Chapter 1

Introduction
1.1 Background

1.1.1 Challenges of the 21st century

If 20th century was an expansive era seemingly without boundaries - a time of jet plane, space travel and an internet - the early years of the 21st century have showed us the limits of our small world [1]. Continuous hikes in the petrol, diesel prices and frequent regional blackouts remind us that the resources of energy like fossils fuels and oil refineries which were being taken for granted must be in tight supply. There has been an enormous increase in the global demand for energy in recent years which may result in energy crisis by the end of 21st century. The overall availability of natural resources and energy in upcoming years is shown in Fig. 1.1 [2].

![Conventional Fossil Fuels](Europe.TheOilDrum.com)

**Figure 1.1:** The overall availability of natural resources of energy in future

Moreover, environmental pollution caused by burning of conventional energy sources is a serious day-to-day problem faced by the developing and the developed nations in the world [3]. The common pollutants include toxic organic compounds like chlorinated and non-chlorinated aliphatic and aromatic compounds, dyes, detergents and surfactants, agro wastes like insecticides, pesticides, herbicides and pathogens like bacteria, fungi and viruses [4]. The pictorial example of the water pollution is shown in Fig. 1.2.
Hence, strict environmental legislations on the safe disposal of recalcitrant pollutants drive the research community to develop clean and green processes to degrade the pollutants before they are admitted into the atmosphere and water bodies.

1.1.2 Solar energy - a source of abundant energy

The sun is a massive source, giving $1.5 \times 10^{18}$ kWh of energy per year which is approximately 28,000 times higher in comparison with the energy consumption by the world for one year [5]. A comparison of the energy available from the sun per year and sum of the energies obtained from all non-renewable sources is presented in Fig. 1.3. Solar energy is a long lasting, non - polluting and silent source of energy. Hence, efficient use of solar energy will not only protect our resources but also make an economic contribution in reducing the environmental pollution.

One of the first technologies that come to mind when discussing solar energy is the growing use of solar cells and thereby photocatalysis which convert sunlight directly into usable form of energy like electric energy and chemical energy. Photocatalysts are silent, non-polluting and long-lived materials that typically convert 10 to 15 percent of the solar energy received into usable form [6, 7].
1.1.3 Heterogeneous photocatalysis – a single step solution for future fuel and water treatment

History dates back to 1972, when Fujishima and Honda discovered that water can be split, i.e. simultaneously oxidized to oxygen and reduced to hydrogen, when a bias potential is applied to an “illuminated” TiO$_2$ single crystal electrode [8]. This remarkable discovery marked the onset of photo induced redox reactions on semiconductor surfaces. Over the last 10 years, the scientific and engineering interest in the application of semiconductor photocatalysis has grown exponentially. This is evident from the number of publications in international journal since 1990 to the current date. Hence, photocatalysis can be regarded as a well understood field. However, many challenges and opportunities are present in this area which includes the production of catalysts at large scale and its practical applications in the decontamination of the environment, and the generation of clean energy.

Some of the highlights of the photocatalysis reaction are:

- This process aims to use the renewable source of energy i.e. solar light
- As the contaminant is attracted strongly to the surface of the catalyst, the process will continue to work at very lower concentrations allowing sub part-per-million consents to be achieved [9].
Photocatalytic reaction takes place at room temperature.

These reactions do not suffer the drawbacks of photolysis reactions as organic pollutants are usually completely mineralized to non-toxic substances such as CO₂, HCl and water [10].

The photocatalysts are generally inexpensive and can be supported on various substrates such as, glass, fibers, stainless steel, inorganic materials, sand, activated carbons (ACs) etc., attaining continuous re-use [11].

Photogenerated holes are extremely oxidizing and photogenerated electrons are reducing which produce superoxides from dioxygens.

Generally, non consumable chemicals are required for the process.

Semiconductor materials with superior physicochemical and optical properties are being employed for potential use as a photocatalyst. These are the materials whose valence band (VB) and conduction band (CB) are separated by an energy gap or band-gap. When a semiconductor molecule absorbs photons with energy equal or greater than its band-gap, electrons in the valence band can be excited and jump up into the conduction band, and thus hole is generated in the valence band. The holes mediate the oxidation of organic compounds by the formation of hydroxyl radicals, and the electrons mediate reduction and oxidation reactions by the formation of superoxide radicals. A pictorial representation of the mechanism of photocatalysis reaction on the surface of TiO₂ nanoparticles is shown in Fig. 1.4.

Figure 1.4: Pictorial representation of mechanism of photocatalysis
Several metal oxides such as TiO$_2$ [12], ZnO [13], MoO$_3$ [14], ZrO$_2$ [15], WO$_3$ [16], $\alpha$-Fe$_2$O$_3$ [17], SnO$_2$ [18], SrTiO$_3$ [19] and metal chalcogenides like ZnS [20], CdS [21], CdSe [22], WS$_2$ [23] and MoS$_2$ [24] can be used as photocatalysts. However, according to the thermodynamic requirement, the VB and CB of the semiconductor photocatalyst should be positioned in such a way that, the oxidation potential of the hydroxyl radicals ($E_0$ (H$_2$O/OH$^\cdot$) = 2.8 V vs NHE) and the reduction potential of superoxide radicals ($E_0$ (O$_2$/O$_2^\cdot$) = −0.28 V vs NHE), lie well within the band gap. In other words, the redox potential of hole must be sufficiently positive to generate hydroxyl radicals and that of the electron must be sufficiently negative to generate superoxide radicals.

**Fig. 1.5** depicts the band structure diagram of different materials, along with their redox potential. It is clear that, TiO$_2$, ZnO, SrTiO$_3$ and ZrO$_2$ exhibit favorable band-gap positions compared to the other materials. The material selection is also based on the stability of the material towards photocorrosion. For eg. ZnO and CdS have only one stable oxidation state (±2) and hence are prone to decomposition by holes according to the following reactions:

![Figure 1.5: Band gap of various semiconductors](image-url)
Furthermore, ZnO undergoes incongruous dissolution, yielding Zn(OH)\(_2\) on the surface, thereby leading to the deactivation of the material over a period of time. However, Ti in TiO\(_2\) is capable of reversibly changing its oxidation state between +4 and +3 and hence it is more favored compared to the other materials. In addition to the above advantages, other factors like the chemical structure, biocompatibility, physical, optical and electrical properties have made it a “photocatalyst of choice” over other photocatalysts [27].

### 1.2 TiO\(_2\) – “Photocatalyst of choice”

TiO\(_2\) has served as a “benchmark photocatalyst” for the degradation of a wide class of organic compounds and microorganisms in the UV range. It is the most widely investigated photocatalyst due to high photo-activity, low cost, low toxicity and good chemical and thermal stability [28]. The structure, mechanism and applications of TiO\(_2\) as a photocatalyst can be explained as follows.

#### 1.2.1 Structure of TiO\(_2\)

TiO\(_2\) exists in three mineral forms, viz: anatase, rutile and brookite which are shown in Fig. 1.6 [29]. In all three forms, titanium (Ti\(^{4+}\)) atoms are coordinated to six oxygen (O\(^2-\)) atoms, forming TiO\(_6\) octahedra.

**Figure 1.6: Polymorphic phases of TiO\(_2\): (a) anatase, (b) rutile and (c) Brookite**
Anatase is made up of face (vertice) sharing arrangements of octahedra at (001) planes (Fig. 1.6a) resulting in a tetragonal structure. In case of rutile, the octahedra share edges at (001) planes to give a tetragonal structure (Fig. 1.6b) and in brookite both edges and corners are shared to give an orthorhombic structure (Fig. 1.6c) [30, 31].

Amongst the various phases, brookite phase has been scarcely used as photocatalyst and hence only the properties of anatase and rutile phases of TiO$_2$ are compared in Table. 1.

**Table: 1 Properties of anatase and rutile phase of TiO$_2$**

<table>
<thead>
<tr>
<th>Property</th>
<th>Anatase</th>
<th>Rutile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight (g mol$^{-1}$)</td>
<td>79.88</td>
<td>79.88</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1825</td>
<td>1825</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>2500-3000</td>
<td>2500-3000</td>
</tr>
<tr>
<td>Light absorption (nm)</td>
<td>&lt;390</td>
<td>&lt;415</td>
</tr>
<tr>
<td>Mohr’s hardness</td>
<td>5.5</td>
<td>6.5-7</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.55</td>
<td>2.75</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>31</td>
<td>114</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Lattice constant (Å)</td>
<td>a = 3.78</td>
<td>a = 4.15</td>
</tr>
<tr>
<td></td>
<td>c = 9.52</td>
<td>c = 2.96</td>
</tr>
<tr>
<td>Density (g cm$^{-3}$)</td>
<td>3.79</td>
<td>4.13</td>
</tr>
<tr>
<td>Ti-O bond length (Å)</td>
<td>1.98</td>
<td>1.98</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>3.2</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Anatase phase of TiO$_2$ is more active for photocatalysis applications, even though rutile possesses a smaller band gap, this is because of the following reasons:
• The conduction band position of anatase TiO$_2$ is more negative compared to rutile, which results in the higher reducing power of anatase towards the adsorbed reactants resulting in a higher photocatalytic activity [32].

• As we are aware of the fact that the recombination reactions adversely affect the photocatalytic activity, the degree of recombination is found to be higher in case of rutile than the anatase phase which might limit its activity [33].

• The photocatalytic activity of TiO$_2$ increases with increase in the density of physically adsorbed OH$^-$ groups on its surface. The surface hydroxyl groups accept holes generated by UV and solar irradiation to form hydroxyl radicals and prevent electron-hole recombination increasing the photocatalytic activity. Generally, the surface of the anatase phase of TiO$_2$ is hydroxylated whereas, rutile TiO$_2$, being obtained at higher temperatures, has a very low density of physically adsorbed hydroxyl groups leading to lower Photoactivity [34].

1.2.2 Mechanism of photocatalysis on TiO$_2$

In all the following reactions, Ti$^4$ represents the four coordinated surface functionality of TiO$_2$ or the “active site”. From laser flash photolysis studies Hoffmann et al. have found that the characteristic time scale for the generation of charge carriers is of the order of femto seconds (fs). The charge carriers thus generated get trapped on the TiO$_2$ surface, which occurs over a time scale of tens of nano seconds (ns) as shown in reaction (1.3).

Reaction (1.4) represents the trapping of the holes by the surface hydroxyl groups present on TiO$_2$ reactions (1.5) and (1.6) represent the reversible trapping of the electrons on the surface of TiO$_2$ (shallow traps) and the irreversible trapping or relaxation of the electrons to the bottom of the CB (deep traps), respectively.

$$\text{Step 1: Charge carrier generation}$$

$$\text{TiO}_2 + h\nu \xrightarrow{H\nu \geq E_{BG}} h^+_{VB} + e^-_{CB} \quad (1.3)$$

$$\text{Step 2: Charge carrier trapping}$$

$$\text{Ti}^4\text{-OH}^- + h^+_{VB} \rightarrow \text{Ti}^4\text{-OH}^• \quad (1.4)$$
Surface trap
\[ \text{Ti}^4\text{OH}^- + e_{CB}^- \rightarrow \text{Ti}^3\text{OH}^- \] (1.5)

Deep trap
\[ \text{Ti}^4 + e_{CB}^- \rightarrow \text{Ti}^3 \] (1.6)

Reactions (1.7) – (1.8) represent the electron–hole recombination reactions, which occur at the surface states of the TiO₂, or in the bulk medium due to the delocalization of the electrons and holes. These are the detrimental reactions in photocatalysis as they affect the interfacial charge transfer processes and hence the quantum efficiency of the photoprocess.

**Step 3: Electron–hole recombination**

\[ \text{Ti}^4\text{OH}^* + e_{CB}^- \rightarrow \text{Ti}^4\text{OH}^- \text{ (Free electron with a trapped hole)} \] (1.7)
\[ \text{Ti}^3 + h^+_{VB} \rightarrow \text{Ti}^4 \text{ (Free hole with a trapped electron)} \] (1.8)
\[ h^+_{VB} + e_{CB}^- \rightarrow \text{heat} \text{ (Free hole with a free electron)} \] (1.9)

Reaction (1.10) represents the generation of hydroxyl radicals (OH•) by the reaction of surface adsorbed water molecules with the holes, and reactions (1.11) – (1.16) show the formation of superoxide (O•⁻²), hydperoxy (HOO•) and hydroxyl species through the electron pathway. All the above radical species are referred to as the “active species”. When the reactions are carried out in non-aqueous (organic) medium, the surface bound hydroxyl species present in the semiconductor plays a major role in reaction (1.4), and the contribution of reactions (1.10) – (1.16) for the overall oxidation of the substrate is negligible.

**Generation of hydroxyl radicals in the aqueous medium:**

\[ \text{Ti}^3\text{-H}_2\text{O} + h^+_{VB} \rightarrow \text{Ti}^4\text{OH}^* + \text{H}^+ \text{ (Hole pathway)} \] (1.10)

Electron pathway:
\[ \text{Ti}^3 + \text{O}_2 \rightarrow \text{Ti}^3\text{-O}_2^* \] (1.11)
\[ \text{Ti}^4\text{-O}_2^* + 2\text{H}^+ + e_{CB}^- \rightarrow \text{Ti}^4\text{-H}_2\text{O}_2 \] (1.12)
Once the active species are generated, the reactants are adsorbed onto the surface of the photocatalyst [reactions (1.17) – (1.19)].

**Adsorption–Desorption of a reductant (any organic substrate S)**

\[ \text{Ti}^{4+} + S \quad \rightarrow \quad \text{Ti}^{4-}S \quad (1.17) \]

\[ \text{Ti}^{4-} \text{OH}^+ + S \quad \rightarrow \quad \text{Ti}^{4-} \text{OH}^+ \text{S} \quad (1.18) \]

**Adsorption–Desorption of an oxidant (eg. metal ion):**

\[ \text{Ti}^{4+} + M^{n+} \quad \rightarrow \quad \text{Ti}^{4-} \text{M}^{n+} \quad (1.19) \]

This is followed by the oxidation of the reductant and the concomitant reduction of the oxidant by the attack of the hydroxyl radicals and CB electrons, respectively [reactions (1.20)–(1.23)]. The above two processes occur at characteristic time scales of 100 ns and milliseconds, respectively. This means that, the oxidizing power of the VB hole or the hydroxyl radicals is always higher than that of the reducing power of the CB electrons. Moreover, these interfacial electron transfer steps compete with the electron-hole recombination reaction (10 ns) and hence, the practical efficiency or quantum yield is always lesser than that of the theoretical yield.

**Photooxidation of a reductant:**

**Direct hole attack:**

\[ \text{Ti}^{4-}S + \text{Ti}^{4+} (h_{VB}) \quad \rightarrow \quad \text{Ti}^{4+} \rightarrow \text{Ti}^{4+} \rightarrow \text{Ti}^{4-} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (1.20) \]

**Hydroxyl radical attack:**

\[ \text{Ti}^{4-}S + \text{Ti}^{4-} \text{OH}^+ \quad \rightarrow \quad \text{Ti}^{4-} \rightarrow \text{Ti}^{4-} \rightarrow \text{CO}_2 + \text{H}_2 \quad (1.21) \]

\[ \text{Ti}^{4-}S + \text{OH}^+ \quad \rightarrow \quad \text{Ti}^{4-} \rightarrow \text{Ti}^{4-} \rightarrow \text{CO}_2 + \text{H}_2 \quad (1.22) \]

\[ \text{Ti}^{4-} \text{OH}^- \text{S}^- \quad \rightarrow \quad \text{Ti}^{4-} \rightarrow \text{Ti}^{4-} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (1.23) \]
The organic compounds degrade through the formation of intermediates (I), which transform finally to CO\(_2\) and H\(_2\)O. Reaction (1.24) shows that the products desorb from the surface thereby freeing the TiO\(_2\) active site. Similarly, when metal ions are present in the system, they are reduced to their thermodynamically stable oxidation states by the CB electrons [reaction (1.25)].

**Adsorption–Desorption of the organic intermediate:**

\[
\text{Ti}^4+ + \text{I} \rightarrow \text{Ti}^4\text{-I} \tag{1.24}
\]

**Photoreduction of a metal ion:**

\[
\text{Ti}^4\text{-M}^{n+} + \text{me}^- \rightarrow \text{Ti}^4\text{-M}^{(n-m)+} \tag{1.25}
\]

Therefore, the overall photocatalysis reaction can be depicted as follows (1.26), wherein, the oxidants are reduced and the reductants are oxidized by the action of UV radiation on the semiconductor photocatalyst [27].

\[
(\text{Ox}_1)_{\text{ads}} + (\text{Red}_2)_{\text{ads}} \rightarrow \text{Red}_1 + \text{Ox}_2 \tag{1.26}
\]

### 1.2.3 Synthesis of TiO\(_2\)

For photocatalytic applications, synthesis of “nano-sized TiO\(_2\)” is preferred compared to bigger sized TiO\(_2\) particles because of the following reasons:

- **The high surface to volume ratio:** It results in high surface area and high porosity, which ensures enhanced reaction rates due to the high level of interaction of the reactants with the active sites.

- **The quantum confinement at the nano scale:** It results in enhancement in the transport of electrons and holes from the bulk to the surface of the materials.

The synthesis routes for “nano-sized TiO\(_2\)” can be broadly classified as solution phase and gas phase techniques. Solution phase synthesis is the most preferred technique for the preparation of TiO\(_2\) in the form of powders whereas gas phase technique is widely
employed for the synthesis of thin films of samples. Some of the solution phase and gas phase methods are given in Fig. 1.7.

![Diagram of synthesis methods]

**Figure 1.7: Classification of methods for synthesis of TiO₂**

Each of the above synthesis methods possesses a unique advantage over the other techniques and the characteristics of the final product vary from one method to another. As we are dealing with the photocatalysis in the powder form, some significant characteristics of the solution phase method are explained as follows.

**A) Sol-gel method**

Sol-gel is a multi step process involving chemical and physical processes associated with hydrolysis, polymerization, gelation, condensation, drying and densification [35]. This process generally starts with the mixing of metal alkoxides or salts in water or in a suitable solvent (usually an alcohol) at ambient or slightly elevated temperatures. Schematic diagram of various steps involved in the sol gel process are shown in Fig. 1.8.
In sol gel process, controlling the pH of the starting solution is very much important to avoid the precipitation as well as to form the homogenous gel, which can be achieved by the addition of basic or acidic solutions. Apart from the above, organic compounds with hydrophilic functional groups (hydroxides or carboxylates) such as citric acid, succinic acid, oxalic acid, tartaric acid, acrylic acid, etc. and polymers like polyacrylic acid (PAA) and polyvinyl pyrrolidone (PVP) can be used with metal ion sources to form the sol as well as to control the particle size and uniformity of the products. Chelation of metal ions by carboxylic acid groups leads to a homogeneous distribution of the constituent ions in the obtained gel [36]. The picture of the TiO$_2$ gel formed during the sol-gel process is shown in Fig. 1.9.

Figure 1.9: TiO$_2$ gel formed during the sol-gel process
The gel intermediate is further heated between 150°C and 300°C to eliminate volatile organic components, excess water, etc., which results in the dried intermediate powders. Single phase nanocrystalline metal oxides are obtained after calcining the dried gel powder at 400-800 °C depending on the chemical nature of the precursors.

- **Advantages**: Improved homogeneity and purity from raw materials, good mixing for multi-component systems, effective control of particle size, shape, and properties
- **Disadvantage**: High calcination temperature

**B) Hydrothermal method**

Hydrothermal synthesis includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures. It can be defined as a method of synthesis that depends on the solubility of minerals in hot water under high pressure [37]. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called autoclave in which a nutrient is supplied along with water. A gradient of temperature is maintained at the opposite ends of the growth chamber so that the hotter end dissolves the nutrient and the cooler end causes seeds to take additional growth [38].

![Figure 1.10: Apparatus required for hydrothermal reaction](image)

The synthesis of TiO$_2$ is usually carried out in small autoclaves (Morey type), provided with Teflon liners, as shown in Fig. 1.10. The conditions selected for the synthesis of TiO$_2$ particles are: $T \leq 200°C$, $P < 100$ bars. The use of Teflon liners helps to obtain pure and homogeneous TiO$_2$ particles. Solutions of NaOH, KOH, HCl,
HNO$_3$, HCOOH and H$_2$SO$_4$ have been used as mineralisers and it is found that HNO$_3$ was a good mineraliser for obtaining mono-dispersed nanoparticles of TiO$_2$ with homogeneous composition [39].

**C) Solvothermal method**

The solvothermal method is almost identical to the hydrothermal method except that the solvent used here is nonaqueous. However, the temperature can be elevated much higher than that in hydrothermal method, since a variety of organic solvents with high boiling points can be chosen. This method normally has a better control on the size and shape distributions and the crystallinity of the TiO$_2$ nanoparticles compared to hydrothermal methods. It is found to be a versatile method for the synthesis of a variety of nanoparticles with narrow size distribution and dispersity. The solvothermal method has been employed to synthesize TiO$_2$ nanoparticles and nanorods with/without the aid of surfactants [40].

- **Advantages**: Low temperature synthesis, different morphologies of TiO$_2$ can be obtained
- **Disadvantages**: Long duration of synthesis, safety issues related to handling pressure

**D) Sonochemical method**

Sonochemistry is the research area in which molecules undergo a chemical reaction due to the application of powerful ultrasound radiations (20 kHz–10 MHz). The chemical effects of ultrasound do not come from a direct interaction with molecular species. Instead, it arises from acoustic cavitation: the formation, growth, and implosive collapse of bubbles which is formed in a liquid (as shown in Fig. 1.11) [41].

The stage leading to the growth of the bubble occurs through the diffusion of solute vapor in to the volume of bubble. The last stage is the collapse of the bubble, which occurs when the bubble size reaches its maximum value. Upon the collapse of bubbles, chemical bonds are broken due to which very high temperature (5000–25,000 K) is attained [42]. Since this collapse occurs in less than a nanosecond very
high cooling rate of ~ 1011 K s⁻¹, are also obtained. This high cooling rate hinders the organization and crystallization of the products [43].

Figure 1.11: Processes involved during sonochemical reaction

Ultrasound has been very useful in the synthesis of a wide range of nanostructured materials, including high-surface area transition metals, alloys, carbides, oxides and colloids. The sonochemical method has been applied to prepare various TiO₂ nanomaterials by different groups of researchers.

- **Advantages**: High crystallinity at a lower calcination temperature, mesoporous TiO₂ with higher surface area can be obtained
- **Disadvantage**: Generally mixed phase TiO₂ is obtained i.e rutile/brookite as a minor phase together with anatase as the major phase

**E) Microemulsion method**

Microemulsion may be defined as a thermodynamically stable, optically isotropic solution of two immiscible liquids consisting of microdomains of one or both liquids stabilized by an interfacial film of surfactant [44]. It provides a micro-heterogeneous medium for the generation of nanoparticles. The formation of particles in such systems is controlled by the distribution of reactants in the droplets and by the dynamics of inter-droplet exchange of reactants. The surfactant-stabilized microcavities provide a cage-like effect that limits particle nucleation, growth and agglomeration. It occurs in two forms: O/W (oil in water) and W/O (water in oil) which are analogous to aqueous and non-aqueous mediums, respectively as shown in Fig. 1.12. The micelles are formed in aqueous medium, where the hydrophobic
hydrocarbon chains of the surfactants are oriented toward the interior of the micelle, and the hydrophilic groups of the surfactants are in contact with the surrounding aqueous medium. On the other hand, reverse micelles are formed in non-aqueous medium where the hydrophilic head groups are directed toward the core of the micelles, and the hydrophobic groups are directed outward. The stability of the emulsions depends on the particle size, particle-particle interaction, particle water interaction and particle-oil interaction.

- **Advantage:** Size of the particles can be controlled by varying the ratio of surfactant to water
- **Disadvantages:** At high concentration of precursors uncontrolled aggregation and flocculation can be observed

![Image of micelles](image.png)

**Figure 1.12: Oil in water and water in oil type of micelles**

**F) Co-precipitation method**

The formation of the precipitate from a homogeneous liquid phase occurs because of physical transformation (change of temperature, pH, solvent evaporation, reactant concentration, *etc.*) or chemical process (addition of bases or acids, use of complex forming agents). In almost all cases, the formation of a new solid phase in liquid medium results from two elementary processes which occur simultaneously or sequentially: (1) nucleation, *i.e.*, formation of the smallest elementary particles of the new phase which are stable under the precipitation conditions; (2) growth or agglomeration of the particles [45].
The kinetics of nucleation and particle growth in homogeneous solutions can be adjusted by the controlled release of the anions and cations. Careful control of the kinetics of the precipitation can result in monodisperse nanoparticles. By controlling the factors that determine the precipitation process such as the pH, and concentration of the reactants / ions, nanoparticles with narrow size distributions can be obtained.

For the synthesis of oxides, the co-precipitation method involves precipitation of hydroxides by the addition of hydrolyzing agents like NaOH, NH₄OH, urea, etc. to a raw material followed by heat treatment like calcination to crystallize the oxide. Lower processing temperatures result in better metal dispersion than higher temperature treatments. This point is very important since a minimum particle size is desired in order to achieve a maximum metal surface area per unit weight of metal. One of the limitations of co-precipitation method is the tedious control of particle size and size distribution, due to the rapid (uncontrolled) precipitation resulting in the formation of larger sized particles instead of nanoparticles.

- **Advantages:** Simple and rapid preparation, easy control of particle size and composition and various possibilities to modify the particle surface state and overall homogeneity
- **Disadvantage:** This process is not suitable for the preparation of highly pure, accurate stoichiometric phase

### 1.2.4 Applications of TiO₂

The effective utilization of clean, safe, and abundant solar energy by the TiO₂ photocatalyst will lead to promising solutions not only for the energy crisis but also for serious environmental challenges. These applications can be roughly divided into “energy” and “environmental” categories which are shown in Fig. 1.13 [46].

In addition to these applications, TiO₂ is widely used as a pigment in cosmetics like sunscreens, ointments, toothpaste [47], etc. Discussing all these applications is out of the scope of this thesis hence; applications of TiO₂ related to water treatment and antibacterial properties are detailed below.
A) Application of TiO$_2$ in water treatment

Water is the most precious natural resource in the world embracing over 70% of the earth’s surface [48]. In spite of this, the accessibility of safe drinking water is a high priority issue for the survival of mankind as well as animals. This is because of the fact that water resources such as rivers, lakes and oceans are being contaminated by human beings through waste disposal. One of the industry that is under the strong radar of the environmental agencies is the “Dyeing units and the Dyestuff industries” as a whole [49]. The pollution that accompanies this industry is primarily due to the non-biodegradable nature of the dyes along with the strong presence of toxic trace metals/acid/alkali and carcinogenic aromatic amines in the effluents. Hence, the degradation of these dyes using solar energy is the current topic of interest. The detailed discussion about dyes as a pollutant, and their photocatalytic degradation is given below.

i) Dyes: one of the pollutants

Dyes find numerous applications in our daily life in clothing, food, paper, leather, cosmetics, plastics, drugs, electronics and printing. Nearly 80% of the synthetic dyes produced in the world are consumed by the textile industry. One of the major
bottlenecks in the textile industry is the dye fixation, i.e., spent dye baths, residual dye liquors and water from washing operations containing dye in the hydrolyzed and unfixed form. Nearly 10% of the dyes are discharged into the effluent as a result of this process. Conventional treatment of waste water like neutralization of acidic and alkaline liquors, flocculation and chemical oxidation result in 70– 80% of decolorization, however, the organic carbon load is retained in the effluents [50]. Biodegradation methods are effective in reducing the biological oxygen demand of the effluent, but reducing the chemical oxygen demand and toxicity to permissible levels is a challenging task [51].

In addition to this, dyes are the most widely used organic substrates which can be used to test the photocatalytic activity of nano-sized catalysts. This is because of the simplicity in the analysis of the dyes. The degradation of a dye can be characterized in two ways: percent decolorization and percent mineralization. Decolorization refers to the reduction in concentration of the parent dye under consideration at its characteristic wavelength, but does not refer to the complete removal of the organic carbon content. This is due to the formation of colored dye intermediates, which absorb at different wavelengths. Complete degradation or mineralization occurs only when all the organic carbon is converted to CO$_2$ which can be easily achieved by photocatalysis reaction. Hence, the role of AOPs in the degradation of dye waste waters is very critical.

Among all the dyes, the photodegradation of azo dyes has been investigated extensively, as these dyes constitute 50% of the commercial dyes. Degradation of azo dyes involves the cleavage in the vicinity of the azo bond and results in the formation of naphthol intermediates, which further gets transformed to benzoic acid.
intermediates [52]. Hence, in the present work, one of the azo dye i.e. methyl orange has been used as a model pollutant to investigate the photocatalytic activity of the synthesized TiO₂ nanoparticles. The structure of the methyl orange dye is given in Fig. 1.14.

**B) Application of TiO₂ as antimicrobial agents**

Microorganisms like pathogenic bacteria, fungi, viruses and protozoa in drinking water as well as in air are hazardous to human and animal life, as they lead to infectious diseases like cholera, gastroenteritis, malaria, yellow fever, tuberculosis, anthrax, etc [53]. Conventional low cost disinfectants include chlorine, chlorine dioxide (ClO₂), hypochlorite (OCl⁻) and ozone, which are used in a wide range of pH. However, the applications of the above disinfectants result in the formation of halo-methanes and halo-acetic acids, which are carcinogenic even at low concentrations [54]. Hence, photolytic (UV-C radiation at 254 nm) and photocatalytic disinfection (UV-A at 365 nm or visible radiation) using TiO₂ as the photocatalyst has been researched extensively over the past two decades.

TiO₂ and its modified forms exhibit superior photocatalytic activity in UV as well as in visible light for the disinfection of a wide class of gram-positive and gram-negative bacteria and other microorganisms, in a broad range of initial concentrations i.e. 10⁵–10⁹ cfu mL⁻¹ [55]. CFU refers to the number of viable microbial colonies, which are measured by counting the cell aggregates on an agar plate. It is also observed in most of the studies that, the optimum catalyst concentration required for the degradation of microorganisms is lesser than that required for the degradation of organic compounds. In the present work, *Staphylococcus aureus* (Gram-positive) and *Escherichia coli* (Gram-negative) are chosen as model organisms for the analysis of the bactericidal activity of the synthesized TiO₂ nanoparticles.

### 1.2.5 Drawbacks of TiO₂

- The large band gap of titania (3.2 eV) which makes TiO₂ inactive in visible light region [56].
- Massive recombination of photogenerated charge carriers limits its overall photocatalytic efficiency [57].
The use of slurries limits the industrial applications of photocatalysis, the separation of semiconductor powders after liquid phase reactions being troublesome and expensive [58].

1.3 Ways to modify the TiO₂

Various strategies have been adopted for improving the photocatalytic efficiency of TiO₂. They can be summarized as morphological modifications and chemical modifications as shown in Fig. 1.15.

Morphological modifications include parameters like increasing the surface area, porosity, crystallinity of the TiO₂ whereas, chemical modifications involve incorporation of additional components in the TiO₂ material.

1.3.1 Morphological modification

The efficiency of TiO₂ can be enhanced by controlling the morphology of TiO₂, in the form of nanoparticles, nanospheres, nanotubes, foams, mesoporous and monodispersed phases as listed in Fig. 1.16 [59]. One-dimensional nanostructures (nanowires, nanorods, nanotubes, nanopillars, nanocylinders, nanoneedles, and nanowhiskers) are better than the bulk TiO₂ as they exhibit higher catalytic activity in photocatalytic applications due to higher surface area and lower rate of recombinations [60]. Mesoporous TiO₂ is relatively more efficient than non mesoporous TiO₂ material for photocatalytic applications due to its continuous particle framework, which may be beneficial as compared to separate individual nanoparticles, in particular for catalyst recovery [61]. Monodispersed nanospheres
exhibit an optimal diameter for which the benefits of high surface area and reduced bulk recombination overcome the detrimental effects such as surface recombination and low crystallinity leading to higher photocatalytic activities [62].

![Morphological modification of TiO₂]

Although morphological modifications enhance the activity of TiO₂, chemical modifications are generally needed to increase the visible light absorption capacity of TiO₂, which will be reviewed in the next section:

### 1.3.2 Chemical modification

Several methods have been developed to modify TiO₂ by shifting its optical response to the visible range. Some of them are listed in Fig. 1.17.

![Types of chemical modifications in TiO₂]
A) Doping

Doping intentionally introduces impurities into pure TiO$_2$ for modulating its physical, chemical and optical properties. The choice of dopant is dependent upon its properties like ionic radii, conductivity and chemical stability. They are of different types such as metal ion, non metal ion and codoping. The pictoral representation of metal ion and non-metal ion doping is shown in Fig. 1.18.

i) Metal ion doping

Metal ion doping/cationic doping involves the substitution of Ti group of TiO$_2$. Two types of metal ions generally used to substitute the Ti ion in TiO$_2$ are as follows

Transitional metal ion doping:

Doping with a transition metal ion increases the formation of Ti$^{3+}$ ions, leading to the enhancement in the photocatalytic activity, as larger number of Ti$^{3+}$ states may cause more oxygen defects which facilitate the efficient adsorption of oxygen on the titania surface [63]. The formation of O$^{2-}$ upon chemisorption of oxygen requires the presence of a surface defect site which can be enhanced by transition metal ion doping [64].

![Figure 1.18: Pictorial representation of metal and nonmetal doping in TiO$_2$](image)

Since the redox energy states of many transition metal ions lie within the band gap states of TiO$_2$, the substitution of metal ions in TiO$_2$ introduces an intraband state close to the CB or VB edge, inducing visible light absorption at sub-band gap energies [65]. The red shift in the band gap absorption is attributed to the charge transfer transition between the $d$ electrons of the dopant and the CB (or VB) of TiO$_2$. 

Cationic doping of TiO$_2$ with transition metals such as Cu, Zn, Co, Ni, Cr, Mn, Mo, V, Fe has been extensively studied. Among them, introduction of Fe ion into the TiO$_2$ lattice accelerates anatase to rutile phase transition resulting in decrease in the activity [66] whereas, doping with Cu significantly increase the visible light absorption of the catalysts increasing its activity in visible and even in sunlight [67].

Rare earth metal ion doping:
Doping rare earth ion in TiO$_2$ is found to increase the photocatalytic activity for the degradation of organic contaminants by stabilizing the reactive anatase phase [68]. Lanthanide ions are well-known for their ability to form complexes with various Lewis bases (acids, amines, alcohols, thiols, etc.) by the interaction of the functional group of the pollutant with the f-orbital of lanthanides [69]. It is expected that incorporation of lanthanide ion into the TiO$_2$ matrix could provide a means to concentrate the organic pollutants at the semiconductor surface, and therefore the photocatalytic degradation is promoted [70].

Among the lanthanide metals (La, Ce, Er, Pr, Gd, Nd, or Sm) Gadolinium appears to be the best dopant when the sol–gel method is used; however, when aqueous synthesis is carried out, neodymium has emerged as the best dopant [71].

ii) Non-metal ion doping
Non-metal doping/anionic doping involves the substitution of O$_2$ group (oxygen site) in TiO$_2$. Wide variety of anionic species such as N, S, C, B, P, I, or F have been used for the same. There are two different mechanisms through which nonmetals can improve the activity of the TiO$_2$.

- Band gap narrowing: Doping with nonmetals introduces intraband states (energy levels of the valence band of the dopant nonmetals) close to/above valence band of the O$_2$ species resulting in the narrowing of band gap of TiO$_2$ [72].

- Oxygen vacancies: Nonmetal doping leads to the formation of oxygen deficient sites in the grain boundaries of TiO$_2$ which increase its visible light absorption [73].
iii) Codoping
Codoping involves the substitution of both Ti and O$_2$ groups of TiO$_2$ by the metal and non metal ion respectively. Codoping with two or more dopants is reported to achieve significant synergistic effects compared to the single ion doped or undoped TiO$_2$ counterparts [74]. Strong interactions between these dopants within the TiO$_2$ matrix alters the charge carrier transfer and also shifts the band gap absorption to the visible region for example, in case of Fe$^{3+}$ and Ho$^{3+}$ (as a dopant in TiO$_2$), Fe$^{3+}$ broadens the absorption profile, improving the visible light absorption of TiO$_2$, and also generates more electron-hole pairs, while Ho$^{3+}$ doping restrains the increase of grain growth and leads to crystal expansion retarding the recombination of charge carriers resulting in the faster degradation of MO compared with single ion doping or undoped TiO$_2$ under UV light [75].

B) Coupling with semiconductor
TiO$_2$ coupled semiconductor photocatalyst is a novel approach to achieve a more efficient charge separation. It increases the lifetime of the charge carriers and enhances charge transfer to adsorbed substrates. The mechanism for this can be explained as follows.

The excitation of one semiconductor injects electrons into the lower lying conduction band of the second semiconductor. The hole formed in this process accumulate in the valence band of the first semiconductor to form a hole center. Consequently, the excited electron/hole pair get separated effectively which leads to the enhanced photocatalytic activity [76]. The pictorial representation is shown in Fig. 1.19.

Metal oxides, such as CuO, Cu$_2$O, Fe$_2$O$_3$, WO$_3$, MoO$_3$, ZnO, SnO$_2$ and so on, have been considered for band-gap engineering of TiO$_2$ as these oxides have compatible band gap structure with that of TiO$_2$.

Among these oxides, low band-gap CuO or Cu$_2$O are used as sensitizers to use visible radiation [77], whereas other large band-gap oxides (e.g. ZnO, SnO$_2$) are coupled with TiO$_2$ for extrinsic trapping of photogenerated charge carriers to enhance photoactivity [78]. Coupling TiO$_2$ with SnO$_2$ attracts much attention as the band gaps of SnO$_2$ and
TiO$_2$ are 3.88 and 3.2 eV, respectively, and the CB edge of SnO$_2$ is $\sim$0.5 V above that of TiO$_2$ [79].

![Figure 1.19: A pictorial representation of charge transfer between two semiconductors](image)

Figure 1.19: A pictorial representation of charge transfer between two semiconductors

**C) Noble metal deposition**
Noble metal doping creates high Schottky barriers in TiO$_2$ lattice which acts as electron traps promoting interfacial electron transfer, thereby suppressing the recombination [80]. Noble metal islands deposited on the TiO$_2$ surface efficiently trap the electron and the free hole in the valence band can successively participate in the oxidation reactions. It has been reported in the literature that the noble metals such as Pt, Ag, Au, Rh, Ru deposited on TiO$_2$ have high Schottky barriers among the metals and thus act as electron traps, facilitating electron–hole separation and promotes the interfacial electron transfer process [81]. The Ag ion deposition on TiO$_2$ surface is a very common practice nowadays as it imparts its inherent antibacterial activity to the TiO$_2$ catalyst as well as improves its photocatalytic activity [82].

**D) Anatase TiO$_2$ with exposed reactive {001} facets**
In photocatalytic process, recombination tends to occur on the grain boundaries and crystalline defects of TiO$_2$. In such cases, the use of TiO$_2$ with highly exposed reactive facets (001) and low defect density can be important strategy to prolong the separation of charge carriers [83]. The picture of the reactive {001} facet of TiO$_2$ is shown in Fig. 1.20.
The addition of suitable electron acceptors in the titania suspension inhibits the charge carrier recombination [84]. These electron acceptors can have several beneficial effects such as

- Increase the number of trapped electrons which hinders its recombination with holes;
- Generate more free radicals and other oxidizing species;
- Increase the oxidation rate of intermediate compounds; and
- Avoid problems caused by low oxygen concentration as the solution phase may at times be oxygen starved because of either oxygen consumption or slow oxygen mass transfer [85].

1.4. Plan and scope of the research work

The brief literature survey presented in the beginning fairly describes the importance, structure, preparation methods and drawbacks of TiO$_2$ nanoparticles. Various methods used to modify TiO$_2$ including both morphological and chemical modifications are also discussed. The objective of the present work was to synthesize TiO$_2$ and modified TiO$_2$ nanoparticles bearing nanosize, crystalline anatase phase and high surface area. To achieve these properties, a conventional sol gel method was modified by combining it with hydrothermal and sonochemical methods. This combinatorial

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**Figure 1.20:** {001} Facets of anatase phase of TiO$_2$
methods yield products with better morphological properties such as higher surface areas, nanocrystallinity etc. Additionally, to achieve enhanced charge separation, some of the catalysts were coated with silver ions by sonochemical and photochemical method of deposition. Amongst the two, sonochemical method of deposition yields product with better optical and morphological properties.

To increase the visible light absorption, TiO$_2$ nanoparticles have been doped with various concentrations (0-5%) of Nd ions which enhanced the anatase phase stability, surface area and visible light absorption capacity of the sample. 1.0% Nd doping appears to be optimum, yielding highest degree of degradation. Further, 1% Nd doped catalyst was coated with Ag ions which restricted the recombination reaction of charge carriers. The photoactivity of the catalysts is significantly increased with Nd doping and Ag coating. The catalysts are found to be active in solar light irradiation though the degradation yields are lower in comparison with UV light. The antibacterial activities of these synthesized materials have been investigated by using *S. aureus* and *E. coli* bacteria as model organisms. 1% Nd doped and Ag coated catalysts show bactericidal activity under solar light irradiation.

Though nano TiO$_2$ has positive properties which makes it more efficient than the bulk TiO$_2$, its separation and recycling are the obstacles for its commercial use. Hence, magnetically separable TiO$_2$ nanoparticles have been fabricated by coupling them with Fe$_3$O$_4$ nanoparticles. Coupling Fe$_3$O$_4$ with TiO$_2$, imparts magnetic separability to the TiO$_2$ catalysts but impedes its photocatalytic activity. Decrease in the activity is attributed to the increase in recombination rate due to the small band gap of Fe$_3$O$_4$ nanoparticles. Thus, one of the composites (15% Fe$_3$O$_4$-TiO$_2$) was coated with silver nanoparticles which exhibits highest photoactivity. The sample is also found to be an active bactericidal agent with lower MIC values.
References


