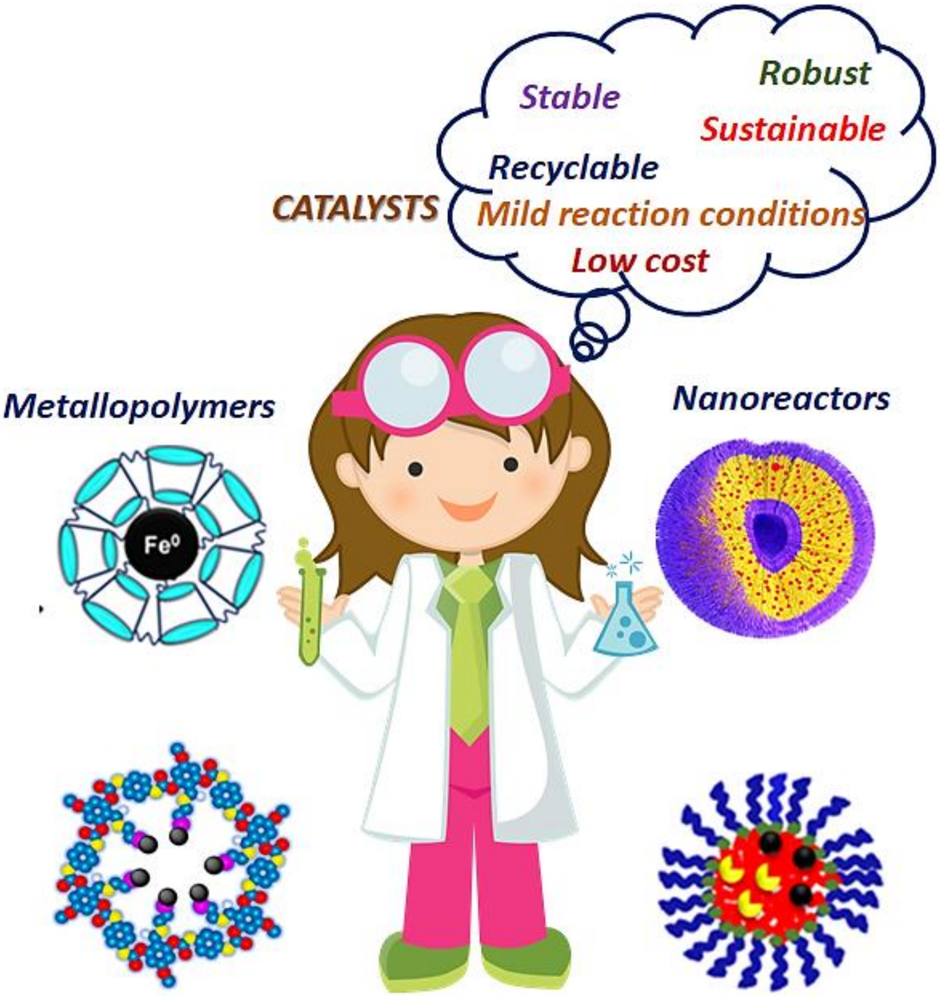
Chapter 1

Introduction



1.1 BACKGROUND AND LITERATURE REVIEW

Catalysis is one of the important area in science because various catalytic reactions used in different fields such as environment, health, pharmacy and chemical industry involves at least one catalytic step[1]. Desired products can be achieved in high yield without side products using catalysts. The rapidly expanding fields of nanoscience and nanotechnology are essential for the expedite advancement in catalysis. Nanocatalysis, an important branch of nanoscience, in which metal nanoparticles are utilized as catalytically active materials, has gained enormous attention during the past few decades. Various materials with metal nanoparticles as catalytic active sites have been reported such as core-shell nanocatalysts[2], magnetic nanocomposites[3], mixed metal oxides[4], integrated nanocatalysts[5], carbon-based nanocatalysts[6], zeolites[7], metal organic frameworks (MOFs)[8], covalent organic framework (COFs)[9], enzymes[10], carbohydrates[11], surfactants[12], polymers[13] etc (**Figure 1.1**).

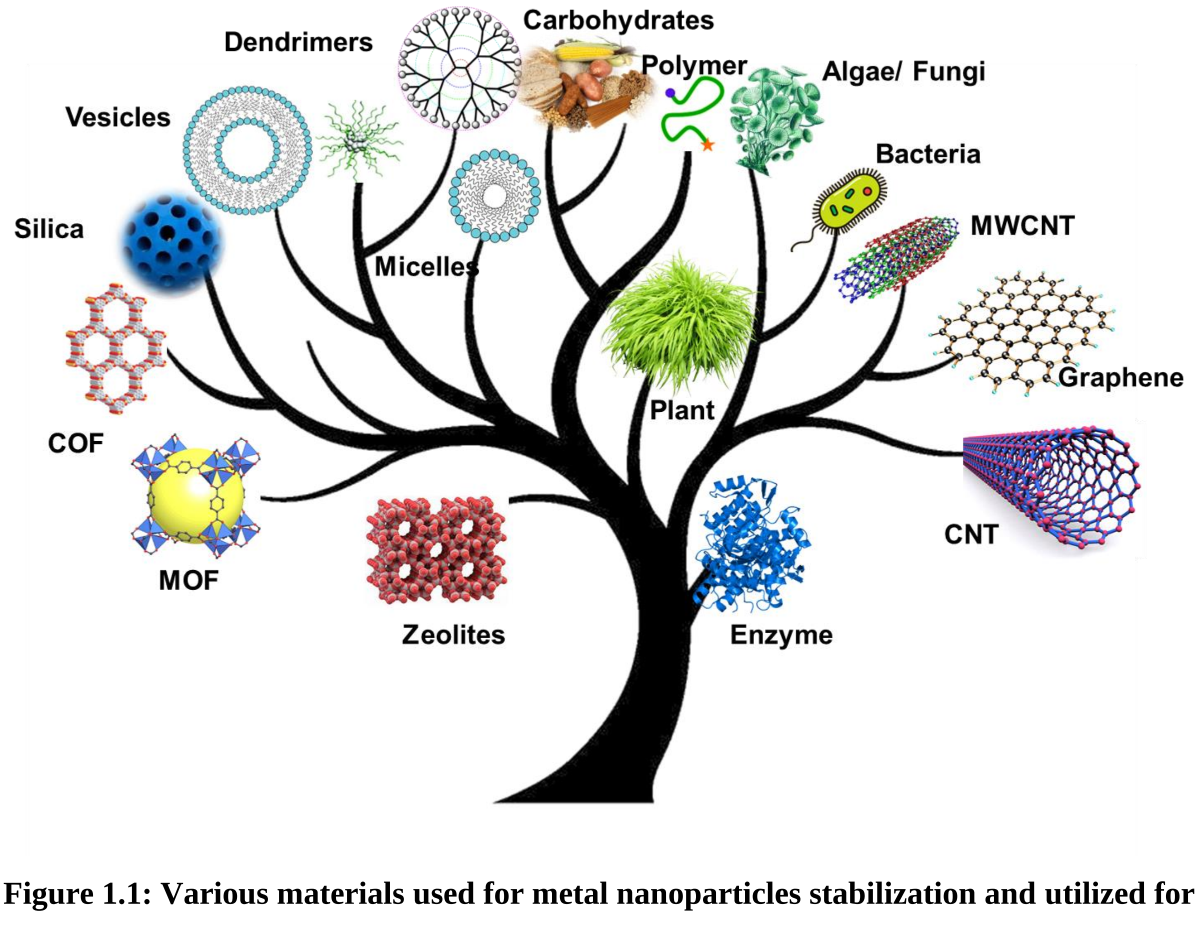


Figure 1.1: Various materials used for metal nanoparticles stabilization and utilized for catalytic applications

1.1.1 METAL NANOPARTICLES

Metal nanoparticles (MNPs) are defined as nanosized metals with at least one of the dimensions within 1 to 100 nm[14]. They are synthesized fundamentally by two approaches namely top down and bottom up **(Figure 1.2).**[15] Top down approach includes mechanical milling[16], etching[17], sputtering[18], laser ablation[19] and electro-explosion[20]. Bottom up approach for MNPs synthesis includes sol-gel process[21], spinning[22], supercritical fluid synthesis[23], laser pyrolysis[24], chemical vapour deposition[25], chemical reduction[26] and green synthesis[27].

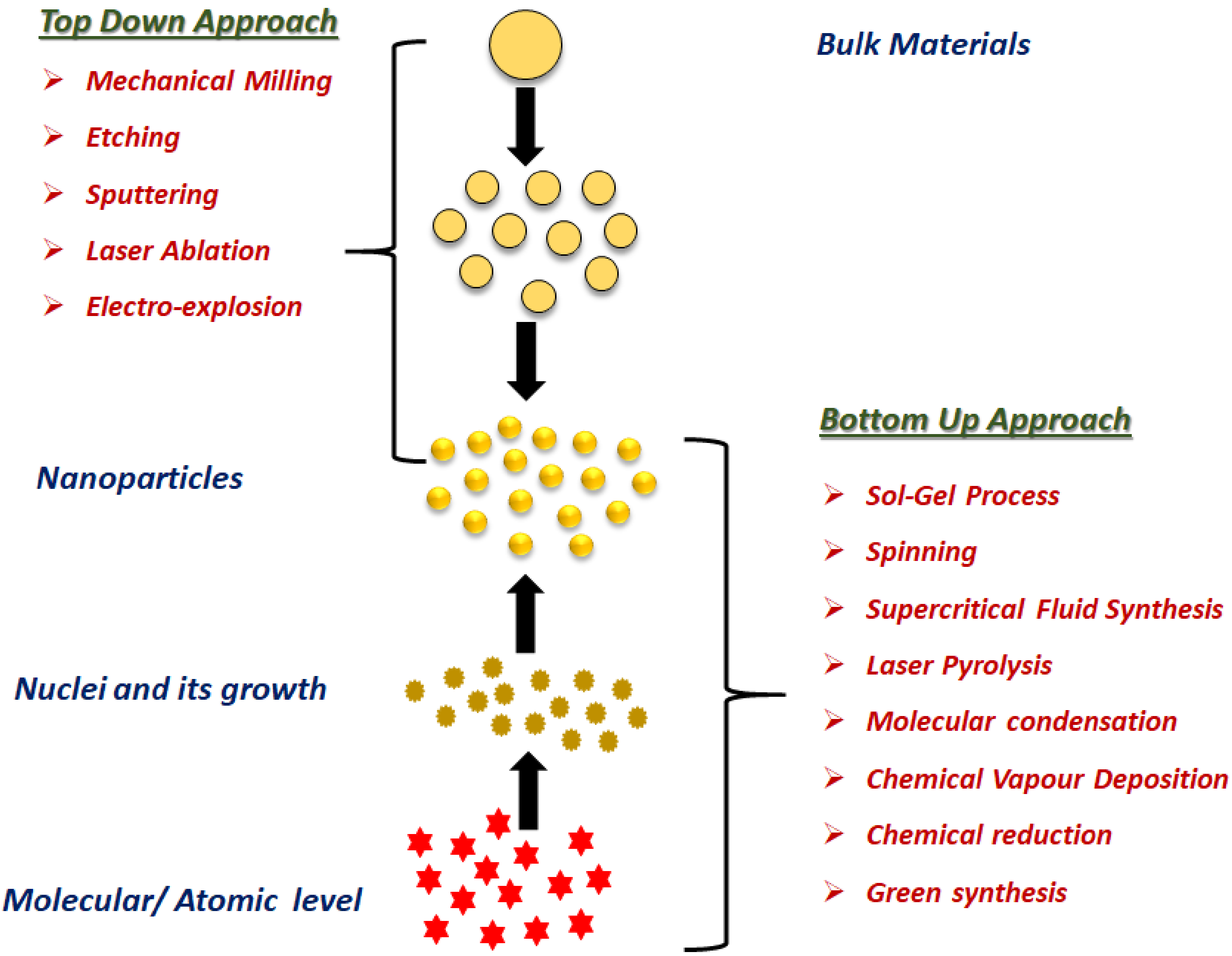


Figure 1.2: Synthesis of nanoparticles via top-down and bottom-up approach

There are different types of MNPs such as noble metal nanoparticles (Ag, Au, Pt, etc.)[28],[29],[30], magnetic nanoparticles (Fe_2O_3, Fe_3O_4, etc.)[31],[32], semiconductor nanoparticles (ZnO, TiO_2, etc.)[33], [34] and metallic chalcogenides (PbS, ZnSe, etc.)[35], [36].

MNPs play important role in heterogenous catalysis due to superior surface-to-volume ratio, abundant rich active surface atoms, and distinctive electronic structures as compared with their bulk counterparts[37]. They have been utilized for catalyzing various organic transformations such as Reduction, Oxidation, Aza Michael Coupling, Reductive amination, multicomponent A3 coupling, Suzuki Miyuara coupling, Suzuki coupling, Heck coupling, Sonogashira coupling, Stille and Hiyama coupling reactions shown in **Figure 1.3**.

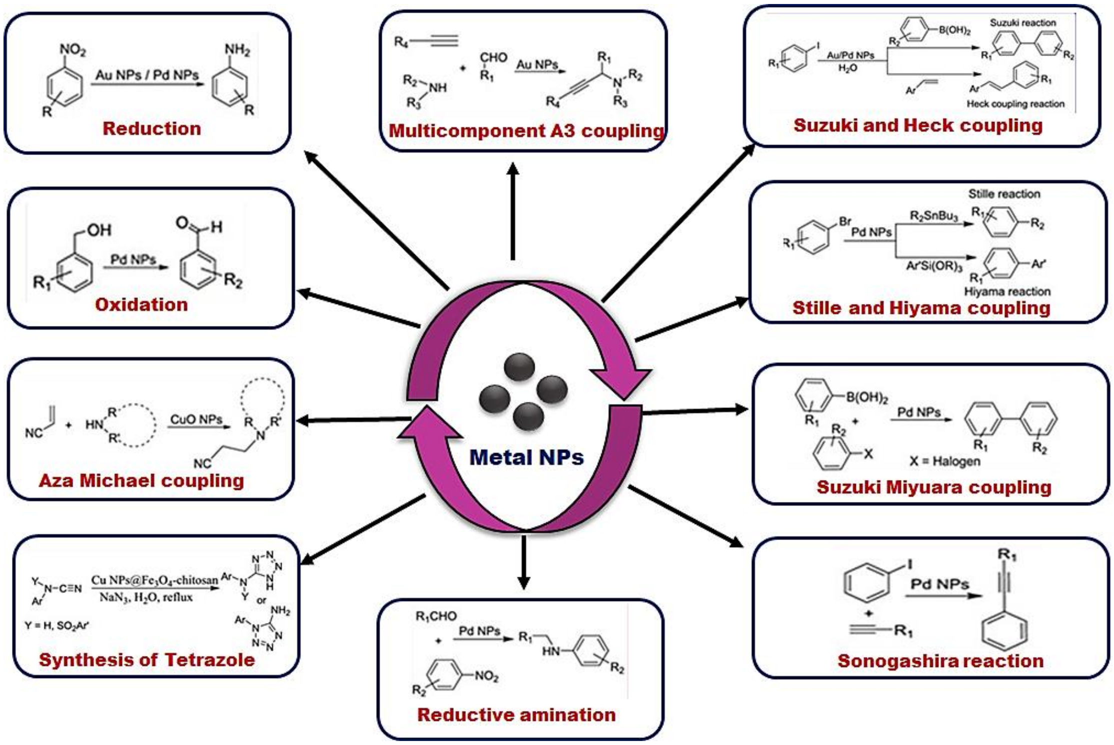


Figure 1.3: Schematic showing various metal nanoparticles catalyzed organic reactions

Conventionally, MNPs possess high surface energy due to which they are thermodynamically unstable, prone to migration and agglomeration during catalysis, especially at high reaction temperatures. These structural alterations are accompanied by a dramatic decrease in catalytic activity and selectivity.

Overcoming these limitations have been the focus of the researchers working in this field by devising various strategies to heterogenize MNPs for catalytic application. In this regard, it is anticipated that stabilizing MNPs by capping agents or encapsulating them within suitable materials will physically isolate them, halt their migration, and prevent them from coalescence which can improve their catalytic stability[38]. Some other benefits include increased stability, recyclability, improved selectivity, and maximized electronic interactions between MNPs and capping agents. Enhanced catalytic activity and selectivity could be accomplished by taking advantage of metal-support interactions between MNPs and capping molecules. Furthermore, it has been established that the size, shape, type of capping molecules on the NP surface and the support features affects the catalytic properties[39]. So far, many systems have been designed for catalytic applications but still there is need for the development of better catalytic systems and catalytic processes for the benefit of society. In light of this view, the advancement in designing environment friendly catalysts is important. Catalysts derived from natural sources, requires less tedious process, avoids long hours of synthetic procedures, can be utilized in aquoues medium at ambient reaction conditions and can be reused for multiple cycle of reactions will play great role in sustainability.

1.1.2 METALLOPOLMERS

Metallopolymers are unique class of functional materials in which metal centers are incorporated in the polymers. In the recent past, they have been utilized for several applications such as biomedicine, optics, catalysis, shape-memory and self-healing [40].

With suitable functionalities, these polymers can support MNPs resulting in formation of metallopolymers that can aid to perform reactions under relatively mild conditions. Metallopolymers offer advantage of easy separation and regeneration from the reaction mixture due to immobilization of metal catalyst in the heterogenous polymer matrix[41].

The spatial confinement within the metallopolymer provides longevity of the catalytic activities by protecting the encapsulated catalysts from contamination or hydrolytic degradation[42]. Thus, the fabrication of metallopolymers with appropriate rationale can turn out to bring a new advent in sustainable chemistry due to their ubiquitous assistance in the synthesis of commercially important compounds.

1.1.2.1 POLYMERS AS SUPPORT

Polymers can act as superior materials among the numerous capping agents, supports, or encapsulating materials developed so far, for stabilizing MNPs. This is because polymers have many benefits, such as the ability to control MNPs composition and morphology, reactivity on their surface brought by a particular polymer, and functional groups[37]. They can also impart beneficial qualities like flexibility and robustness. MNPs are stabilized in the polymer matrix via ionic, electrostatic, hydrophobic and covalent interactions. The structure and catalytic activity of MNPs/polymer composites are influenced by structure, morphology and functionality of the polymer. To serve this purpose, several polymers porous, conductive, branched polymers along with biopolymers have been utilized to design MNPs-polymer nanocomposites catalysts for various catalytic reactions.

1.1.2.2 POROUS ORGANIC POLYMERS

Porous organic polymers (POPs) have attracted widespread attention because of their potential to merge the properties of both porous materials and polymers.[43] The porous organic polymers have been widely used for the stabilization of MNPs. These are classified as conjugated micro- and mesoporous polymers (CMPs), covalent organic frameworks (COFs), hyper crosslinked polymers (HCPs), covalent triazine frameworks (CTFs) and porous aromatic frameworks (PAFs)[44]. By varying the polymerization conditions and types of reagents, cross-linking can occur, which will lead to the formation of macro- (>50nm), meso-(2-50 nm) and microporous (≤2 nm) materials. They can act as important supports for heterogeneous nanocatalysts due its high surface area, ability of control size of NPs, and large pore volume which allows easy access of substrates and products. The type and functionality of pores govern the above-mentioned features. For example, Kundu et al. reported pyrene-based microporous sulfonated organic polymers for the synthesis of biodiesels via esterification/transesterification of long chain fatty acids/esters at room temperature **(Figure 1.4)**[45]. These porous polymers showed nanofiber-like or spherical morphology, very high surface acidity, and excellent catalytic activity. Some examples of porous polymers used for catalysis has been listed in **Table 1.1**.

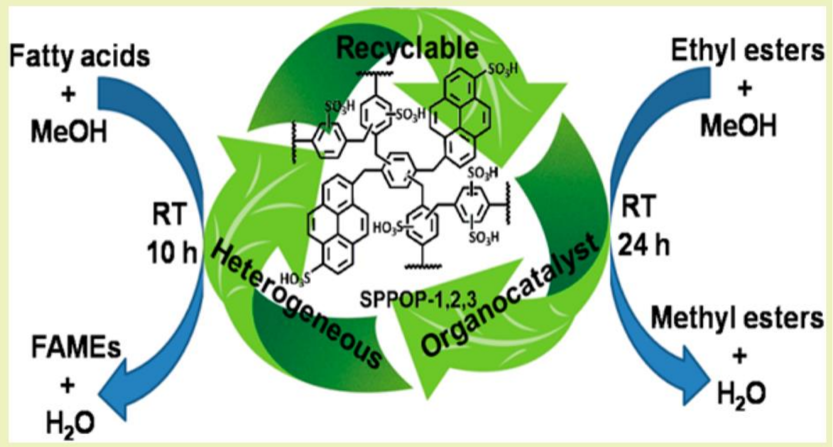


Figure 1.4: Pyrene based sulfonated microporous polymers for the synthesis of biodiesels (Reproduced with permission from. *ACS Sustainable Chem. Eng.* 2015, 3, 8, 1715–1723, Copyright 2015, American Chemical Society.)

Table 1.1: Some examples of porous polymer capped metal nanoparticles used for different chemical reactions.

Porous organic polymer	Metal NP	Porosity of polymer (Size)	Reaction	Ref.
poly(triphenylimidazole) (PTPI-Me)	Pd	Mesoporous and Macroporous (2-100 nm)	Cyanation reaction of aryl iodides	[46]
Crosslinked toluene on the surface of Co/C NPs	Pd	Mesoporous (~4 nm) to Macroporous (>200 nm)	Hydrogenation of alkenes	[47]
Spirobifluorene-based	Pd and Pt	Microporous (0.8 nm)	Hydrogenation of 4-Nitrostyrene	[48]
polythiophene polymer (PTPA)	Au	Microporous - mesoporous (2-6 nm)	Catalytic reduction of Congo red and MB	[49]
1,3,5-triazine (TRIA-POP)	Pd	Mesoporous (2.9 nm)	Hydrodeoxygenation of vanillin	[50]
Hyper-cross-linked polymer bearing carbazole and α,α′-dibromo-p-xylene monomeric units (HMP-1)	Pd	Microporous (1.6 nm)	N-formylation of Various amine	[51]

1.1.2.3 CONDUCTIVE POLYMERS

Conductive polymers are a class of organic polymers that are capable of conducting electricity. They possess conjugated single and double bonds along the polymer backbone or composed of rings connected through carbon-carbon single bonds such as phenylene, anthracene, naphthalene, anthracene, pyrrole and thiophene[52]. They are widely used for synthesis of nanocomposites to catalyze photocatalytic, electrocatalytic and reactions where electron transfer is involved. Some examples of conducting polymers are polyacetylene (PA)[53], polyaniline (PANI)[54], polypyrrole (PPy)[55], polythiophene (PTH)[56], poly(para-phenylene) (PPP)[57], etc. For instance, Muthuraj and Co-workers have reported a facile in situ synthesis of polypyrrole (PPy) polymer-incorporated silver molybdate (Ag_2MoO_4) nanocomposite utilized as a photo and electrocatalyst for the degradation of pollutants like methylene blue (MB), (Cr(VI)), and ciprofloxacin (CIP) shown in **Figure 1.5.**[58]

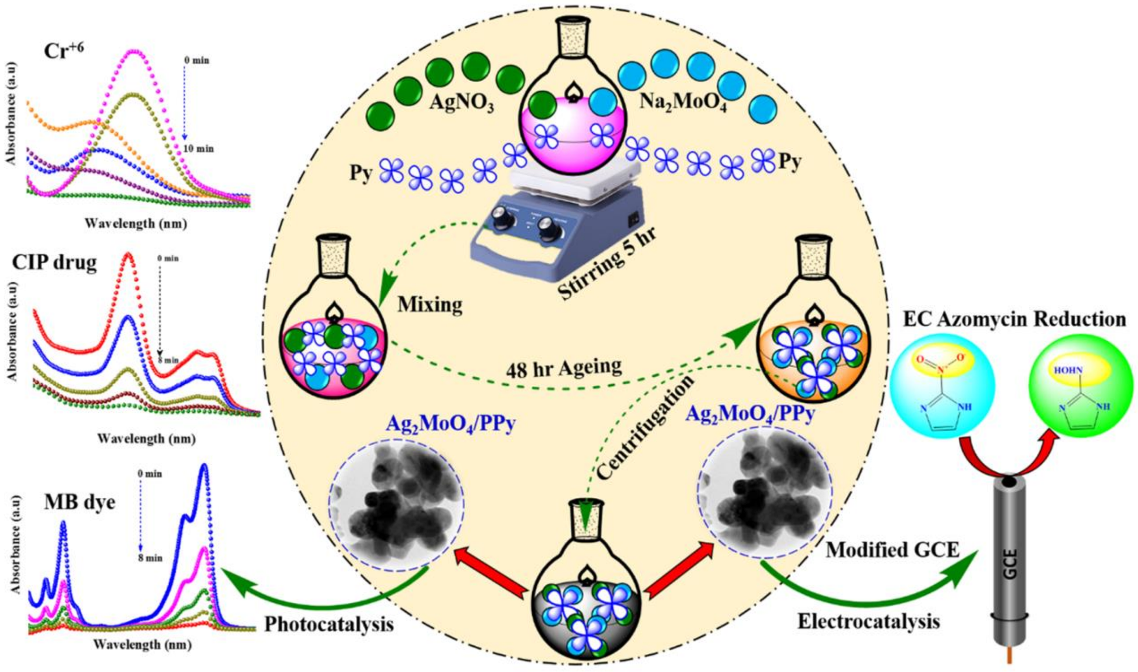


Figure 1.5: Schematic representation of synthesis procedure and the photocatalytic applications of Ag2MoO$_4$/PPy Nanocomposite (Reproduced with permission from *ACS Applied Materials & Interfaces* 2019 *11* (41), 38321-38335, Copyright 2019, American Chemical Society.)[58]

Table 1.2: Nanoparticles stabilized by conducting polymers used as catalysts

Conducting polymer	Metal NP	Reaction	Ref.
PANI	Pt	Reduction of substituted nitrobenzene	[59]
PANI enveloped reduced graphene oxide	Pt	Dimethylamine-borane (DMAB) dehydrogenation reaction.	[60]
Poly(1,8-diaminocarbazole)	Au/Pt	Electrocatalytic oxidation of formic acid	[61]
PANI	CeO_2	Photocatalytic reduction of dyes	[62]
Graphene oxide grafted with polypyrrole (PPy)	Cu_2O	Methanol oxidation reaction	[63]

1.1.2.4 BRANCHED POLYMERS

Branched or hyperbranched polymers are special class of polymers having unique topological structure. They can influence MNP formation by additional steric stabilization of growing MNPs and catalytic activity by creating space between branches for reacting molecules. For example, poly(amidoamine) dendrimer with hydroxyl functionalities employed for Copper encapsulation which was utilized for hydrogenation of carbonyl and olefin group **(Figure 1.6)**[64].

Table 1.3: Examples of branched and hyperbranched stabilized metal nanoparticles for catalytic reactions.

Branched/ Hyperbranched polymer	Metal NP	Reaction	Ref.
PEI	Pt	Reduction of 4-NP	[65]
Hyperbranched PEG-b-PCA (poly(citric acid)) shell grafted on the surface of Fe_3O_4	Pd	Mizoroki−Heck cross-coupling reactions	[66]
G4OH PAMAM dendrimer	Pd	Reversible Dehydrogenation/Hydrogenation of N-Heterocycles	[67]

Figure 1.6: Schematic representation showing the copper nanoparticles encapsulated in poly(amidoamine) dendrimer with hydroxyl for hydrogenation of carbonyl and olefin group (Reproduced with permission from *ACS Catal.* 2013, 3, 2, 182–185, Copyright 2013, American Chemical Society.)[64]

1.1.2.5 BIOPOLYMERS

Carbohydrates are one of the most promising biopolymers for the stabilization of MNPs as they are biocompatible, available in bulk and biodegradable. It exists in different size, molecular chains and functionalities which aids in reduction and stabilization of MNPs. The need for sustainable polymers has also been a purview of researchers for developing them. Thus, past few years have seen an uprising trend in the utilization of carbohydrates such as alginate, cyclodextrin, chitosan, cellulose, dextran, starch etc for catalytic application. For instance, Tam and Co-workers have reported a green approach to anchor silver nanoparticles onto the surface of cellulose nanocrystals coated with mussel-inspired polydopamine (PDA) at room temperature and utilized it as nanocatalysts for the reduction of 4-Nitrophenol(**Figure 1.7)**[68].

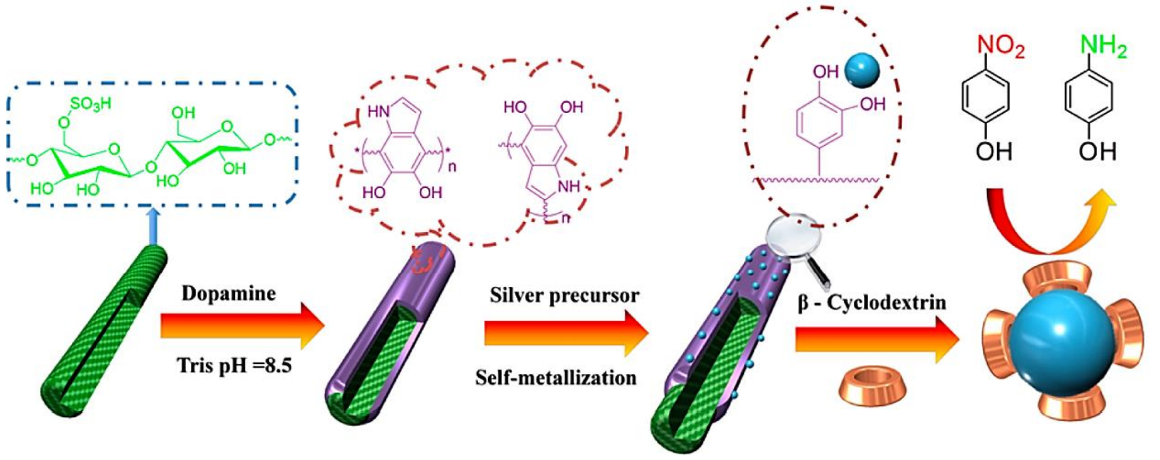


Figure 1.7: Schematic representation of the strategy for the synthesis of Polydopamine coated cellulose nanocrystals, and the plausible mechanism of metallization of AgNPs , and binding with β-CD(Reproduced with permission from *Ind. Eng. Chem. Res.* 2015, 54, 13, 3299–3308 , Copyright 2015, American Chemical Society.)[68]

Table 1.4: Some examples of polysaccharide-derived metallopolymers for catalytic applications

Polymer	Metal Nanoparticle (Size)	Catalytic Reaction	Reference
β-CD polymer crosslinked with citric acid (poly (CTR-β-CD))	Ru (1.8 nm)	Hydrogenation of biomass-derived Furanic compounds	[69]
β-cyclodextrin-functionalized surface of magnetic Fe_3O_4	Pd (17 nm)	Reduction of Nitroarenes	[70]
Honeycomb structured Bionanocellulose (NCmw)	Pd (10.6 nm)	Suzuki−Miyaura and Sonogashira cross-coupling reactions.	[71]
Chitosan coated Fe_3O_4 (CS-Fe_3O_4).	Cu (10 nm)	Azide-alkyne cycloaddition.	[72]
Alginate	NiPt (2.72-5.24 nm)	Hydrogen generation	[73]
Carboxymethyl guar gum polymer	Ni (60-80 nm)	Reduction of 4-nitrophenol	[74]

1.1.3 NANOREACTORS

The advancement in environment-friendly catalytic processes is a growing necessity and a topic of current interest due to the detrimental impact of the manufacturing process of pharmaceuticals and fine chemicals on the environment. The major impetus behind this initiative is the replacement of volatile organic solvents which are the primary cause of environmental pollution due to their excessive usage.

A switch from carrying out the reaction in "organic media" to other greener options such as water or no solvent, can advance organic chemistry sustainably and aid in pressing the rigorous environmental concerns**.** According to green chemistry principles, water is an acceptable choice of solvent due to its ubiquitous, non-toxic and non-inflammable nature. In fact, water is attractive from both environmental and economic perspectives. However, its utility is limited in organic chemistry due to the poor solubility of organic compounds and catalysts in water as well as low E-factor of the chemical processes [75],[76]. To address these issues, several researchers across the world are working to achieve maximum outcomes of the organic reaction in water, which is a major challenge. The catalytic reactions in the confined hydrophobic core of micelle and vesicles is an emerging research area and an effective strategy to address the above-mentioned issues.

In the recent past, polymer-derived nano architectures with varying morphologies have been explored for drug delivery applications but not much explored for catalysis as shown in **Figure 1.8**. Polymer micelles and vesicles, self-assembling aggregates, can be used to design robust and recyclable functional materials as catalytic nanoreactors through molecular manipulation and control.

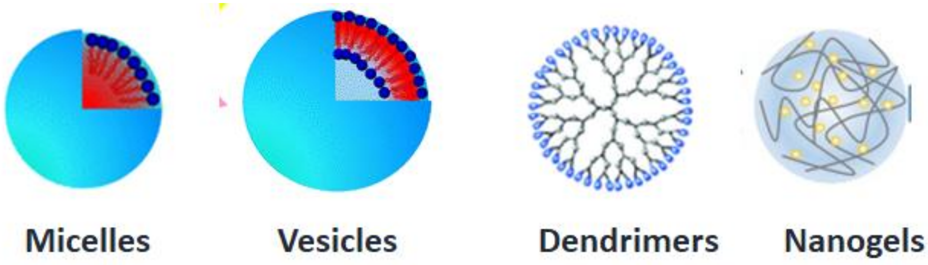


Figure 1.8: Different morphologies of the polymer nanoassemblies

The micellar and vesicular solutions are introduced as highly efficient, substrate-sorting scaffolds for the enhancement of the catalytic behavior.

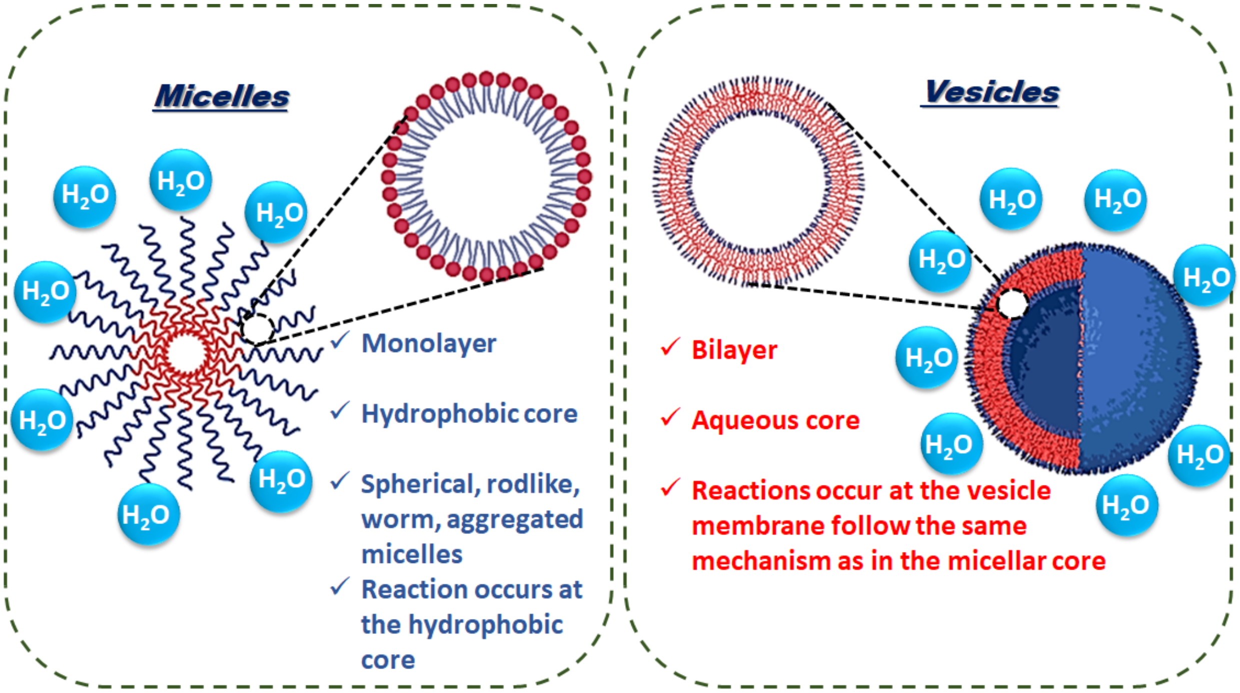


Figure 1.9: Schematic representation of structural difference of micelles and vesicles

1.1.3.1 Micelles

Micelles belong to a specific class of nano architectures. Their thermodynamics, formation kinetics, dynamics of exchange and its geometrical shapes depend on the chemical nature of the amphiphilic monomers and the conditions. In aqueous phase, amphiphiles spontaneously self-assemble into micelles, which can bind reactants and the catalyst at two distinct positions i.e., the hydrophobic surface (polar substrates/ catalyst) and the hydrophobic core (apolar substrate/ catalyst). Most of the catalytic reactions occur between these two positions of a micelle. Micellar nanoreactors act as a "pseudo phase" that can enhance the solubility of reactants and the catalyst in the concentration range of 10^{-1} to 10^{-3} M which is much better than the solubility of most of the organic species in water but still lower than their ability to solubilize in the organic solvents. Moreover, interactions play a major role in determining the reaction rate and selectivity. Since, micelles can stabilize catalysts, MNPs, reagents, reactants, etc. due to their relatively confined environment which can enhance the stability and the lifetime of the catalytic nanoreactors. Various cationic, anionic, and neutral amphiphilic molecules have been reported for accelerating the challenging catalytic reactions in water. Since the catalyst can be precisely housed in the hydrophobic portion of the amphiphile, micellar nanoreactors can be exploited for a range of catalytic reactions. For instance, Que et. al have reported gold nanoparticles (AuNPs) covered with well-defined poly(ethylene glycol)-b-polystyrene (PEG-b-PS) amphiphilic diblock copolymers containing a thiol group. They have reported excellent catalytic activity of this catalyst for the reduction of 4-Nitrophenol (shown in **Figure 1.10**)[77]

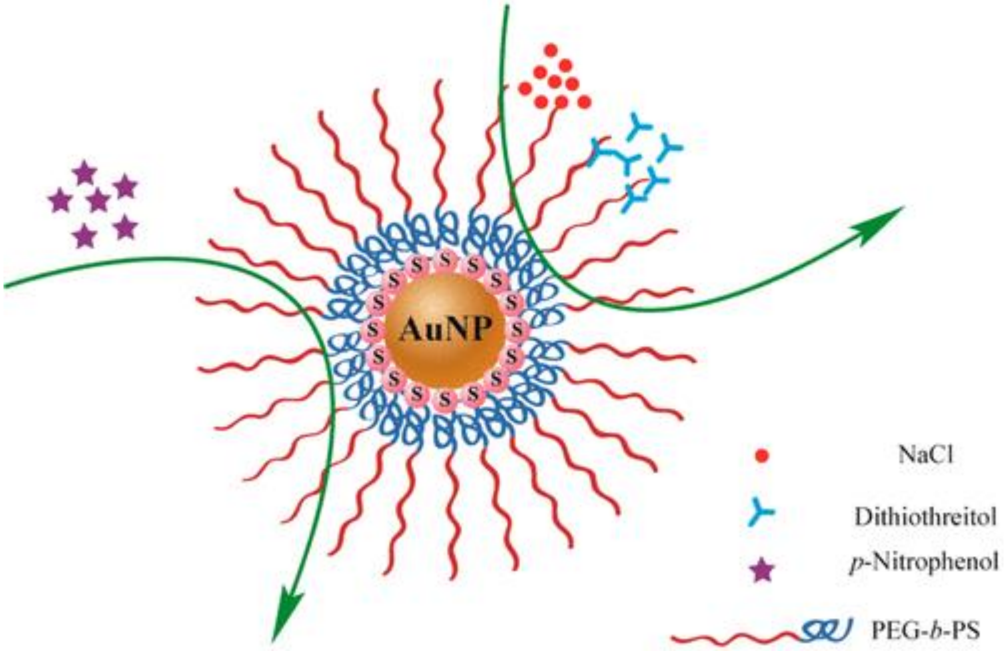


Figure 1.10: Schematic diagram showing the catalytical reactions occurring in hydrophobic core of polymer micelle (Reproduced with permission from *J. Phys. Chem. C* 2015, 119, 4, 1960–1970, Copyright 2023, American Chemical Society.)[77]

1.1.3.2 Vesicles

Polymer vesicles are hollow bilayered structures self-assembled from a specific type of synthetic amphiphilic polymers [78]. The intrinsic properties of vesicles such as size, membrane permeability, and stability can be tuned due to their synthetic nature. Polymer vesicles are highly robust in nature and hence is a suitable candidate for catalytic nanoreactors[79]. They consist of a hydrophilic core and hydrophobic membrane. For example, Du and Co-workers have reported a multifunctional homopolymer vesicle which was self-assembled poly(amic acid) (PAA) at room temperature for the reduction of 4-Nitrophenol (shown in **Figure 1.11**)[80].

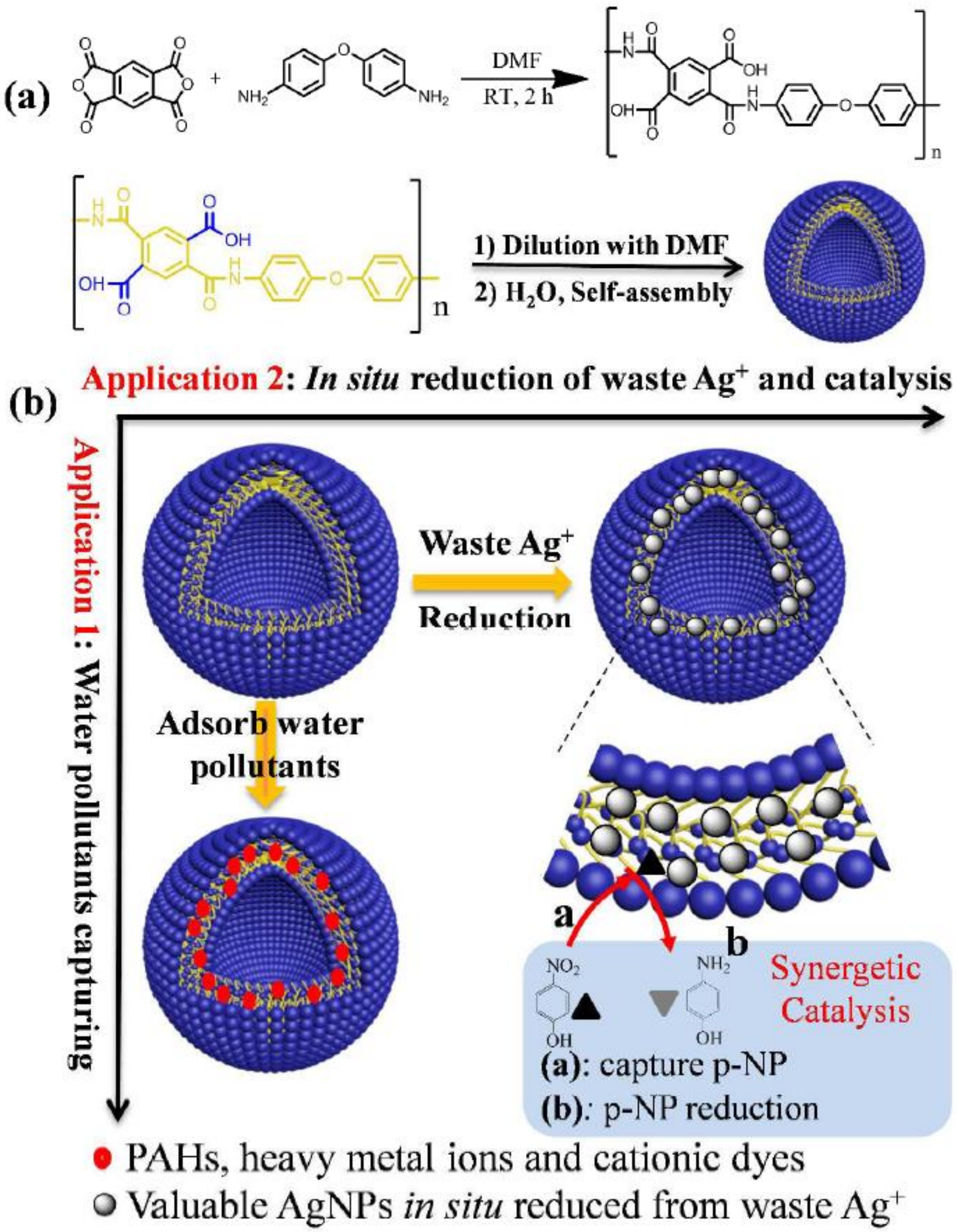


Figure 1.11: Schematic diagram showing the synthesis of polymer vesicles and catalytic reaction occurring in hydrophobic bilayer of polymer vesicle (Reproduced with permission from *ACS Appl. Mater. Interfaces* 2018, 10, 1, 713–722, Copyright 2018, American Chemical Society.)[80]

Since, the compartmentalization between the hydrophobic and hydrophilic portions in a vesicle can accommodate both hydrophilic (i.e, enzyme) and hydrophobic (i.e., metal catalyst) moieties in a single catalytic system to perform tandem catalysis. The hydrophobic membrane accommodating the catalyst and substrates provide more proximity to each of them and enhances the reaction rate[81]. The complex structure of vesicles provides sufficient steric hindrance preventing side reactions. Mechanisms and dynamics of vesicular catalysis are still under exploration.

There are different methods for the preparation of micelles and vesicles are reported in the literature such as simple dissolution, oil in water emulsion, solvent evaporation, lyophilization, dialysis and co-precipitation method.

Table: Some examples of surfactant and polymer derived nanoreactors for catalyzing different chemical reactions.

Surfactant/ Polymer	Metal NP	Nanoreactor Morphology	Type	Catalytic Reaction	Reference
FI-750-M	Pd	Micelle	Surfactant	sp^2-sp^3 coupling of nitroalkanes to aryl bromides	[82]
SPGS-550-M	Pd	Micelle	Surfactant	Arylations of Indoles	[83]
PS-750-M	Pd	Micelle	Surfactant	Reactivity of carbenes	[84]
Bistriazole-based dendritic amphiphile micelles	Cu/ Ag	Micelle	polymer	Reduction of 4-NP	[85]
Thiol-functionalized BSA-polymer conjugate composition (BSA-SH/PNIPAAm)	Au	Vesicle	Polymer	Reduction of 4-Nitrophenol	[86]
PEGylated surfactant ionic liquid	Pd	Vesicle	Surfactant	Chemoselective reduction of nitroarenes	[87]
Dodecylamine and cholesterol	Cu	Vesicle	Surfactant	Benzimidazole synthesis	[88]

1.2 THESIS AIMS AND HYPOTHESIS

Heterogeneous catalysis is highly preferred in the industry as it facilitates ease of separation and recovery of the catalyst. However, homogeneous catalysis displays the advantage of usually being much more selective. Nanocatalytic systems are one of the promising candidates for heterogenous catalysis. Metal nanoparticles have potential for catalyzing various organic processes. But aggregation is a major challenge with metal nanoparticles as a catalyst. Several capping agents and supports have been employed to solve this issue. Amongst them, polymers are conventional capping agents for metal nanoparticles because they can control their morphology and size, passivate surface, provide stability, and impart valuable properties such as flexibility and robustness. With suitable functionalities, polymers can support metal nanoparticles resulting in formation of metallopolymers that can aid in reactions at relatively mild conditions. This spatial confinement within the metallopolymer provides longevity of the catalysts by protecting the encapsulated catalysts from contamination or hydrolytic degradation.

The challenge of combining superior selectivity of homogeneous catalyst with the recoverability and reusability factor of heterogeneous catalyst puts forward the need for developing innovative and smart materials that smartly address the demands of green catalysis. Nanoreactors allow rapid and selective chemical transformation with excellent product yield. Most of the nanoreactors are surfactant derived and less explored for catalysis compared to biomedical applications.

Thus, the fabrication of metallopolymers and nanoreactors with appropriate rationale can turn out to bring a new advent in sustainable chemistry due to their ubiquitous assistance in the synthesis of commercially important compounds.

The classical approach of synthesis suffers from certain demerits such as use of expensive catalysts, harsh reaction conditions (bases and toxic solvents), formation of undesirable and hazardous by-products. Low yields, difficulty in product separation, and lack of catalyst recyclability are also identified as key limitations. This was done by synthesizing different polymer architectures such as crosslinked polymers, covalent organic frameworks, vesicles and micelles for stabilizing desired metal nanoparticles. They were rationally designed for the additional feature of recyclability and reusability. The work was executed in the following steps:

1. Development of crosslinked polymers stabilized zerovalent iron nanoparticles

β-Cyclodextrin, a well-known host for hydrophobic substrates with multiple hydroxy groups can aid in capping the metal nanoparticles to act as catalyst. However, due to its good solubility in water, the native β-CD may not be efficient capping agent hampering the recycling ability of the catalyst. β-CD derived crosslinked polymers can be ideal stabilizing agents due to stable, biodegradable and amphiphilic nature. β-CD was selected as a precursor and was covalently conjugated to α-hydroxy acids such as citric acid and lactic acid. These environmental friendly crosslinked polymers were endowed with functionalities like –OH, –COOH to stabilize the metal nanoparticles via ionic interaction. They can facilitate reactions in aqueous medium in less time and with high recyclability. Two crosslinked polymers were synthesized (i.e, citric acid crosslinked β-CD (CDCA) and lactic acid crosslinked β-CD (CDLA). Two nanocatalyst derived from CDCA capped zerovalent iron nanoparticles (nZVI) and CDLA capped nZVI were synthesized via ultrasonication method. The synthesized nanocatalysts were assesed for their ability to catalyze reduction of nitroaromatics via ultrasonication.

2. Development of covalent organic frameworks encapsulated palladium nanoparticles

Covalent Organic Frameworks (COFs) exhibit many properties that are advantageous for heterogeneous catalysis. They can act as hosts for catalytically active metallic nanoparticles and minimizes their aggregation. The large spatial separation allows multiple catalytic sites to be incorporated into the COF. For the development of this COF based catalyst, urethane linkage for formation of COF was utilized in a unique manner. The urethane linkages will provide the robustness. Monoformylphloroglucinol was rationally selected as one of the monomer for the COF synthesis, which can provide a pendant formyl group for the post-modification of COF. The formyl group was functionalized with cysteamine molecules. Benefiting from the dangling thiol groups in the pore, functionalized COF possess as the coordination sites for the transition metal cation such as Pd^{+2} due to its strong affinity towards the sulfur group. These were subsequently reduced to palladium nanoparticles. They were assesed for their ability to catalyse Suzuki Miyuara Cross Coupling reaction.

3. Development of polymer vesicles encapsulated copper nanoparticles

An amphiphilic co-polymer with carboxyl functionalities was rationally designed via urethane linkages. The free carboxyl group helps in stabilization of copper nanoparticles. The rational to choose urethane linked amphiphilic co-polymer was the intrachain H-bonding assisted in self-assembly into vesicles. The vesicles consist of hydrophilic core and hydrophobic membrane was tested by the hypothesis that hydrophilic dye will be encapsulated within the hydrophilic interior and hydrophobic dye in bilayer of vesicles. By this hypothesis, the hydrophobic substrates and the catalyst was efficiently encapsulated in the hydrophobic membrane and the reaction was facilitated. The close proximity between the reactant and the catalyst will aid in efficient and rapid catalysis. This nanoreactors were assessed for their ability to catalyze synthesis of benzimidazole, an industrially important compound via cascade route.

4. Development of polymer micelles loaded *Candida antarctica* Lipase B and zerovalent iron nanoparticles

For the development of biobased polymer micelles, tyrosine is used as a backbone of the molecular architecture with polyethylene glycol as the hydrophilic component and a long aliphatic acid chain as a hydrophobic component. This tyrosine-derived amphiphilic polymer self-assembles to form nanomicelles. The nanomicelles resemble the surfactant micelles as they possess a hydrophobic core that facilitates the organic transformation in an aqueous medium. Nanomicelles enhance the stability of the encapsulated metal catalyst, solubility of the hydrophobic reactants, and bring the catalyst and the reactant in close proximity. These polymer micelles were loaded with CALB and iron nanoparticles to behave as nanoreactors, further ability to catalyze chemoenzymatic cascade synthesis of p-aminophenol from the p-nitrophenyl ester was evaluated.

All the metallopolymers and nanoreactors synthesized by different strategies were assessed for their capabilities to catalyze different reactions. Several reaction parameters, kinetics, mechanisms and recyclability were investigated.

1.3 References

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