CHAPTER - I

INTRODUCTION

1.1 General

The prefix "nano" means one billionth. One nanometer (abbreviated as 1 nm) is 1/1,000,000,000 of a meter, which is close to 1/1,000,000,000 of a yard. To get a sense of the nano scale, a human hair measures 50,000 nanometers across, a bacterial cell measures a few hundred nanometers across, and the smallest features that are commonly etched on a commercial microchip are around 130 nanometers across. The smallest things visible with the unaided human eye are 10,000 nanometers across. Just ten hydrogen atoms in a line make up one nanometer. The scale of things represented in figure (1.1) gives the sense of nanoscale.

Nanoscience is the study of the fundamental principles of molecules and structures with at least one dimension roughly between 1 and 100 nanometers. These structures are known as nanostructures. Nanotechnology is the application of these nanostructures into useful nanoscale devices.

Nanostructures are not just smaller than anything we have made before but they are the smallest solid things possible to make. Nanoscale is unique because of its size, scale, and variation in the properties of materials like conductivity, hardness, melting point etc. The most exotic properties of the atomic and molecular world such as wave-particle duality and quantum effects also have effects at nanoscale [1].
1.2 History of Nanotechnology

It is rather difficult to fix a date for the discovery of Nanoscience as the existence of nanomaterials and nanotechnology in both living and nonliving things can be traced back to the beginning of Science. For instance, cells in animals and plants are the glaring examples of the multifunctional nano-machine together with naturally occurring or man-made colloidal particles which fall very much in line with nanomaterials. In ancient times, nanoparticles were used by the Damascans to create
swords with exceptionally sharp edges and by Romans to craft iridescent glassware. The illustration in figure (1.2), is the Lycurgus Cups known since AD 400 were made of a glass that changes color when light is shown upon them. These contain colloidal gold particles dispersed throughout the glass in such a way that the glass appears green in daylight (reflected light), red when light is transmitted from the inside of the vessel [2].

![Figure 1.2: The Lycurgus Cup made from glass appears green in reflected light and red in transmitted light.](image)

The idea of atom-by-atom construction was first put forth in a scientific manner by the Nobel Prize winning physicist Richard Feynman in 1959 in his famous lecture called “There is Plenty of Room at the Bottom” [3]. In his speech, he predicted that an entire encyclopedia would one day fit on the head of a pin and a library with all the world books would fit in three square yards. Few years later in 1963, Sandomirskii theoretical predication showed that the band gap energy of
semiconductors can vary with thickness [4]. Also the hypothesis was verified experimentally by Stasenko in 1968, which were called quantum size effect in a related event of nanotechnology [5]. The term “Nanotechnology” was first used and defined in 1974 by Norio Taniguchi of the Tokyo Science University in Japan. According to him, “Nanotechnology mainly consists of processing, separation, consolidation, and deformation of materials by one atom or one molecule” [6]. Ekimov reported the finding of three-dimensional quantum confinements of nanoparticles in 1981 [7]. 1987 is considered to be the beginning of the present-day nanotechnology revolution after Eric Drexler’s “Engines of Creation”. Drexler envisioned a molecular nanotechnology discipline that would allow manufacturers to fabricate products from the bottom-up with increased molecular control. This technology would allow every molecule to be inserted into its specific place, so that the manufacturing systems using this process would be clean, efficient, and highly productive. Around the same time, the development of scanning probe microscopy by IBM scientists allowed to fulfill Feynman’s vision of atom-by-atom construction of molecules [8]. Furthermore, the discovery of Fullerene by S. C. O’Brien in 1987 [9] and carbon nanotubes by Iijima in 1991 [10], were other cornerstones to give a boost to the research on nanotechnology.

1.3 Synthesis Approaches of Nanomaterials

Several hundreds of nanomaterials belonging to inorganic, organic, or polymeric or composite categories have been obtained by the following general approaches, i.e.
(a) A top-down approach and
(b) A bottom-up approach.

The following objectives are considered as important while choosing a technique, they are

(i) the synthesis method should be reproducible;
(ii) the method should produce monodispersed nanoparticles;
(iii) the surface of the nanoparticle should be defect free;
(iv) the method should be economical, scalable, and environment friendly.

1.3.1 Top-down methods

The top-down approach involves in breaking down of the bulk material into nanosized structure and particle. This approach is inherently an extension, which has been used for producing micron-sized products. This involves the slicing or successive cutting of bulk materials to get nanosized particles or to produce their desired structure with appropriate properties. This technique is quite useful to produce nanosized particles on a large scale by using mechanical force. However, the imperfection of surface structure, poly dispersion, surface dislocation, formation of aggregates, and clustering usually accompanied with the nanoparticles.

Some of the methods include

(i) ball milling
(ii) photolithography
(iii) electron beam lithography
(iv) anodization
(v) plasma-etching etc.
1.3.2 Bottom-up methods

In the bottom-up technique, the chemical approach is involved. It involves more effective build-up of a material from the bottom: atom by atom, molecule by molecule, or cluster by cluster. All the living beings in the nature only undergo growth by this approach and it has been in industrial use for the production of variety of chemicals. The major advantages of the bottom-up approach lie in the production of nanostructures with less defects, more homogeneous chemical composition, better control of size and shape, etc.

Some of the common methods belonging to bottom-up approaches are,

(i) precipitation/wet chemical/soft chemical method
(ii) reduction of metal salt/solution method
(iii) hydrothermal/Solvothermal method
(iv) hot thermolysis/colloidal synthesis
(v) flame synthesis
(vi) photochemical synthesis
(vii) sol-gel method
(viii) self-assembly
(ix) biometric, etc.[11].

1.4 Classification of Nanomaterials

Nanomaterials can be nanoscale in one dimension (eg. surface films), two dimensions (eg. strands or fibres), or three dimensions (eg. particles). They can exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and irregular shapes. Common types of nanomaterials include nanotubes, dendrimers, quantum dots and fullerenes. Nanomaterials have applications in the field of nanotechnology, and displays different physical chemical characteristics from normal
chemicals (i.e., silver nano, carbon nanotube, fullerene, photocatalyst, carbon nano, 

silica).

Figure (1.3) illustrates the classification of nanomaterials (A) 0D spheres and 

clusters, (B) 1D nanofibers, wires, and rods, (C) 2D films, plates, and networks, (D) 

3D nanomaterials [12].

![Classification of Nanomaterials](image)

**Figure 1.3: Classification of Nanomaterials**

1.4.1 Zero-Dimensional Nanostructures

Zero-Dimensional nanomaterials are materials where in all the three 

dimensions are measured within the nanoscale. For example, nanoparticles or well 

dispersed nanopowders and quantum dots can be called Zero-Dimensional 

nanomaterials. A quantum dot exhibits Zero-Dimensional confinement, which means 

that the electrons are confined in all three dimensions. Quantum confinement 

describes the increase in energy which occurs when the motion of a particle is 

restricted in one or more dimensions by a potential well [13].

One can tune the optical and electronic property of the quantum dots by 

changing the size of the dots. When large numbers of atoms are brought closer to 

form a solid, the allowed discrete energy levels become a continuous energy band. 

The energy band structure thus obtained directly impacts the optical as well as the
electronic properties. A very few commonly used quantum dots are cadmium selenide (CdSe), zinc sulphide (ZnS), Zinc oxide (ZnO) etc. [14,15].

1.4.2 One-Dimensional Nanostructures

Materials which are at the nano scale in atleast one dimension are referred as One-Dimensional nanomaterials. Nanotubes, nano rods and nano wires are the examples of one-dimensional nanostructures on account of their novel electrical and mechanical properties attracting the researchers for many years. Leading researchers make clear the synthesis and properties of one-dimensional nano structure for various morphologies and compositions for their considerable application on spintronics, information storage and the design of FET [16, 17].

One-dimensional nano tubes of length several centimeters and cross section of a few nano metre thick have been synthesized [18]. Moreover, it has been reported that TiO$_2$ nanotubes with varying thickness were successfully prepared [19].

In metal oxides, one-dimensional nano belts were first discovered by Z.W. Pan [20]. In nano belts, the thickness of the belt is much smaller than its width. Very recently, the nano belts of TiO$_2$ were effectively prepared by electrochemical anodization technique [21, 22].

Nano wires are another one-dimensional nano structures. They have a specific axial direction while their side surfaces are less well defined [23, 24]. The radius of nano wire is very small, negligible compared to their length. According to the existing reports, Titanium dioxide (TiO$_2$), Indium tin oxide (In$_2$O$_3$), Zinc oxide (ZnO) and Aluminium oxide (Al$_2$O$_3$) nano wires are successfully synthesized [25-28].
1.4.3 Two-Dimensional Nanostructures

The nanostructures which have two dimensions outside the nanometric scale range are called Two-Dimensional nanostructures. These two-dimensional structures display plane-like structures and are found in thin films, nano coatings and nano layers. Thin films are good for high efficient conversion of light to electrical power as in photovoltaic cell devices due to their large surface area for the photo-electro-chemical process to take place.

The simplest shape of a two-dimensional nanostructure is a plane with depth below 100 nm and the other dimensions are larger than nanometric dimensions. They may exhibit some new size related properties even if the external thickness remains in the nanometric size range, the interior grains may be outside the nano scale, and those structures are categorized as two-dimensional nano structured material. As per interior structural dimensions or exterior dimensions, the two-dimensional nano structures are named as internal nano structured and non-internal nano structured layers [29]. A large amount of researchers have investigated synthesizing wide band gap semiconducting metal oxide materials TiO$_2$, SnO$_2$ and ZnO [30-32].

1.4.4 Three-Dimensional Nanostructures

When all three dimensions are outside the nanometric range, it is called the nanostructures as three-dimensional nano structures [33]. One can obtain a three-dimensional nano crystalline material by first obtaining an amorphous phase by solidifying the melt and then by crystallizing the glassy phase at relatively low temperature. Most commonly, gas condensation, mechanical alloying, chemical precipitation, spray conversion etc. are a few methods used to prepare three dimensional nano crystallites.
The high speed large areas of fabrication methods facilitate the use of these materials to find practical application in photonics, catalysis, micro fluidics, drug release etc. The 3-D micro flowers [34] and 3D hollow spheres [35] of TiO$_2$ are produced and investigated by various researchers.

1.5 Introduction to TiO$_2$ Nanoparticles

The nanoparticles are getting more and more familiar in many fields as they found applications due to their structure, size, elemental composition and the quantum size effects. They find application in the field of optoelectronics, catalysis, medicine, sensor devices etc. TiO$_2$, being a metal oxide, is studied for its potential and promising applications such as catalysis, gas sensing, white pigments for paints cosmetics, solar cells, transducer, and photochemical degradation of organic pollutants [36, 37]. Crystalline structure, morphology, and particle size are the important factors which affect the applications of TiO$_2$ [38].

Titanium dioxide occurs mainly in three crystalline phases, namely anatase, rutile and brookite. The three phases differ in their physical properties, such as refractive index, dielectric constant, and chemical and photochemical reactivity [39]. Among these structures, rutile is the thermodynamically most stable phase and anatase is preferable for both photocatalysis and dye-sensitized solar cells due to their large band gap (Anatase $\sim$3.2 eV and Rutile $\sim$3 eV). This means both the phases of TiO$_2$ can be activated by visible and UV light illumination with the wavelength equal to or less than 420 and 385 nm, respectively [40]. Also TiO$_2$ is an ideal material for generating photonic band gap materials and other photonic applications due to its low absorption in the visible and near infrared regions with higher refractive index.
(n= 2.4 for anatase and n=2.9 for rutile) [41]. The property of quantum confinement in nanoparticles can modify the optical properties of semiconductors. However, TiO$_2$ nanoparticles have a relatively small exciton radius (~1 nm), and thus there is no quantum confinement effect observed [42].

**1.6 Brief Review on TiO$_2$ Nanoparticles**

**1.6.1 History of TiO$_2$**

An English mineralogist, William Gregor in 1791, analyzed black magnetic sand found on the Cornwall beach. He observed that almost 50% of the sand was a formerly unknown metal oxide. Four years later, in 1795, M. H. Klaproth analyzed a red ore found in Hungary, obtained a white oxide, and realized that this was the same white oxide which Gregor had separated from the black sand. Klaproth borrowed his name for the oxide, titanium oxide, from the Titans of Greek mythology. In 1918, commercial production of titanium oxide was started in Norway and in the United States. In 1939, titanium dioxide replaced toxic lead carbonate as the most common white pigment. After that, titanium dioxide was used as a pigment for many years [43]. The bleaching property of TiO$_2$ in dye, under UV light irradiation was reported by C. F. Goodeve and J. A. Kitchener in the year 1938 [44]. The terminology, “photocatalyst” for TiO$_2$ was first pointed out by Kato and Mashio in 1956 [45]. At the time of “oil crisis” in 1972, Fujishima and Honda discovered hydrogen production from water by TiO$_2$ photocatalysis [46]. This revolutionary work set fire to researchers to display unique properties of titanium dioxide in many areas. In 1991, Gratzel published a paper on dye sensitized solar cells by using TiO$_2$ colloidal film, tuning the popularity of TiO$_2$ into worldwide [47].
1.6.2 Crystalline Structures of TiO$_2$

Titanium dioxide has one stable phase, rutile (tetragonal) and two metastable polymorph phases, brookite (orthorhombic) and anatase (tetragonal). Both Metastable phases become rutile (stable) when subjecting the material at temperatures from 400°C-1000°C [48].

1.6.3 TiO$_2$ in Anatase Phase

The anatase polymorph is one of the familiar metastable phases of TiO$_2$ together with brookite phase. Anatase polymorph possesses crystal structure of tetragonal with two TiO$_2$ formula units (six atoms) per primitive cell. In this polymorph, each Ti atom is coordinated to six O atoms and each O atom is coordinated to three Ti atoms. In addition, TiO$_6$ octahedron is slightly distorted, with two Ti-O bonds slightly greater than the other four, and with some of the O-Ti-O bond angles deviating from 90°. This distortion is greater in anatase phase than in rutile phase. Lattice parameters values of anatase phase TiO$_2$ are: a = b = 3.784Å and c = 9.515Å with c/a ratio of 2.5145. Anatase belongs to space group of $I4_1/amd$ [49]. When anatase phase TiO$_2$ is made into calcination process above 900°C, the anatase structure is transformed into rutile structure [50]. Other authors also have found that 600°C would be enough for phase transition from anatase to rutile when thermal treatment takes place [51-54]. The anatase structure is preferred over other polymorphs for photocatalytic applications. So it can be mainly used as a photocatalyst for the decomposition of organic compounds and nitrogen oxides [50]. Figure (1.4) shows the 3D structure of anatase phase TiO$_2$. 

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1.6.4 TiO$_2$ in Rutile Phase

Rutile phase polymorph of TiO$_2$ possesses tetragonal crystal structure similar to anatase phase. In this structure, each Ti atom is coordinated to six O atoms and each O atom is coordinated to three Ti atoms. Also, TiO$_6$ octahedron is slightly distorted, with two Ti-O bonds slightly greater than the other four, and with some of the O-Ti-O bond angles deviating from 90° which is identical to anatase phase. This distortion is lesser in this rutile phase when compared to anatase. Lattice parameter values of rutile phase TiO$_2$ are: $a = b = 4.5936$ Å and $c = 2.9587$ Å with $c/a$ ratio of 0.6441. The space group of rutile is $P4$_2$/mnm$ [49]. Rutile is the most stable polymorph of TiO$_2$ at higher temperatures. Both anatase and brookite are transformed to rutile when they are subjected to heat treatment [55]. Direct synthesis of single phase rutile TiO$_2$ is also possible at lower temperatures [56]. The 3D structure of Rutile phase TiO$_2$ is shown in figure (1.5).
1.6.5 TiO₂ in Brookite Phase

TiO₂ in Brookite phase belongs to the orthorhombic crystal system with space group of Pbca. The unit cell of brookite phase TiO₂ is composed of 8 formula units of TiO₂ and is formed by edge-sharing TiO₆ octahedra (Figure (1.5)). It has a larger cell volume and minimal dense of the 3 forms. Hence, it is not often used for experimental investigations and is more complicated. The angles of O-Ti-O bond and the interatomic distances are homogeneous to those of rutile and anatase. Lattice parameter values of brookite phase TiO₂ are: \( a = 9.515 \text{ Å} \), \( b = 5.447 \text{ Å} \) and \( c = 5.145\text{Å} \) [49]. The 3D structure of brookite phase TiO₂ is shown in figure (1.6). Single phase brookite TiO₂ is difficult to synthesize. Therefore, this phase is mostly obtained together with rutile or anatase phase TiO₂[57].
Figure 1.6: 3D Structure of Brookite Phase TiO$_2$

Table (1.1) indicates comparison of three polymorphs of TiO$_2$.

**Table 1.1: Unit Cell Parameters of TiO$_2$**

<table>
<thead>
<tr>
<th>Unit Cell Parameters</th>
<th>Anatase</th>
<th>Rutile</th>
<th>Brookite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal Structure</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Lattice Constants (Å)</td>
<td>a=b=3.784, c = 9.515</td>
<td>a=b=4.5936, c = 2.9587</td>
<td>a=9.515, b=5.447, c = 5.145</td>
</tr>
<tr>
<td>Point group</td>
<td>4/mmm</td>
<td>4/mmm</td>
<td>1 mmm</td>
</tr>
<tr>
<td>Space group</td>
<td>$I4_1/ amd$</td>
<td>$P4_2/ mnm$</td>
<td>$Pbca$</td>
</tr>
<tr>
<td>Atoms per cell</td>
<td>4</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>Band gap</td>
<td>3.2</td>
<td>3</td>
<td>3.31</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>3.79</td>
<td>4.13</td>
<td>3.99</td>
</tr>
<tr>
<td>Volume (Å$^3$)</td>
<td>34.061</td>
<td>31.2160</td>
<td>32.172</td>
</tr>
<tr>
<td>Ti-O bond length (Å)</td>
<td>1.937(4), 1.965(2)</td>
<td>1.949(4), 1.980(2)</td>
<td>1.87~ 2.04</td>
</tr>
<tr>
<td>O-Ti-O bond angle</td>
<td>77.7°, 92.6°</td>
<td>81.2°, 90.0°</td>
<td>77.0 - 105°</td>
</tr>
</tbody>
</table>
1.7 Applications of TiO$_2$ Nanoparticles

1.7.1 Solar Hydrogen Production

There is a constant search for clean and renewable energy, which can effectively be replaced with petroleum. Decades of R&D efforts have shown that hydrogen is the best substitute of petroleum. The production of hydrogen can reduce our requirement of imported oil and natural gas. Hydrogen can be produced through various routes; most attractive routes are photoelectrochemical and photocatalytic decomposition of water. In 1972, Fujishima and Honda demonstrated photoelectrolysis of water on n-type TiO$_2$ single crystal electrode for solar energy conversion and storage in the form of hydrogen [58]. Because of its large band gap (3 - 3.2 eV), TiO$_2$ absorbs only the ultraviolet part of the solar emission, consequently has low conversion efficiencies. Numerous attempts have been made to shift the spectral response of the TiO$_2$ into the visible range to increase the efficiencies of the photo electrochemical solar cells either by dye sensitization or doping with species that essentially reduce the band gap of the TiO$_2$.

1.7.2 Solar Cells

A new type of solar cell, based on dye using n-type TiO$_2$ semiconductor is known as dye-sensitized solar cell (DSSC), was first reported by M. Gratezel and B. O’Regan in the year 1991 [47]. In these DSSCs, the hole-transmitting medium is a redox species in an electrolyte, liquid or gel (quasi solid-state). The classic DSSC is composed of a layer of nanocrystalline TiO$_2$ particles on a conducting substrate, a platinum counter electrode, and an adsorbed Ru-dye as a sensitizer and an electrolyte. Using such constructions, 11% conversion efficiency has been achieved. Usually, TiO$_2$ nanoparticles are deposited on a conducting glass substrate, and sintered to
convert the particles to an anatase crystal phase to improve the electronic conduction between the conductive glass and the TiO$_2$ nanoparticles. On the TiO$_2$ surface is adsorbed a dye, which serves as a light absorber (sensitizer), and is anchored (attached) to the surface of the TiO$_2$ nanoparticles by specific functional groups. A key requirement for the dye is that the LUMO of the dye molecule is energetically positioned slightly higher than the conduction band of TiO$_2$. Under irradiation with sunlight, HOMO–LUMO transitions in the dye occur. Excited electrons can then be injected from the LUMO into the conduction band of the semiconductor electrode. For typically used Ruligand dyes, the electron injection from the dye sensitizer to the conduction band of TiO$_2$ occurs through a metal-to-ligand charge transfer (MLCT) [59].

### 1.7.3 Water Purification

TiO$_2$ has excellent stability, good photocatalytic performance, and hydrophilic properties which make it effectively as a self-cleaning coating material. TiO$_2$ is widely used as a photocatalyst for environmental applications. It decomposes industrial waste water which contains dilute toxic chemicals under UV light [60]. However, TiO$_2$ is active only in the wavelength range shorter than 387 nm [61]. The solar irradiation contains only small fraction (5%) of UV radiation and is very small when compared to fraction of visible light (45%). Hence, enhanced photocatalytic efficiency requires shift in the optical response of TiO$_2$ from the UV ($\lambda \leq$387 nm) into the visible spectral range ($\lambda \geq$420 nm) [62]. Common way to attain this visible light response is to modify the particle size, crystallinity, crystalline phase, doping with ions and the surface modification [61].
1.7.4 Self-cleaning Coatings

Self-cleaning coatings have very much interest in number of applications such as rear-view mirrors, antifogging glasses, antireflection mirrors, self cleaning windows and buildings etc. Usually, two types of self-cleaning coatings can be developed-hydrophobic and hydrophilic. On a hydrophilic coating, water is made to spread out (water sheeting) over the surface, which carries away dirt and other impurities, whereas using the hydrophobic technique, water droplets slide and roll over the surface, thereby cleaning them [62].

Another property linked with the photo-induced hydrophilicity is the anti-fogging application. When the steam cools down on the surface of mirrors and glasses it creates many water droplets called fogging on the surface. No water drops are formed on a highly hydrophilic surface. Instead of water drops, a uniform thin layer of water is formed on the surface and prevents fogging. Once the surface turns into the highly hydrophilic state, it remains unchanged for several days or a week. Thus, various glass products, mirrors and eye glasses could be imparted with antifogging functions using this technology with simple processing and at low cost. In fact, Japanese-made cars are being equipped with antifogging, highly hydrophilic side-view mirrors [45]. Figure (1.7) illustrates the application of TiO$_2$ in anti-fogging mirror.

Figure 1.7: (a) Ordinary mirror (b) TiO$_2$ nanoparticles coated anti-fogging mirror
1.7.5 Gas Sensors

The nanoparticles of metal oxides such as SnO$_2$, CuO, Cr$_2$O$_3$, V$_2$O$_5$, WO$_3$, ZnO and TiO$_2$ are particularly very much interesting because of their reactivity with their surrounding gas atmosphere. Among these metal oxides, TiO$_2$ possesses high sensing behavior and could sense various hazardous gases CO$_X$, NO$_X$, CH$_4$, H$_2$S, SO$_2$, H$_2$, LPG, NH$_3$ and O$_2$ [63]. The sensing mechanism of TiO$_2$ nanoparticle is based on the charge transfer interactions between the TiO$_2$ and chemisorbed species that modify the surface conductivity of the TiO$_2$ [64].

1.7.6 Cancer Treatment

TiO$_2$ has its wide application in the field of medicine especially in the treatment of cancer which is considered as a fatal disease. In mid-1980s Fujishima and coworkers used the strong oxidizing power of illuminated TiO$_2$ to kill tumor cells [65]. According to them, polarized illuminated TiO$_2$ film electrodes and TiO$_2$ colloidal suspensions are used in killing HeLe cells. They examined a series of experimental conditions [66], including the effect of superoxide dismutase, which enhances the effect, due to the production of peroxide. In addition, it is found that those illuminated TiO$_2$ microelectrodes can selectively kill a single cancer cell. Photoexcited TiO$_2$ nanoparticles also significantly suppress the growth of HeLe cells implanted in nude mice, compared with those receiving TiO$_2$ alone or UV irradiation alone. This technique is ineffective if the cancer cells had grown beyond a certain size. Also, it is proved that the wavelengths of 300–400 nm, which are used in photocatalytic reactions, are safe and do not cause mutation to the cell [65].

1.7.7 Air Purification

In recent years, it has been shown that the photocatalytic detoxification of volatile organic compounds is generally more efficient in the gas phase compared to the liquid phase. This technology is used in air treatments, including the utilization of
pollutant air stripping from the liquid phase. It is reported that the use of illuminated TiO$_2$ can result in the overall degradation of volatile organic compounds (VOCs) together with nitrogen oxides and sulfur oxides in air [23]. Photocatalytic oxidation (PCO) is a cost-effective method than incineration, carbon adsorption, or bio-filtration for flow rates up to 20,000 cfm (ft$^3$/min) for treating a 500 ppm VOC-laden stream gas phase reaction [25].

1.7.8 Photocatalysis

Various classes of azo dyes, such as monoazo, diazo, triazo classes etc. can be oxidized using heterogeneous photocatalysis such as TiO$_2$ [26]. Using TiO$_2$ nanoparticles the destruction of pollutants can be promoted by both artificial and sources employing solar technologies. This method has advantages because it is a destructive method and could occur under ambient condition. Also it is shown that it may lead to the complete mineralization of organic carbon into CO$_2$ [27].

1.8 Scope of the Thesis

The continuous development of science brings about smaller, faster and more accurate technological tools of increased performance. Among the several semiconductor materials, TiO$_2$ has got better attention due to its superior physical and chemical properties. Different modifications of TiO$_2$ extend its application to various fields such as photocatalysis, photo induced organic transformations, thermal reactions, photovoltaics, non linear optics etc. The synthesis and characterization of high-aspect-ratio Titanium dioxide nanostructures have attracted considerable attention recently owing to their multiple potential applications. Among the various chemical methods of preparing TiO$_2$ nanoparticles, the Sol-Gel process seems advantageous because of its low temperature and creating fine particles.
In this present study, an attempt has been made to prepare UV light active pure and metal ions doped TiO$_2$ nanoparticles by Sol-Gel method. The photocatalytic efficiency of the pure and metal ions doped systems are measured by monitoring the degradation of methyl orange dye.

This thesis consists of six chapters.

The first chapter deals with general introduction, review and scope of the present work.

Various preparation methods and the synthesis of pure and metal ions doped TiO$_2$ nanoparticles are provided in chapter two. The structural, morphological and chemical composition characterization techniques and results obtained in the present study are briefly explained in chapter three.

The spectroscopic investigation and optical studies of the present work are discussed in chapter four. The photocatalytic application studies of pure and metal ions doped TiO$_2$ nanoparticles are briefly explained in chapter five.

The summary and conclusion derived out of the present study along with the suggestions for future work are provided in chapter six.

Finally in the appendix section, a brief resume of the candidate and the list of papers published in International Journals, National proceedings, and papers presented/attended in National/International conferences by the candidate are added.
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