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Preparation and catalytic applications of nanomaterials: A review

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Abstract

Catalyst plays a very important role in the chemical industries. Catalysts have been used in processes like the workup of fuels such as oil, gas and coal, purification of effluents and industrial waste gases etc. Heterogeneous catalysts are gaining much attention as compared to the homogeneous catalysts as it confers more selectivity and provides better yield. Research in new catalytic materials or optimization of existing catalyst systems is of enormous importance in order to increase the efficiency of the catalyst resulting in higher product yields and purities. Currently, the research is more focused towards the nanostructured catalyst with enhanced physiochemical properties. Nanoscale catalysts have high specific surface area and surface energy, which ultimately lead to the high catalytic activity. Nano-catalyst improves the selectivity of the reactions by allowing reaction at a lower temperature, reducing occurrence of side reactions, higher recycling rates and recovery of energy consumption. Therefore, these are widely used in green chemistry, environmental remediation, efficient conversion of biomass, renewable energy development and other areas of interest. In this review prospects, paradox and perspective of preparation and catalytic application of nanomaterials in organic synthetic chemistry is reviewed, and an outlook of their developments is discussed.

Keywords: Nanomaterials, Catalytic applications, Organic Synthesis, Nanoparticles, Catalytic nanomotors.

1.0 Introduction

Nanotechnology is considered one of the key technologies of 21st century. Nanomaterials are man-made, possessing special properties and functions with, at least one external dimension that measure 100 nanometers (1nm = 10^{-9} m) [1-3]. These nanomaterials include nano-objects such as nanoparticles, nanofibers (rods, tubes) and nanoplates, which can consist of different materials, and therefore derived agglomerates and aggregates[4-6]. The increasing uses of such synthetic nanomaterials have increased the scope of its application in different fields. With the widespread industrialization of nanotechnology, nanomaterials applications in areas of medical diagnostics, areas of material modification, degradation of environmental pollutants and biotechnology are phenomenally increasing. This results to the necessity of its modification into different structure with desirable features. One of the foremost features is the catalytic application.

The use of catalysts in chemical technology is of great importance. Use of small amounts with high activities is particularly desirable for economic and environmental considerations. One possible strategy is the use of supported metal catalysts and hence, the application of the active material on a porous material with high specific surface areas (eg., Mesoporous SiO_2 nanoparticles) [7-13].

Due to the defined microporous crystalline structure of the Nanomaterials, they are characterized by a high shape selectivity and activity. Defined by the generation of defects, acid-base centers can be introduced into these materials, which make it suitable for use in organochemical reactions[14, 15]. A major advantage of the defined nanoporous structure is the diffusion caused by the small pore openings. Thus, catalyst efficiency increases, as many reactions can only take place by diffusion control.

In addition catalyst it supports with high surface area such as one-dimensional have recently attracted attention of researchers worldwide. These include layered double hydroxides, nanobubbles, quantum dots etc[16-18].

Based on the material catalytic nanoparticles can be broadly classified into the three types as shown in Figure 1.

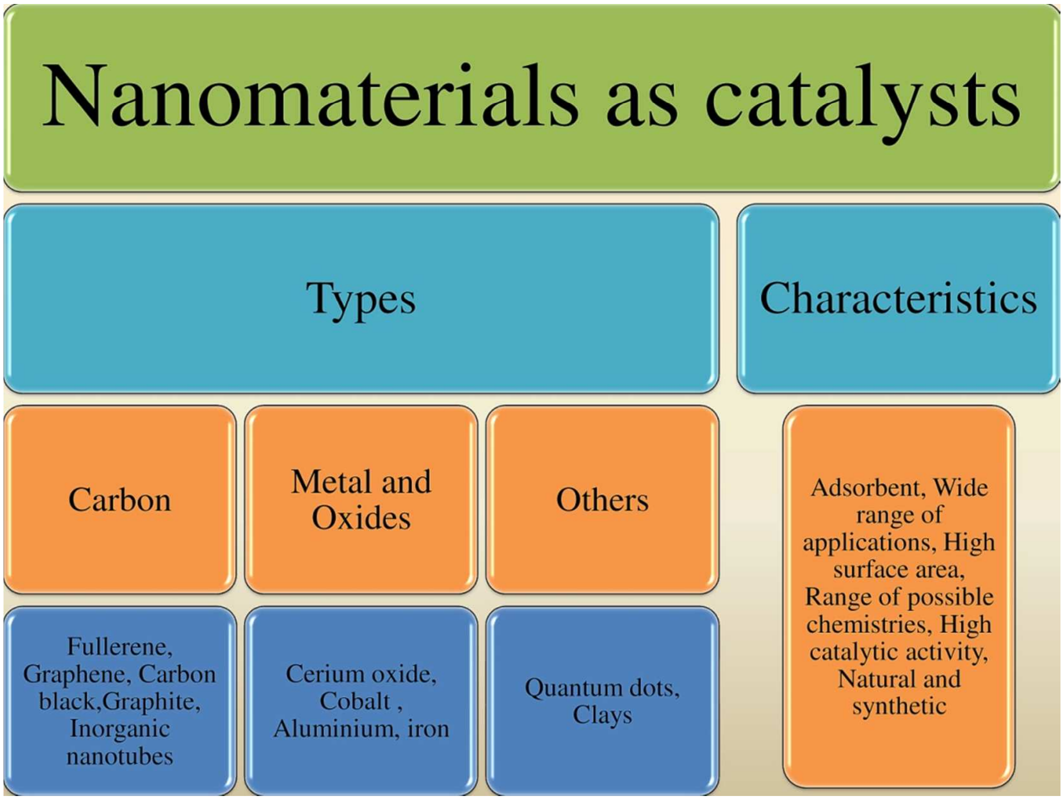
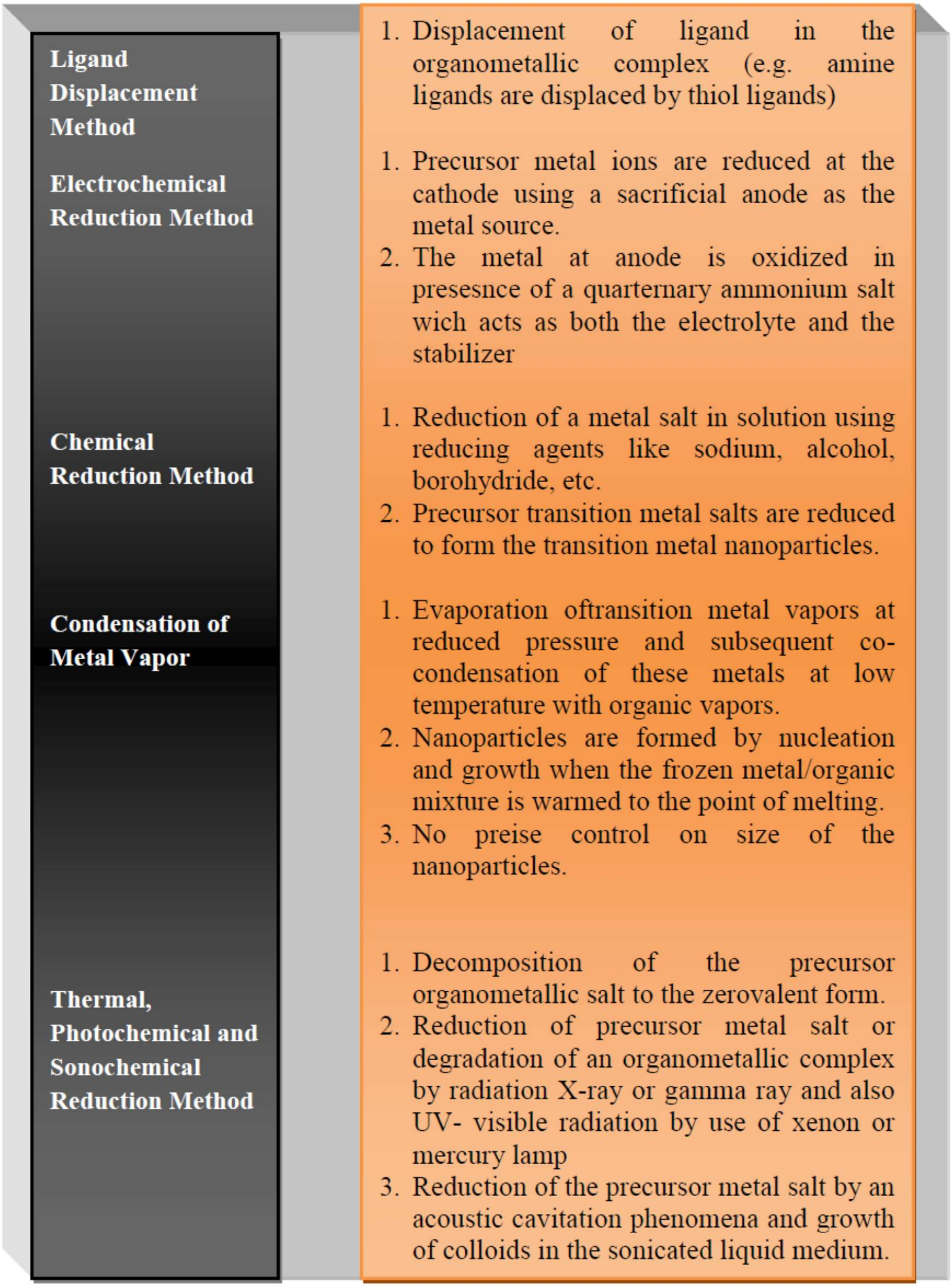


Figure 1. Types of Catalytic Nanomaterials and its characteristics [19-21].

There are many methods for the synthesis of the catalytic nanomaterials, most common among them [22-24] are described as follows.



Ligand Displacement Method	1. Displacement of ligand in the organometallic complex (e.g. amine ligands are displaced by thiol ligands)
Electrochemical Reduction Method	1. Precursor metal ions are reduced at the cathode using a sacrificial anode as the metal source. 2. The metal at anode is oxidized in presesnce of a quarternary ammonium salt wich acts as both the electrolyte and the stabilizer
Chemical Reduction Method	1. Reduction of a metal salt in solution using reducing agents like sodium, alcohol, borohydride, etc. 2. Precursor transition metal salts are reduced to form the transition metal nanoparticles.
Condensation of Metal Vapor	1. Evaporation oftransition metal vapors at reduced pressure and subsequent co-condensation of these metals at low temperature with organic vapors. 2. Nanoparticles are formed by nucleation and growth when the frozen metal/organic mixture is warmed to the point of melting. 3. No preise control on size of the nanoparticles.
Thermal, Photochemical and Sonochemical Reduction Method	1. Decomposition of the precursor organometallic salt to the zerovalent form. 2. Reduction of precursor metal salt or degradation of an organometallic complex by radiation X-ray or gamma ray and also UV- visible radiation by use of xenon or mercury lamp 3. Reduction of the precursor metal salt by an acoustic cavitation phenomena and growth of colloids in the sonicated liquid medium.

Figure 2. Common methods for the synthesis of the Catalytic Nanomaterials.

Figure 2 shows a brief summary of the common synthesis methods of the catalytic nanomaterials.

The characterization of the catalytic nanomaterials is done with the help of small-angle X-ray scattering, nitrogen physio-sorption, thermal response measurements with conventional X-ray diffractometry, Temperature-Programmed Ammonia Desorption (TPAD) and electron microscopic methods [25-27].

There is a wide application of the Nanocatalysis in the chemical and pharmaceutical industries which results to the increment of the energy efficiency with involvement of the green technology with minimum chemical waste generation. Waste water treatment, safer catalytic reagents with optimum feed stock utilization etc [28-30](Figure 3).

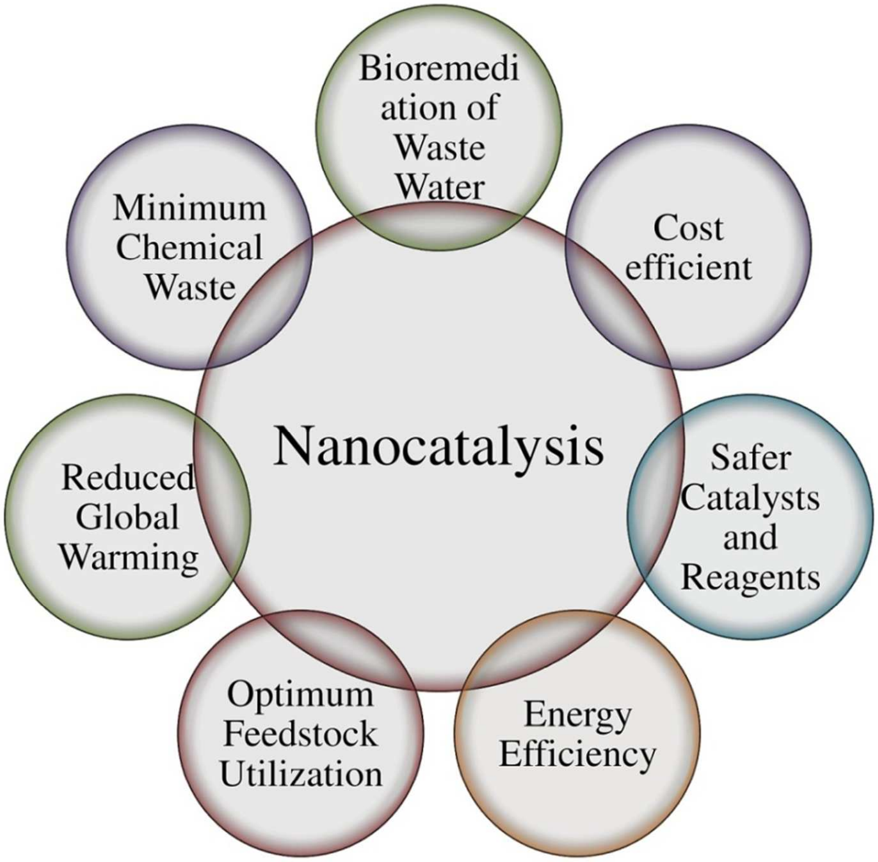


Figure 3. A glimpse of selected applications of Nanocatalyst.

Present review discusses the state of art in preparation and catalytic application of the Nanomaterial with respect to their present and future prospect.

2.0 Mesoporous Silica Nanomaterials (MSN's)

Zeolites sparked a revolution in the field of catalysis due to the special structure and performance. However, processing problem has been encountered with the zeolites such as the catalytic cracking of heavy oil macromolecules and immobilization of the macrocyclic complexes. Scientists had discovered mesoporous materials at early 18th century. Since, that time mesoporous materials had become attraction for the material, chemical, physical and other disciplines. Mesoporous Silica Nanocatalyst is having the wide catalytic applications (Table 1). As, nanostructured mesoporous materials have large surface area, high activity and a great adsorption capacity[31-34] (Figure.4).

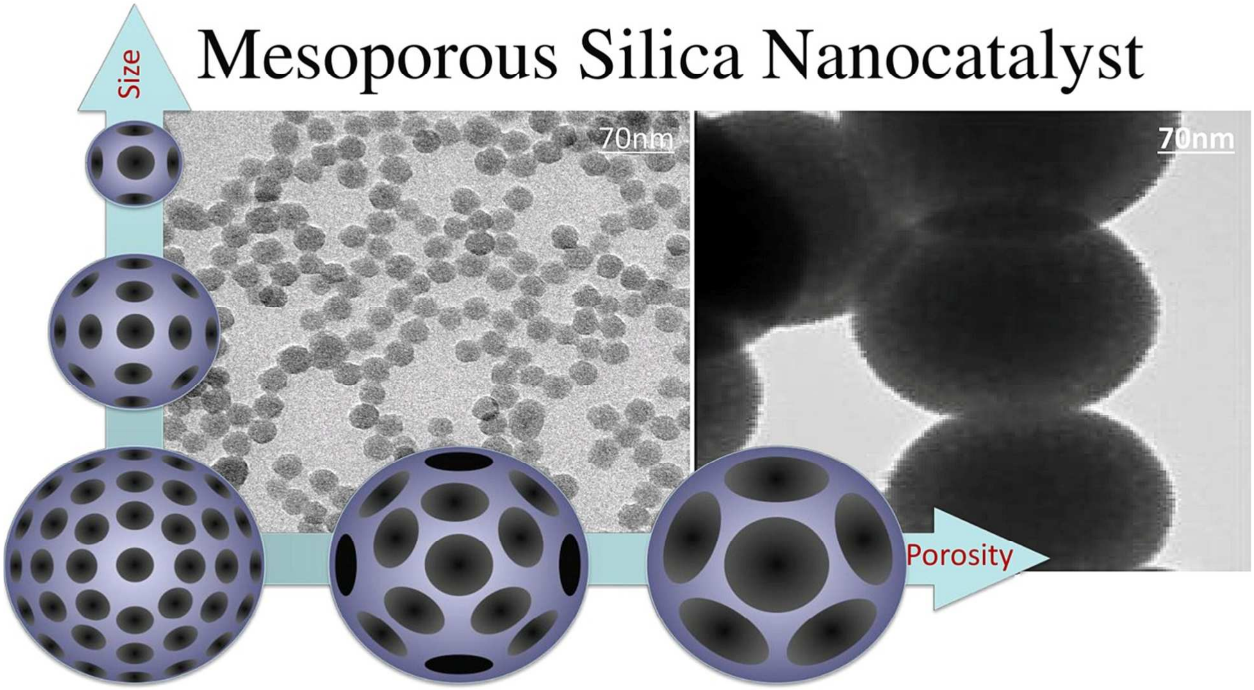


Figure 4. Variation in the pore size and particle size of the Mesoporous silica Nanocatalys.

However, modification were made like large aperture zeolites can be easily fixed or installed in the nanocatalyst. Hence, its adjustable uniform pore size can be used as carrier for the nanoparticles, size effect, surface effect and quantum effect provide additional features in it. Mesoporous nanomaterial possess regular pore diameter and extra high surface area in the range of the 1.5nm to 50nm along with the distinct absorption capacity[35-36]. These characteristics open up their potential use in the catalytic cracking and the manufacturing of fine materials. There are wide application of the mesoporous silica shell nanosperes in the catalysis such as hydrogenation catalysis magnetic acid catalysis and nano noble-metal catalysis etc [37-38].

MSN's may be solid or hollow prepared by TEOS (tetraethylorthosilicate) and Stober method.

2.1. Preparation of solid magnetic mesoporous silica nanospheres

Wu *et al.*[39], first proposed the synthesis of mesoporous magnetic composite by using sol - gel procedure. The same is schematically represented in figure 5

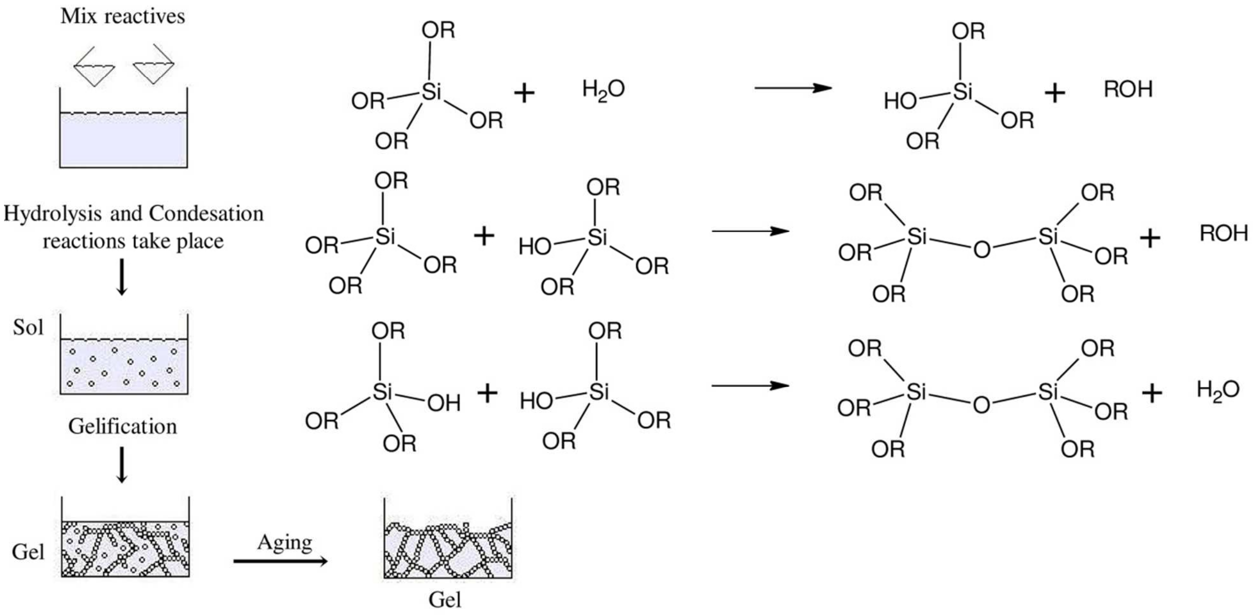


Figure 5. General steps involve in the synthesis of the solid mesoporous silica nanospheres

He reported that the magnetic layer of silicon covered in a thin layer silicon oxide coated Fe_3O_4 particles was synthesized using molecular template and sol-gel techniques. In the sol gel method, sodium silicate was used as the silica source. Drop wise addition of the dilute sulfuric acid forms a thin layer of silicon oxide on the surface of the magnetic particles. The purpose of the mother liquor is to protect against nuclear magnetic immersion under industrial conditions. Further, this silicon oxide layer is conducive to self-assembly of the surfactant. The TEOS (Tetraethylorthosilicate) was used as silica source and cationic surfactant molecules through ad-hoc Loaded silicon species, forming a silicon oxide mesoporous structure.

Lu *et al.*[40] reported that the magnetic nanoparticles with outer surface of SBA-15 have mesoporous nanocrystalline composite material with good magnetic response have an advantage of avoiding clogged pores. But the uneven size and shape of the resulting composite, is not conducive to biological applications. They chose methyl methacrylate as a monomer inhibitor to SBA-15, 2, 2'- azobisisobutyronitrile, by polymerization reaction PMMA / SBA-15 complex. Then the composite was immersed in a toluene suspension containing cobalt nano-particles. Subsequently toluene was dried and removed at 50°C, and then dipped in a methanol solution containing oxalic acid and furan. Finally, the composite was dried at 80 ℃, baked in an argon atmosphere at 850 ℃. The furan conversion to methanol to a thin carbon layer covering the cobalt nanoparticles Surface particles, while a heat treatment furan methanol carbonized polymerization gave Co / SBA-15-1.

2.1.1 TEOS (tetraethylorthosilicate) hydrolysis method

This method uses tetraethyl orthosilicate (TEOS) under basic conditions of hydrolysis and condensation ethyl orthosilicate which leads to the formation of the SiO_2 sol. coated magnetic particles surface.

Kim *et al.* [41] reported the synthesis of monodisperse Fe_3O_4/SiO_2 mesoporous nanospheres,which can be used to control drug release and absorption. However, for specificity the procedure is as follows:

First, the magnetic Fe_3O_4 particles in a non polar organic solvent was stabilized with the help of hydrophobic oleic acid; and then, by cetyltrimethyl ammonium bromide. CTAB used as a surfactant to obtain an aqueous dispersion of the nanocrystals; finally, soluble and stable magnetic nanocrystals containing CTAB-oleic acid solution. Use TEOS sol - gel prepared by the reaction of the magnetic medium Porous silica microspheres, and then with ethyl acetate to remove the organic templating agent. Magnetic silica microspheres have super paramagnetic and uniform size, but the magnetometer is very low, disordered mesoporous shell structure limits its biological separation application.

Zhang *et al* [42] showed that the TEOS hydrolysis method using super-paramagnetic single nano-magnetic crystals dispersed successfully embedded into the mesoporous silica microspheres.

2.1.2 Stober method

Stober *et al.*[43] proposed sol-gel method using alcoholic solution to prepare monodisperse SiO_2 nanospheres. Major step involves the formation of a stable alcoholic medium using the suitable proportions of the tetraethyl orthosilicate, water and alkali.

2.2 Preparation of hollow magnetic mesoporous silica microspheres

2.2.1 TEOS hydrolysis method

The synthesis process is:

First, iron stearate monodispersed Fe_3O_4 nanocrystals were dispersed in chloroform. These acid ligand coated magnetic nanocrystals are fluorocarbon vesicles, and then under high temperature conditions, the silicone precursor rapidly hydrolyzed to produce complex and CTAB micelles by S^+ I^- electrostatic interactions to form the self-assembly. These composite micelles embedded magnetic nanoparticles combines to form self-assembly which results in a shell mesoporous structure.

2.2.3 Stober method

Zhao *et al.*[44] synthesized a new air-gel method - using the sol heart magnetic mesoporous microspheres. Magnetic microsphere is a kind of a structure which has high burden load capacity and relatively strong magnetization intensity.

2.3. Catalytic application of the Mesoporous Silica Nanomaterials

Mesoporous silica nanomaterials not only have excellent properties of magnetic nanomaterials, but also have excellent catalytic activity[45-48] .It has the properties of conventional catalysts as well as magnetic separation capacity. In the chemical production processes, it enhances the chemical reactions and separation process, but also simplifies the entire process. There is a wide use of the mesoporous silica nanomaterials in the field of the magnetic acid catalysis, hydrogenation catalysis, nanotechnology research catalysis and photocatalysis[49-53].

2.3.1 Magnetic acid catalysis

In magnetic nano-probe reaction solid acid catalysis, the accession of the external magnetic field magnetized the whole process due the rotation of the external magnetic field and the magnetic motion of the particles. The Lorentz force generated by changing the size of the magnetic field results in disturbance of reactant molecules constantly making it easier for the magnetic catalyst attacking the carbonyl carbon forming positive ions, thereby facilitating nucleophilic reagent attack, so that the conversion of the esterification reaction is catalyzed[54].

2.3.2 Catalytic hydrogenation

Hydrogenation catalyst is selected from the ferromagnetic negative substances. The noble metal present in the catalyst, Fixed bed processes approach of catalytic hydrogenation is compared with lower bed pressure and it was find out that the Mesoporous Silica Nanomaterials enhances

the catalytic hydrogenation[55,56]. Major advantage of using the Mesoporous Silica Nanomaterials in the catalytic hydrogenation is the transfer efficiency, less side effects, and high productivity[57-59].

2.3.3 Photochemical catalysis

TiO_2 Mesoporous Silica Nanomaterials is used in the photochemical catalysis because of its high chemical stability, light corrosiveness and compatibility to human body.[60] Xushi *et al*[61]p repared the magnetically isolated TiO_2 / SiO_2 / $NiFe_2O_4$ (TSN) nanoparticles. This photocatalyst showed superparamagnetic properties. The results showed that TiO_2 nanoparticles lead to the formation of the SiO_2 / $NiFe_2O_4$ (SN) TiO_2 layer photocatalytic degradation of methyl orange proved the fact that SiO_2 significantly improves the decolorization of the catalyst.

Table 1 Applications of the Mesoporous Silica Nanomaterials for catalysis.

Use	Material	Reference
Olefin epoxidation	Ti / V-MS	Chen et al 1998[62]
Olefin oligomerization	Cr-MS	Pelrine et al1996[63]
Aromatics oxidation	Ti-MS	Tanev et al1994[64]
Photocatalysis	Ti-MS	Anpo et al1998[65]
MPV reduction	Al-MS	Anwander et al1998[66]
Olefin metathesis	Mo-MS	Ookushi et al1998[67]
Olefin Polymerization	MAO-MS	Tudor et al1995[68]
Hydrocracking	Ni-Mo-Al-MS	Corma et a1997[69]
Base catalysis , catalytic alkylation	$(CH_2)xNR_2$-MS	Brunel et al1995[70]

2.4 Advantages and disadvantages of Mesoporous Silica Nanomaterials

- High specific surface area of the MSN's provide high efficiency for the adsorption and catalysis.
- Large pores allow the implementation of large molecules and allow them to chemically modify in variety of ways.
- Different functional groups can be selectively and effectively functionalise the MSN's because of the presence of the silanol groups on internal surface of the MSN's[71-73].
- Presence of the ≡Si-OH group on the surface of the MSN's help in easy immobilization of the organic functional groups on the silica surface due to the presence of the hydrogen bonding or covalent bonding.

- One of the major drawback of the Grafting Method of the synthesis of the MSN,s is that, the organosilanes at the initial stage of the synthesis would react at the external surface of pores. This further impairs molecules deeply into the centre of the pore, leading to a non-uniform distribution of organic functional groups.
- All the synthesis methods of the MSN's are facing two major problems first organosilanes may instantaneously change the physical properties of the reaction solution. Secondly, phase separation problem may occur due to the poor solubility of the organosilanes in the surfactants or if its condensation or hydrolysis rates differ greatly from that of TEOS.

3.0 Magnetic Nanoparticles

The magnetic nanoparticles (MNPs) are formed with the help of magnetic elements like Cobalt (Co), iron (Fe), Nickel (Ni) and their oxides like Chromium di-oxide (CrO_2), cobalt ferrite (Fe_2CoO_4), maghemite (Fe_2O_3, γ-Fe_2O_3) and magnetite (Fe_3O_4)[71-73]. These are engineered to the size of <100nm and can be influenced under the applied magnetic field [73,74] .The MNPs do not have any particular physical or chemical properties, because they depend largely on their synthesis and chemical structure. They may also exhibit superparamagnetism[75,76]. Three dissimilar types of magnetic nanomaterials are used at present: Oxides: ferrite, Metallic, Metallic with a shell. General applications of MNP are shown in Figure 6. [77,78]

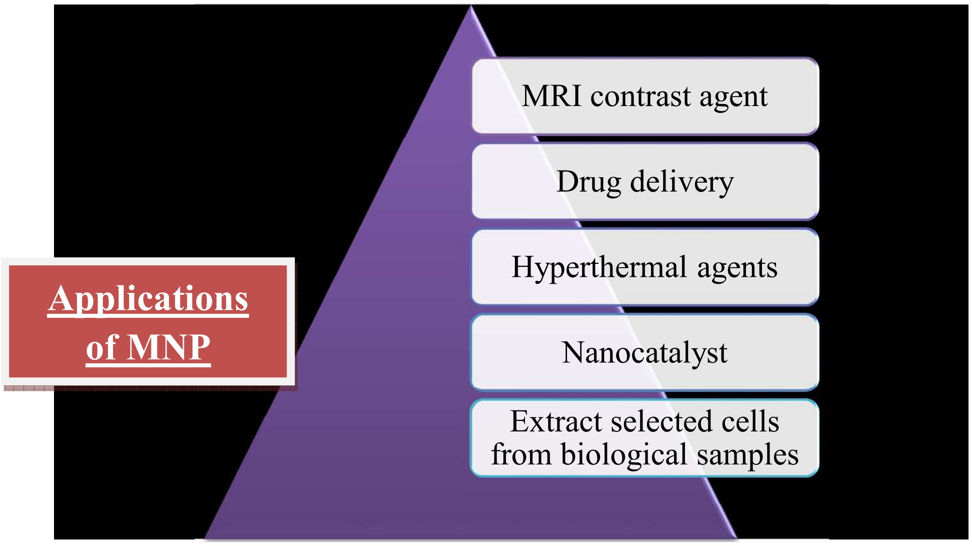


Figure 6. Few selected Application of Magnetic Nanoparticles.

3.1 Preparation

The magnetic materials used are either metals or metal oxides[79-81]. The bulk preparation of MNP's is easy, morphology, phase purity, dimension of nanometer scale and crystal structure has to be kept in mind while manufacturing the MNP's[82-84].There is a high level of complexity with their production.

The simple grinding method may be used and considered as beneficial, but following conditions have to be taken care of, while using this method-

- This method can only be used for metal oxides, because metals are malleable.
- When the size and shape of the MNP does not affect the results.

Hence different methods have been devised for this purpose.

Preparation of the nanoparticle is differentiated on the category of the precursor used, along with the features of processing, distinguished categories are[85]:-

1. Preparation from macroscopic materials by dispersion (Figure 7).

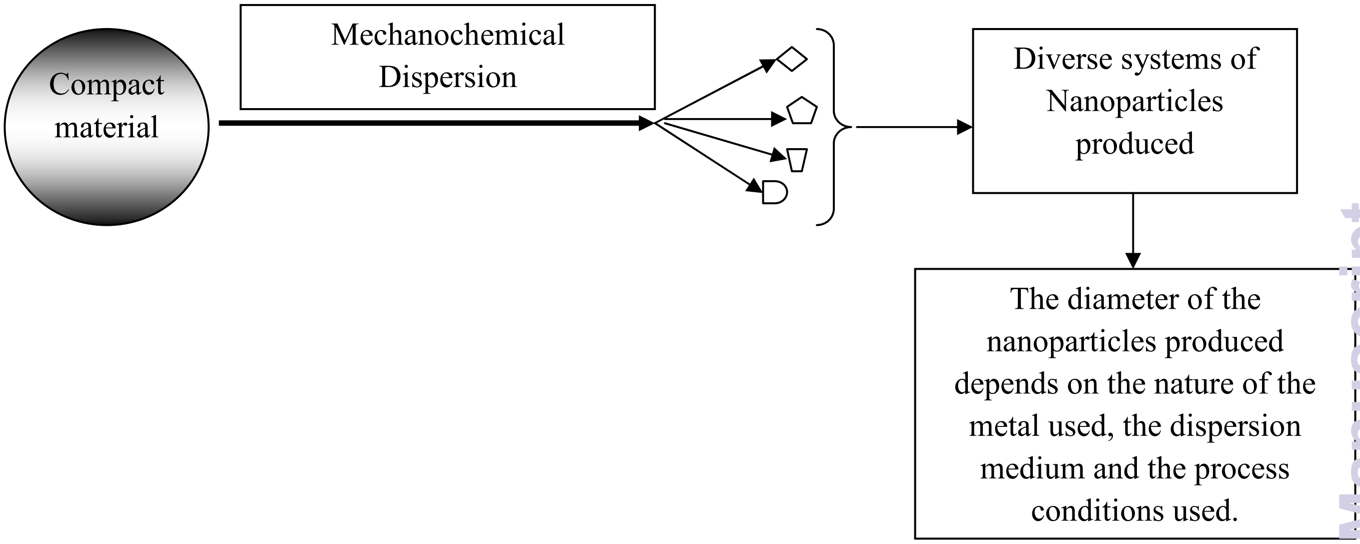


Figure 7. Method of nanodispersion of a compact material.

2. Chemical synthesis, i.e., targeted change in the substance composition with termination of the nascent phase growth at the nano-size stage (Figure 8).

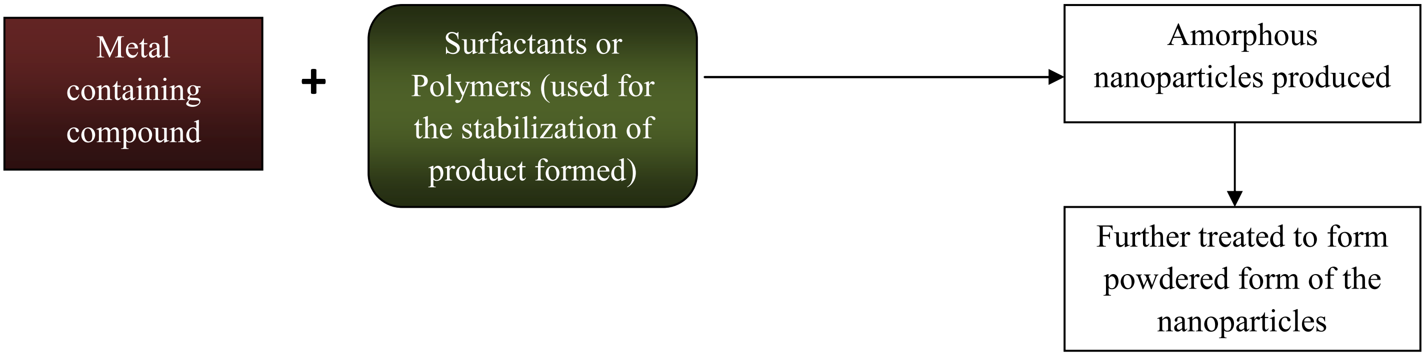


Figure 8. Thermolysis of metal-containing compounds.

The synthesis of magnetic nanoparticles can also be classified under physical and chemical methods, as shown in Table 2. When high-energy treatment is required for the production of magnetic nanoparticles in the gas or solid stage, then the method is known to be as physical. But, when synthesis is conceded at restrained temperature and in solutions, then the method of preparation is said as chemical[86,87]. Both the methods stand their importance individually for the production of the magnetic nanoparticles.

Physical Methods	Chemical Methods
➢ Condensation [88-90]	➢ Thermolysis of metal-containing compounds [94,95]
➢ Methods of nanodispersion of a compact material [91-93]	➢ Decomposition of metal-containing compounds on ultrasonic treatment [96,97]
	➢ Synthesis in reverse micelles [98,99]
	➢ The reduction of metal-containing compounds [100-102]
	➢ Synthesis of magnetic nanoparticles at a gas ± liquid interface [103-105]

Table 2. Classification of Physical and Chemical Methods of Preparation of Magnetic Nanomaterial.

3.2 Catalytic Applications

As, catalyst used can either be homogeneous or heterogeneous in nature. A homogeneous catalyst gets mixed up very easily with the reactants, due to the same phase they both share, but the heterogeneous catalyst is in solid phase thus they do not get mingled with the reactants. Both have their advantages and disadvantages respectively. At one place, the homogeneous catalyst, due to their mixing property with the reactants, provide a very fast reaction process. But removing and obtaining a homogeneous catalyst is a difficult task .On the other hand, the heterogeneous catalysts can be easily removed because of their negative integration properties in the reaction mixture as well as they do not offer speedy reaction results, as per expected. Hence, to overcome such disadvantages nanoparticles are used, as they can easily be administered in the reaction solution and due to their large surface area they can enhance the reaction rate according to the catalyst used, and moreover these nanoparticles, can be removed easily from the solution due to the unique properties they endure [106-111]. Under the categories of such special nanoparticles, magnetic nanoparticles are involved. These nanoparticles when introduced in an external magnetic field show powerful magnetic moments, and otherwise these remain in the solution like any other nanoparticle. These catalysts can be immobilized on the MNP, which in the absence of an external magnetic field remains dispersed like any other nanoparticle. MNP can be removed easily by applying a simple magnetic field, which helps in the separation of the catalyst and thus can be reused again [112]. For carrying out this function of catalysis, different types of magnetic nanostructures have been devised. A good example of MNP is the removal of contaminants (pesticides) from the groundwater system, chemical nerve agents from the battle field and decontamination of organophosphate. Through conventional methods their removal is very difficult. Hence, functional magnetic particles are produced for such functions.

3.2.1 The use of MNP's in catalysis as follows

1. Due to rapid industrialization, the level of pollution has increased alarmingly. So to control this situation catalysts are being used. As, there is a recovery problem with the homogeneous catalyst, it is being replaced with heterogeneous catalyst. For the achievement of this purpose, nanocatalysts are being prepared. Silica coated magnetic nanoparticles (SMNPs) are being produced, that acts as the catalyst, that may be regained from the solution. These SMNPs can function as an efficient, recoverable and selective catalyst in diverse industrially considerable organic transformations [113].

2. Certain bimetallic nanoparticles, like, Ni-Ag, supported on reduced grapheme oxide (Ni-Ag-RGO hybrid), also show magnetic properties, which were administered in the experiments with the help of a sample magnetometer. Additionally, these bimetallic nanoparticles, showing the magnetic properties, demonstrated catalytic activities for the

reduction of 4-nitrophenol and the photodegradation of methyl orange. The catalytic activity was observed by examining the change in the concentration of the reactants, with respect to time, with the help of ultraviolet-visible absorption spectroscopy. Therefore, after reaching the finishing point of the reaction, the catalysts can be removed from the system under a specific magnetic field, hence achieving recyclability and lesser pollution in the environment [114.]

3. Quite different from the conventional preparation of Nickel (Ni) nanoparticles. New nanoparticles of Ni were produced from $NiCl_2 \cdot 6H_2O$ by hydrazine hydrate in assorted solvent, containing ethanol , along with water, and in the attendance of hydroxy propyl methyl cellulose (HPMC) as protective and steadying agents. Field-emission-scanning-electron microscopy (FESEM), Fourier-transform infrared (FTIR) spec-troscopy, and X-ray diffraction (XRD), were used to examine the morphology and dimension, the characterization and the structural properties of polymer steadied Ni nanoparticles. With the help of magnetic measurements, the conclusion obtained was that these Ni nanoparticles are ferromagnetic in nature. Moreover with the decrease in temperature, the saturation magnetization (MS), coercivity and remanent magnetization (MR), were observed to be increased. Experiments showed that the HPMC stabilized Ni nanoparticles are fairly dissimilar from the bare Ni nanoparticles being used. Furthermore, these nanoparticles acts as catalyst in the Suzuki coupling reaction, and are highly active and recyclable as well [115].
4. A new and different category of magnetic nanoparticles being experimented and synthesized are magnetic bromochromate hybrid nanomaterial, Fe_3O_4-SiO_2-TEA [CrO_3Br]. This acts as a catalyst. Transmission electron microscopy (TEM), vibrating

sample magnetometer (VSM), and scanning electron microscopy (SEM) techniques are used to study the physical properties, magnetic properties and morphology respectively [116].

3.3 Advantages and disadvantages of the MNPs

- Due to the phenomenon of the superparamagnetism MNPs are not remain magnetized after the action of magnetic field this will ultimately reduce the risk of the particle aggregation[117].
- Most of the MNP’s are made up of the biocompatible material such as magnetite (Fe_3O_4) which do not cause *in vivo* concerns[118].
- Immobilization of the organic catalyst is a concern for most of the catalytic application on heterogeneous substrates. Magnetic nanoparticles help in this concern as a substrate by help in the recycling of organic catalyst from the reaction mixture.
- Due to the size similarity of the nanoparticles to that of the biomolecules they may poses size related properties close to that of biomolecules. This further act as a efficient and specific catalysts.
- However, MNP’s help in recycling and reuse of the enzymes form the reaction medium. There is still a disadvantage of the reactivity and selectivity of the MNP’s. This further requires the innovative approaches to overcome this problem.

4.0 Layered Double Hydroxides

Layered double hydroxides (LDHs), also known as hydrotalcite compounds which are composed of two or more metallic elements of Hydroxide-like crystal structure.

Chemical composition of LDH is generally expressed as:

$$\mathrm{M\ (II)}_{1\text{-}X}\ \mathrm{M\ (II)}_{X}\ \mathrm{(OH)_2}\ (\mathrm{A}^{n-})_{x/n}\ \times \mathrm{y\ H_2O},$$

Where, M (II) = divalent cation, M (III) = trivalent cation, A= interlayer anion, n- = charge on the inerlayer ion, and X and Y are fraction constant[116].

Octahedral metal ions and oxygen form a cell layer parallel to each other, where M is the radius of the inner circle of similar domain .Isomorphous substitution (High metal ion) makes laminates with a permanent positive charge and this,positive charge is located between the layers [119].

Because of the diversity in LDHs layered composition, the interlayer anion exchangeability occurs with other materials, especially organic and biological Material which finally results in its compatibility with them. Therefore these materials have a wealth of physical and chemical properties (such as acid-base catalysis, redox catalysis, photoelectrochemical etc.)

With the development of modern analytical techniques and testing methods, attention of the research is more on the structure and properties of LDHs which results to the expansion of its application in the catalytic exhibition to medicine, environmental protection and other fields.

In recent years, lot of work has been done in the field of supramolecular chemistry and self-assembly concept, which results in the rapid research and development related to LDHs in the precursor Preparation, characterization, supramolecular structure model, intercalation kinetics and mechanism of the assembly[120-122].

4.1 Preparation of LDH

The LDHs are prepared by Reconstruction and Co-precepetation method.

4.1.1. Reconstruction method

Salts of metal were calcinated for 4 hours at 500^0C in nitrogen at the heating rate of 5^0C min^{-1}. Then this solid was added to a solution which contains decarbonated water with the guest molecule. The pH of the solution was adjusted to 7-8 by using sodium hydroxide. It was then precipitated and filtered at the room temperature. After that it was washed thoroughly by using decarbonated water and then it was dried under vacuum.

4.1.2 Co-precipitation method

The mixture of the two different salts of metal in a decarbonated water was added drop wise into an aqueous solution over the hours which contains an organic guest species with the vigorous stirring under the atmosphere of nitrogen. To induce the co- precipitation, the pH of the solution was adjusted to 7-8 by using 0.1 N sodium hydroxide during the course of titration. Then it was precipitated and agitated for 24hours. After that it was filtered and washed thoroughly by using decorbonated water. It was then dried under the vacuum. With the help of ion- exchanging, interlayer anion of layered double hydroxides the biomolecules layered double hydroxides hybrids can be prepared. However, the co-precipitation method is much useful than reconstruction method because it gives 3 times more yield (Figure 9).

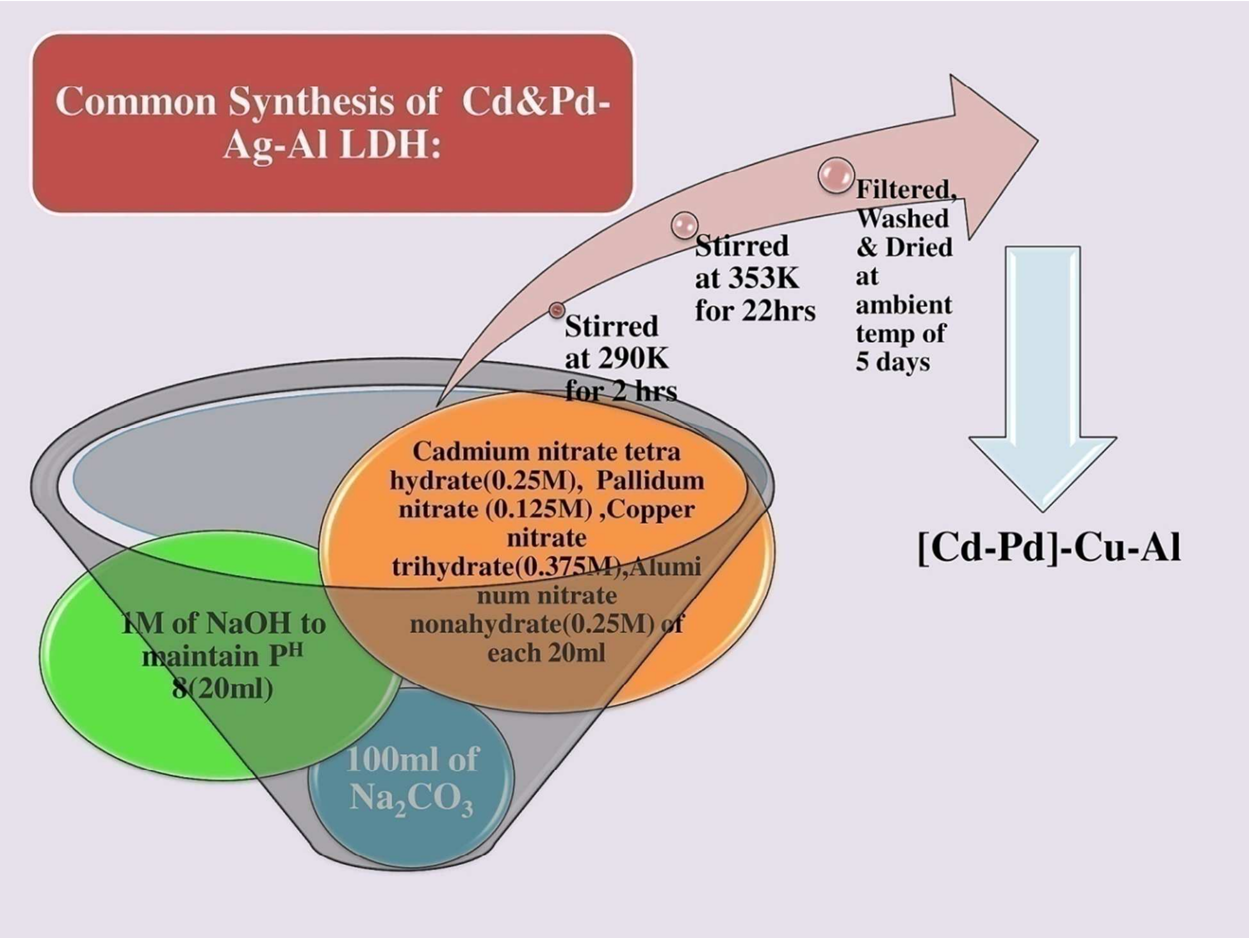


Figure 9 Showing an example of the common steps involved in the synthesis of the LDH.

4.2 Catalytic applications of the LDH

LDHs have large specific surface area, interlayer anion exchangeability and salkaline oxides. Therefore, can be used in catalytic reactions.Major reactions takes place in the multi layers. Introduction of certain anionic acid-catalytic properties can effectively enhance the conversion rate and selectivity of the reaction.

4.2.1 Laminates of different metal elements LDHs application

Metal hydroxide-LDHs have a larger surface area for exposure and strong alkaline nature. It has a solid base which generally activates in mild reaction conditions, easy to separate, less corrosive to reaction apparatus, etc. Due to these unique properties they are widely used in catalytic biomass. Such as LiAl-LDHs, MgAl-LDHs, MgFe-LDHs are used as an esterification catalyst[123, 124].

“Photocatalyst LDHs” itself generally does not have photocatalytic activity, its modification, change its physical and chemical properties and give it Photocatalytic activity. Such as firing form a composite oxide, intercalation oxide [125,126], laminates doping [127-129] and other methods can modify the material to a semiconductor.

By increasing the band gap energy of the catalyst and reducing the photo-generated electrons and holes recombination rate enhances the catalytic activity of the catalyst.

Seftel et al. found that in ZnSnLDH .ZnO / SnO_2 promotes close contact between the two electronic semiconductors to increase the efficiency of charge separation and show stronger photocatalytic activity[130].

Wang et al. prepared theZnSn-LDH by co-precipitation of the ZnO / SnO_2 composite oxide, photocatalytic degradation of methyl orange shows excellent photocatalytic Ability and good light stability [131,132].

4.2.2 Based anions between different layers of LDHs

4.2.2.1 Simple anion intercalation.

Vera et al. studied the inter-Mg Al LDHs structures. Four pairs of catalytic Butylcarbitol due to alcohol (MBOH) converted to acetylene and acetone. The results showed the specific surface area of MgAl LDHs is smaller, but still showed high catalytic activity.

4.2.2.2 Poly-anion intercalation.

Some poly-anions shows excellent redox catalytic activity, these poly-anion exchange between the layers of LDHs to achieve effective separation of the catalyst from the reaction system.

Maciuca et al. demonstrated the tungstate intercalated LDHs catalytic oxidation of sulfide by $H_2O_2$and proves the good catalytic activity and selectivity of LDH [133].

4.2.3 Catalyst support material

4.2.3.1 Enzyme carriers.

The use of LDHs layered structure can be used as carrier materials in the number of biological enzymes.

4.2.3.2 Hydrogenation catalyst carrier.

Francovet al. demonstrated the intercalation of Pd precursor to Al Mg LDHs and Pd / Mg / Al co-precipitation. Pd catalyst applied to 2-butyne - 1,4diol resulting the catalytic hydrogenation. The results showed that intercalation after reduction with Pd catalyst. LDHs show good catalytic activity and selectivity[134].

4.3 Advantages and Disadvantages of the LDHs

- LDH's offers multi advantages as a host of catalytic nanoparticles. Brucite-like layer composition help in incorporating different active catalytic molecules which further help in the dispersion of the catalytic molecules within the layers.
- As compare to the traditional methods of the synthesis of the metal catalysts LDH precursors has their own advantages in the synthesis such as uniform distribution of the

active metal cations in the Brucite- like layer[135,136] and Strong metal and its oxide instructions between the metal oxide and metal nanoparticles.

- By the transformation of LDH's into MMOs (mixed metal oxides) *in situ* structural change to a crystalline solid nature of metal nanoparticles can be controlled[137].

5.0 Micro/ Nanobubbles

Liquid film administers three distinctive phenomena- Films, droplets and bubbles. In many different industrial areas, bubbles play a very critical role, and with the increase in technological aspects these have been of great interest and work by the scientists [138-144] Bubbles when in the size of micro and nano scale, are said to be micro and nano bubbles respectively.

Micro and Nanobubbles (MNB) due to their compact size, of about 5-100 nm in height and 0.1-0.8 μm in the radius of curvature. It consists of definite exceptional attributes because they stay in the liquid for a considerable amount of time, compared to the usual macro bubbles present in the liquid (Figure 10).

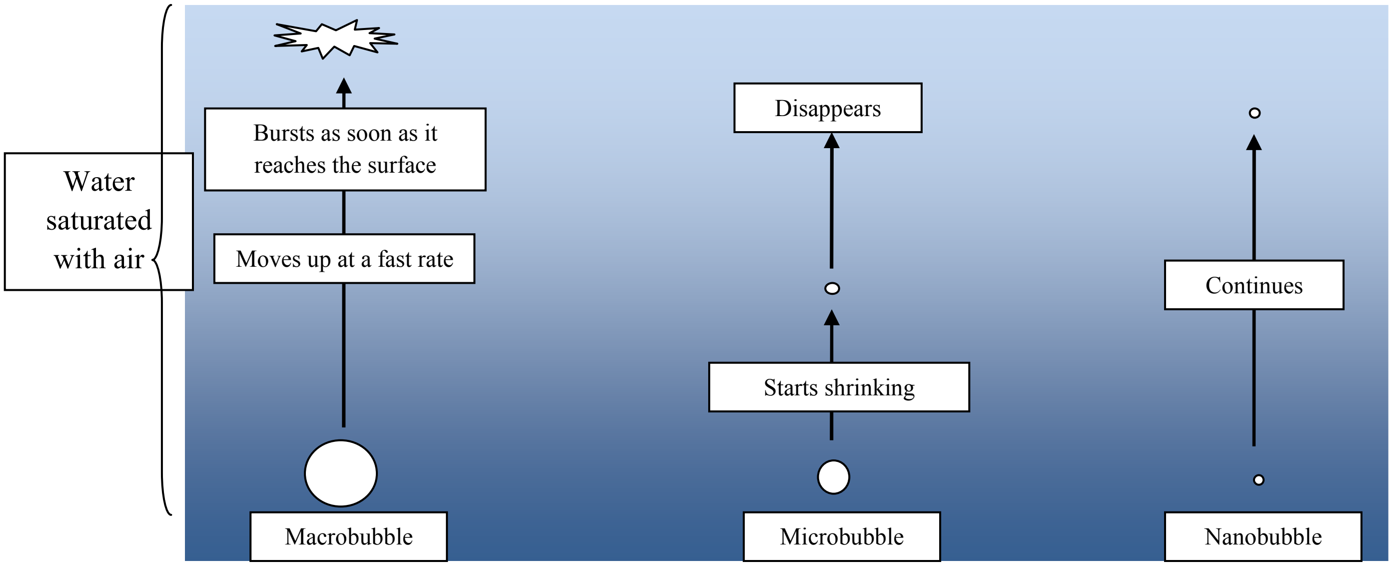


Figure 10. Comparison shown among macrobubbles, microbubbles and nanobubbles on the basis of their capability of being retained in air saturated water.

MNBs emerge at the interface of a polar solvent (e.g. water) saturated with air at a high concentration and a hydrophobic surface. Their existence was measured with the help of tapping mode atomic force microscopy (AFM), and with the help of other techniques like, cryofixation,neutron reflectometry. [145-152].The hydrophobic surface is covered in an asymmetrical and consistent fashion. Due to elevated time spent in the liquid and high surface area per volume ratio, the gas suspension increases in the liquid medium. Furthermore, there are high amount of radicals formed at the gas-liquid interface, which are introduced into the medium after their collapse[153,154]. Such characteristics of MNB make them useful in various different fields (Figure11).

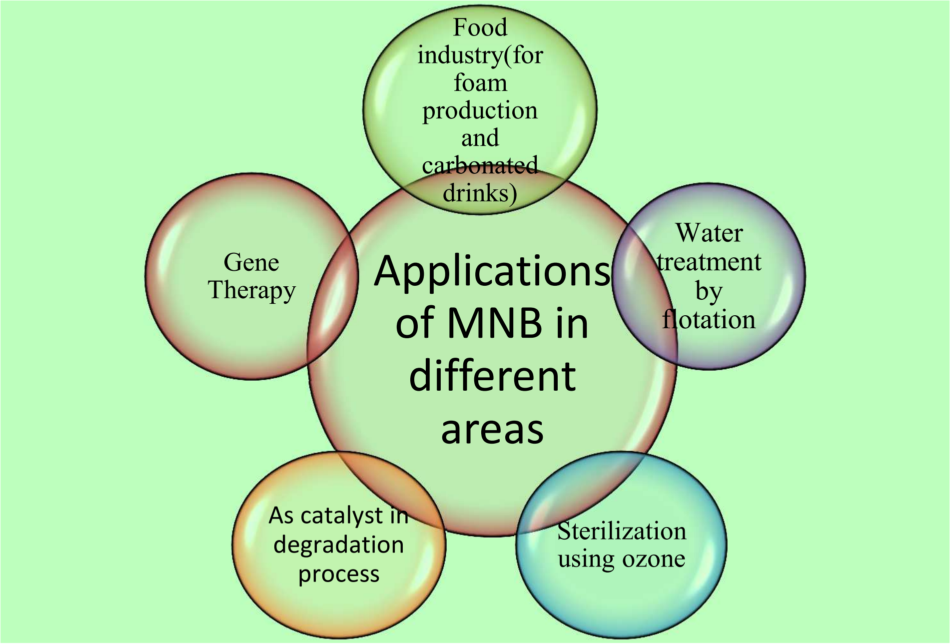


Figure 11 The applicability of MNB in various areas.

Nanobubbles can either be beneficial or not, because of their exceedingly constant nature [155].The gas suspension and the free radical production by the MNB's are permanent in the solution. On the other hand, such contents when once introduced into the system cannot be removed.

The flow of the liquid in the neighboring surface is affected by the presence of the nanobubbles. Even the particles present in the liquid are considerably influenced by the presence of nanobubbles on the plane of the hydrophobic material. But many studies of MNBs are reported to engage in playing an essential role in the physiological activities in the cell [156-160] Excluding all these facts, the main concern is that how can the micro and nannobubbles can be created and stabilized. The studies are being conducted for the formation of these MNBs, which largely depends on the surfaces used, not focused on their formation and stability. They appear on the hydrophobic surfaces, but in the case of hydrophilic surfaces, these appear when there is a considerable difference between the solubility of the air in the two miscible fluids present.

5.1 Preparation

When a Microbubble is formed, it grows and collapses in the solution, this process is known to be as Cavitation [161]. On the basis of the generation techniques of a microbubble, the cavitations is largely divided into four different groups-

- **Acoustic cavitation:**

  Ultrasonic waves are used to stimulate the cavitation. Pressure differences are produces because of these sound waves.

- **Optic cavitaion:**

  Photons of high intensity light are used for cavitation. The light, of required intensity, is made incident on the solution. As the light ruptures the air saturated liquid, microbubbles are formed.

- **Particle cavitation:**

  Other particles are used to produce microbubbles, like a proton can be used, as it is made incident on the liquid at a particular speed to form microbubbles.

- **Hydrodynamic cavitation:**

  The pressure differences in the flowing liquid, due to the geometry of the system, induce cavitations.

Desired physical and chemical alterations can be introduced with the use of acoustic and hydrodynamic cavitations, while optic and particle cavitations are incapable of inducing such an effect on the properties of the microbubble formed.

With the advancement in technology, few more methods have been devised to produce MNB’s. Among such methods, two widely used are -

- Decompression (as shown in figure 12),[162] and
- Gas-water circulation (as shown in figure 13) [163]

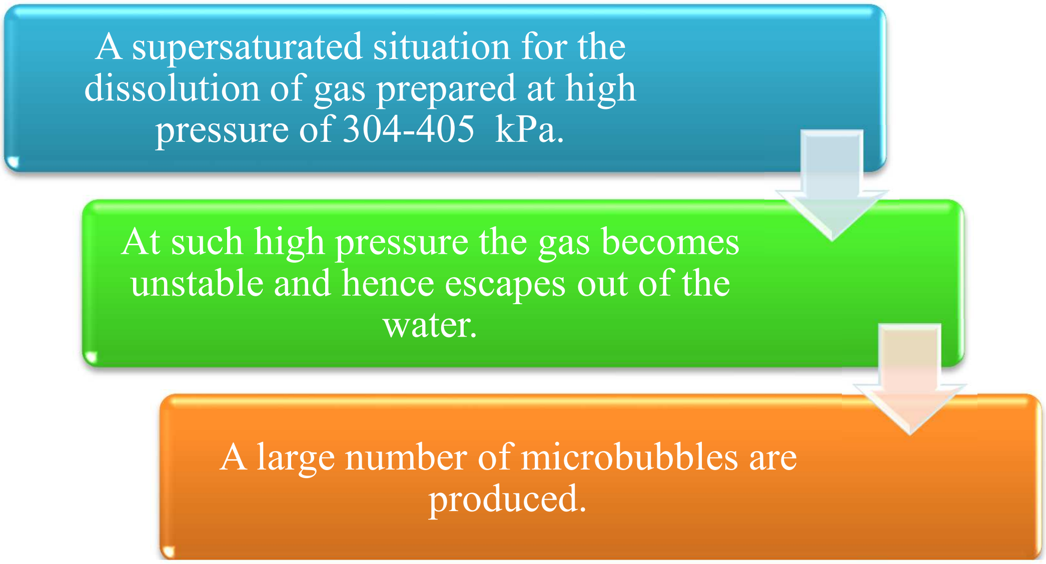


Figure 12 Steps depicting the Decompression process for preparation of MNB.

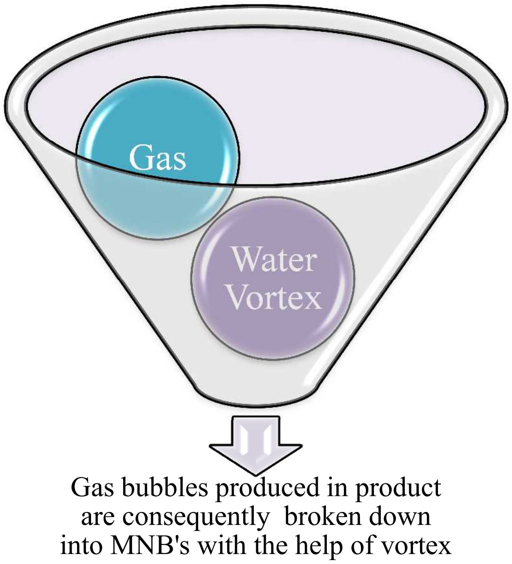


Figure 13 Steps depicting the Gas-water circulation process for preparation of MNB.

The ozone microbubbles can be produced, more efficiently, with the help of decompression, in spite of gas- water circulation method.

A palladium electrode, along with ultrasonication, can also be used, except decompression and gas- water circulation methods, to generate MNB's, with diameter of around 300-500nm.

Another method of producing the nanobubbles from water using highly oriented pyrolytic graphite (HOPG) surfaces. When this surface operates as a negative electrode, then hydrogen nanobubbles are produced, while if the surface is active as a positive electrode, then oxygen nanobubbles are formed. Hence, according to the nanobubbles required, the HOPG surface is charged. With the increase in voltage, the volume of the nanobubbles also increases simultaneously. AFM is used to study the development of the nanobubbles formed, during the electrolysis method being carried out, interrelated with the total current used.

5.2 Catalytic Applications

Due to an increasing interest and acceptance in the field of formation and applicability of MNB's, many new areas have been introduced with the advantages being provided by them. Theoretically, it is calculated that due to high pressure, and size in nanobubbles, the air should escape out of the bubble in microseconds. But, practically another aspect was noticed of the MNB's, i.e. under the appropriate circumstances, these MNB's can shape freely and remain stable for a comprehensive period of time. Hence, such property can be used for various different fields, like-

- The MNBs can be used for bioremediation purposes. Due to the large surface area of MNB, and high stagnation time in the water, sparging with MNB proves to be a better option of increasing the content of oxygen, than sparging with the macrobubbles. Hence, the water purification can be achieved with the help of MNB technology[164-166].
- Moreover, the MNBs have grown interest in the field of Gene therapy technology. Gene therapy technology includes the introduction of gene of interest in the desired cell or mass of cells. Usually viral and non viral vectors are used traditionally, but due to certain disadvantages perceived by both of them, novel ideas are being investigated for the purpose. Hence, the MNBs are being seen as the most promising way for this function [167].

Other applications of the MNBs have been reported showing certain catalytic properties which can also be used in catalytic applications.

- Nanobubbles of platinum, are synthesized with silica cores, and in the presence of KBH_4, they represent phenomenal catalytic properties in the degradation of rhodamine B.[168]
- Nanobubbles are also being made to use in the diagnostic and therapeutic areas. The physiochemical characteristics and toxic retort of the nanobubbles made of different

formulations, was checked on *N*-formyl-methionyl-leucyl-phenylalanine (fMLP)-activated human neutrophils. This experiment ensured that the nanobubbles present in diagnostic areas shows catalytic properties as well. [169]

- Thermal decomposition method was used to produce CdS–TiO_2 nanocomposites. By using four different categories of TiO_2 in the construction of these nanocomposites, exploration can be done regarding the optical and photocatalytic activities of the nanocomposites formed.[170]
- A method was proposed for fabricating highly crystalline nanoporous layers of ZnO with the help of the hydrogen bubbles which act as a gas template for the formation of the porous ZnO macrostructures. Further, they had introduced the formed layer into the solid-state dye-sensitized solar cells which achieved 2.1% power conversion efficiency.[171]

5.3 Advantages and Disadvantages of the MNBs

- Liquid bubble and deformity of the emulsion globule provide the advantage in synthesis of the catalytic nanobubbels.
- Considerable progress has been made in the synthesis and applications of the catalytic nanobubbels which involves the templating strategies (hard, soft and sacrificial) overall hard templating strategy have many disadvantages such as difficulty in achiving heigh product yield in multistep synthesis process[172].
- High cost, Low efficiency and tedious synthesis procedure may lead to the difficulty in synthesis of the catalytic micro/nanobubbels for large-scale application[173].

6.0 Semiconductor Quantum Dots

Also known as semiconductor nanocrystals belonging to the group II-VI or III-V. The group consist aromatic and nanoparticles elements which are soluble in water, having size 2 ~ 20nm. Between the nanocrystalline grains (Figure 14).

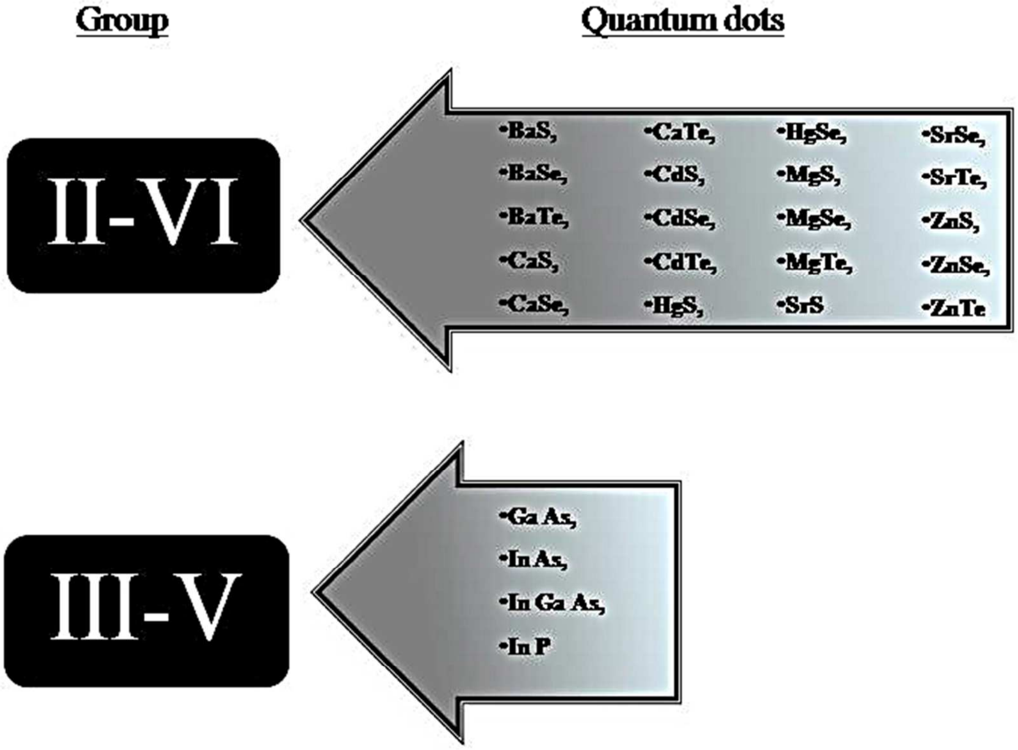


Figure 14 Showing the elements from groups II-VI and III-V commonly used to form Quantum Dots

In recent years research is more focused on the CdS, CdSe, CdTe, ZnS, quantum dots[174-177]due to its unique nature. More attention has been paid to its electronic arrangement phase. Quantum dots can absorb a higher amount of light waves and produce energy level jump due to the down low energy state order. It will emit a longer wavelength (red line bias) light. Different size quantum dots emit different fluorescent wavelength such as cadmium selenide (CdSe) particle emits blue fluorescence at 2.1 nm diameter, green fluorescence at 5 nm and red fluorescence at10 nm. Compared to conventional organic dye molecules, quantum dots have strong brightness, good light stability and using a single wavelength laser can stimulate various characteristics of different wavelengths of the transmitted wave. Application of the Nanoquantum dots increases rapidly which is evident by the no. of publications in this field which widely consists of its use in optical sensing, single electron transitions, drug delivery, catalysts, etc.

6.1 Preparation of quantum dots

During the synthesis of the Quantum dots, researchers are involved in the increase of the quantum yield, stable performance and use of the special functional groups. Currently, quantum dots preparation mainly divided into metal organic synthesis[178-181] and water consistency [182-185]. Metal organic synthesis involves the dissolution of the agents (e.g. trioctylphosphine oxide (TOPO)) in a ligand solution followed by organometallic decomposition which leads to nucleation and growth at high temperature. The advantages of this method is the prevention of the reactive oxygen species or free radicals effect of the quantum dots, size uniformity, perfect crystal growth and high photo stability [186,187] (Figure 15).

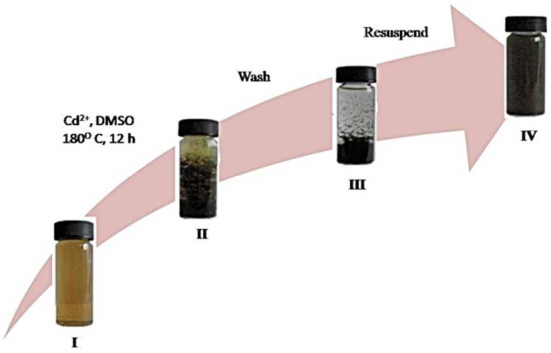


Figure 15 Different steps involved into the synthesis of the Quantum Dots

Machine-phase synthesis of water-soluble and biocompatible quantum dots is very poor. Mercapto carboxylic acids needed after ligand exchange in order to enter in biological systems. Crystal formed have imperfection, uneven particle size, and low quantum yield. These are the major drawbacks.

6.2 Catalytic properties of Graphene Quantum Dots

Gao and Wang synthesized the graphene -CdS quantum dots composites and explored its photocatalytic properties with the help of the Rhodamine B and Methylene blue solution[188,189]. Degradation Studies indicated that the composite material has high activity and stability. Visible light can be used as a practical catalyst.

graphene Quantum Dots effectively reduced the charge recombination rate resulting in the increase in the catalytic activity.

Lee et al. studied the graphene composites for Rhodamine B -CdSe and light industrial dye degradation effect, indicating that the composite organic dyes and general industrial dyes have some photocatalytic degradation[190].

Gao et al. found that graphene -CdS composite materials have high photocatalytic degradation and good disinfecting properties under irradiation. (Figure 16 a and b)

Studies showed that graphene and semiconductor quantum dot composites reinforce photocatalytic activity.

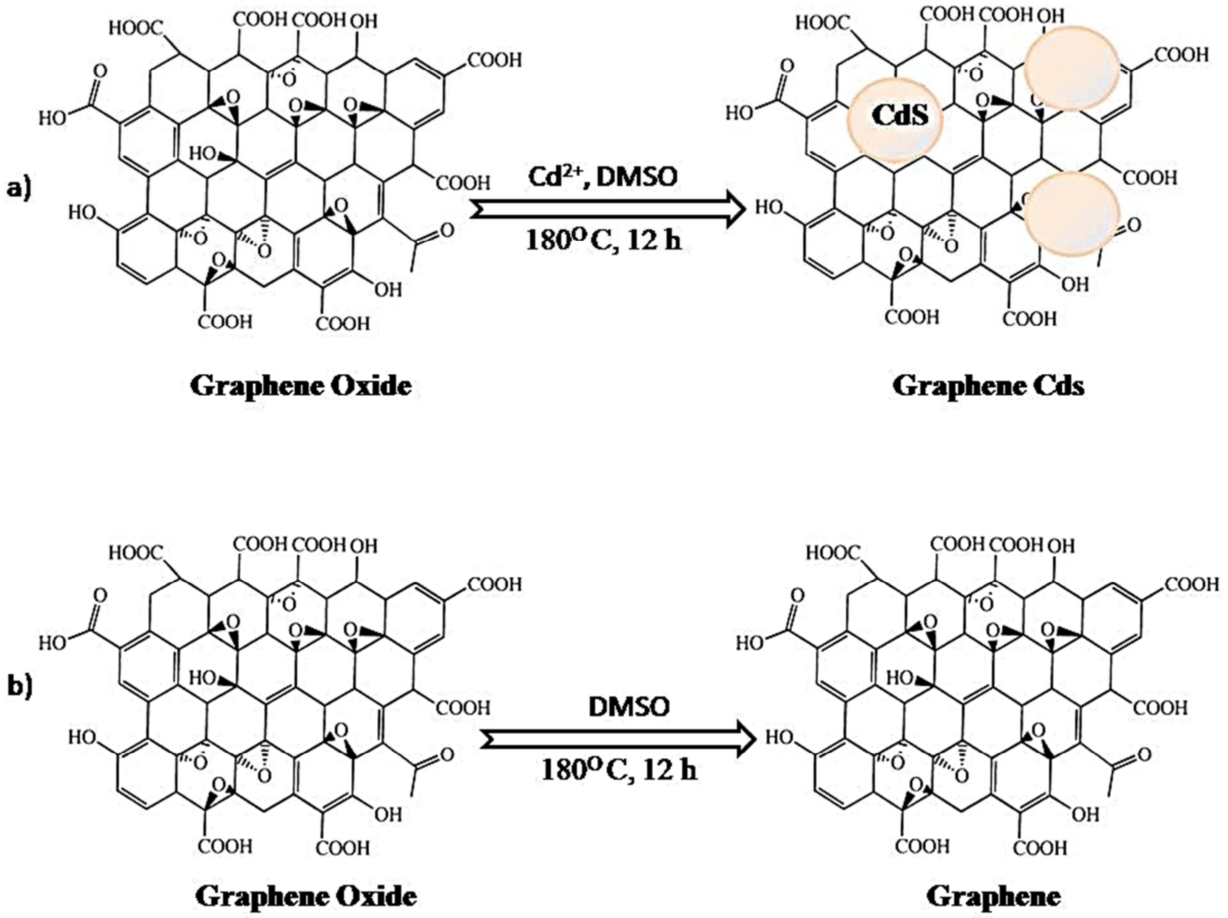


Figure 16 Graphene -CdS composite materials have high photocatalytic degradation and good disinfecting properties under irradiation.

6.3 Advantages and disadvantages of the Semiconductor quantum dots

- QDs can be used in the field of Chemophotocatalysis because of their high photostability, high resistance to metabolic degradation and fluorescence properties.
- QDs exist in different forms such as quantum dust, beads and small crystals which provide a wide scope for its application.
- Different routes such as colloidal synthesis, lithographic techniques can be used for the manufacturing of QDs.

- Irrespective of the size of the QDs UV or blue wavelength beam can be used to excite them[191].
- QDs are non-biodegradable in nature because of extended lifetime.
- Sometimes, QD shows quantum yield deterioration because of the low ratio of the emitted to the absorbed energy
- A potential drawback when used in biological applications is the fact that due to their large physical size, they cannot diffuse across cellular membranes. The delivery process may actually be dangerous for the cell and even result in destroying it[192].

7.0 Hybrid Nanomaterials

There are diverse natural nanomaterials, but their existence was noticed and administered by scientists until recently, and thus they have been used for the different technological aspects, for the betterment of the society. Moreover there is a quantity of nanomaterials which are being used in an integrated form, i.e. the already formed nanomaterials are used as the building blocks, in order to form a new set of nanomaterials, known to be as hybrid nanomaterials [193-197]. These hybrid nanomaterials are found to be more efficient than their unadulterated equivalent, because the properties of the isolated components are inherited in the new hybrid nanomaterials, thus yielding newer properties that are essentially dissimilar to the original ones [198-200]. These nanomaterials are used as the building blocks, may be integrated in the form of an organic-organic, organic-inorganic or protein-organic/inorganic hybrid system [201-203]. The interaction between the two parts of the hybrid nanomaterial, i.e., organic and inorganic, comes under any one of the classes, as shown in Figure 17-

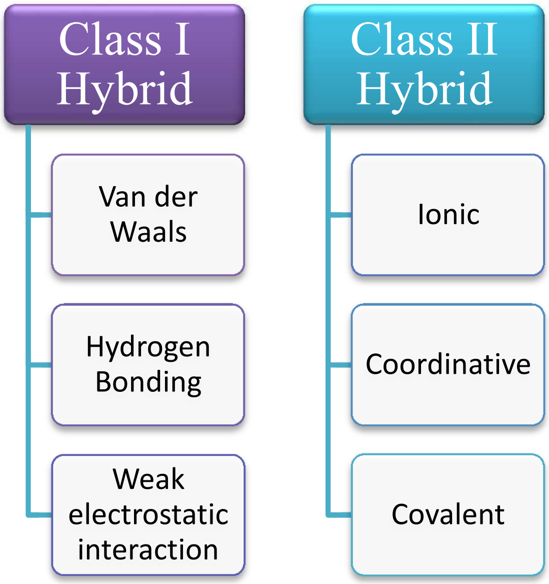


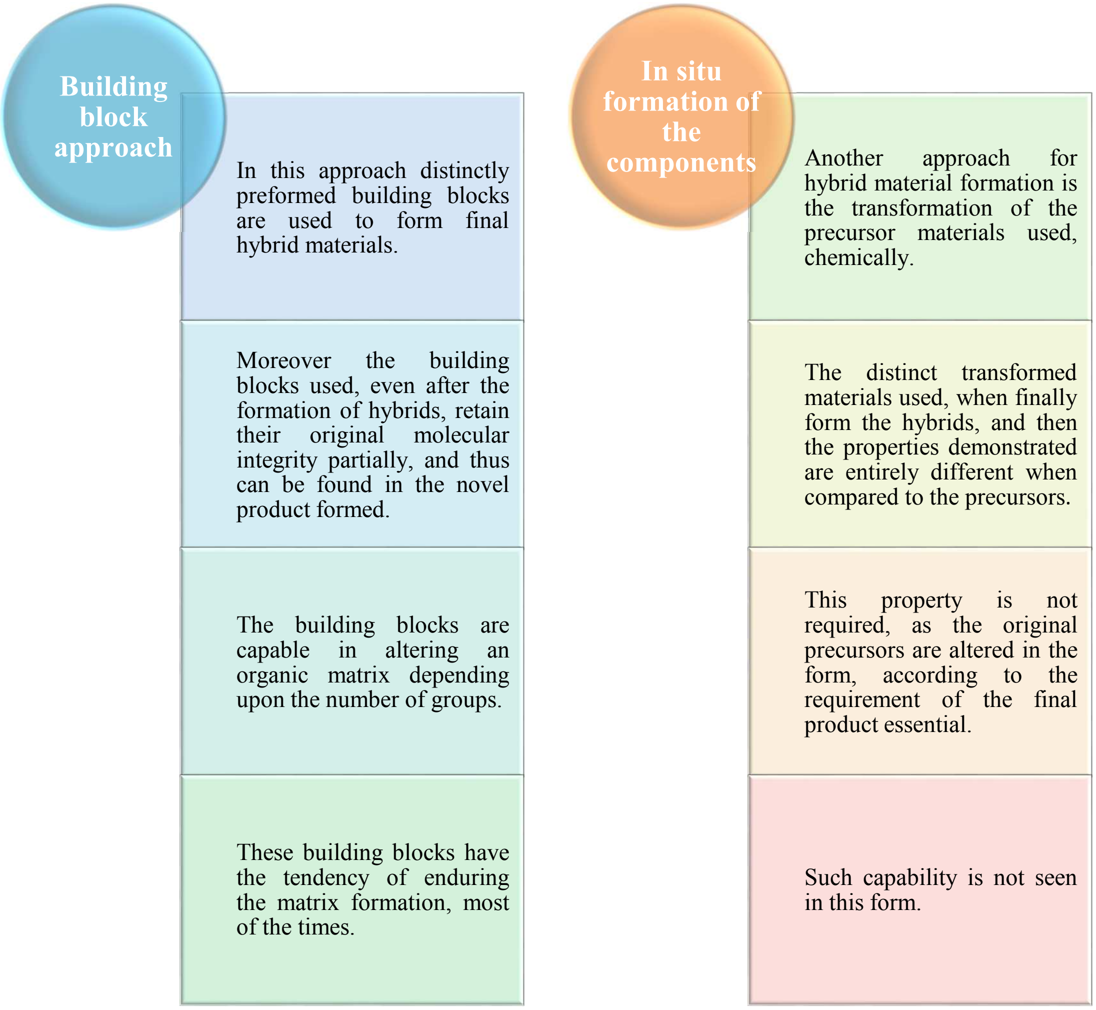
Figure 17 Showing the difference between the two classes of interactions in hybrid nanomaterials.

Class I Hybrid show weak forces of interactions between the two phases, while there are strong forces governing in the Class II Hybrid nanomaterials [204,205].

The field of hybrid nanomaterials is innovative and diverse because it allows the incorporation of two very divergent materials with characteristic properties into one, which opens up the possibilities of numerous, and indefinite properties, functions and applications of the new product formed. Moreover, there is an opportunity that the hybrid material formed may have multifunctional properties. These may also find relevance in the field of new generation nanophotocatalytic and optoelectrocatalytic material designing, due to the assorted functionality possessed. [206,207]

7.1 Preparation

Hybrid nanomaterials have found its place in the scientific world from the last decade, but its presence has been in nature from the very beginning[208,209]. In the form of bone, corals and nacre, hybrid nanomaterials represent nature's most intricate work of combining the biological organic molecules, with the inorganic components, and the complexity of this work cannot be completely mimicked by the scientists in the production of these materials [210-212]. The synthesis of synthetic hybrid materials can be attained with any of the two methods as shown in Figure 18. [213-216]



In this approach distinctly preformed building blocks are used to form final hybrid materials.

Moreover the building blocks used, even after the formation of hybrids, retain their original molecular integrity partially, and thus can be found in the novel product formed.

The building blocks are capable in altering an organic matrix depending upon the number of groups.

These building blocks have the tendency of enduring the matrix formation, most of the times.

Another approach for hybrid material formation is the transformation of the precursor materials used, chemically.

The distinct transformed materials used, when finally form the hybrids, and then the properties demonstrated are entirely different when compared to the precursors.

This property is not required, as the original precursors are altered in the form, according to the requirement of the final product essential.

Such capability is not seen in this form.

Figure 18 Explains the two processes by which the hybrid materials can be prepared.

Along with the organic/inorganic hybrid nanomaterials, polymer/inorganic hybrid nanomaterials are also being studied in the recent times and thus find its place in miscellaneous applicable areas, like, optics, coatings, catalysis, etc. [217]

In such hybrid nanomaterials, polymers offer the structural purpose, along with the mechanical features and process ability, if required, for the final product formed, while the inorganic precursor establishes the particular functionalities and properties in the finished hybrid material. Thus, the concluding material produced bears a unique result from both the precursors.

The four likely assembly of approach that may be used for the production of polymer /inorganic hybrid nanomaterial [218,219] are shown in Figure 19.

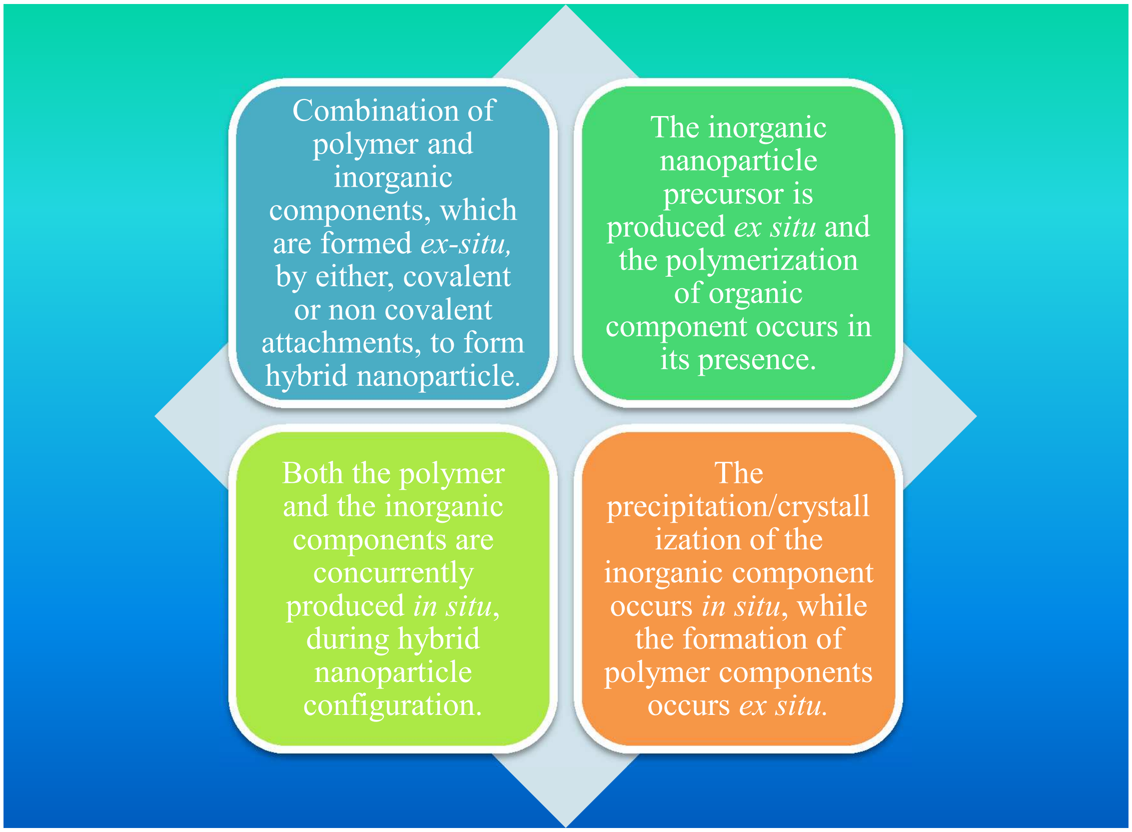


Figure 19 Approaches to form polymer/inorganic hybrid nanomaterials

7.2 Catalytic applications

The polymerization of inorganic nanomaterials with the organic components, gives an extensive assortment of applications, due to the considerably improved electronic, magnetic, mechanical and optical properties. The areas in which they are being used are shown in Figure 20. The applications involving the targeting form of function, depends on how the hybrid nanomaterial functions and its properties, which are governed by its morphological, structural and chemical parameters. These nanoparticles illustrate the elevated catalytic activities, along with commendable hydrogen storage capabilities due to its exceptionally large surface/volume ratios, which eventually boost up the surface effects.

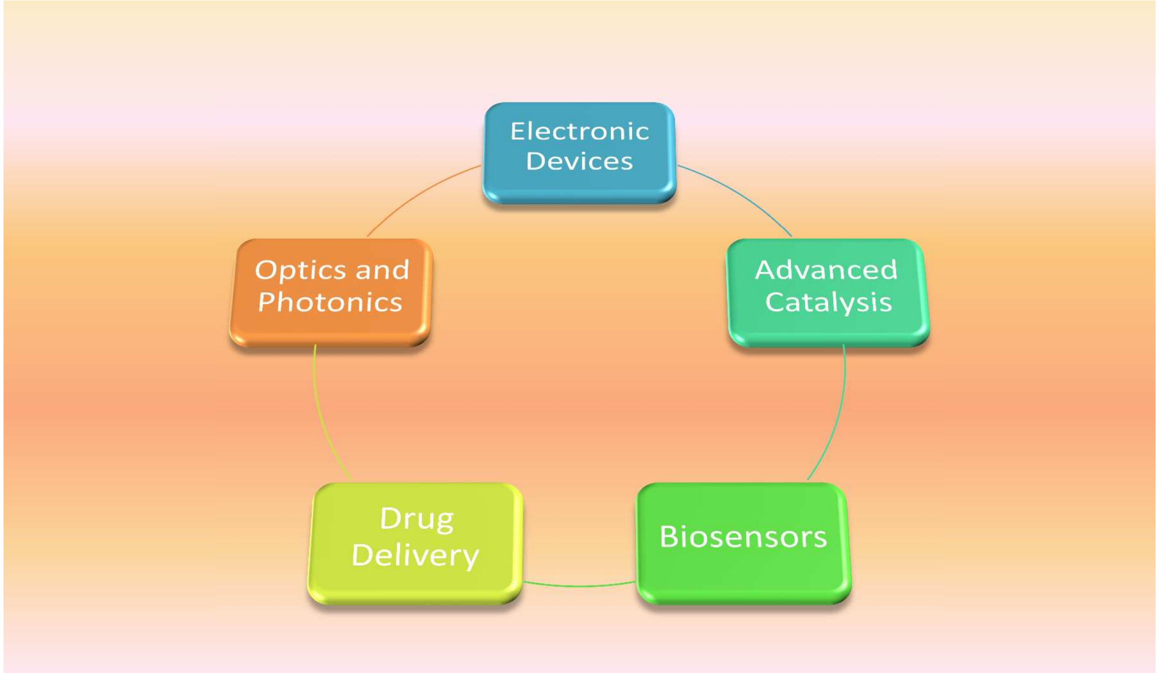


Figure 20 Wide ranges of applications of the Hybrid nanomaterials

Zhu *et.al*, [220] had shown the aqueous-phase synthesis of the graphene/SnO_2 composite (GSCN) hybrid nanostructures obtained through the reduction of graphene oxide (GO) using $SnCl_2$ in the presence of polyelectrolyte poly diallyldimethylammonium chloride (PDDA). Further they had shown the catalytic application of the same for the reduction of p–nitrophenol into p-aminophenol by $NaBH_4$.

Wang *et.al,* [221] had synthesized the organic–inorganic hybrid ionic liquid polyoxometalate (IL–POM) nanomaterials with the help of the solid-state chemical reaction at room temperature. Further, IL–POM shows the good catalytic activities and sensitive responses to the reduction of nitrite, bromate and hydrogen peroxide.

8.0 Metal - Organic Frame works

In the last ten years, metal-organic frameworks (MOF,s) have played a crucial role in the field of the catalysts after the zeolites, activated carbons and another class of porous materials [222-227]. MOFs are different from other porous materials due to its modular design called as Metalloxoclusters [228].Yaghi et al., first proposed the metal-organic Scaffolding of six Terephthalate anions (1,4-benzenedicarboxylate BDC) to a three-dimensional cubic network composition Zn_4O (BDC)[229]. Depending upon the orientation of the Benzene rings of the terephthalate anions and with the involvement of the Van der Waals radii, the resulting pores have, the diameter of 15.1 Å and 11.0 Å. The total pore volume (Vp) of MOF is up to 1.55 cm^3g^{-1} and has a specific surface area of 3800 m^2g^{-1} [230]. In further work, the working group of Yaghi was able to show that the pore size of the cubic MOF network can be freely varied by using linear linker of variable length over a range from 12.8 Å to 28.8 Å (van der Waals radii the network-atoms not involved)[231]. On the basis of this first highly porous metal-organic framework compound, subsequent MOF materials with extremely high pore volume and specific surfaces with maximum pore size will be synthesized with a variety of metals and linker molecules. The synthesis of metal-organic frameworks is not limited to the use of zinc and dicarboxylic. MJ Rosseinsky and his co workers have reacted salicylaldehyde to give an immobilized ligand for the complexation of Vanadium [232]. Now a days MOFs are synthesized from almost all the transition metals and some main group elements such as magnesium, aluminum, and beryllium. MOFs are also synthesized as a linker with to di- and polyfunctional carboxylates and molecules be used with nitrogen, phosphorus or sulfur donor functions. The modular structure of metal-organic framework allows the synthesis of a variety of different MOF structures and the specific design of tailored functional materials for the desired application. The application field of the porous metal-organic frameworks is very diverse. Due to their high specific surface area and pore size, they are used as an efficient storage for gases such as Hydrogen or methane. The controllability of the pore size and functionality makes MOFs also attractive materials for substance separation and catalytic transformations for obtaining various fine chemicals.

8.1 Synthesis of the Metal Organic Frame works

As mentioned earlier, synthesis of metal-organic frameworks is not limited to the use of zinc and dicarboxylic. The combination of several coordinating functions within a linker molecule is also possible. Solvothermal synthesis of the metal-organic frameworks is possible in polar solvents such as formamides, alcohols and water. As a result of this technique, the pores of the freshly synthesized MOF materials are always filled with the solvent molecules [233,234]. By treating the sample under vacuum at elevated temperature may lead to large pore volume and high specific surface area of the MOF's [235,236]. In some of the MOF structure not all coordination sites of the metal atoms occupied by donor groups of the linkers. The existing vacant coordination sites are vacant for the further MOF synthesis with time also occupied by the coordinated solvent molecules of the unsaturated metal atoms [237].

Almá˘si et al., had synthesized the two novel coordination polymers of MOF's with composition {[Ln(BTC)(H_2O)]·DMF}n(where Ln = Ce(III) and Lu(III), BTC = benzene-1,3,5-tricarboxylate, DMF = N,N_-dimethylformamide) under solvothermal conditions. Further, the catalytic activity of the MOF polymer has been evaluated with the help of the Knoevenagel condensation reactions in a series of aromatic and non-aromatic aldehydes with different active methylene compounds (malononitrile, methyl cyanoacetate)[238].

Neves et al., had incorporated the complex of [MoO_2Cl_2 (bpydc)] (H_2bpydc = 2, 20 bipyridine-5,50-dicarboxylic acid) into a ZrIV-based Metal–Organic Framework (UiO-67) by partial replacement of 4,40-biphenyldicarboxylic acid (H_2bpdc) in the solvothermal synthesis. The resultant MOF catalyst is capable in the epoxidation of cis-cyclooctene (Cy8) and limonene (Lim) with tert-butylhydroperoxide as oxidant [239].

8.2 Application of metal-organic frameworks in heterogeneous catalysis

Due to the variable pore size and functionality, metal-organic framework compounds not only used for the storage and separation of various gases but also open up a wide Range of applications in heterogeneous catalysis [240-242]. Because of their pore sizes generally range from 10 to 35 Å, MOFs are ideal for application in catalytic reactions. Other than this, MOF's have the additional property of the crystallinity. This leads to a defined pore structure and provides an accurate knowledge of the type and distribution of catalytically active centers. As the periodic structure of the network, these active centers are also uniform. Due to the uniformity of the catalytically active centers, MOFs have the advantage of the homogeneous catalysis along with the heterogeneous catalysis.

Despite these advantages of MOF's, there are some disadvantages as well such as thermal and chemical stability of metal-organic frameworks, in some cases significantly lower than that of the zeolites. On the other hand, the metal atoms of the nodes usually coordinatively saturated and thus no longer accessible to the reacted substrates.

The use of the MOF's in heterogeneous Catalysis is mainly based on three different principles such as the use of coordinatively binding with metal atoms, result of existing reactive functional groups and as a catalyst support [243].

Metal - Organic Frameworks with catalytically active metal atoms

There are many publications which deal with the implementation of catalytic reactions with MOFs containing active metal centers. The catalytic activity of these metal-organic frameworks is caused by the existence of coordinatively unsaturated metal atoms. The free coordination sites are generated by removal of coordinated solvent molecules at the initial stage of the MOF synthesis. The range of reactions carried out involves hydrogenations over oxidations to Lewis acid catalyzed Cyanation reactions, such as, the Friedel-Crafts reaction, or Mukaiyama aldol addition.

Monge et al, has synthesized the first Indium terephthalate based hydrogenated metal-organic frameworks, which has been characterized and found very successful in the hydrogenation of nitro aromatic compounds [244]. MOF with active metal atoms are widely used to catalyze oxidation reactions such as: the oxidation of alkanes or carbonyl compounds to alcohols, the oxidation of alcohols to Aldehydes or ketones, the epoxidation of olefins, the conversion of thiols to disulfides [245,246], the sulfoxidation of sulfides [247] and the selective oxidation of carbon monoxide to carbon dioxide for the purification of hydrogen[248,249].

A selective oxidation of linear and cyclic alkanes to alcohols was observed by KS Suslick and co-workers. They had also observed an organometallic scaffolding connection with a manganese porphyrin - linker as Inserting catalyst [250].

Volkmer et al, had showed the systematic approach for the synthesis of cobalt -based metal-organic Frameworks, which are used in the oxidation of olefins. He is capable to introduce the methyl group in the 3- and 5- Position of the pyrazolyl units of the Co (BPB) (BPB = 1,4- bis (4' pyrazolyl) benzene) , with the help of the catalytic activity by the oxidation of Cyclohexene [251].

Corma et al. had performed a carbon-carbon - linking reaction, for the coupling of Phenylboronic acid and 4- bromoanisole. This reaction is a metal -mediated cross-coupling rather than than the Lewis acid initiates extending mechanism and the Suzuki coupling[252].

In addition to the above-mentioned reactions, publications exist for synthetically rather less relevant MOF - catalyzed acetalization of aldehydes[253] and the three-component coupling of an aromatic alkyne, an aldehyde and an amine followed by cyclization then extraction of indole derivatives[254].

9.0 Catalytic Nanomotors

Catalytic nanomotors are the nano sized micrometer actuators, ubiquitous in nature having inorganic structures that use chemical energy ATP to perform mechanical work. The nanomotors have autonomous, non -Brownian motion that stems from propulsion via catalytic generation of chemical gradients[255]. These catalytic motors do not require external magnetic, electric, or optical fields as energy sources. They are analogs of naturally occurring bionanomotors which utilize energy obtained from the environment to do work. Nanomotors can occur naturally in organic molecules, combine natural and artificial parts to form hybrid nanomotors or be purely artificial .Nanomotors are commonly divided into two categories biological and nonbiological[256].Biological nanomotors can broadly divided into three categories: DNA base, Protein based, Chemical motor molecule. One of the typical examples of a biological Nanomotor is the organelle ribosome, which consists of ribosomal RNA (rRNA) and protein Figure.21[257] Nonbiological are made from natural and artificial part. F1F0 ATP synthase bacterial flagella, kinesin, dynein, myosin, actin, microtubule, dynamin, RNA polymerase, DNA polymerase, helicases, topoisomerases, and viral DNA packaging motors are some other prominent biological nanomotor[258].There are various fabrication techniques consist of template directed electroplating, lithography, physical vapor deposition, and other advanced growth methods[259].

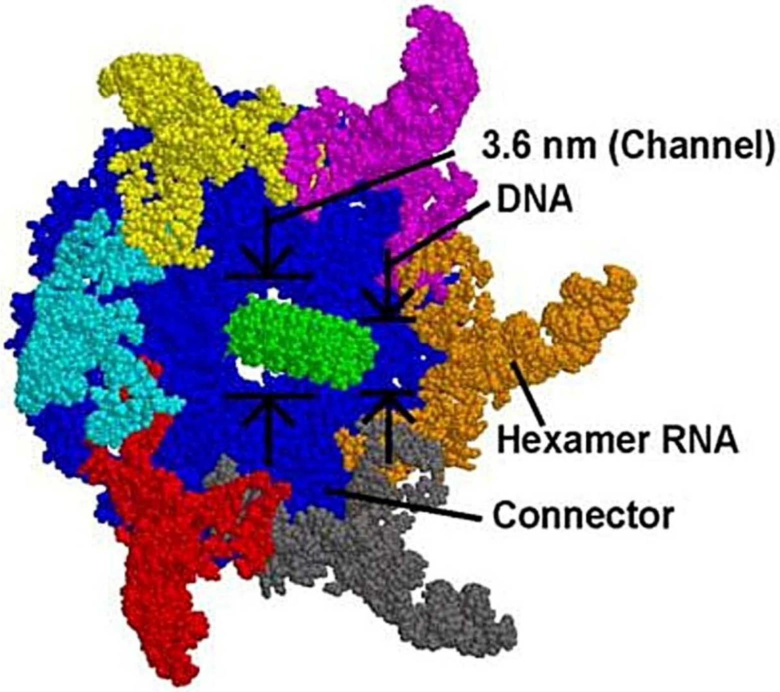


Figure 21 DNA Nanomotor (Reproduced with permission from Tae Jin Lee et al[259]).

9.1 Biological nanomotors

The chemically powered motor protein classes, myosins, linear stepper motor-kinesins and dyneins, perform variety of cellular signaling functions in biology such as organelle and vesicle transport[260]. These molecular motors are proteins that use adenosine triphosphate (ATP) as a chemical fuel for the conversion of chemical energy into mechanical work to carry out coordinated movements within cells. As, ATP is hydrolyzed to adenosine diphosphate (ADP) and then into adenosine monophosphate (AMP). ATP hydrolysis is presumed to drive protein conformation changes that result in sliding or walking movements[261]. A kinesin is another motor protein which requires ATP hydrolysis for their movement along the microtubule filaments. The kinesins are responsible for anterograde or outward transport of cargo from the cell center [262].Dynein produces the axonemal beating of cilia and flagella and also transports cargo along microtubules towards the cell nucleus[263]. In bacterial flagella, the molecular engine powered by the flow of ions across the inner, or cytoplasm, membrane of a bacterial cell envelope. Each motor drive a protruding helical filament and the rotating filaments provide the propulsive force for cells to swim. Ion flux is driven by an electrochemical gradient controlled by H+ and Na+ .This gradient consists of a voltage component and a concentration component. The interior of the cell is at an electrical potential about 150mV below the outside and has a slightly lower concentration of H+ or Na+[264].

9.2 Manmade catalytic nanomotors

The most practical method researchers used to design functional artificial motors by combining naturally and artificial parts to form hybrid nanomotors such as the transportation of inorganic cargo was shown to be possible through the catalysis of actin filament polymerization[265]. In artificial nanomotors, hydrogen peroxide H_2O_2 is commonly used chemical fuel[266]. It spontaneously decomposes into water and oxygen, but at a very slow rate. Catalyst can greatly increase the rate of reaction as shown in figure 22. Although, H_2O_2 is generally the most commonly used source of energy, other chemical fuels that are more biocompatible such as glucose have been used as well.

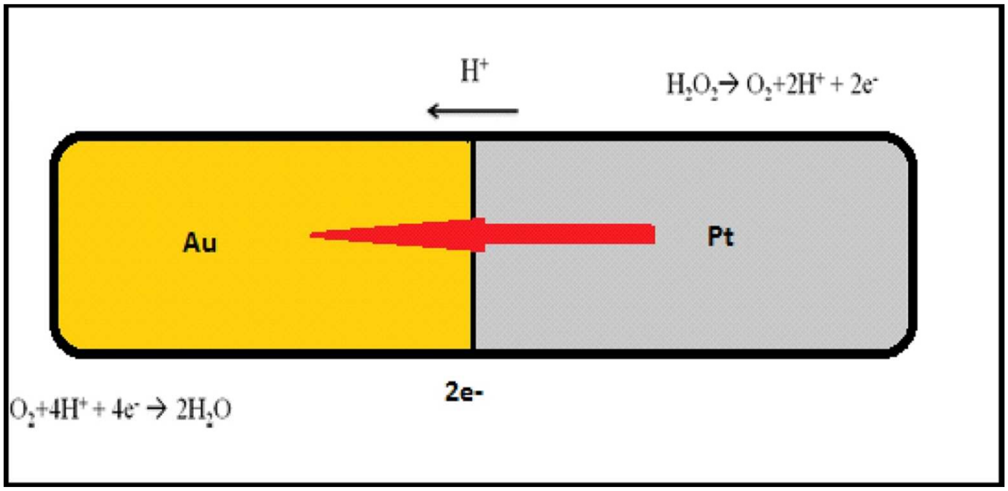


Figure 22 When placed in an aqueous solution of hydrogen peroxide .its decomposition reaction at the Pt end lowers the interfacial tension between the solid and the liquid, thus generating a gradient of interfacial tension along the rod. This results in a net force to propel the rod in the direction of the Pt end [266,267].

9.3 Methods used for fabricating catalytic nanomotors

The methods used for synthesis are template directed electroplating (TDEP) and physical vapor deposition (PVD). In template directed electroplating a porous Al_2O_3 membrane with uniformly sized pores is used as a template for the electrochemical deposition of an array of metallic nanorods which can be released from the template. Physical vapor deposition is economic and an easy method that consists of coating substrates by the heating and evaporation of metals and metal-oxides. PVD is the deposition of a thin film onto a substrate. In this case, the substrate is placed directly above the source material at a 0° vapor incidence angle (the vapor direction is parallel to the substrate surface normal) and is coated with a film of the evaporated material[267].

9.4 Applications

Catalytic nanomotores emerge from Nanobiotechology. Nano motors are found in living systems. The purpose of creating nonbiological nanomotors is to get the desired physiological function in nanoscience. Nanotechnology has advanced heterogeneous catalysis[268]. Heterogeneous catalysis can generate localized potential gradients in nonbiological systems and plays the role similar to enzyme-catalyzed reactions in biological systems .Use of gradient in interfacial tension between a solid and a liquid is one of the example of it.On other hand in the macroscopic world, motions are generated by the presence of a gradient. Pistons in the cylinders of a combustion engine are pushed by pressure gradient, and shafts in electric motors are turned by magnetic or electric field gradients[269]. Catalytic nanomotors have recently been used to act as sensors for the presence of DNA and bacterial rRNA[270].

9.5 Advantages and disadvantages of the Catalytic Nanomoters

- Catalytic nanomotors only need chemical fuel to work. So they can be used to manufacture autonomous catalysts for Microelectromechanical System (MEMS).
- The properties of catalytic nanomotors can be changed by changing their dimensions and compositions.
- Catalytic motors can be used in biology and medicine by using bio-compatible enzymes such as glucose oxidase irrespective of inorganic catalysts.
- The major disadvantage of catalytic nanomotors is their direct manipulation for different purposes such as control motion and multi-component nanomotors.[271]

- The use of multifunctional micromotors limited due to its short lifespan.[272]

10.0 Future Prospects of the Catalytic Nanomaterials

Nanotechnology and nanoscience are considered as a very important part for future technological progress, due to the enormous potential for manipulation in this ultra small nanoscale system[273-276].

10.1 Sustainable Preparation and catalytic application

Research in the field of catalytic nanomaterial is more focused towards the green-inspired approaches to synthesize the nanomaterials[277-280]. Bale et al. investigated that the proteins such as soybean peroxidase, poly-l-lysine and bovine serum albumin can be used to synthesize the silver nanoparticles on the carbon nanotubes[281].

Table 3 Summarizes the sustainable preparation and catalytic application of the Nanomaterials.

Nanomaterial	Method of preparation	Catalytic application	Reference
ZnO nanoparticles, nanorods and nanowires	Nanomaterials (NMs) prepared and coated on multi-channel porous alumina ceramic membrane. The structures and morphologies confirmed by X-ray diffraction method and scanning electron microscopy.	Shape dependent oxidative decomposition of ZnO NMs of Butane. It could completely oxidize butane into carbon oxides (CO_x). Better carbon balance and CO_x selectivity were obtained with the ZnO Nanowaires and Nanorods than with the Nanoparticles.	Gandhi et al, 2014[282]
Multi-wall carbon nanotubes (CNTs) and graphene oxide (GO) nanomaterials	Multiwall carbon nanotubes were synthesized using functional groups like carboxyl, alkyl and amine groups.	The catalytic activity of cyt c increases up to 78-fold in the presence of graphene oxide and up to 2.5-fold in the presence of other functionalized carbon-based nanomaterials (CBNs)	Patila et al, 2013.[283]
Strontium(II)-added $ZnAl_2O_4$ nanomaterials with spinel structure	Modified sol–gel method using ethylenediamine and then sintering at 900 °C. Analysis done by XRD FTIR, HRSEM, DRS, PL Spetroscopy.	Sr addition improves the performance of zinc aluminate for selective oxidation of alcohols and decreases the grain size.	Kumar et al, 2012.[284]
Au–Pt nanomaterials with cage-bell structures	Au nanoparticles with narrow size distributions prepared, Ag coating done on them. Pt^{II} ions reduced using citrate in the presence of core–shell Au–Ag nanoparticles, core-shell-shell Au–Ag–Pt nanoparticles formed Ag removed using bis (p-sulfonatophenyl)phenylphosphane and hydrosol containing the	Catalytic activity toward oxygen reduction in proton-exchange membrane fuel cells because of higher surface areas than their solid counterparts. Nano-channels on the Pt shell permit the access of the inner	Qu et al, 2012[285]

	Au–Pt nanomaterials with cage-bell structures obtained.	surface areas. Electronic coupling effect occurs between the inner-placed Au core and the Pt shell.	
Coiled Carbon Nanotubes (CCNTs)	CCNTs used as support to prepare platinum catalysts via modified ethylene glycol method. Evaluation of two and three kinds of above catalysts mixed with different mass ratios was done.	Mixed catalysts also demonstrated improved oxygen reduction reaction activities. CCNTs had an uncommon feature by which can construct a multi-dimensional network to facilitate the mass transportation and electrons/protons transfer.	Shuihua et al, 2014[286]
CuO materials-microspheres, nanosheets, nanowires	CV scans analysis shows water oxidation under a potential of ~0.90 V at pH 9.2. Characterization by XRD, SEM, TEM, HRTEM, XPS.	Catalytic activity toward oxygen evolution of the nanomaterials was investigated. CuO nanowire had lowest over potential for water oxidation and CuO microsphere material had the best catalytic current densities from 1.10–1.40 V.	Liu et al, 2015[287]
Organic–inorganic hybrid ionic liquid polyoxometalate (IL–POM) nanomaterials	Facile synthesis method of solid-state chemical reaction at room temperature with the reactants of four ILs and Keggin-type structure phosphomolybdic acid.	IL–POM CPEs exhibit catalytic activities and sensitive responses to the reduction of nitrite, bromate and hydrogen peroxide.	Wang et al, 2012[288]
Silica based strong metal nanocatalyst	Electrostatic metal deposition methods	To determine the correlation between strong electrostatic interaction during	Jiao et al, 2008[289]

		impregnation and the high dispersion of reduced metals,	
Graphite Oxide	Laser reduction method for the synthesis of laser converted graphene (LCG) from graphite oxide (GO).	For heating water for a variety of potential thermal, thermochemical, and thermomechanical applications.	Abdelsayed et al, 2010[290]
Covalent Organic Frameworks (COF)	Cerius Modeling(crystal building module) Software	Activation of COF-102 and COF-103 for gas adsorption measurements. Low Pressure (0 – 760mTorr) Argon Adsorption Measurements for COF-102	Rabbani and El-Kadetri 2007[291]

10.2 Future Implications of the Catalytic Nanomaterials

Many other materials besides gold and the carbon nanotubes have been investigated as catalysts. The potential application of these solids is related to its high specific surface area and the ability to control the selectivity by variations in size and dispersion of the nanoparticles in media. The catalytic systems based on aluminum oxide, impregnated with platinum and palladium nanoparticles with a high degree of dispersion, for example, are employed in automotive devices to reduce emissions of pollutants[292].

The materials employed as electrodes of fuel cell components are the doped cerium nanoparticles[293]. In particular, cerium oxide doped with gadolinium and samarium are considered promising as compared to the commercial-based electrolyte Zirconium stabilized with yttrium, to allow the use of operating temperatures lower than 800°C due to the employed as the electrolyte in solid oxide fuel cells. Another example is presented by the colloidal platinum-ruthenium nanoparticles obtained by the reduction of platinum and ruthenium ions with citric acid and sodium borohydride, which are active in the catalytic oxidation of methanol, reaction of industrial interest for the anode catalyst preparation cells of direct methanol fuel (DMFC, Direct Methanol Fuel Cell)[294]. The reaction medium was adequate for nanoparticles of these metals with sizes between 2 and 3 nm, proving its potential application as catalytic anode in DMFC.

The cobalt oxide nanoparticles mixed oxide supported on zirconium-cerium also have potential application as catalysts exhibiting high performance at low methane oxidation temperature[295]. Other studies have shown the potential of platinum catalysts supported on mixed oxides of cerium and zirconium in autothermal reforming of iso-octane in carbon dioxide monoxide conversion to high temperatures and the removal of nitrogen oxides from automobile exhaust gases[296-299].

Inclusion of the bio-inspired approaches in the synthesis of the nanomaterials and its catalytic application in the recoverability, biodegradability and bioremediation are the upcoming fields of the nanocatalysts.

11.0 Conclusions

The nanostructured materials show great promise and opportunities for a new generation of materials with controlled and optimized properties for different applications, including catalysis. In this case, it is desired to achieve perfect activity and selectivity similar to those of enzymes. The nanocatalysts have complex structures of different materials on a large scale with a high surface to volume ratio, which gives them the unique properties, especially reactivity. Among these materials, the LDH's and MSN's are the most striking examples of nanocatalysts, being active in different reactions. However, knowledge about the nature of the catalytic sites is still limited due to the lack of studies on the conditions of the reactions. Metallic nanoparticles also have great potential for application in catalysis due to their electronic properties, adsorptivity, mechanical and thermal properties. Other nanomaterials have potential applications in catalysis, such as Quantum dots, Nano Bubbles, and Catalytic Nanomoters. Despite the large volume of work in nanocatalysts, there is a need to increase the performance of these materials and experimental techniques that can produce materials on a large scale, with reproducible characteristics.

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