CHAPTER I
INTRODUCTION

Nanotechnology

“There’s plenty of room at the bottom”, an initiative talk delivered by Richard Feynman on 29th December 1959, in the annual meeting of the American Physical Society at the California Institute of Technology, USA, motivated several researchers to think about the possibility of manipulating things at the atomic level. The existence of nanomaterials can be historically traced back to even before the introduction of some modern concepts in science and technology. Nanoparticles were used as colorants in ceramics by ancient people [1]; colloidal gold was used in medical treatment to cure dipsomania, arthritis etc., as early as from 19th century; systematic experiments conducted on nanomaterials had also been started from the days of well known Faraday’s experiment in 1857 [2]. Interest on nanostructured systems has been arisen because of many reasons that include the discovery of novel materials, processes and phenomena at the nanoscale as well as the development of new experimental and theoretical techniques that provide fresh opportunities for the development of innovative materials with unique properties and this field is expected to open new avenues in science and technology. Despite its increasing prominence in the scientific, regulatory and public spheres, there is still no single definition of “nanotechnology”. In essence, nanotechnology is the science and engineering of creating materials, functional structures and devices on a nanometer scale. In scientific terminology, “nano” means billionth of a meter or $10^{-9}$ m. “Nano” means dwarf in Greek and nanoscience deals with the study of atomic and molecular particles.

Nanotechnology is a relatively new research topic that attracts increasing interest from scientists and engineers all over the world due to its novel applications. Nanotechnologists use special tools called atomic force microscope and scanning tunneling microscope in order to view and measure these tiny pieces of matter as well as to manipulate them into what nanoscientists call “nanostructures,” such as nanotextured surfaces, nanotubes and nanoparticles. In nanoscale, materials become stronger, less weight, exert higher ductility and gain a host of enhancement in characteristics. How these materials gain such improvements is a much more complicated matter. The size of the nanoparticles strongly
influences their property those were different from that of the bulk materials [3]. This can make materials chemically more reactive (in some cases materials that are inert in their larger form are reactive when produced in nanoscale) and affect their strength, optical or electrical properties.

Also, when the crystallites of a material are reduced to the nanometer scale, there is an increase in the role of interfacial defects, grain boundaries, triple junctions and elastically distorted layers. The properties of materials can be different at the nanoscale for two main reasons. First, nanomaterials have a relatively larger surface area when compared to the same mass of material produced in the bulk form (Figure 1.1).

![Figure 1.1: Increase in the surface area of a material while volume remains constant](image)

Second, quantum effect begin to dominate the behavior of materials at the nanoscale, particularly affecting their optical, electrical and magnetic properties (Figure 1.2 & 1.3).

![Figure 1.2: Changes in the optical properties of a bulk material upon size reduction](image)
Recently, scientists and engineers are becoming “new-age alchemists” by diving into a new scientific realm known as nanotechnology to create materials those can change the way of life that we live today [4]. Nanotechnology differs from particle physics in a sense that the latter science attempts merely to understand the tiniest things in the universe while the former use these tiny particles for practical purposes. This is what that differentiates nanotechnology from more theoretical sciences: it possesses very distinct purposes and clear goals (even though the science behind it might seem so complicated as to be nearly impossible for the average human to fully understand). Nanotechnology can be used to manipulate the metals in order to make them lighter or to build better semiconductors and microchips. Also, nanotechnology has countless medical applications that include treatment to kill cancer cells. Even tennis racquets and other sports equipments are often built using nanotubes of carbon molecules which greatly enhance both strength and performance. Research in nanotechnology promises breakthroughs in various areas such as materials and manufacturing, nanoelectronics, medicine, health care, energy, biotechnology, information technology and national security. It is common belief that nanotechnology is a diverse and powerful field and will result in revolutionary achievements for the creation of new products.

**Nanosystems in nature**

Nature has many objects and processes that function on a micro to nanoscale. The nanoscale happens to be the size regime of the fundamental building blocks of biology.
In nature, there are numerous examples of nanotechnology based systems, already highly optimized through millions of years of evolutionary development. For example, the size of some optically tuned nanoparticles lie precisely in the range of DNA and typical proteins (Figure 1.4). Few cases of what nature can do in nanoscale are shown in Figure 1.5. The inner ear of a frog (left) has nanomechanical cantilevers that measure deflections as small as 3 nm due to sound. The eye of an ant (right) uses nanoscale features to greatly enhance its visual sensitivity. Also, the wings of butterfly were shown to be intricately colorful because of nanoparticles that act as a photonic crystal. A human hair is approximately 80000 nm wide and a red blood cell is approximately 7000 nm wide [5].

The water repellent surface of the lotus (*Nelumbo nucifera*) leaf and flower is due to nanosized wax papillae on the upper side of each epidermal cell. As a result, rain drops make a high contact angle with the papillae and roll off carrying dust and dirt particles, leaving the surface clean. This self cleaning property of highly hydrophobic surfaces, termed as the lotus effect, has opened the possibilities of fabricating super hydrophobic surfaces for a variety of applications [6].

In addition, biological nanomotors are unique, microscopic engines created by nature: ATP synthase and bacterial flagella motor which makes possible for the bacteria to move independently in space. The tip of the flagellum rotates through electrostatic interactions between its rolling grounds, which is about 50 nanometers in diameter (rotor).
and still enshrined in the cell membrane complex (stator). The rotation is ensured by a transmembrane gradient of positive ions Na⁺ and mainly H⁺ [7]. Chlorophyll in plants is a Mg-porphyrin complex and is a typical natural photocatalyst which captures sunlight to convert water and carbon dioxide into oxygen and glucose without which survival of the living beings would be a big question.

![Figure 1.5](image_url)

Figure 1.5: (a) Lotus leaf, (b) Butterfly wings and (c) Flagella of E-coli bacterium

These are only few of the countless examples of how nature employs nanotechnology in different ways. It is both fascinating and humbling to observe that despite all of the advances in nanoscale synthesis and characterization, in most cases we are still unable to build nanotechnology based devices that even come close to reveal nature.

**Nanomaterials**

Materials with atleast one dimension in nanoscale are termed as nanomaterials. There are already many utility enhanced products in the market and efforts are being made that would turn polymers into efficient solar energy converters simply by mixing them with nanocrystals [8].

Much of nanoscience and nanotechnology concepts are concerned with producing new materials with advanced properties. Nanomaterials can be constructed by two methods such as ‘bottom-up’ and ‘top-down’ approaches. In bottom-up approach, it is done by building atom by atom or molecule by molecule. One way of doing this is self-assembly in which the atoms or molecules arrange themselves into a well defined structure due to their natural properties. Crystals grown for the semiconductor industry provide an example of self assembly as does chemical synthesis of large molecules. They may also be done by top-down technique, producing very small structures from larger
pieces of material, for example by etching to create circuits on the surface of a silicon microchip. A second way in top down approach is to use tools to move, each atom or molecule individually. Although this ‘positional assembly’ offers greater control over construction, it is currently very laborious and not suitable for industrial applications. In order to understand the inter-relationship between structure and properties, nanocrystalline materials need to be characterized on both atomic and nanometer scales. There are various experimental techniques that can be used to study the nanomaterials.

Microscopic techniques

- Scanning electron microscopy (SEM)
- Atomic force microscopy (AFM)
- Transmission electron microscopy (TEM)
- Scanning tunneling microscopy (STM)
- Field-ion microscopy (FIM)
- Neutron microscopy

Other techniques

- Powder X-ray diffraction (XRD)
- Nuclear magnetic resonance spectroscopy (NMR)
- Raman spectroscopy
- Mossbauer spectroscopy (MB)
- Fourier transform infra-red spectroscopy (FT-IR)
- UV-visible spectroscopy (UV-vis.)
- Photoluminescence spectroscopy (PL)

Owing to the ultrafine scale of these materials, TEM, X-ray and neutron diffraction are necessary and useful to understand the structure of nanocrystalline materials.
Semiconductor nanomaterials

Solid materials can be categorized as metals or semiconductors, depending on their ability to conduct electrical charge. On a microscopic level, this implies that the metal has overlapping valence and conduction bands, allowing the electrons to move freely and thus giving rise to charge conduction. Semiconductors have fully filled valence bands and the entirely empty conduction band separated from valence band by a forbidden range of energies. Thus, conduction in such materials requires a finite energy to promote the electrons from the valence to conduction band. While metals do not show much change in their electronic properties but to very low sizes, semiconductors exhibit interesting variations in their properties at sizes of about 10 nm (100 Å) and below. The structure of the nanocrystalline materials plays an important role in determining electronic properties. The same material can crystallize in different structures upon size reduction depending on the reaction conditions. The direct consequence of a reduction in the nanocrystalline size on the electronic structure of semiconducting materials is a pronounced increase in the band gap due to the quantum confinement effect [9].

Owing to the unique size dependent physical and chemical properties, semiconductor nanocrystals constitute an important class of nanomaterials that render them applicable in the emerging field of nanoelectronics [10]. Therefore, developing reliable protocols for the synthesis of nanometer scale semiconductor particles is a problem of great importance. Among nanocrystalline semiconductors, metal oxides and metal sulphides are significant due to their optical, electronic and magnetic properties. Oxide nanoparticles like ZnO, SnO₂, In₂O₃ and sulphide nanoparticles like CdS, ZnS, PbS etc., are tremendously explored and finds application as fluorescent biological labels [11], in optoelectronics such as non-linear optics, flat panel displays, light emitting diodes (LEDs), transistor components [12], catalysis [13], photocatalysis [14], sensors [15], photoelectric and thermoelectric materials [16], photoimaging, photodetection [17] etc.,. These interesting properties of semiconductor oxide/sulphide nanocrystals are because of electronic quantum confinement and the large number of exposed atoms on the surface [18]. Quantum confinement in luminescent semiconductors enables tuning of the absorption and emission via particle size and shape [19]. Transition metal sulphides are useful as dry lubricants, catalysts and solar cells [20]. There are few reports on the synthesis of nanoparticles of transition metal
sulphides like iron and nickel which showed magnetic properties [21]. Iron sulphide with structural formulae Fe$_3$S$_4$ and Fe$_7$S$_8$ are magnetic minerals and called as greigite and pyrrhotite respectively. These magnetic sulphides behave as a soft magnet and are mostly studied from geomagnetic field paleoclimatic magnetism point of view [22].

**Current applications of nanomaterials in various fields**

**Solar cells**

Solar cells are photovoltaic devices that can convert sunlight into electricity. They are much in demand as they offer an inexhaustible and environmentally benign energy source. Most solar cells are made of amorphous silicon. The problem with this is that the silicon must be of a very high purity and have a near perfect crystal structure. This makes it very expensive to produce and efficiency of such a cell is also very low, typically converting only 13-18 % of sunlight to electricity. However, low efficiency wouldn’t matter if huge arrays of cells could be produced cheaply. After all, nature’s solar cells, chloroplasts in plants are less than 1 % efficient.

Most solar powered devices rely on the same principle: a photon of sunlight boosts an electron in the material into a mobile state so that it can be used to generate electricity. The problem with this simple mechanism is that the electrons are negatively charged and will leave a positively charged hole. These opposite charges attract one another and therefore will tend to recombine, squandering the absorbed energy as heat or as re-emitted light. Silicon solar cells use an electric field to push the negatively charged electrons and positive charged holes apart so as to make the system more effective [23].

**Nanocrystalline amplification of light absorption**

By using nanocrystalline semiconductor films, it is possible to amplify the light absorption of the molecular monolayer to obtain visible color changes. The nanocrystalline layers are highly porous and usually the real surface of a 5 μm thick layer is about 500 times the projected area. Therefore, as light passes through the layer, it crosses several hundreds of monolayers of colored molecules giving a strong absorption.

The creation of an ultra fast, single electron transistor would lead to the development of "quantum" computers with supercomputer powers with the size of a thumbtack. However, there is still a long road ahead before atomic or molecular
transistors can be assembled into viable, dense and fast logic-circuits and at present these single electron devices are not competitors for silicon transistors. But they will serve both scientifically, for studying electron motion through nanoscale objects and technologically, for developing chemical techniques to fabricate electronic devices on single molecules [24].

**Sunscreen s and cosmetics**

Nanosized titanium dioxide and zinc oxide are currently used in some sunscreens, as they absorb and reflect ultraviolet (UV) rays and yet are transparent to visible light and so are more appealing to the consumer. The use of nanoparticles in cosmetics has raised a number of concerns about consumer safety.

**Clays**

Clays that contain naturally occurring nanoparticles have long been important as construction materials and are undergoing continuous improvement. Clay particle based composites containing plastics and nanosized flakes of are also finding applications in car bumpers.

**Tougher and harder cutting tools**

Cutting tools made of nanocrystalline materials such as tungsten carbide, tantalum carbide and titanium carbide are more wear and erosion resistant and last longer than their conventional (large-grained) counterparts. They find applications in the drills used to bore holes in circuit boards.

**Paints**

Incorporating nanoparticles in paints could improve their performance, for example by making them lighter and giving them different properties. Thinner paint coatings (light weight), used for aircraft would reduce their weight, which could be beneficial to the environment. Other novel and long term applications for nanoparticles might lie in paints that change color in response to change in temperature or chemical environment or paints that have reduced infra-red absorptive and so reduce heat loss.

Concerns about the health and environmental impacts of nanoparticles may require the need for the durability and abrasion behavior of nano-engineered paints and
coatings to be addressed, so that abrasion products take the form of coarse or microscopic agglomerates rather than individual nanoparticles.

**Fuel cells**

Engineered surfaces are essential in fuel cells where the external surface properties and the pore structures affect the performance. The hydrogen used as the immediate fuel in fuel cells may be generated from hydrocarbons by catalytic reforming, usually in a reactor module associated directly with the fuel cell. The potential use of nano-engineered membranes to intensify catalytic processes could enable higher efficiency and small scale fuel cells. These could act as distributed sources of electrical power. It may eventually be possible to produce hydrogen locally from sources other than hydrocarbons, which are the feedstocks of current attention.

**Displays**

The huge market for large area, high brightness, flat-panel displays as used in television screens and computer monitors is driving the development of some nanomaterials. Nanocrystalline zinc selenide, zinc sulphide, cadmium sulphide and lead telluride synthesized by sol–gel techniques (a process for making ceramic and glass materials, involving the transition from a liquid ‘sol’ phase to a solid ‘gel’ phase) are candidates for the next generation of light emitting phosphors. CNTs are being investigated for low voltage field-emission displays; their strength, sharpness, conductivity and inertness make them potentially very efficient and long-lasting emitters.

**Batteries**

With the growth in portable electronic equipment (mobile phones, navigation devices, laptop, computers, remote sensors), there is a great demand for light weight, high energy batteries. Nanocrystalline materials synthesized by sol–gel techniques are candidates for separator plates in batteries because of their foam like (aero-gel) structure, which can hold considerably more energy than conventional ones. Nickel metal hydride batteries made of nanocrystalline nickel and metal hydrides are envisioned to require less frequent recharging and to last longer because of their large grain boundary (surface) area.
Catalysis

Among the entire applications, the most significant one is the use of nanomaterials as catalysts/photocatalysts for organic reactions, degradation of pollutants like dye stuffs, pesticides etc., and conversion of air pollutants like CO and NOx into useful products [25]. The search for an alternative cleaner, safer and environment friendly technology is one of the priorities in chemistry research. The minimization of wastes together with the use of renewable feedstock, green reagents and catalysts are important parameters to achieve more sustainable processes [26]. Earlier research efforts in the area of catalysis have focused on large volume, low value products of petrochemical industries. Nowadays, these catalytic technologies are well established in industries such as oil refining and petrochemicals. Industries that produce fine and specialty chemicals always depend on the product innovation for their massive profits and not process development which in turn acquired by a new technology known as catalysis. The whole world relies on some common phenomena for the production of fuels, commodity chemicals, fine chemicals, pharmaceuticals as well as for strengthening environmental safety measures. Catalytic processes have been used by mankind for several thousands of years. The process of fermentation known since primitive times involved in the conversion of fruit juice into wine, malt into beer, in making vinegar, bread and cheese. The complex chemical reactions that occur during fermentation depend upon catalytically active enzymes produced by micro-organisms [27]. Catalysts are materials which themselves are not consumed during chemical reactions, but serve to accelerate those reactions and set them on course to create the desired products.

Catalysis as a whole comprises of both homogeneous and heterogeneous, depending upon the phase behavior of the catalyst. In heterogeneous catalysis, the catalyst is in a different phase from the reactants whereas in homogeneous, the catalyst and the reactants are in the same phase. Biocatalysts are often recognized as a separate group and thought to be a mixture of homogeneous and heterogeneous catalysts, because the enzyme is in solution itself, while the reaction takes place on the surface of the enzyme.
**Homogeneous and heterogeneous catalysis**

Homogeneous catalysis has gained enormous relevance in various reactions such as oxidation, transfer hydrogenation, formylation, Heck/Suzuki coupling reactions etc., with high reaction rates and turn over number (TON). The properties of homogeneous catalysts can be tuned by the nature of ligands [28]. Though homogeneous catalysts are highly selective and specific in their activity at low temperature and pressure, the main disadvantages are difficulty in separation of the catalyst from the product, degradation of the catalyst and high initial cost especially, if noble metals are required. On the other hand, heterogeneous catalysis involves a reaction, in which one or more of the constituents are in different phases and heterogeneous catalyst is normally insoluble in the reaction medium and can be easily separated. The catalyst may be pure, mixed with other catalysts or dispersed on an inert support e.g., metals and metal oxides. The advantages of using heterogeneous catalysts are their low cost, ease of recovery and adaptability to either batch or continuous flow reactors. Since catalysis is predominantly known for its importance in process efficiency and product selectivity in reactions starting from large scale industry to small-scale sector, non-specific and non-selective catalysts will not be applicable. It is evident that the key to cleaner process of fine chemicals and pharmaceuticals is the concept of selectivity and it is the major concern towards the green chemical aspects in atom economy and selectivity.

**Nanomaterials in catalysis**

Nanosized noble metal particles have occupied a central place in heterogeneous catalysis for many years, long before the recognition of nanotechnology [29]. Reduction in size parameters of a substance to nanometer scale causes appreciable change in the properties of the material, which can be used in practice for development of novel materials and technologies. This manifestation has not only reflected in physical properties like melting point, optical absorption, electrical and magnetic properties but also in the reactivity of the substance. This has direct consequence in generation of new functional nanomaterials especially in catalysis and adsorbents. The majority of industrial catalysts contain an active component in the form of nanoparticles < 20 nm in size and all the elementary reaction steps occur at the atomic scale level and hence, catalysis seems to be
intrinsically a nanoscale phenomenon. The importance of nanomaterials towards the performance of catalysts has stimulated wide efforts to develop methods for their synthesis and characterization, making this area of study an integral part of nanoscience [30].

Main driving forces for the development of nanocatalysts include:

(i) production of high value products with inexpensive raw materials

(ii) energy efficient and environmentally benign chemical conversion processes

(iii) increasingly stringent environmental regulations and

(iv) low cost catalysts with reduction or replacement of precious metals

Today, catalysis is an essential application of metal/metal oxide nanoparticles in addition to their applications in diverse fields of photochemistry, nanoelectronics, optics and drug delivery [31-38]. The use of nanoparticles in catalysis has appeared in 19th century with photography and the decomposition of hydrogen peroxide using Ag and Pt NPs respectively. Pioneering catalytic applications of nanoparticles were reported in 1940 by Nord for nitrobenzene reduction, in 1970 by Parravano for hydrogen atom transfer between benzene and cyclohexane and oxygen atom transfer between CO and CO₂ using Au NPs [39]. Similarly Ni NPs were used for the transfer hydrogenation of carbonyl compounds [40] and acetylene polymerization with Cu nanoparticles, ring opening metathesis polymerization on Au catalysts, cycloaddition reactions on Ni nanoclusters and carbonylation of methanol by Rh colloids [41].

It is not only the metal nanoparticles are excellent catalysts, but also metal oxides such as TiO₂, ZnO, Nb₂O₅, SnO₂, NiO, CuO etc., in the dimensions of several nanometer have been used as heterogeneous catalysts in variety of organic reactions.

**Nanomaterials in photocatalysis**

During the last few decades, environmental pollution causes serious impacts to human beings, animals, plants and even buildings. The presence of harmful organic compounds in water supplies and the discharge of wastewater from chemical industries, power plants, landfills and agricultural sources is a topic of global concern. Traditional water treatment processes include filtration, flocculation, biological treatment, thermal/catalytic oxidation and chemical treatment using chlorine, potassium...
permanganate, ozone, hydrogen peroxide and high energy ultraviolet light [42-45]. All these processes, currently in use have some limitations of their own as listed below and none is cost-effective:

- Phase transfer methods remove unwanted organic pollutants from wastewater, but they do not eliminate the pollutants entirely;
- Cost of biological treatment is low, however, some of the toxic compounds present are found to be lethal for micro-organisms intended to degrade them and there is a class of non-biodegradable organic products noted as bio-recalcitrant organic compounds;
- While chemical treatments based on aqueous phase hydroxyl radical chemistry are powerful to oxidize toxic organic compounds present in water, these processes either use high-energy ultraviolet light or strong chemical oxidants of hazardous and therefore, undesirable nature [43].

Moreover, several intermediates which are more hazardous are formed in these processes, have very low efficiencies, overall treatment cost becomes high if, destruction of intermediates and complete mineralization are to be achieved, especially for treating dilute waste water streams [42].

Photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. In catalysed photolysis, light is absorbed by an adsorbed substrate and hence the photocatalytic activity depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals (hydroxyl radicals: •OH) that able to undergo secondary reactions. Its comprehension has been made possible ever since the discovery of water electrolysis using titanium dioxide. Commercial application of the process is called advanced oxidation process (AOP). There are several methods of achieving AOPs that can but do not necessarily involve TiO₂ or even the use of UV light. Generally, the defining factor of photocatalysis is the production and use of the hydroxyl radical. When light falls on semiconductor nanomaterials, the electron present in the valence band jumps to the conduction band, as a result of it, a positive hole is generated. The recombination of the electron and the hole must be prevented as much as possible if a photocatalysed reaction is to be favored. The ultimate goal of the process is to have a reaction between the
activated electrons with an oxidant to produce a reduced product and also a reaction between the generated holes and a reductant to produce an oxidized product. Due to the generation of positive holes and electrons, oxidation-reduction reactions take place at the surface of semiconductors. In the oxidative reaction, the positive holes react with the moisture present on the surface and produce hydroxyl radical. When nanoparticles act as photocatalysts, the reaction is termed as heterogeneous photocatalysis, where in the catalyst and the reactants constitute different phases.

Figure 1.6: Mechanism of semiconductor photocatalysis

Up to date, several strategies have been attempted to improve the efficiency of photocatalytic reaction using different kind of semiconducting materials as photocatalyst as well as various kind of sensitizers to increase the efficiency of degradation. In this regard, it is significant to discuss about the photocatalysis for benign environment.

Heterogeneous photocatalysis using semiconductor metal oxide/sulphide nanoparticles is an advanced oxidation process (AOP), which was shown to be an effective means of
removing organic pollutants from water streams [45]. Compared with traditional oxidation processes, heterogeneous photocatalysis has the following advantages [46-48]:

- It utilizes low-energy, ultraviolet light with semiconductors acting as photocatalysts and leads to complete mineralization of pollutants to environmentally harmless compounds.
- The photocatalytic reactions allow thermodynamically unfavorable reactions to occur and allow destruction of non-biodegradable refractory contaminants.
- While catalytic processes normally require high temperature or high pressure, photocatalytic oxidation is a promising technique for many purposes due to its ability to operate at or slightly above ambient conditions.

However, the rate of the photocatalytic reaction is determined by the illuminated surface area of photocatalysts, light intensity, rate of adsorption of reactants and the properties of photocatalysts. Many metal oxides such as TiO$_2$, ZnO, Nb$_2$O$_5$, SnO$_2$, NiO and CuO and sulphides such as CdS, ZnS, WS$_2$, MoS$_2$ and other chalcogenides such as CdSe, CdTe etc., have been used as photocatalysts to degrade many synthetic dyes and organic pollutants. Among these catalysts, TiO$_2$ is highlighted because of its superior catalytic efficiency, chemical stability, low cost and less toxicity. It is biocompatible, environmentally benign and has been widely used in paints as pigments [34, 36, 49-50]. Recent research efforts dedicated to TiO$_2$ materials have been most fascinated with the discovery of photocatalytic splitting of water on TiO$_2$ electrode [51, 52].
Survey of previous work

Interest in heterogeneous catalysis by semiconductor metal oxide/sulphide nanoparticles increases enormously as reflected by the large number of publications during the last few years. It is a general belief that some of the metals (especially noble metals like Pt, Pd or Rh) are active catalysts while some other coinage metals like gold and silver are not active as catalysts in bulk state. This concept has been abandoned today, since gold is found to be active even for exotic reactions like oxidation of carbon monoxide to carbon dioxide at room temperature. Also, semiconductor photocatalysis has important applications in achieving sustainable energy generation and treating environmental pollution. Nanoscale CdS, ZnS, ZnO, SnO₂, WO₃, WSe₂, Fe₂O₃ etc., have been the most widely used photocatalysts. Combining a semiconductor nanomaterial with special reagents like H₂O₂ is being thoroughly investigated as a means to increase photocatalytic activity and demonstrations on the enhancement are plentiful.

Though voluminous reports are available in the literature on the preparation methods, characterization and utility of metal oxide/sulphide nanoparticles in catalysis and photocatalysis, some of them relevant to our work alone were reviewed and presented in this part of the introduction chapter along with few reports on hydroxyapatite those have been published recently.

Allylic oxidation of cyclo-olefins over silver doped vanadium pyrophosphate (Ag-VPO) catalyst was carried out in an argon atmosphere using tert-butyl hydroperoxide (TBHP) as an oxidant. Attack of the activated C–H bonds was preferred instead of the epoxidation of C=C bond and the corresponding α, β-enones were obtained as the main products by J. Liu et al.,. It is a high yielding, safe and eco-friendly method [53].

![Scheme 1.1: Allylic oxidation of cyclohexene](image-url)
Spherical, nickel nanoparticles has been successfully synthesized by the chemical reduction of nickel chloride with hydrazine at room temperature without any capping agent and inert gas protection by Z. G. Wu and his research team. The effect of concentration of the precursor nickel salt and the molar ratio of hydrazine to Ni\(^{2+}\) on the properties of the resultant products were investigated by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). This synthetic method is proven to be simple and very facile. In addition, it is very interesting to note that the obtained nickel nanoparticles can be isolated in the solid state and stabilized for several months in the atmosphere [54].

Azadi and co-workers studied the catalytic performance of cermets made of 10 % nickel or nickel oxide nanoparticles supported on YSZ (yttria-stabilized zirconia) for chemical looping combustion (CLC) and steam reforming (SR) of methane at 700 °C. Steam reforming of methane over the reduced catalyst resulted more than 70 % hydrogen and about 15 % carbon monoxide. Chemical looping combustion of methane within sufficient lattice oxygen could potentially lead to 40–65 % hydrogen rich gas products [55].

Watanabe et al., reported the preparation of nickel nanoparticulate catalysts supported on hollow Al\(_2\)O\(_3\) ball by spraying a mixed solution of nickel and aluminum nitrates in atmospheric pressure plasma. A wall of each ball (10 nm in thickness) consisted of uniformly dispersed oxide bricks of ~30 nm sizes, which were identified as densely packed NiO, NiAl\(_2\)O\(_4\) and Al\(_2\)O\(_3\) crystallites. Highly dispersed Ni particles (< 10 nm in diameter) have been formed on the ball surfaces by H\(_2\) reduction of NiO crystallites, surrounded by the nano-sized oxide bricks of NiAl\(_2\)O\(_4\) and Al\(_2\)O\(_3\). The catalytic activity of the Ni catalyst thus prepared for methane steam reforming reaction was tested for
polymer electrolyte fuel cells (PEFCs). The results showed that the catalyst possessed superior performances for the reaction in the activity and the resistance to coke deposition even under a low H₂O/CH₄ molar ratio [56].

Treatment of a stoichiometric amount of hydroxyapatite (HAp), [Ca₁₀(PO₄)₆(OH)₂], with [PdCl₂(PhCN)₂] gave a new type of palladium grafted hydroxyapatite. Analysis by means of powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray analysis (EDAX), IR and Pd K-edge X-ray absorption fine structure (XAFS) proves that a monomeric PdCl₂ species is chemisorbed on the HAp surface, which is readily transformed into Pd nanoclusters in the presence of alcohol. Nanoclustered Pd⁰ species can effectively promote the alcohol oxidation under an atmospheric O₂ pressure, giving a remarkably high turnover number with an excellent turnover frequency of oxidation of 1-phenylethanol under solvent-free conditions. In addition to advantages such as a simple work-up procedure and the ability to recycle the catalyst, the present Pd catalyst does not require additives to complete the catalytic cycle [57].

Selective, catalytic Knoevenagel condensation with Ni nanoparticles impregnated on SiO₂ or TiO₂ supports is achieved in quantitative yield. In this liquid phase reaction, under mild reaction conditions Ni–TiO₂ catalysts showed an efficiency of 100 % conversion and 100 % selectivity in an environmentally benign process [58].

D. Dutta et al., prepared Ni⁰ nanoparticles by impregnating Ni(CH₃COO)₂ into the nanopores of modified montmorillonite (Mt) followed by polyol reduction. The Mt was activated with HCl under controlled condition for generating desired pore sizes. The porous materials were characterized by XRD, TEM, SEM, UV–visible spectroscopy, FT-IR and XPS analysis. N₂ adsorption data revealed specific surface area (BET) in the range of 296–548 m²/g, specific pore volumes of 0.4–0.6 cm³/g and pore diameters of 0–6.8 nm. These supported Ni⁰ nanoparticles showed efficient catalytic activity in transfer hydrogenation of acetophenone to 1-phenylethanol with about 98 % conversion with nearly 100 % selectivity [59].

Karvembu et al., prepared copper(II) oxide nanoparticles by simple precipitation method and tested as an efficient and inexpensive catalyst for C-N cross coupling
reaction of benzimidazole with various aryl halides. The catalyst was characterized by
scanning electron microscopy, transmission electron microscopy, Brunauer-Emmett-
Teller (BET) surface area and powder X-ray diffraction analysis. Benzimidazole
undergoes reaction with aryl bromides, aryl chlorides or aryl fluorides in the presence of
K$_2$CO$_3$ at moderate temperature with yield ranging from 55 to 92 % [60].

\[
\text{N} + \text{Ar-X} \xrightarrow{\text{CuO NPs, K$_2$CO$_3$, DMAC, 120°C}} \text{N-arylbenzimidazole} + \text{HX}
\]

(Where X = Cl, Br, F)

Scheme 1.2: N- Arylation of benzimidazole with various aryl halides using CuO
nanoparticles

Monodisperse gold nanoparticles (Au NPs) have been synthesized by Sheng
Peng et al., at room temperature via a burst nucleation of Au upon injection of the
reducing agent t-butylamine borane complex into a 1, 2, 3, 4-tetrahydronaphthalene
solution of [HAuCl$_4$.3H$_2$O] in presence of oleylamine. The as-synthesized Au NPs
showed a size dependent surface plasmonic properties between 520 and 530 nm and were
deposited on graphitized porous carbon support as a highly active catalyst for CO
oxidation showing 100% conversion at 45 °C [61].

Nanosized ZnO powder was synthesized by Jun Wang et al., and applied as a
sonocatalyst after high temperature activation for degradation of acid red B and
rhodamine B. At the same time, the effects of operational parameters such as solution pH
value, initial concentration of the dye stuff and loading of the catalyst have been
examined and reported in this paper. The degradation ratios of acid red B and rhodamine
B in the presence of the sonocatalyst were much higher than that with only ultrasonic
irradiation. However, the degradation ratio of acid red B was about two times higher than
that of rhodamine B. The difference of the degradation ratios can be illustrated by the
chemical forms of acid red B and rhodamine B in aqueous solution and the surface
properties of nanosized ZnO particles. In addition, the kinetics of sonocatalytic reactions
of acid red B and rhodamine B have also been studied and found to follow pseudo first-order kinetics. All the experiments indicated that the sonocatalytic method in the presence of nanosized ZnO powder was an advisable choice for the treatment of either non-transparent or low transparent organic waste water in future [62].

Figure 1.8: UV–vis. spectra of acid red B and rhodamine B solutions during sonocatalytic degradation

K. Hwan and co-workers synthesized various nanocrystal (e.g. CdS, CdSe and Cu$_2$S)-carbon nanotube (NC-CNT) and NC-TiO$_2$ hybrid nanostructures using the solvothermal method and compared their photocatalytic ability in the visible light assisted degradation of methylene blue (MB) dye. The free CdS NCs exhibited higher degradation efficiency than the CdSe and Cu$_2$S NCs. The photocatalytic abilities of the NCs were found to determine the relative degradation efficiency of their CNT and TiO$_2$ hybrid nanostructures. These results suggest that the oxidative N-demethylation degradation involves the transfer of holes from the NCs to MB. The hybridization of the NCs with the TiO$_2$ NCs and CNTs enhances the oxidative degradation rate to the same extent, suggesting that the interfacial electron transfer process from the NCs to the attached CNTs (or TiO$_2$), which retards the recombination of the electrons and holes, is comparable for both hybrid nanostructures [63].

A series of N and N/Zr-doped titanium nanomaterials were synthesized by Rahima A. Lucky et al., via an acetic acid modified sol–gel route using supercritical carbon dioxide (scCO$_2$) as both the synthesis and drying medium using titanium isopropoxide (TIP), triethyl amine (TEA) and zirconium propoxide as precursors. The effects of N and N/Zr
doping on the morphology, phase structure, mean crystallite size, textural properties, thermal, crystallization behavior and photocatalytic degradation of methylene blue was investigated. SEM and TEM analysis showed that pure titania nanofibers were formed from TIP and acetic acid whereas the doped samples gave a flake like structure. The SEM and TEM images showed that a porous material consisting of ca. 10–15 nm crystals were formed. XPS spectra indicated that the N(1s) peak for both N-doped titania and Ti–Zr binary metal oxide were centered at 400 eV, indicating effective doping of nitrogen in the TiO₂ matrix. From the XRD analysis, it was observed that a small amount of nitrogen and zirconia inhibited the crystal growth, resulting in smaller crystallite materials. The BET analysis revealed that small amount of zirconia and nitrogen (0.4 at %) increased the surface area. All the synthesized doped samples gave superior photocatalytic degradation of methylene blue compared to degussa P25 powders. These results show that scCO₂ is a new promising route to provide N and N/Zr-doped advanced photocatalytic nanomaterials [64].

![Degradation rate graph](Figure 1. 9: Variation in the degradation rate for Zr modified N-doped TiO₂ nanomaterials)

Faisal and co-workers published the synthesis of ZnO–CeO₂ nanoparticles by simple and efficient low temperature process and employed for the development of effective chemical sensor as well as photocatalyst for the removal of environmental contaminants. Field emission scanning electron microscopy (FE-SEM), powder X-ray diffraction (XRD), Raman spectroscopy and Fourier transform infrared spectroscopy
(FT-IR) were used to confirm the morphology and structure of the synthesized ZnO–CeO₂ nanomaterial which revealed well crystalline aggregated nanoparticles with average diameters of 50±10 nm. The composition of the nanoparticles was obtained by using EDS spectroscopy while the optical property was measured using UV–vis. absorption spectrum. Photocatalytic degradation of acridine orange (AO) and methylene blue (MB) dyes carried out using these nanoparticles showed 92.1 % degradation of the former substrate and 80.7 % degradation in the case of the latter in 170 min. of irradiation time. ZnO–CeO₂ nanoparticles fabricated ethanol sensor exhibited higher sensitivity in short response time [65].

![Figure 1.10: Typical (a) low-magnification image of ZnO–CeO₂ nanoparticles (b, c) high-resolution FE-SEM images and (d) EDS spectrum of the synthesized ZnO-CeO₂ nanoparticles](image)

Nanocrystalline tungsten oxide (WO₃) was synthesized by Upendra A. Joshia and co-workers via sol-gel process and applied as photocatalyst for the degradation of methyl orange under visible light and compared with that of commercial bulk WO₃ for the same reaction. These materials were fully characterized using powder X-ray diffraction (XRD), UV-vis. diffuse reflection spectroscopy (UV-DRS) and transmission electron microscopy (TEM). The photocatalytic oxidation of iso-propanol was used as a model reaction to follow the concomitant reduction of molecular oxygen. No reactions occurred in the absence of platinum, which is an essential co-catalyst for the multi-electron reduction of oxygen. The platinized WO₃ catalysts were stable for multiple oxidation–reduction cycles. The results from the catalytic activity measurements showed that platinized nanocrystalline WO₃ is a superior oxidation photocatalyst when compared with bulkWO₃ [66].
Nanocrystallites of both non-stoichiometric and stoichiometric copper selenides (Cu$_{2-x}$Se, CuSe and Cu$_3$Se$_2$) were synthesized via sonochemical irradiation at room temperature by Yi Xie et al., The influence of solvents, surfactants and ultrasonic irradiation on the morphology and crystalline phase of products has been investigated. The morphological difference of the products was mainly affected by the solvents and surfactants, which can self aggregate into lamellar structures or micro-emulsions and then these unique structures can act as both supramolecular template and micro-reactor to direct the growth of copper selenides. On the other hand, it was also found that the sonochemical irradiation and solvents played an important role in the formation of different phases of copper selenides [67].

X. Song et al., reported a combination of solvothermal and calcination process to synthesize NiO hierarchical architectures with controllable morphologies and sizes. First, several hollow α-Ni(OH)$_2$ hierarchical architectures assembled by α-Ni(OH)$_2$ nanosheets had been synthesized through the solvothermal method. The nucleation mediated mechanism overwhelmingly determined the morphology of hollow α-Ni(OH)$_2$ architectures through tuning the nucleation rate. The hollow α-Ni(OH)$_2$ spheres could be formed in the case of high nucleation rate. However, the hollow α-Ni(OH)$_2$ tubes would be obtained at low nucleation rate. Second, the hollow NiO hierarchical architecture could be obtained from the precursor without changing their morphologies by a simple calcination procedure. The as-prepared hollow NiO hierarchical architectures showed high photocatalytic property to decompose acid red 1 pollutant and could also be easily recycled under an external magnetic field, displaying great potential in environmental pollutant for clean up applications [68].
Microwave assisted photocatalytic degradation of pentachlorophenol (PCP) in aqueous TiO$_2$ nanotubes suspension was introduced by Z. Gao and co-workers. In this study, TiO$_2$/SiO$_2$ (Ti:Si = 10:1) nanoparticles were first prepared by ultrasound assisted hydrolysis and then treated by 10 M NaOH at 110 °C for 20 h. to form titania nanotubes that have been characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), N$_2$-adsorption, UV–vis. absorption spectra and ESR spectroscopic data. From the experiment, it was clear that the samples prepared are nanotubular structure with opened ends and the diameter of nanotubes is about 10 nm with about 100 nm lengths with surface area of 286 m$^2$/g. The ESR signals show that there are more •OH on the surface of TiO$_2$ nanotubes than that on the surface of TiO$_2$/SiO$_2$ nanoparticles. The results indicated that the degradation rate in the microwave assisted photocatalysis process (MPC) is faster than that in other processes including microwave assisted photolytic (MDP), microwave alone process (MP) and dark process (DP). The photocatalytic activity of TiO$_2$ nanotubes is higher than that of P25 and TiO$_2$/SiO$_2$ nanoparticles and it may be contributed to the capacity of absorption to the UV–vis. irradiation and specific surface area among the photocatalysts. PCP is effectively degraded in the MPC on TiO$_2$ nanotubes. Along with the degradation of PCP, pH of solution decreases from 10.32 to 7.5 and the dechlorination is completed in 12 min. The major intermediates of PCP in MPC on TiO$_2$ nanotubes were identified by GC-MS, including tetrachlorophenols, trichlorophenols, tetrachlorocatechol, tetrachlorohydroquinone. Based on the results, the possible photocatalytic degradation pathways of PCP on TiO$_2$ in MPC were proposed [69].
Bismuth oxide/titania, an interfacial composite semiconductor possessing 100 nm with high photocatalytic activity under solar light was prepared at low temperature by J. Jing and co-workers. The material was characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET), X-ray photoelectron spectroscopy (XPS) and diffuse reflection spectra (DRS). The results indicated that deposited titania nanoparticles on bismuth oxide surface have micro-nano structure and this composite material exhibits porosity and increased surface hydroxyl groups. Furthermore, the as-prepared photocatalyst shows higher photocatalytic activity for the degradation of 4-chlorophenol than pure titania or P25 under sunlight [70].

A study by Q. Lana et al., on the photodegradation of pentachlorophenol (PCP) with two types of iron oxide/oxalate systems as a function of pH was reported. Two iron oxides of hematite and goethite were selected. The experiments were conducted at pH values 3.5, 5.0, and 7.0 showed that PCP photodegradation proceeded rapidly at pH 3.5 and slowed down with the increase in pH. To account for the effect of pH on the degradation kinetics, the surface charge of iron oxides, the adsorption of PCP and oxalic acid on to the iron oxides at different pH values were examined. The presence of oxalic acid gave the iron oxides a negative charge at pH values above 3.5, which caused the decrease of PCP adsorption with increasing pH value. On the other hand, iron oxides adsorbed oxalic acid to form photoactive Fe(III)–oxalate complexes. Compared with
-FeOOH, -Fe₂O₃ had a much stronger ability to adsorb oxalic acid and showed better photocatalytic activity. Furthermore, the detection results of H₂O₂ during the process of photodegradation showed that a low pH favored the H₂O₂ generation [71].

ZnO–SnO₂ hollow spheres and hierarchical nanosheets are successfully synthesized using an aqueous solution containing ZnO rods, SnCl₄·H₂O, and NaOH by hydrothermal method. The effects of hydrothermal temperature and time on the morphology of ZnO–SnO₂ are investigated by By Wei-Wei Wang. The formation process of ZnO–SnO₂ hollow spheres and nanosheets is discussed. The samples were characterized using powder X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and UV-vis. absorption spectroscopy. Both hollow spheres and hierarchical nanosheets showed higher photocatalytic activities in the degradation of methyl orange than that of ZnO rods or SnO₂ [72].

CdS–TiO₂ and CdS-C60/TiO₂ were prepared by Za-Da Meng et al., using C60, cadmium acetate dihydrate [(CH₃COO)₂Cd·2H₂O], sodium sulphide (Na₂S·5H₂O) and titanium(IV) isopropoxide by a sol–gel method. The prepared catalysts were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX) and transmission electron microscopy (TEM). Excellent catalytic degradation of rhodamine-B solution was observed using the CdS-C60/TiO₂ composites under ultrasonic irradiation. C60 coupled CdS-TiO₂ can enhance the Brunauer–Emmett–Teller (BET) surface area and increase the decolorization rate for rhodamine-B solution. The results also showed that increase in the content of CdS enhance the catalytic activity [73].

Figure 1.14: TEM image obtained from (a) CdS-C60 and (b) CdS-C60/TiO₂ composites.
Lixiayang et al., studied the degradation of \( p \)-nitrophenol (PNP) under solar light by a \( \text{Cu}_2\text{O}/\text{TiO}_2 \) p-n junction network which is fabricated by anodizing \( \text{CuO} \) particles-loaded \( \text{TiO}_2 \) nanotubes (NTs). The network is composed of \( p \)-type \( \text{Cu}_2\text{O} \) nanowires on the top surface and \( \text{Cu}_2\text{O} \) nanoparticles on the inner walls of the \( n \)-type \( \text{TiO}_2 \) NT arrays. The \( \text{Cu}_2\text{O}/\text{TiO}_2 \) network shows much higher degradation rate (1.97 \( \mu \)g/min cm\(^2\)) than the unmodified \( \text{TiO}_2 \) NTs (0.85 \( \mu \)g/min cm\(^2\)). The enhanced photocatalytic activity can be attributed to the extended absorption in the visible region resulting from the \( \text{Cu}_2\text{O} \) nanowire networks and the effective separation of photogenerated carriers driven by the photoinduced potential difference generated at the \( \text{Cu}_2\text{O}/\text{TiO}_2 \) p-n junction interface [74].

A manuscript published by Y. Hu et al., described the coating of CdS nanoparticles on the surface of colloidal carbon spheres by a facile two-step, microwave-assisted method and studies on the photocatalytic activity of the C@CdS core-shell spheres. For the coating of CdS nanoparticles, cadmium ions were incorporated into the hydrophilic shell of colloidal carbon spheres and reacted with an introduced sulphur source under a microwave field to obtain the C@CdS hybrid spheres. Using this process, the as-prepared hybrid structures, preserved the good dispersity and uniformity of initial carbon spheres and the thickness of the CdS nanoparticles shell could be varied or controlled by the irradiation time. A photoluminescence spectrum showed that the C@CdS hybrid spheres featured a broad green emission at around 494 nm (\( \lambda_{\text{ex}}=337 \) nm). Additionally, CdS nanospheres were successfully prepared in aqueous solution via a microwave-assisted route and the effect of irradiation time on the products was also investigated. The studies on the photocatalytic property demonstrated that these fabricated functional hybrid structures exhibited a higher photocatalytic degradation activity when exposed to visible light irradiation than that of CdS nanospheres under the same conditions [75].

Wurtzite CdS and CdSe nanostructures with complex morphologies such as urchin-like CdS nanoflowers, branched nanowires and fractal nanotrees (Figure 1.15) have been produced via a facile solvothermal approach in a mixed solution of diethylene triamine (DETA) and deionized water (DIW) by W. T. Yao and co-workers. The morphologies of CdS and CdSe nanocrystals were easily controlled via tuning the volume ratio of DETA and DIW. Urchin-like CdS nanoflowers made of CdS nanorods are in a form of
highly ordered hierarchical structures, while the nanowires are branched and the fractal CdS nanotrees are a buildup of branched nanopines. The results demonstrated that solvothermal reaction in a mixed amine/water can access a variety of complex morphologies of semiconductor materials. The photocatalytic activity of CdS particles with different morphologies has been tested by the degradation of acid fuchsine under both UV and visible light, showing that the as-prepared branched CdS nanowires exhibit high photocatalytic activity for degradation of acid fuchsine [76].

![Figure 1.15: FE-SEM images of CdS prepared at 180 °C for 12h (a) low-magnification image and (b) a typical single CdS nanoflower](image)

A series of nano hydroxyapatite–gelatin (Gel–HAp) composites with different gelatine concentrations were synthesized by a thermally assisted low power ultrasonic irradiation by Ravi Krishna Brundavanam and co-workers using Ca(NO₃)₂ and KH₂PO₄ in the presence of gelatin in an aqueous solution. The synthesized products were heat treated between 100 °C and 400 °C. The effect of addition of gelatin on the nucleation and growth of synthesized nano-HAp was investigated. Characterization performed using powder X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and Fourier transform infrared spectroscopy (FT-IR) indicated that gelatin has been appended to the nano-HAP forming regular spherical shaped crystals of nano sized Gel–HAp [77].

Rajkumar and co-workers prepared hydroxyapatite (HAp) nanorod embedded poly (vinyl alcohol) (PVA) composite using different weight percentages of PVA. The role of PVA composition on the crystallite size, degree of crystallinity, functional groups and morphology of HAp nanocomposites were characterized by XRD, FT-IR and
TEM analysis. The results indicated that the size and crystallinity of HAp nanoparticles decreases with increase in PVA concentration in the composite and this shows the size control effect of PVA concentration on HAp nanorods [78].

Hydroxyapatite nanoparticles were prepared using a sol–gel technique in order to study the effects of agitation rate and temperature on particle size by Nabil Salimi et al., Agitation rates were investigated at 200 rpm, 1200 rpm, 2200 rpm using an overhead stirrer, and 3000 rpm and 7000 rpm using a mechanical blade homogenizer at 20 and 40 °C, respectively. Primary particles between 43 and 68 nm were obtained as determined by TEM images, while from Scherrer formula using XRD data, these were found to be between 38 and 56 nm. Above 2200 rpm the agitation rate did not significantly affect the size of the particle and inferred that kinetic coagulation had led to the formation of stable aggregates. An increase in process temperature from 20 to 40 °C had a slight effect on particle size. The different particle sizes were explained in terms of power input and turbulence within the mixing zone. Different particle morphologies were obtained at different agitation rates which were dependent on equipment selection. Cuboid like particles was obtained at lower agitation rates with the overhead stirrer, while elongated particles were obtained at high shear created by the homogenizer [79].

Nanosized InVO₄ with orthorhombic structure was successfully synthesized at a relatively low calcination temperature of 600 °C using an amorphous heteronuclear complex as precursor by L. Zhang et al., The photocatalytic activity of InVO₄ catalyst has been evaluated by the decomposition of formaldehyde (FAD) under UV light and visible light irradiation. The as-synthesized InVO₄ catalyst showed higher photocatalytic activity for the FAD decomposition compared to the sample prepared by the conventional solid state reaction. The photocatalytic activity of the as-prepared sample was discussed on the basis of the electronic band structure and bulk material structure [80].

Indium tin oxide nanoparticles prepared by co-precipitation were re-dispersed in benzyl alcohol and modified successfully with titanium dioxide using titanium tetrachloride as precursor was reported by R. Pan and co-workers. The photocatalytic properties of the modified nanoparticles were compared with commercial P25 photocatalyst. It was found that the average diameter of the initial indium tin oxide nanoparticles was 10.7 nm and
that of the surface-modified nanoparticles was 14.5 nm and the modified particles possessed a higher photocatalytic activity than commercial P25 photocatalyst for the photodegradation of rhodamine B in aqueous medium at pH 5 [81].

Applicability of the nanomaterials as discussed in the previous pages purely depend on the phase, size, morphology, porosity, surface area and other physiochemical characteristics of them. It is very difficult to control the size and shape of the material under physical or chemical routes. However, bio-inspired techniques have shed some light on the controlled synthesis of nanomaterials/composites.

Biological methods comprise the use of micro-organisms, small molecules of biological origin, biological templates and small peptides for the synthesis of various metal oxide/sulphide nanoparticles. Variety of biological materials such as silk fibroin, butterfly wings, eggshell membrane (ESM), skeletal plates, DNA, etc., have also been used as templates [82-86]. For example, bio-supramolecular templates such as cage-shaped proteins [87], rod-like viruses [88], and fibrillar protein [89] have been utilized to prepare well-defined nanoparticles and nanowires by biomineralization and also been used as capping agents for some nanoparticles. Living organisms can exert tight control on the synthesis of materials [90]. Therefore, most of the work till date is centered on the use of micro-organisms for the synthesis of sulphide nanoparticles. Recently, it was found that highly evolved organisms like plants, microbes (diatoms), algae and heterotrophic human cell lines and some biocompatible agents are regarded as potent eco-friendly green nanofactories that have been used extensively for the production of various inorganic nanoparticles [91].

Tube shaped proteins were effectively used to produce one-dimensional nanostructured materials by Rikako Tsukamoto et al.. Tobacco mosaic virus (TMV) is one of the ideal biological molecules for this purpose. TMV is a tube shaped supramolecule, 300 nm in length with an outer diameter of 18 nm. It composed of 2130 identical coat protein molecules, which are self assembled in a helical manner together with the TMV RNA and it has a hollow central channel with a 4 nm diameter. The channel has been used to synthesize nickel and cobalt nanowires by palladium (Pd) activation and electroless deposition [92].
Well-organized, porous hierarchical tin oxide (SnO$_2$) with connective hollow interiors has been synthesized by using butterfly wings as templates via an aqueous sol–gel soakage process followed by calcination. The biomorphic porous hierarchy was constructed by a layer of flexural wall that was assembled by SnO$_2$ nanocrystallites with a diameter of around 7 nm. The wall thickness was tunable under the control of the impregnants concentration as well as the immersion time. The biomorphic SnO$_2$ showed good sensing to ethanol and formaldehyde, due to its small nanocrystalline building blocks and unique porous hierarchical architecture. More interestingly, the response was found to be controllable and dependent on the wall thickness. The response decreased with the increase of wall thickness, which should be ascribed to the increasing difficulty of gas diffusion to the interior of the walls [93].

Hierarchical, biomorphic ZnO films are prepared by a simple soakage procedure associated with succedent calcination treatment, using natural eggshell membrane (ESM)
as the template by Q. Dong et al.. The hierarchy of ESM architecture is faithfully achieved by the assembly of ZnO nanocrystallites into interwoven meshwork at three dimensions. The thermal evolution, phase, morphology and pore size distribution of the samples are characterized by thermogravimetric analysis (TGA), powder X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectroscopy, field emission scanning electron microscopy (FE-SEM) and nitrogen adsorption measurement [94].

Figure 1.18: Mechanism for the formation of ZnO NPs using ESM

Ag/ZnO metal-semiconductor nanocomposites with hierarchical micro/nanostructure have been prepared by hydrothermal synthesis in the presence of bovine serum albumin (BSA) by S. Gao and co-workers. Their study suggested that the biomolecule assisted hydrothermal method is an efficient route for the fabrication of Ag/ZnO nanocomposites by using BSA both as a shape controller and a reducing agent of Ag⁺ ions, respectively. Moreover, Ag nanoparticles on the ZnO act as an electron sinks, improving the separation of photo-generated electrons and holes, increasing the surface hydroxyl contents of ZnO and thus enhancing the photocatalytic efficiency of ZnO. This is a good example for the organic combination of green chemistry and functional materials [95].
Hierarchical nanocomposite films with Pd-PdO nanoparticles anchored uniformly on the inner surface of TiO$_2$ nanotubes were achieved through a stepwise bio-redox/artifical oxygenation approach using the natural eggshell membrane (ESM) as a template by H. Su et al.. The Pd content ratio of Pd-PdO loading could be arbitrarily varied from 0 to 53 wt %, and the ESM-morphic nanocomposites Pd-PdO/TiO$_2$ exhibited porous and multiphasic features, facilitating light transport and molecule accessibility to the active site during photocatalytic reactions. The photocatalytic activity of target nanocomposites was determined by the degradation of rhodamine B. The composites with a ratio of 10 wt % TiO$_2$ (5 wt % Pd of Pd-PdO loading) presented a high degradation efficiency of 99.3 % and showed good stability with a second run of about 95.3 % and a third run of 94.6 %. These composites with structural particularity and complexity are expected to find potential applications in various fields such as photovoltaic devices, gas sensors, antistatic coating, dye-sensitized solar cells, etc., [96].

Figure 1.19: TEM images of Pd-PdO/TiO$_2$ nanocomposites: (a) the longer incubation periods revealing that Pd-PdO nanocrystallites grow inside the co-adjacent TiO$_2$ tubes (marked by the dotted line), (b) a single tube and (c) the enhanced magnification of the boxed area in (b)
Mitsuhiro Okuda et al., developed an environmental friendly method for the synthesis of cerium oxide nanoparticles (CeO$_2$ NPs) and their 2D/3D array formation using the cage shaped protein apoferritin. Apoferritin was used as a bio-template for CeO$_2$ NPs synthesis and the cavity served as a restricted chemical reaction space where the trivalent Ce ions were oxidized and formed CeO$_2$ NPs through a process similar to iron oxide formation [97].

Figure 1.21: Synthesis of homogenous cerium oxide nanoparticles using apoferritin protein

Tetragonal SnO$_2$ with hierarchical interwoven structures with a size of about 5 nm were formed, assembled into tubular fibers and further intertwined to construct hollow...
interconnective fibrous mesh works was prepared by a convenient soaking technique followed by a calcination treatment at 823 K by Qun Dong et al., using the biomaterial eggshell membrane (ESM) immersed in aqueous Sn colloid medium and a calcination treatment in succession. The unique hierarchical SnO$_2$ nanomaterials are proposed to find applications in gas sensors, photocatalysis and dye-sensitized solar cells etc., [98].

The mechanical behavior and microstructure of bio-inspired fibers spun from solutions of recombinant spidroin like proteins were extensively characterized by M. Elices et al., and compared with those of natural spider silk fibers. It is confirmed that high performance bio-inspired fibers indistinguishable from natural spider silk up to large strains can be produced through genetic engineering and conventional spinning technologies. It is also found that fibers spun from spidroin like proteins that contain different motifs of sequence exhibit variations in their microstructure in terms of crystallinity and chain alignment, but these differences are not reflected in distinct tensile properties. This similarity in terms of their mechanical behavior indicates that bio-inspired fibers are largely independent of their exact sequence of recombinant proteins and in particular, of their proline content. Finally, it is shown that the largest difference between natural and bio-inspired fibers is found at very large deformations, marking the ultimate challenge in the synthesis of silk like fibers [99].

Recently, the reticular hierarchical structure of butterfly wings (Papilio Paris) was introduced as a template for the preparation of Au/TiO$_2$ photocatalyst with an average size of 7 nm. Au nanoparticles have been homogeneously dispersed in TiO$_2$ substrate by depositing the Au nanoparticles on TiO$_2$ matrix by a water–ethanol, sol–gel procedure combined with subsequent calcination. Benefiting from such unique structure and composition, the biomorphic Au/TiO$_2$ exhibits high harvesting capability and presents superior photocatalytic activity. Especially, the biomorphic Au/TiO$_2$ at the nominal content of gold to titanium of 8 wt % shows the highest photocatalytic activity and can completely decompose methyl orange within 80 min., which is obviously higher than that of commercial P25 powders [100].
Figure 1.22: (a) Photograph of the entire wings of butterfly; (b) and (c) FE-SEM images of the black scales

Figure 1.23: (A) Photocatalytic degradation of methyl orange under visible light radiation in the presence of (a) control TiO$_2$, (b) biomorphic TiO$_2$, (c) biomorphic Au/TiO$_2$ and (d) commercial P25 powders, (B) Recycling test of the biomorphic 8.0 wt % Au/TiO$_2$ sample for the photocatalytic degradation of methyl orange

The use of an alkalotolerant actinomycete (*Rhodococcus* sp.) in the intracellular synthesis of gold nanoparticles with 5–15 nm dimensions was reported by Absar Ahmad and co-workers. Electron microscopic analysis of thin sections of the gold actinomycete cells indicated that gold particles with good monodispersity were formed on the cell wall as well as on the cytoplasmic membrane. The particles are more concentrated on the cytoplasmic membrane than on the cell wall, possibly due to reduction of the metal ions by enzymes present in the cell wall and on the cytoplasmic membrane. The metal ions were not toxic to the cells and the cells continued to multiply after bio-synthesis of the gold nanoparticles [101].
Kannan Badri Narayanan and Natarajan Sakthivel reported a facile environmental friendly “greener synthesis” of anisotropic nanostructures and isotropic spherical gold nanoparticles using the cell free filtrate of fungus, *Sclerotium rolfsii*. They found that NADPH-dependent enzyme present in the cell free filtrate of *S. rolfsii*, when incubated with the aqueous chloroauric acid solution has the ability to synthesize gold nanoparticles within 10–15 min. at ambient temperature. The morphologies of synthesized nanoparticles were anisotropic like triangles, hexagonals, decahedrals, rods and isotropic sphericals. The controlled synthesis of well-defined size, shape and composition has enormous applications in the fields of bio-labeling, bio-sensing, drug delivery, cancer therapy and catalysis [102].

![UV–visible spectra of colloidal gold solution synthesized by proteins of (A) cell-free filtrate and (B) heat-denatured cell-free filtrate at 90 {\degree}C for 1 h](image)

**Figure 1.24**: UV–visible spectra of colloidal gold solution synthesized by proteins of (A) cell-free filtrate and (B) heat-denatured cell-free filtrate at 90 {\degree}C for 1 h

A new method to prepare nanostructured dimagnesium silicide (Mg$_2$Si) by the reduction of diatomaceous earth (diatoms) using a gas-displacement solid state reaction with magnesium vapor was reported by Jeannine R. Szczech and Song Jin. The resulting semiconducting Mg$_2$Si preserves the general morphology of the original diatoms and their nanosized grains at least down to the size of 30 nm. This reaction represents a possible method for the production of large quantities of low-cost nanoscale thermoelectric materials with potential for enhanced performance [103].

Based on the significance of metal oxide/sulphide nanoparticles in diverse fields and also in continuation of our research group’s interest on the preparation of potential inorganic nanomaterials through novel methods, we planned to undertake a systematic
study on the preparation of some semiconductor metal oxide/sulphide nanoparticles using biomaterials (eggshell membrane and tomato peel) as the template in order to achieve different morphologies with control in the particle size of the resulting material. In addition, an effort was undertaken to prepare the novel biomaterial, hydroxyapatite by the controlled movement of phosphate ions towards calcium via an eggshell membrane. All the nanomaterials have been thoroughly characterized with regard to their morphology, crystalline phase and chemical composition using several state of the art instrumental facilities. From the application point of view, the newly prepared materials have been utilized in some catalytic and photocatalytic reactions as a heterogeneous catalyst.
REFERENCES


44


