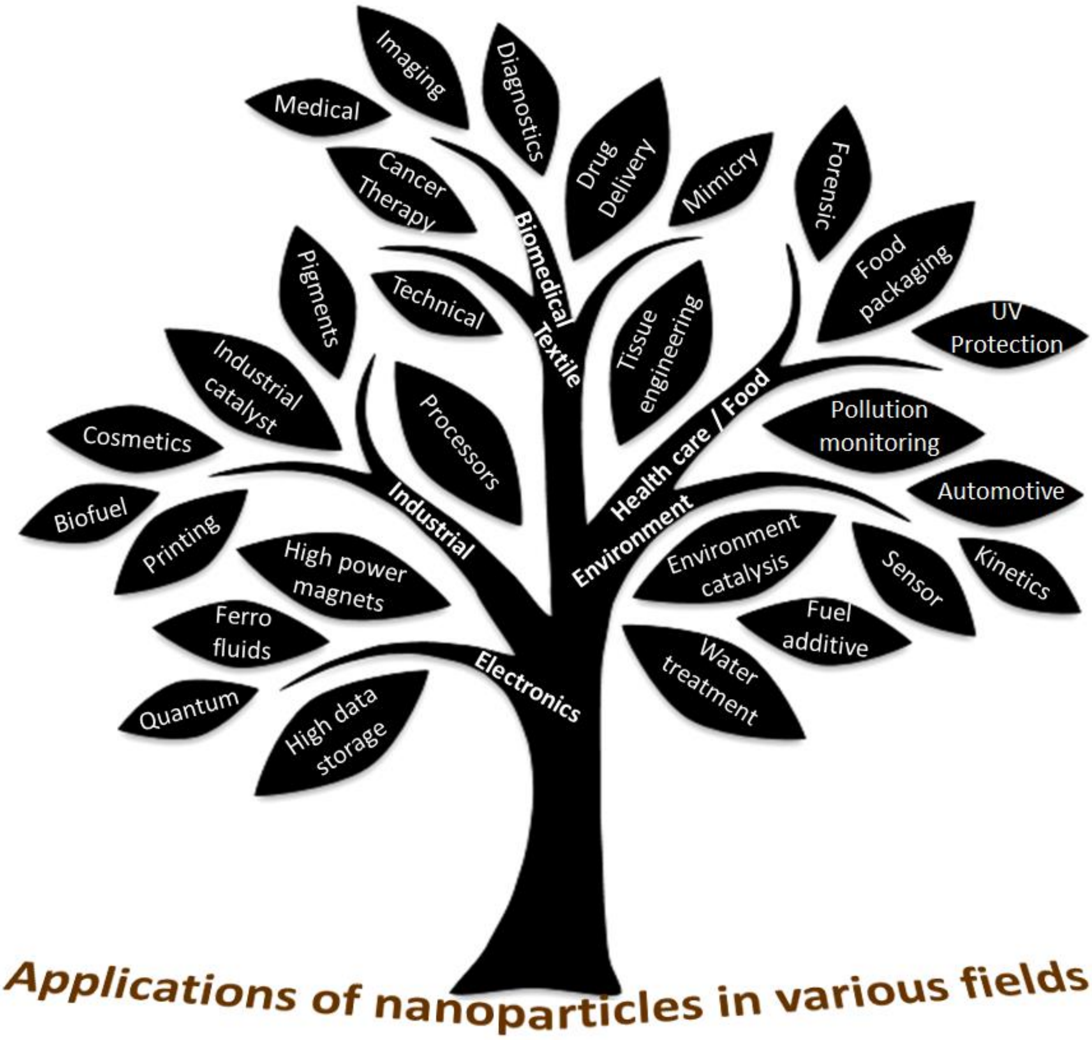

Figure 1.6: *Application of Nanoparticle in various fields*

Considering the unique properties, nanomaterials have been utilized for various purposes by industries and humankind for thousands of years in variety of applications. such as environmental, catalytic, electronic, magnetic and optoelectronic, biomedical, pharmaceutical, cosmetic, agriculture, energy storage and sensing applications(Tiquia-Arashiro & Rodrigues, 2016).

1.4.1. Application of Nanosystems in organic catalysis

Catalysis has changed and is still evolving our world. Generally homogenous catalysts are used extensively due to their high reactivity and selectivity, and requirement of low catalyst loading. In spite of many benefits, poor catalyst reusability and metal contamination in the final product, significant amount of wastes and imposing hazardous impact on the surrounding environment are the common problems faced for using homogeneous catalysts. Recovery and reuse of the catalyst are crucial from economic and environmental point of view. These drawbacks and requisites led to heterogenization of the catalyst which involves grafting of the homogeneous catalyst to a solid support such as polymers, silica, alumina, etc. However, the heterogenous catalysts have serious limitations like low reactivity, selectivity, non-robustness, leaching of metals from the catalyst and cost. So, there is a need for a development of new catalytic system, which are highly active like homogeneous catalysts and are easily separable and recoverable like heterogeneous catalysts. Therefore, nanomaterials were recently used as efficient alternatives for the immobilization of homogeneous catalysts because by reducing the size of the catalytic support, the surface area of the catalyst is increased and thus a semi-homogeneous media is generated, which can be used as a bridge to improve the gap between homogeneous and heterogeneous catalysts (Ghorbani-choghamarani et al., 2016; Savitha et al., 2016).

Shaping of metals into the nano size structures allows one to modulate both quantitatively (surface to volume ratio) and qualitatively (types of facets and surface atom coordination) the catalytically active areas with respect to extended (bulk) systems (Fortunelli & Vajda, 2016). The properties of noble transition metal nanoparticles make them potential materials for nanocatalysis. Now a days, an important part of synthetic chemistry is established on the usage of valuable transition metal catalysts such as Ru, Co, Rh, Ni, Pd and Pt, mainly Pd. Palladium catalyzed reactions are now recognized as very important toolbox in organic synthesis, due to their diverse applications in several organic transformations like oxidation, reduction (hydrogenation), Heck reaction, Suzuki coupling, Stille, Sonogashira, Hiyama, Negishi, Kumada, C-F bond formation etc. (Anjum et al., 2020; Hooshmand et al., 2019; Leonhardt et al., 2010; Sahin & Gubbuk, 2022) that find widespread applications in pharmaceutical and other chemical industries.

A majority of commercial heterogeneous catalysts are made of small nanoparticles (less than 20 nm) that are highly dispersed on solid supports with large surface area (Niu & Li, 2014). Therefore, nanomaterials have recently been used as efficient alternatives for the immobilization of homogeneous catalysts. This is because, by decreasing the catalytic support size, the surface area of the catalyst is increased and thus a semi-homogeneous media is obtained, which can be used as a bridge to improve the gap between homogeneous and heterogeneous catalysts (Ghorbani-choghamarani et al., 2017) (Figure 1.7). In this regard, Iron oxide nanoparticles have been reported as a solid support, especially in the forms of ferrite and magnetite, or Fe_2O_3 and Fe_3O_4, respectively. The magnetic property of the support allows magnetic separation of the catalyst using an external magnet, thus avoiding centrifugation and filtration. it also reduces loss of catalyst and improves the reusability (Baran, 2019).

Heterogeneous catalysts based on bimetallic systems, in particular noble metals with non-noble metals such as Pd with Nickel, have received enormous scientific and industrial attention because bimetallic nanocatalysts prove to be economical with improved catalytic activity, selectivity and stability(Nan et al., 2020).

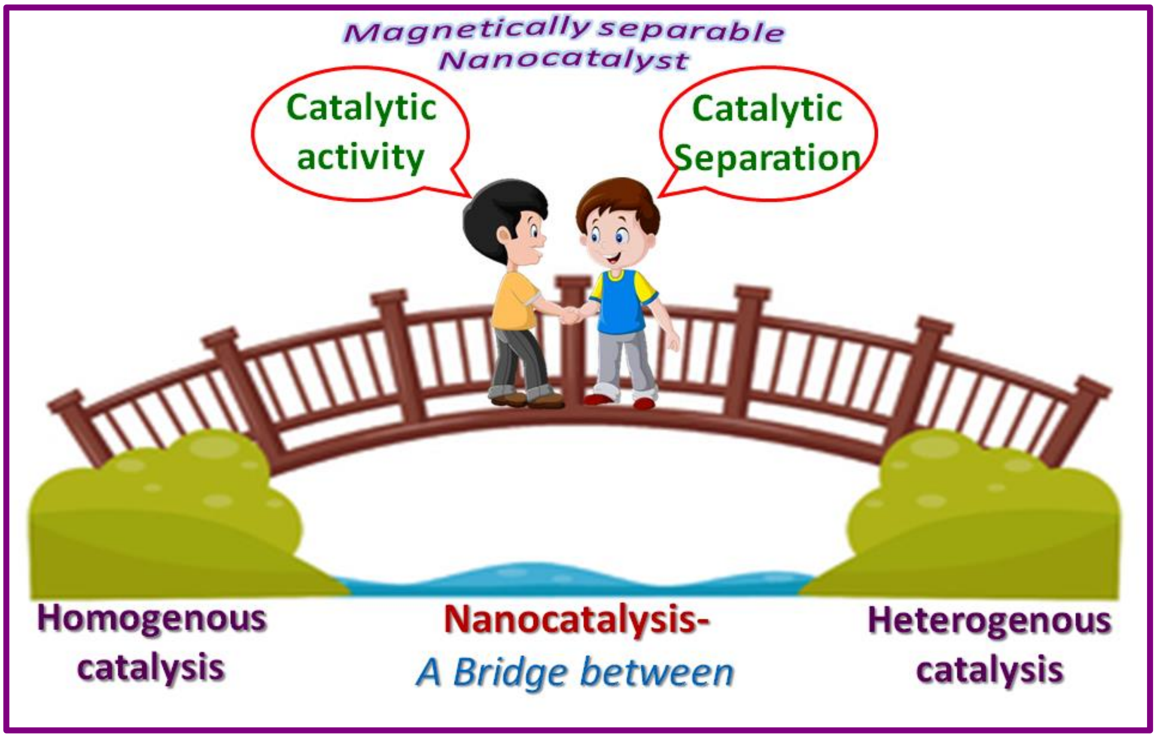

Figure 1.7: *Representative diagram of Nanocatalysis (a bridge gap between homogenous and heterogenous catalysis) and magnetically separable nanocatalyst*

Suzuki coupling reaction in water

The Suzuki coupling reaction, which combines aryl boronic acids with aryl halides to produce biaryl compounds, is the most significant C-C coupling reaction via sp^2–sp^2 linkages which are widely used in different areas due to its attractive characteristics including the benign reaction conditions, commercial availability of precursors, functional-group compatibility, great resistance to air and moisture, and participation of nontoxic, stable, and easily accessible boronic acids (Hooshmand et al., 2019). Nobel prize in chemistry for 2010 was awarded to Ei-ichi Negishi, Akira Suzuki and Richard Heck, due to the significant industrial importance of Suzuki coupling reaction and their important contribution to this research field (Martín et al., 2012).

The homogeneous catalytic system consists of Pd (II) and Pd (0) composites with appropriate ligands in organic or biphasic solvent system. It frequently encountered several issues such as separation and recyclability of catalyst after reaction and more importantly the high cost of the ligands which are sensitive to air and therefore, the reactions require inert atmosphere and majority of the reactions are performed in organic solvents (Borah et al., 2014). Palladium immobilized on solid support are promising candidates as heterogeneous catalysts for carrying out Suzuki coupling reactions (Bao et al., 2019a). Superparamagnetic heterogenous metal nanocatalyst enables further facilitates the separation step of catalyst (magnetically separable), easy isolation step, high atom economy, efficient recovery and recyclability of the catalyst (Augustyniak et al., 2016). (Figure 1.8)

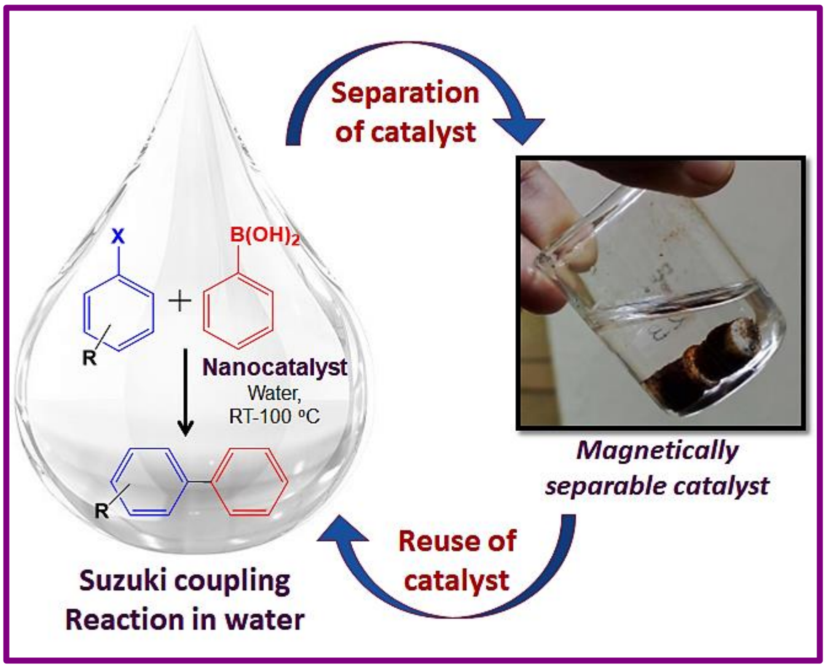

Figure 1.8: *Diagram for Suzuki coupling and magnetically separable catalyst*

There are several metal ions capable of catalysing this reaction, but the palladium catalysts are the key players (Dong et al., 2021).

However, Palladium is a precious metal with a low planetary abundance and a high cost, so it is crucial to substitute another metal or decrease the dosage of Pd to get over these drawbacks. It also becomes imperative to find alternative secondary sources of palladium due to its low abundance and wide applicability.(Nan et al., 2020).

In recent years, a lot of research has been done on the recovery of metals from industrial effluents. However, the majority of the investigations have concentrated on recovering Cu, Ag, and Au, and little work has been done on isolating Pd. (S. J. Lee et al., 2021). In order to recover Pd(II) from waste process streams, conventional methods like chemical precipitation, adsorption, leaching, ion exchange, electrolysis and electrochemical reduction and innovative separation techniques like membrane separation, biosorption, electro-kinetic process, magnetic nanoparticle-based process, hydrothermal sulfidation flotation, foam fractionation, and molecular recognition gel technology techniques have been reported (Nagireddi et al., 2018). Among these adsorption is one of the preferred method for the separation of metals(Parajuli & Hirota, 2009).

To increase the efficiency of Pd catalysts, research was also directed towards the development of Pd-based bimetallic nanoparticle catalysts, such as Pd-Au, Pd-Ag, Pd-Rh, Pd-Ru, Pd-Cu, Pd-Co or Pd-Ni, for several C-C coupling reactions. Pd–Ni nanoparticles are notably efficient for Suzuki coupling reactions than the mono metallic Pd or Ni catalysts mainly due to the enhanced electron flow on surface of the catalyst (Zhang et al., 2018) and can also become less expensive due to the involvement of inexpensive Ni metal (Bao et al., 2019b; Ghanbari et al., 2017).

Nickel in Pd-Ni alloy nanoparticles played an important role to resist Pd-oxidation, which was attributed to the standard reduction potential of Pd^{2+}/Pd^0 (0.83 V), higher than that of Ni^{2+}/Ni^0 (-0.23 V). So, Pd^0 with rich electrons transferred from Ni to Pd exhibited higher catalytic activity and easily executed the oxidative addition of aryl halide in Suzuki coupling reactions. Bao et al. had prepared Pd–Ni bimetal by using carbon nanofibers (CNF) as carrier and used it for Suzuki coupling reaction (Bao et al., 2019a). Nan et al. had synthesized Carbon nanotube (CNT) based nanocatalyst (Ni@Pd/CNT) and was used in catalytic carbonylative cross-coupling (Nan et al., 2020). Ghanbari et al had prepared Pd-Ni alloys on Fe_3O_4 magnetic nanoparticle cores by ultrasonic irradiation and was investigated in the Suzuki-Miyaura C-C coupling reaction and 4-nitrophenol reduction (Ghanbari et al., 2017).

Due to strict and growing environmental regulations, industries need to introduce greener solvents in place of organic solvents, as well as environmentally friendly and recyclable catalysts. Water has gained tremendous importance among the different greener solvents due to its environmental acceptability, non-toxicity, non-flammability, availability and cost. The Suzuki–Miyaura coupling reaction progresses effectively when using water as a solvent (Figure 1.8) due to high stability of boronic acids in water and also the ability of water to dissolve most of the bases favouring the transmetalation step of the catalytic cycle and thus increasing the overall reaction rate (Borah et al., 2014; Hoffman et al., 2015).

1.4.2. Application of Nanoparticles in Environmental remediation

Environmental pollution is undoubtedly one of the biggest issues faced by the society today. New methods are constantly being explored for the remediation of toxins in air, water, and soil. It relies mainly on using various technologies such as, adsorption, biological oxidation, chemical oxidation and incineration (Khin et al., 2012). The use of nanotechnology in environmental applications has been a major area of research interest with a focus on pollution prevention and the removal of environmental contaminants from different contaminated soils, sediments, solid wastes, air and water (Das et al., 2018).

Most environmental applications of nanoparticles fall into three categories(Khan et al., 2019): 1) Formation of sustainable and environmentally benign products for the prevention of pollution; 2) Remediation of contaminated hazardous materials; 3) Sensors for pollutants.

Application of Nanosystems for detection of pollutants by Surface enhanced Raman spectroscopy (SERS)

Nanomaterials are becoming important in the design of detection system due to their fascinating properties like surface plasmon resonance (SPR), high fluorescent quantum yield, biocompatibility, chromogenic functionality, and electrocatalytic functionality (Yadav et al., 2019). In order to enhance the sensing performance with improved sensitivity, stability, and selectivity, functionalized nanomaterials are used as optical or electroactive labels, colour generators, and/or amplifiers as well as catalytic tools for electron-transfer catalysis, (Farzin et al., 2019) to fabricate optical sensors surface-enhanced Raman scattering (SERS) substrates, as well as electrochemical sensors. (Xie et al., 2022)

In 1974; the enhancement in Raman spectra of pyridine on roughened silver was first accidentally observed by Fleischmann and co-workers. At that time, the researchers did not understand that these spectra were caused by any remarkable enhancement or novel phenomena and they ascribed the enhancement to a surface-area effect. In 1977, Albrecht and Creighton and Jeanmaire and Van Duyne each independently recognised the phenomenon. Since its discovery over 48 years ago, the application of surface enhanced Raman spectroscopy (SERS) in various fields has grown rapidly (B. Sharma et al., 2012).

SERS is considered as one of the most potent, ultrasensitive analytical technique for identifying and quantifying trace amounts of analytes and providing structural information based on their distinct vibrational Raman fingerprint and enables many applications, such as water pollution monitoring, detection of illegal and carcinogenic food additives, pesticide monitoring, trace detection for organic substances, identification of explosives, and biological and medical detection and so on (Sheng et al., 2020; Tong et al., 2018).

When the pollutants are in contact with metallic surfaces like Ag, Au or Cu nanoparticles, Raman spectra are amplified by factors up to 10^8 or even larger, enabling single molecule (SM) SERS in some cases. The majority of the visible and near infrared wavelength region, where most Raman observations take place, is covered by the Localized surface plasmon resonance (LSPRs) of all three metals (Ag, Au, and Cu). Since Au and Ag are air stable materials, they are frequently utilised as SERS substrates while Cu is more reactive (Mosier-boss, 2017). It is well-known that silver is more affordable than gold and has a larger optical cross section.

Aggregation of nanoparticles, which is bottleneck of nanoparticles as a sensor, can be regulated by introducing stabilizers during the synthesis of metallic nanoparticles into stable solid substrates. Due to their thermal stability and chemical resistance, polymers such as polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP), gelatin, and sodium poly(D-L) glutamic acid are good stabilizers (Sundaram et al., 2013). The use of biopolymers as a matrix that supports or contains nanostructures, is an alternative technique for producing inexpensive SERS substrates. Among the biomolecules reported for this use, Chitin, Guargum, Cellulose, Alginate, silk, pectin, and chitosan have been investigated (Colusso & Martucci, 2021; Puente et al., 2021).

Balachandran et al prepared pectin supported gold and silver nanoparticles and used them for the detection of Cu-complex of cationic tetrakis (4-N methylpyridyl)porphyrin (Balachandran et al., 2015). Puente et. at., synthesized chitosan stabilized gold and silver nanoparticles and SERS measurements were done using 10^{-4} and 10^{-9} M p-aminothiophenol as a probe molecule (Puente et al., 2021). Vanamudan & Sudhakar, attempted to use guargum as a capping agent for the synthesis of guargum stabilized silver nanoparticles and applied it as a SERS substrate for Rhodamine 6G, Reactive blue-21 and Reactive red-141 dyes (Vanamudan & Sudhakar, 2016). Fateixa et. al., synthesized Ag and κ-Carrageenan gel which was further used as a SERS substrate for the detection of 2,2′-dithiodipyridine (2-dtpy) (Fateixa et al., 2014).

A wide range of nanoparticle morphologies, including nanorods, nanocubes, nanospheres, nanotriangles, nanowires, nanoplates, and nanostars, can be produced depending on the capping agent and reducing agent used (Mosier-boss, 2017). The morphology of formulated nanoparticles has a major impact on the amount of Raman amplification. The significant enhancement of Raman signal is due to two main factors: Chemical enhancements (CM) and Electromagnetic effect (EM) (Figure 1.9). Chemical enhancement mechanism (CM) is based on the enhancement effect due to the charge transfer (CT) between adsorbed molecules and substrate, which can be photo-induced charge transfer or chemical bonding (Tong et al., 2018). The electromagnetic effect arises from the localized surface plasmon resonance (LSPR) on metallic nanomaterial excited by laser under the action of an electromagnetic field. (E. Lee et al., 2017; Prakash, 2019; Sheng et al., 2020).

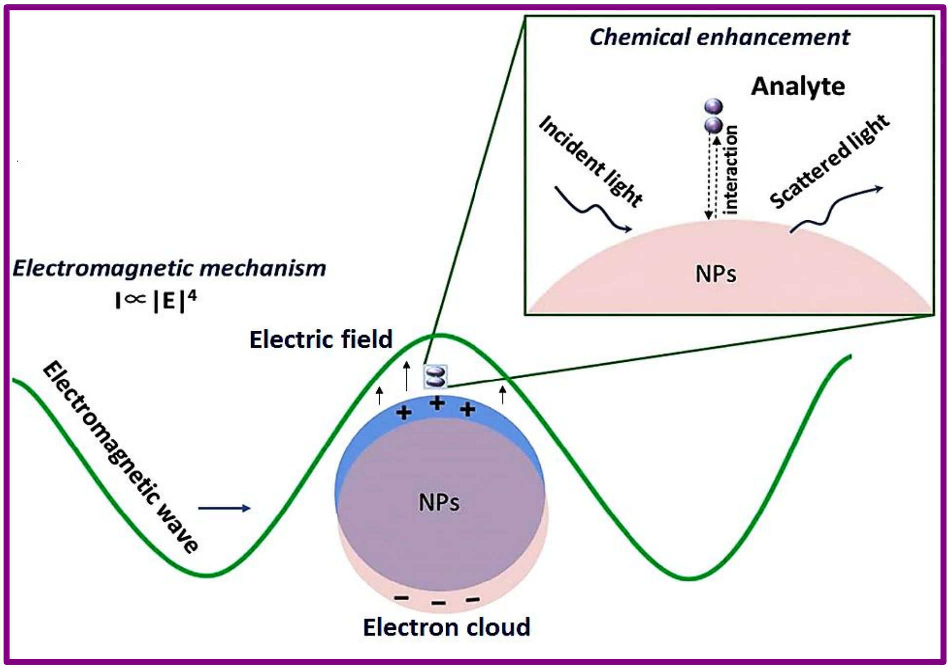

Figure 1.9: *Electromagnetic and chemical SERS enhancement*

In SERS, the so-called hot-spots formed in the gaps between nanoparticles, particle-substrate nanogaps, or at the edges and tips of anisotropic nanoparticles provide sufficiently intense electromagnetic fields to promote a tremendous increase in the Raman intensity of molecules located in these regions, allowing for the detection of a SERS signal even from single molecules (Ding et al., 2019; K. Wang et al., 2018). A large SERS enhancement is observed when the gap between two nanoparticles is less than 10 nm (Y. Wang et al., 2010).

Reduction of p-Nitrophenol

Nitrophenols are one of the most refractory pollutants that can occur in industrial wastewaters and are widely used to make pharmaceuticals, explosives, dyes, pesticides, herbicides, and insecticides as well as a corrosion inhibitor for rubber and wood. They are hypertoxic substances for humans and animals (G. Wang et al., 2021). According to the United States Environmental Protection Agency (U.S. EPA) p-Nitrophenol (p-NP) is one of the top 114 organic pollutants.(Vincent & Guibal, 2004). Several processes such as adsorption, coagulation, flocculation, oxidation, chemical precipitation for the degradation of nitrophenols have been developed to prevent their discharge into the environment (Vincent & Guibal, 2003).

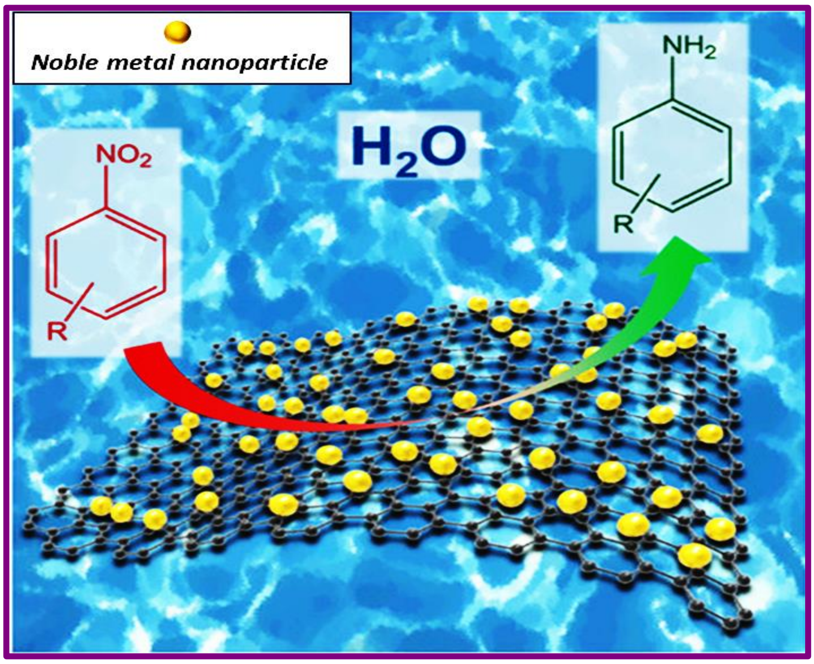

Figure 1.10: *p-Nitrophenol reduction in water*

The reduction of toxic p-NP (Figure 1.10) is a common and facile route to produce harmless aminophenols, which are very significant intermediates for the synthesis of several useful nitrogen-containing organic compounds, such as agrochemicals, pharmaceuticals, polymers, dyes, pesticides, and cosmetics. Moreover, reduction of p-NP is a "model catalytic reaction". It is a stoichiometric reduction process in which single product is obtained from single reactant (P. Zhao et al., 2015).This reduction process is inert to $NaBH_4$, in absence of metal catalyst. The catalytic efficiency of metal nanoparticles for electron transfer is explained by their size dependent redox potential. The redox potential of the nanoparticles should lie between thresholds of potentials of the donor atom (negatively charged, BH_4^-) and the acceptor molecule (positively charged, aromatic nitro compounds) (Pradhan et al., 2001).

Coinage metal nanoparticles have gained more importance in reduction of p-NP due to their high catalytic activity and stability. The catalytic activity of different nanoparticles such as Ag, Au, Cu, Pd, Pt and Ni was studied for the reduction of p-NP as homogenous and heterogenous catalysts. Due to their high activity, excellent efficiency, and higher Fermi potential, which lowers the reduction potential value, metal nanoparticles can function as an active catalyst for many electron-transfer reactions (El-Sheikh et al., 2013). Bimetallic nanoparticles display higher catalytic activity than either constituent monometallic nanoparticle, because of the additional degrees of freedom, structure and composition(Pozun et al., 2013).

Dye degradation

Organic dyes are widely utilised for industrial applications such as textile, leather, ceramics, explosives, paper, plastic, pharmaceutical and food industries. The high usage of organic dyes leads to the environmental (Water) pollution. Most of the dyes used for industrial purposes are carcinogenic and poisonous to plants, animals and humans owing to not being decomposable. Due to this reason, it is essential to control industrial effluents for the creation of a safe and clean environment (Hemmati et al., 2018). There are many ways to remove contaminants from both waterbodies and the environment, most of them are only suitable for certain applications. For e.g., Coagulation, Photodegradation, Chemical Degradation and Reverse Osmosis. Among them, one of the most popular methods for removing pollution from the environment is chemical degradation(Dadashi et al., 2022).

Thus, the development of easy, facile and rapid method for the efficient degradation process of dyes has received greater significance. Noble metal nanoparticles such as Ag, Au, Cu, Ni, Pd, Pt, Rh, Ru are being used for degradation of organic dyes (Begum et al., 2020). The dye degradation process by this method leads to the formation of less toxic and biodegradable products (Benhadria et al., 2022).

From the above discussion and detailed literature review it was evident that development of novel sustainable palladium based bimetallic, magnetic nanostructures with catalytic potential for C-C coupling reactions as well as environmental remediation would be interesting.

Monitoring of water quality is of tremendous importance. Surface enhanced Raman spectroscopy (SERS) is an attractive analytical tool that offers several advantages such as fingerprint recognition, multiplex capabilities, high sensitivity as well as being non-destructive. Development of SERS substrate by a green process that is sustainable would be of great advantage.

Among all metal nanoparticles, Pd nanoparticles have gained a lot of interest recently because of their ability to be utilised as homogeneous or heterogeneous catalysts in many reactions due to their high surface to volume ratio. (Ganapuram et al., 2015; Hemmati et al., 2018; Kora & Rastogi, 2016) and Ag nanoparticles as SERS substrates

The main objectives of present research are:

1. Synthesis of metallic and bimetallic Palladium-Nickel based magnetic capped nanostructures using chitosan and DTPA.
2. Evaluation of catalytic potential of these nanostructures for C-C coupling reactions and environmental remediation of Nitrophenols.
3. Recovery of Palladium from ELP using cross linked chitosan and evaluate its valorization as heterogeneous catalyst for C-C coupling reactions and environmental remediation of Nitrophenols and dyes
4. Synthesis of chitosan supported silver nanostructure with potential application as SERS substrates for nitrophenols and dyes

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