Chapter II
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Literature Survey

As always, a waste management process faces the law of conservation of mass and consideration must be given to the fate of the products of a treatment process. If contaminants are removed from the aqueous phase to render water safe for discharge or useable for recycle, an early question is into what phase are they delivered? For example, adsorption and biological treatment create solid waste management problems. The central attraction of advanced oxidation (AO) processes is that organic contaminants are commonly oxidized to CO$_2$ [1]. The relatively small amounts of organic matter, and the ultimate fate that organic matter might experience under other treatment regimes, does not imply a significant contribution to greenhouses gases. Thus, the advanced oxidation processes (AOP) offer an attractive option to use the gas phase as the carbon sink.

2.1 Photocatalysis

Photocatalysis has become an emerging technology for the treatment of waste water all over the world [2]. It is being used for solving the problem of environmental pollution and even has remedial effect from harmful bacteria as reported by Toshiyuki et al. [3] The photocatalytic activity of a number of semiconducting materials has been established and photocatalysis has been predicted as a promising technology for waste water treatment. Ternary oxides are being used as effective photocatalysts for carrying out a number of chemical reactions [4]. The field of photocatalysis has been extensively reviewed by Stein Bach [5-7]. Considering that the photocatalytic reduction is an environmentally friendly treatment process, it is possible to be employed widely in environmental protection [8].

2.2 History of Photocatalysis

Catalysis can be thought of as an umbrella term to describe any process in which a substance through intimate interaction(s) with the reactant(s) and through a lower energy pathway accelerates an otherwise thermodynamically favored but kinetically slow reaction [9]. Unique processes can be found under the umbrella of catalysis, including photocatalysis, thermal catalysis, acid-base catalysis, redox
catalysis, and enzyme catalysis. Photocatalysis in particular has become an increasingly important field and a heavily researched topic by all fields of science, including physicists, chemists, and surface scientists, and is pursued today to solve an ever widening variety of environmental problems. The term *photocatalysis* has been used since the 1920s, although the name itself has drawn scrutiny since it incorrectly implies a catalytic reaction driven by light. Photocatalysis, however, broadly defines a photoreaction that is accelerated by the presence of a catalyst. In the mid 1920s, the semiconductor ZnO began attracting attention for use as a sensitizer for the decomposition of both organic and inorganic photoreactions, and TiO$_2$ was soon after investigated for its photodegradation characteristics [10]. Most of the primitive work in semiconductor photochemistry took place during 1960s, leading to the first photoelectrochemical cell for splitting water, using TiO$_2$ and Pt coated electrodes in the early 1970s [11]. In the early 1980s, TiO$_2$ was used for the first time to sensitize reactions in the photomineralization of selected organics. Since that time, research in the field of photocatalysis has been dominated by studies on the photocatalytic oxidation of organic compounds in water, although there is increased interest in oxidizing bacteria and volatile organic chemicals (VOCs) for the purpose of air purification. Currently, photocatalysis has been studied for the oxidative removal of the natural organic matter. Previously published works cover the effects of the presence of common anions and divalent cations, some transition metals such as Cu, Zn, Cr, Mn and also the effect of the hypochlorite ion as well as other chlorinated oxyanions acting as electron acceptors [12-16].

### 2.3 Definition of Photocatalysis

A suitable description of the term *photocatalysis*, whether in homogeneous or heterogeneous media, seems to elude acceptance as attested by the spectrum of specific labels used to describe a variety of mechanistic possibilities for a given process [17, 18]. The term *photocatalysis* refers simply to a catalytic reaction involving light absorption by a catalyst or by a substrate [18, 19], although there is no universal agreement on an appropriate definition. Without reference to a special or specific mechanism, photocatalysis has also been described [17] as the *acceleration of the rate of a photoreaction by the presence of a catalyst*; further, as a label to indicate that *a catalyst may accelerate the photoreaction by*
interaction with a substrate either in its ground state or in its excited state and/or with the primary photoproduct, depending on the mechanism of the photoreaction. This description also encompasses [21] photosensitization, yet such a process, defined officially [19] as a process by which a photochemical or photophysical alteration occurs in one molecular entity as a result of initial absorption of radiation by another molecular entity—the photosensitizer, is by no means necessarily catalytic without the knowledge of the turnover number and/or quantum yield. The issue seems to rest entirely on the role of the photons. Where in a process the quantum yield is greater than one (as occurs in photoreactions involving radicals) the process may be considered catalytic in photons, and where the quantum yield is less than or equal to one, the process may be taken as being noncatalytic in photons.

In chemistry, photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. In catalysed photolysis, light is absorbed by an adsorbed substrate. In photogenerated catalysis the photocatalytic activity (PCA) depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals (hydroxyl radicals: OH·) able to undergo secondary reactions. The IUPAC commission defines photocatalysis as “a catalytic reaction involving light absorption by a catalyst or a substrate” [22]. The definition of a photo-assisted catalysis was also proposed in a later revised glossary stating that “Catalytic reaction involving production of a catalyst by absorption of light” [23]. Similar to the above definitions, an earlier collection of similar terms of Chemical Terminology [24] described the idea of catalysis and a catalyst as follows: “catalysis is the action of a catalyst”, and a “catalyst is a substance that increases the rate of reaction without modifying the overall standard Gibbs energy change in the reaction”. But both of these definitions are less acceptable as they lack behind too many details of the catalytic process.

The term photocatalysis has been characterized in the past by a continued use of labels to describe a variety of mechanistic possibilities for a given process. The turnover quantities, like (numbers, TON; rates, TOR; frequencies, TOF), while being relatively understood in homogeneous photocatalysis, are not simple parameters to estimate and thus have required further considerations in heterogeneous photocatalysis as they necessitate knowledge of the number of
photocatalytically active sites for TON and TOR [25]. These turnover quantities depend on how the photocatalytic process is described. The older definition on catalyst defines catalyst as “any substance which accelerates / alters the rate of a chemical reaction without undergoing any physical or chemical change in it during the overall reaction”. When light is involved with the reaction, the expression photocatalysis can be described as “the acceleration of a photoreaction by the presence of a catalyst”. When the light falls on the catalyst the catalyst may increase the speed of the photoreaction by interacting with the substrate(s) either in its ground state or in its excited state or with the primary product, depending upon the reaction mechanism of the photoreaction [26]. The above statement gives rise to a question that whether photons also interact with the catalyst? These descriptions gives rise to a new terminology photosensitization [27] and such a process can be defined [28] as a process whereby a photochemical change occurs in one molecular as a result of initial photon absorption by another molecular species known as the photosensitizer. Chanon and Chanon define the term photocatalysis as “a general label to indicate that light and substrate (the catalyst or initiator) are necessary entities to influence a reaction” [20]. Teichner and Formenti described heterogeneous photocatalysis as “an increase in the rate of a thermodynamically allowed (ΔG<0) reaction in the presence of an irradiated solid with the increase (in rate) originating from the creation of some new reaction pathways involving photocrearted species and a decrease of the activation energy” [29]. In a heterogeneous photocatalytic process, light induced chemical reactions or molecular transformations occur at the surface of a catalyst. This general process can be further divided into catalyzed or sensitized photoreactions based upon whether the initial excitation occurs at the surface of the adsorbate molecule or the catalyst [30]. A catalyzed photoreaction occurs when the initial photoexcitation occurs in an adsorbate molecule, which then reacts with a catalyst substrate. A sensitized photoreaction occurs when the initial photoexcitation occurs in the catalyst substrate and then energy transfer, which is often in the form of electron transfer, takes place with a ground (non-energetically excited) state molecule.

In an excellent account, Salomon [30] proposed that a broad definition of photocatalysis should be operationally divided into two distinct classes: (i)
**photogenerated catalysis**, which is catalytic in photon, and (ii) **catalyzed photolysis**, which is non-catalytic in photons. The former implicates only ground states of the catalyst and the substrate in the catalytic step which is thermodynamically spontaneous (exoergic), whereas in the latter either the nominal catalyst or the substrate, or both, are in an excited state during the catalytic step. Figure 2.1a illustrates a simple scheme of photogenerated catalysis, whereas Figure 2.1b depicts an example of catalyzed photolysis.

![Diagram of photogenerated catalysis and catalyzed photolysis](image)

**2.3.1 Photogenerated Catalysis - The Langmuir - Hinshelwood Process**

According to Hinshelwood when light is absorbed by the catalyst which leads to the generation of electrons (e\(^{-}\)) and holes, (h\(^{+}\)), during the photocatalytic reaction, which occurs at a photochemically active surface and the following reactions take place:

\[
\begin{align*}
R + S & \longrightarrow R_{ads} \\
R_{ads} & \longrightarrow R + S \\
\text{Catalyst} + h\nu & \longrightarrow e^{-} + h^{+} \\
R_{ads} + h^{+} & \longrightarrow R_{ads}^{+} \\
R_{ads}^{+} + e^{-} & \longrightarrow R_{ads} \\
R_{ads}^{+} & \longrightarrow \text{products} + S
\end{align*}
\]
The Eq. 2.1 corresponds to the adsorption of reagent R on the surface site S of the catalyst while Eq. 2.2 shows the desorption of the adsorbed molecules R_{ads}. Eq. 2.3 illustrates the photoexcitation of the catalyst producing electrons and holes. Eq. 2.4 describes carrier (hole) trapping by the adsorbed molecule to form a reactive radical state, whose decay occurs through recombination with an electron described by Eq. 2.5 Eq. 2.6 is the chemical reaction that yields the products and regenerates the original state of the catalyst surface, S. This description of photocatalysis is most widely accepted.

**2.3.2 Catalyzed Photolysis**

The catalyzed photolysis can be summarized by a simple photochemical process that takes place on an inactive surface of a photocatalyst when light is absorbed by an adsorbed substrate which is given in Eqs. 2.7–2.11.

\[ R + S \rightarrow R_{ads} \quad (2.7) \]
\[ R_{ads} \rightarrow R + S \quad (2.8) \]
\[ R_{ads} + h\nu \rightarrow R^*_{ads} \quad (2.9) \]
\[ R^*_{ads} \rightarrow R_{ads} \quad (2.10) \]
\[ R^*_{ads} \rightarrow S + \text{products} \quad (2.11) \]

Eq. 2.7 corresponds to the adsorption of reagent R on the surface site S of the catalyst while Eq. 2.8 illustrates the desorption of the adsorbed molecules R_{ads}. Eq. 2.9 is the photoexcitation of adsorbed molecules R_{ads} to form excited state R^*_{ads} followed by the rapid decay of excitation (Eq. 2.10) and chemical reaction (Eq. 2.11) to regenerate the original state of catalyst surface S.

**2.3.3 Photogenerated Catalysis - The Eley-Rideal Process**

Another possible heterogeneous photochemical process may be observed when the catalyst is photoexcited and no pre-adsorption of M occurs, as described by

\[ \text{Catalyst} + h\nu \rightarrow e^- + h^+ \quad (2.12) \]
\[ S + h^+ \rightarrow S^+ \quad (2.13) \]
\[ S^+ + e^- \rightarrow S \quad (2.14) \]
\[ S^+ \rightarrow S + h^+ \quad (2.14a) \]
\[ \text{S}^+ + \text{hv} \rightarrow \text{S} + \text{h}^+ \]  
\[ \text{S}^+ + \text{M} \rightarrow (\text{S} - \text{M})^+ \]  
\[ (\text{S} - \text{M})^+ \rightarrow \text{S} + \text{Products} \]  
\[ (\text{S} - \text{M})^+ \rightarrow \text{S}^+ + \text{Products} \]

In the above reactions Eq 2.12 corresponds to the photogeneration of free carriers. Eq 2.13 describes the trapping of carriers (in this particular case, holes) by surface defects (i.e., “potential” surface active centers) S to produce surface active centers S; Eq 2.14 represents the “physical” decay pathway of surface active centers through recombination with charge carriers of the opposite sign, in this case electrons; it may also be a first-order thermal deactivation process (Eq 2.14a) or a second-order photoionization process (Eq 2.14b) Eq 2.15 is a chemical reaction (chemisorption) which yields the intermediate species \((\text{S}–\text{M})^+\) followed by secondary reactions to produce the photoreaction products Eq 2.16, 2.16a.

Based on the above definitions and descriptions of photocatalysis, it can be said that the photocatalysis process deals with mainly three separate steps like light, catalyst and the substrate. Even the adsorption plays a major role in the overall process of photocatalysis. Keeping all the above mentioned factors a new definition for photocatalysis has been proposed.

**Photocatalysis** is the destruction of any organic molecule adsorbed on the catalyst surface by the active radical species formed because of the effect of UV or visible light illumination on the catalyst. Where the word destruction is considered as partial or complete destruction of the organic molecule.

### 2.4 Description of Photocatalysis

A simple description for a chemical reaction in the presence of catalyst is given below. The Eq. 2.17 illustrates a chemical reaction in the absence of catalyst and the Eq. 2.18 gives the same chemical reaction in the presence of catalyst.

\[ \text{A} \leftrightarrow \text{B} \]  
\[ \text{A} + \text{Catalyst} \leftrightarrow \text{B} + \text{Catalyst} \]
The catalytic process can be described as the process in which the rate of a chemical reaction is either increased or decreased by means of a chemical substance known as a catalyst for example the addition of a catalyst changes the rate of establishing an equilibrium state in Eq. 2.18, as compared to the equilibrium state of Eq. 2.17. After the completion of the reaction the catalyst can be separated in the same original state and in the same amount as before the reaction. Unlike other reagents that participate in the chemical reaction, a catalyst is not consumed by the reaction itself. The reaction pathway in the catalytic process is different from that of the reaction pathway without a catalyst. In the catalytic process the rate of the reaction depends on the activation energy. If the activation energy in the catalytic process is lower then the rate of the reaction increases.

In general the definition of the photocatalysis can be stated as the same as that of the catalyst, but here the light plays a prominent role where the chemical reaction occurs by the absorbed light by some reagent A (Eq. 2.19).

\[ A + h\nu \rightarrow B \]  
(2.19)

The corresponding photocatalyzed process is

\[ A + \text{Catalyst} + h\nu \rightarrow B + \text{Catalyst} \]  
(2.20)

In a photochemical reaction the reaction is initiated by the absorption of a quantum of electromagnetic radiation to form an excited state. The photochemical reaction (Eq. 2.19) is irreversible, if light is taken as a quasi-reagent in the reaction, the reversible reaction must follow the pathway as shown in Eq. 2.21.

\[ B \leftrightarrow A + h\nu \]  
(2.21)

where, \( h\nu \) denotes photons of identical energy as those used in the forward reaction (Eq. 2.19).

2.5 Principles of Photocatalytic Reactions

In general, a sensitized photocatalytic oxidation process is one in which a semiconductor upon absorption of a photon of suitable energy can act as a photocatalytic substrate by producing highly reactive radicals that can oxidize organic compounds. A molecular description of a general photocatalytic process is given below in Eq 2.22 – 2.27 [32]. For example, the most commonly used and
researched semiconductor catalyst, TiO$_2$, is used as the substrate, and H$_2$O and O$_2$ are used as adsorbates.

\[
\text{TiO}_2 + \text{hv} \rightarrow \text{TiO}_2 \left( e^-_{\text{cb}} + h^+_{\text{vb}} \right) \quad (2.22)
\]

\[
\text{TiO}_2 \left( e^-_{\text{cb}} + h^+_{\text{vb}} \right) \rightarrow \text{TiO}_2 + \text{heat} \quad (2.23)
\]

\[
\text{TiO}_2 + \text{H}_2\text{O}_{\text{ads}} \rightarrow \text{TiO}_2 + \text{OH}^- + \text{H}^+ \quad (2.24)
\]

\[
e^-_{\text{cb}} + \text{O}_{\text{ads}} \rightarrow \text{O}^-_2 \quad (2.25)
\]

\[
h^+_{\text{vb}} + \text{OH}^- \rightarrow \text{OH}^- \quad (2.26)
\]

\[
\text{OH}^- + \text{Organics} \rightarrow \text{H}_2\text{O, CO}_2, \text{etc} \quad (2.27)
\]

One point that should be obvious from Eq 2.22 – 2.27 is that a photocatalyst’s interaction with other adsorbed molecules is essential. Photoactive semiconductor surfaces can attract electron donors and acceptors through both chemical and electrostatic forces including van der Waals forces, induced dipole-dipole interactions, dipole-dipole interactions, hydrogen bonding, outersphere complexation, ion exchange, surface organic matter partitioning, and sorbate hydrophobicity.

2.6 Semiconductors

A semiconductor is a material that has electrical conductivity between those of a conductor and an insulator; it can vary over that wide range either permanently or dynamically. A material with a small, but not null or negative, band gap (arbitrarily defined as < 3 eV, although some definitions place the upper limit at 4 eV) is referred to as a semiconductor. Semiconductors are most primary light absorbers used in photocatalysis. The favorable combination of electronic structure, light absorption properties, charge transport characteristics and excited-state lifetime make them useful for photocatalytic applications. The theory and properties of semiconductor materials are described in the subsequent section of the thesis.

2.6.1 Structure of Semiconductor

The principles of semiconductor physics are best illustrated using the example of silicon, a group 4 elemental semiconductor. The silicon crystal forms the so
called diamond lattice where each atom has four nearest neighbours at the vertices of a tetrahedron. The four-fold tetrahedral coordination is the result of the bonding arrangement which uses the four outer (valence) electrons of each silicon atom. Each bond contains two electrons, and can easily see that all the valence electrons are taken up by the bonds. Semiconductors can exhibit a wide variety of atomic arrangements; almost all elemental semiconductors have a crystal structure where every atom is tetrahedrally bonded to four other atoms. The best known semiconductors germanium and silicon have the diamond structure and many semiconducting compounds of interest have the closely related structures of zinc blende and chalcopyrite.

2.6.2 Band Gap

The term "band gap" refers to the energy difference between the top of the valence band and the bottom of the conduction band; electrons are able to jump from one band to another. In order for an electron to jump from a valence band to a conduction band, it requires a specific amount of energy for the transition. The required energy differs with different materials. Electrons can gain enough energy to jump to the conduction band by absorbing either a phonon (heat) or a photon (light). A useful way to visualize the difference between conductors, insulators and semiconductors is to plot the available energies for electrons in the materials. Instead of having discrete energies as in the case of free atoms, the available energy states form bands. Crucial to the conduction process is whether or not there are electrons in the conduction band. In insulators the electrons in the valence band are separated by a large gap from the conduction band (Figure 2.2 d), in conductors like metals the valence band overlaps the conduction band (Figure 2.2 a, b), and in semiconductors there is a small enough gap between the valence and conduction bands that thermal or other excitations can bridge the gap (Fig 2.2 c). With such a small gap, the presence of a small percentage of a doping material can increase conductivity dramatically.
Figure 2.2 Possible energy band diagrams of a crystal. Shown are: a) a half filled band, b) two overlapping bands, c) an almost full band separated by a small bandgap from an almost empty band and d) a full band and an empty band separated by a large bandgap [33]

Figure 2.3 Energy structures of various photosemiconductors [34]

Figure 2.3 shows the bandgap positions of several dominant photocatalysts in relation to the oxidation and reduction potentials of H$_2$O. The energy positions of the band edges are shown both on the absolute vacuum scale (AVS) and with respect to the normal hydrogen electrode (NHE) and can be related by

\[ E_{(AVS)} = -E_{(NHE)} - 4.5 \]  \hspace{1cm} (2.28)
Table 2.1 Band positions of some common semiconductor photocatalysts in aqueous solution at pH=1 [35]

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Valence band (V vs NHE)</th>
<th>Conductance band (V vs NHE)</th>
<th>Band gap (eV)</th>
<th>Band gap wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>3.1</td>
<td>-0.1</td>
<td>3.2</td>
<td>387</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>4.1</td>
<td>+0.3</td>
<td>3.9</td>
<td>318</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.0</td>
<td>-0.2</td>
<td>3.2</td>
<td>387</td>
</tr>
<tr>
<td>ZnS</td>
<td>1.4</td>
<td>+2.3</td>
<td>3.7</td>
<td>335</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>3.0</td>
<td>+0.2</td>
<td>2.8</td>
<td>443</td>
</tr>
<tr>
<td>CdS</td>
<td>2.1</td>
<td>-0.4</td>
<td>2.5</td>
<td>496</td>
</tr>
<tr>
<td>CdSe</td>
<td>1.6</td>
<td>+0.1</td>
<td>1.7</td>
<td>729</td>
</tr>
</tbody>
</table>

2.6.3 Thermal and Optical Excitation

Semiconductor materials are insulators at absolute zero temperature that conduct electricity in a limited way at room temperature. The defining property of a semiconductor material is that it can be doped with impurities that alter its electronic properties in a controllable way. Increase in conductivity can be obtained by exposure of the semiconductor to either light or heat, because these stimuli promote electrons from the valance band to the conduction band. Photoconductivity is an optical and electrical phenomenon in which a material becomes more conductive due to the absorption of electro-magnetic radiation such as visible light, ultraviolet light, infrared light, or gamma radiation. When light is absorbed by a material like a semiconductor, the number of free electrons and holes changes and raises the electrical conductivity of the semiconductor. To cause excitation the light that strikes the semiconductor must have enough energy to raise electrons across the forbidden bandgap or by exciting the impurities within the bandgap. When carriers in a semiconductor are excited thermally, electrons are prompted to the conduction band, and an equal number of holes are produced in the valance band. This type of semiconductor is known as an intrinsic semiconductor.
2.6.4 Doping of Semiconductors

Semiconductor doping was originally developed by John Robert Woodyard working at Sperry Gyroscope Company during World War II [36]. The demands of his work on radar denied Woodyard the opportunity to pursue semiconductor doping research [37]. Related work was performed at Bell Labs by Gordon K. Teal and Morgan Sparks [38]. In semiconductor production, doping is the process of intentionally introducing impurities into an extremely pure (also referred to as intrinsic) semiconductor to change its electrical properties. The impurities are dependent upon the type of semiconductor. Lightly and moderately doped semiconductors are referred to as extrinsic. A semiconductor doped to such high levels that it acts more like a conductor than a semiconductor is referred to as degenerate.

The knowledge of doping effects on optical and thermal properties of semiconductors is crucial for the development of optoelectronic compounds. It is advantageous to change the optoelectronic properties of a semiconductor for the photocatalytic process. This can be achieved by introducing impurities/foreign elements into the crystal structure of a semiconductor. The impurity can either occupy a lattice site, an interstitial site, or it can simply be a vacancy. In most applications, a foreign element known as a dopant is added to a semiconductor to change the equilibrium concentration of electrons or holes. The dopant, also called doping agent and dope, is added to the semiconductor lattice in low concentrations in order to alter the optical/electrical properties of the semiconductor. The addition of these dopants creates a new set of energy levels which accompany these impurity sites, and the location of these levels will determine the changes in electrical and optical properties of solid. If the semiconductor is doped with donors, it is referred to as an n-type semiconductor, and if the solid is doped with acceptors it is called as a p-type semiconductors. In n-type materials, electrons are called majority carriers and holes are known as the minority carriers. In p-type semiconductors, the opposite situation holds, wherein the holes are the majority and electrons are the minority carriers.
2.6.5 *n*-type and *p*-type Semiconductors

An n-type semiconductor (n for *Negative*) is obtained by carrying out a process of doping, that is, by adding an impurity of valence-five elements to a valence-four semiconductor in order to increase the number of free charge carriers. When the doping material is added, it gives away (donates) weakly-bound outer electrons to the semiconductor atoms. This type of doping agent is also known as donor material since it gives away some of its electrons. A p-type semiconductor (p for *Positive*) is obtained by carrying out a process of doping that is adding a certain type of atoms to the semiconductor in order to increase the number of free charge carriers. When the doping material is added, it takes away (accepts) weakly-bound outer electrons from the semiconductor atoms. This type of doping agent is also known as acceptor material and the semiconductor atoms that have lost an electron are known as holes or in other words n-type semiconductor materials have been doped with elements which have spare electrons in their outer shells. This gives n-type silicon free electrons (which are negatively charged particles) which can move about at will - with the potential to create current. p-type semiconductor materials have been doped in the opposite way, with elements that have too few electrons in their outer shells. Therefore, the opposite of electrons - holes - are free to move about within the material - with the potential to create current.

2.7 Photogeneration of Electron-hole Pairs

The electron–hole pair is the fundamental unit of generation and recombination, corresponding to an electron transitioning between the valence band and the conduction band. When the light of the suitable wavelength is absorbed by a semiconductor the electrons tend to move from the valence band (V_b) to the conduction band (C_b) due to which electron-hole pairs (e, p) are formed which are having potential energies corresponding to the thermodynamic levels, E_{cb} for the electrons and E_{vb} for the holes, where E_{cb}-E_{vb} = E_{gap}.

2.7.1 Role of Photogenerated Electrons in Photocatalysis

For a semiconductor to have high quantum efficiency, its photoinduced charges must freely migrate to the surface of the particle so that they can participate in reactions with adsorbed species. The migration of electrons to the surface is not
only in competition with electron hole pair (EHP) recombination but also with trapping by coordination defects at the surface and by lattice defects in the particles bulk. The photogenerated electrons that are able to migrate to the surface are primarily used in the reduction of O$_2$ (in both aqueous and gas solutions), other reactive species such as the superoxide radical O$_2^-$ or the singlet oxygen, which can in turn stimulate other radical chain reactions involving H$_2$O$_2$ or O$_3$ [39]. Experiments have proven that the photocatalytic ability of TiO$_2$ is almost completely suppressed in the absence of an electron scavenger to prevent EHP recombination [40]. This may be one possible reason for the negligible photoactivity in many rutile phase TiO$_2$ particles which have a conduction band energy just below that required to reduce molecular oxygen.

2.7.2 Role of Photogenerated Holes in Photocatalysis

The positively charged photogenerated holes that are able to migrate to the surface can either directly oxidize organic species with lower oxidation potentials or they can create the highly reactive and short-lived hydroxyl radical OH• upon the catalyst’s adsorption of H$_2$O. The adsorption of H$_2$O on the surface of TiO$_2$ is an active and debated area of research, although it is commonly accepted that H$_2$O is adsorbed both molecularly and dissociatively [41]. In both molecular and dissociative adsorption of H$_2$O on the surface of TiO$_2$, a probable evolution path is for the localized hole states exposed on the surface to transfer directly to other species where direct oxidation can occur. Dissociative adsorption can have the extra benefit of forming a hydroxyl radical that can desorb from the surface to oxidize organic species [42].

2.8 Properties of a Photocatalyst

These are some of the important properties of a photocatalysts that are necessary for the photodegradation of organics:

- The band gap should be between 2.43 eV and 3.2 eV
- The valence band should be lower than the oxygen oxidation potential
- The conduction band should be higher than the hydrogen reduction potential
- The photocatalyst must be able to split water in protons and hydroxyl anions
- The generation of water from molecular oxygen and hydrogen must be reduced
• Electron transport to the surface is necessary

The photosensitized dissociation of water into H₂ and O₂ and research work in this area has led to the development of many photochemical systems capable of generating either H₂ or O₂ from water upon irradiation with visible light. Heterogeneously dispersed photocatalyst such as TiO₂, ZnO, Fe₂O₃ and CdS, which are considered as photosemiconductor have been extensively researched [43-47]. But most of the investigations have focused on TiO₂ when compared to other photocatalysts. TiO₂ is much more promising as it is stable under UV light irradiation, non-corrosive, environmentally friendly, abundant and cost effective. Moreover, it shows relatively high activity and chemical stability. TiO₂ exist in two major forms, the anatase and the rutile. The anatase form has free electrons in its crystal lattice, hence is an n-type semiconductor [48]. Like other semiconductor photocatalyst, the reduction and oxidation reactions of TiO₂ are the basic mechanisms of photocatalytic hydrogen production and photocatalytic water/air purification, respectively. For hydrogen production, the CB level should be more negative than hydrogen production level (E_{H₂/H₂O}) while the VB should be more positive than water oxidation level (E_{O₂/H₂O}) for efficient oxygen production from water by photocatalysis. But, the energy conversion efficiency from sunlight by TiO₂ photocatalyst is too low, mainly due to the following reason:

Inability to utilize visible light: The band gap of TiO₂ is about 3.2 eV and only UV light can be utilized for the photodegradation. Since the UV light only accounts for about 4% of the solar radiation energy while the visible light contributes about 50%, the inability to utilize visible light limits the efficiency of solar photocatalyst for the degradation process.

In order to resolve the above listed problems and enhance the photodegradation property of the photocatalyst, continuous efforts have been made to promote the photocatalytic activity and enhance the visible light response. Addition of electron donors (hole scavengers), addition of carbonate salts, noble metal loading, metal ion doping, anion doping, dye sensitization, composite semiconductors, metal ion-implantation etc, were investigated and some of them have been proven to be useful to enhance photocatalytic property.
2.8.1 Modification by Metal loading

Usually, addition of noble metals such as Pt, Pd, or Rh to semiconductors is essential. Noble metals, including Pt, Au, Pd, Rh, Ni, Cu and Ag, have been reported to be very effective for enhancement of TiO$_2$ photocatalysis. As the Fermi levels of these noble metals are lower than that of TiO$_2$ [49, 50], photo-excited electrons can be transferred from CB to metal particles deposited on the surface of TiO$_2$ while photo-generated VB holes remain on the TiO$_2$. Accumulated electrons on metal particles can then be transferred to protons adsorbed on the surface and further reduce the protons to hydrogen molecules. Therefore, noble metals with suitable work function can help electron transfer, leading to higher photocatalytic activity. It should be noted that although the loading of noble metal can reduce recombination to some extent.

2.8.2 Modification by Dye Sensitization

Dye sensitization is widely used to utilize visible light for energy conversion. Some dyes having redox property and visible light sensitivity can be used in solar cell as well as photocatalytic systems [51, 52]. Under illumination by visible light, the excited dyes can inject electrons to CB of semiconductors to initiate the catalytic reactions as illustrated in Figure 2.4.

![Diagram of dye sensitized photocatalytic hydrogen production](image)

Figure 2.4 Mechanism of dye sensitized photocatalytic hydrogen production under visible light irradiation [53]

Even without semiconductors, some dyes, for example safranine O/EDTA and T/EDTA, are able to absorb visible light and produce electrons as reducing agents strong enough to produce hydrogen [54]. High hydrogen production rate can be obtained by efficient absorption of visible light and efficient transfer of electrons from excited dyes to the CB of TiO$_2$. The CB electrons can then be transferred to
noble metal particle (Pt) loaded on the surface to initiate water reduction. In order to regenerate dyes, redox systems or sacrificial agents, such as I3/I pair and EDTA, can be added to the solution to sustain the reaction cycle.

\[
\text{dye} \xrightarrow{hv} \text{dye}^* \\
\text{dye}^* \xrightarrow{\text{TiO}_2} \text{dye}^* + e^- \\
\text{dye}^* + e^- \xrightarrow{} \text{dye}
\]

As for principles of the improved photocatalyst activity of modified TiO\textsubscript{2}, three benefits of modification to the photocatalyst semiconductor system have been studied as follows: Inhibiting recombination by increasing the charge separation and therefore, efficiency of the photocatalytic process increased. Increasing the spectrum response range (i.e. excitation of wide band gap semiconductors by visible light). Changing the selectivity or yield of a particular product [55].

### 2.8.3 Modification by Ion Doping

Transitional metal ion doping and rare earth metal ion doping have been extensively investigated for enhancing the TiO\textsubscript{2} photocatalytic activities. Choi et al. [56] carried out a systematic investigation to study the photoreactivity of 21 metal ions doped into TiO\textsubscript{2}. It was found that doping of metal ions could expand the photo-response of TiO\textsubscript{2} into visible spectrum. As metal ions are incorporated into the TiO\textsubscript{2} lattice, impurity energy levels in the band gap of TiO\textsubscript{2} are formed as indicated below

\[
\text{M}^{n+} + h\nu \rightarrow \text{M}^{(n+1)} + e^-_{cb} \\
\text{M}^{n+} + h\nu \rightarrow \text{M}^{(n-1)} + h^+_{vb}
\]

where, M and M\textsuperscript{n+} represent metal and the metal ion dopant, respectively. Furthermore, electron (hole) transfer between metal ions and TiO\textsubscript{2} can alter electron-hole recombination as:

- **Electron trap:** \(\text{M}^{(n+1)} + e^-_{cb} \rightarrow \text{M}^{(n-1)}\)
- **Hole trap:** \(\text{M}^{(n-1)} + h^+_{vb} \rightarrow \text{M}^{(n+1)}\)

The energy level of \(\text{M}^{n+}/\text{M}^{(n-1)+}\) should be less negative than that of the CB edge of TiO\textsubscript{2}, while the energy level of \(\text{M}^{n+}/\text{M}^{(n+1)+}\) should be less positive than that of the VB edge of TiO\textsubscript{2}. For photocatalytic reactions, carrier transferring is as
important as carrier trapping. Only if the trapped electron and hole are transferred to the surface, photocatalytic reactions can occur. Therefore, metal ions should be doped near the surface of TiO$_2$ particles for a better charge transferring. In case of deep doping, metal ions likely behave as recombination centers, since electron/hole transferring to the interface is more difficult. Furthermore, there exists an optimum concentration of doped metal ion, above which the photocatalytic activity decreases due to the increase in recombination.

2.9 Types of Photocatalysts

Photocatalysts may be classified into three groups:

1. Dye molecules used as homogeneous photocatalysts
2. Semiconductors used as heterogeneous photocatalysts and
3. A combination of dye and semiconductor species to give dye-sensitized photocatalysts.

Although the semiconductor photocatalyst functions in a manner similar to the molecular photocatalyst, it possesses several properties characteristic to the solid:

1. The semiconductor photocatalyst functions as a pool of electrons or holes, which is advantageous in multielectron transfer reactions, for example, in water splitting and carbon dioxide reaction.
2. Efficient charge separation occurs at the interface between the semiconductor and a liquid (or gas), owing to the electric field in the space charge layer of the semiconductor.
3. It is possible to modify the catalytic nature of the surface by deposition of redox catalysts such as Pt and RuO$_2$. Doping of rare earth materials is of recent interest to increase the catalyst efficiency.

2.10 Mechanism Involved in the Mineralization of Organics

When a light with energy greater than the band gap energy of a semiconductor is illuminated on its surface, the electron-deficient holes ($h^+$) are formed in the valance band and free electrons ($e^-$) will be available in the conductivity band. The possible mechanism of hydroxyl radical formation on the catalyst surface is depicted in Figure 2.5.
2.11 Supports in Photocatalysis

A number of nanostructured composite materials based on titanium dioxide has been synthesized and investigated for photocatalytic applications in recent years. Aluminum phosphate AlPO$_4$, titanium phosphate TiOHPO$_4$ and hydroxyapatite Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, activated carbon has been used as support materials for the deposition of nanocrystalline titanium dioxide. Supporting TiO$_2$ on high dispersing supporters is an option to prevent agglomeration [58]. The enhanced photocatalytic activity of these composite materials is due to the combination of a very high specific surface, chemical stability, minimal concentration of recombination centers in mesoporous matrixes, and the presence of anatase-enriched titanium dioxide nanoparticles. In heterogeneous catalysis, the active material like a metal, an oxide, or a sulphide is used usually in the form of small particles, typically in the nanometers range. The reason for this small size is that the surface area of the catalyst increases as the particle size decreases. Thus a high dispersion rate (a small particle size) is beneficial to the chemical activity per unit mass of materials. The focus of the present day research is to further increase the efficiency of a photocatalyst, which can be done by depositing the catalyst onto some solid supports. Also the problem of catalyst recovery can be tackled easily by using the catalyst loaded on a solid support.
The various functions that may be achieved by a support in a photocatalytic system and the typical examples of materials, which have been used the purpose have been described in Table 2.2. The properties that have to be selected for the choice of a material destined for performing a given combination of functions fall into two categories: textural and surface chemical.

Table 2.2 Chemical, Physical or structural functions potentially involved in a photocatalytic system and typical suitable materials [59]

<table>
<thead>
<tr>
<th>Function</th>
<th>Support</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Silicas, Alumina</td>
</tr>
<tr>
<td>Adsorbing the substrate to be transformed</td>
<td>♦</td>
</tr>
<tr>
<td>“caging” the substrate or the primary products</td>
<td>♦</td>
</tr>
<tr>
<td>Absorbing light</td>
<td></td>
</tr>
<tr>
<td>Supporting a particulate catalyst</td>
<td></td>
</tr>
<tr>
<td>Anchoring a molecular catalyst or a sensitizer</td>
<td></td>
</tr>
<tr>
<td>Separating redox intermediates</td>
<td></td>
</tr>
<tr>
<td>Organizing the system at supramolecular level</td>
<td></td>
</tr>
</tbody>
</table>

2.11.1 *Micro Textural Properties*

Texture is defined as a structure composed of a large number of more or less ordered similar elements or primitives in a compound. Textures are normally
ranging from micro to macro. Micro texture is a collative term for a material's crystallographic parameters and other aspects of microstructure: such as morphology, including size and shape distributions; chemical composition; and crystal orientation. The micro textural property includes the surface area, the particle size, the pore size, and the connectivity of the porous space. The surface area is an important parameter to be considered while selecting a support for a photocatalyst to know their reactivity or adsorption capacity. The particle size is of primary importance in order to evaluate the ability of the material to give stable suspensions in a liquid. Microporosity controls the cage effects, the molecular sieving properties and eventually the shape selectivity of the photoreaction.

2.11.2 Surface Chemistry

Surface chemistry is of particular importance to the field of heterogeneous catalysis. The surface chemistry also involved in the photocatalyzed reaction and in the photocorrosion process. The adhesion of gas or liquid molecules to the surface is known as adsorption. This might be due to either chemisorption or by physisorption. These too are included in surface chemistry. Important surficial reactions include sorption, ion exchange, dissolution, precipitation and heterogeneous oxidation/reduction processes occurring at the solid/aqueous interface of the catalyst can be known. The nature of the surface groups, their acids-base properties, their hydrophilic balance, their redox properties determine the surface charge of the support in water, its wettability, its interactions with adsorbed molecules, and its ability to form derivatives.

2.12 Application of Photocatalyst

The applications of the photocatalyst are given in Figure 2.6. The detail of the selected application of the photocatalyst is given in Table 2.3 [60].
Figure 2.6 Applications of Photocatalyst in different field [61]

Table 2.3 Selected application of photocatalysis

<table>
<thead>
<tr>
<th>Property</th>
<th>Category</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Self-cleaning</td>
<td>Materials for residential and office buildings</td>
<td>Exterior tiles, kitchen and bathroom components, interior furnishings, plastic surfaces, aluminium siding, building stone and curtains, paper window blinds</td>
</tr>
<tr>
<td></td>
<td>Indoor and outdoor lamps and related systems</td>
<td>Translucent paper for indoor lamp covers, coating on fluorescent lamps and highway tunnel lamp cover glass</td>
</tr>
<tr>
<td></td>
<td>Materials for roads</td>
<td>Tunnel wall, soundproofed wall, traffic signs and reflectors</td>
</tr>
<tr>
<td></td>
<td>Others</td>
<td>Tent material, cloth for hospital garments and uniforms and spray coating for cars</td>
</tr>
<tr>
<td>Air cleaning</td>
<td>Indoor air cleaners</td>
<td>Room air cleaner, photocatalyst equipped air conditioners and interior air cleaners for factories</td>
</tr>
<tr>
<td></td>
<td>Outdoor air purifiers</td>
<td>Concrete for highways, roadways and footpaths, tunnel walls, soundproof walls and buildings walls</td>
</tr>
<tr>
<td>Water purification</td>
<td>Drinking water</td>
<td>River water, groundwater, lakes and water-storage tanks</td>
</tr>
<tr>
<td></td>
<td>Others</td>
<td>Fish feeding tanks, drainage water and industrial wastewater</td>
</tr>
<tr>
<td>Anti-tumor activity</td>
<td>Cancer therapy</td>
<td>Endoscopic-like instruments</td>
</tr>
</tbody>
</table>
Self-sterilizing Hospital
Tiles to cover the floor and walls of operating rooms, silicone rubber for medical catheters and hospital garments and uniforms

Others
Public rest rooms, bathrooms and rat breeding rooms

2.13 Comparison of Advanced Oxidation Processes

Fundamental merits and problems are described for the advanced oxidation processes excluding the financial comparison. The details of the AOPs are discussed in Chapter 1. The brief description, advantages and disadvantages of AOPs are given in the Table 2.4.

Table 2.4 Comparison of advanced oxidation processes [62]

<table>
<thead>
<tr>
<th>AOP technology</th>
<th>Brief description</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Established technology</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| H₂O₂/O₃ | When O₃ and H₂O₂ are simultaneously applied to water they react to form hydroxyl radical. This OH oxidize most organic matters to form by products | • Efficient in treating waste water.  
• Supplemental Disinfectant.  
• More effective than O₃ or H₂O₂ alone.  
• Established technology for remediation applications | • Potential for bromate formation (controllable through adjustment of H₂O₂ and O₃ ratio and pH).  
• Require excess treatment of H₂O₂ due to potential of microbial growth.  
• May require ozone off gas and/or permitting. |

| O₃/UV | Hydroxyl radicals are generated when UV light is applied to ozonated water. Distraction of organics occurs by hydroxyl radical reaction coupled with direct photolysis and oxidation by molecular ozone. | • Supplemental Disinfectant.  
• More effective than O₃ or H₂O₂ alone.  
• More efficient for generating OH. Than H₂O₂/UV process for equal oxidation concentration. | • Energy and cost intensive process.  
• Potential for bromate formation (controllable through adjustment of H₂O₂ and O₃ ratio and pH).  
• Turbidity can interfere with UV light penetration.  
• May require ozone off gas and/or permitting.  
• Interfering compound |
<table>
<thead>
<tr>
<th>High energy electron beam</th>
<th>Electrons react with water molecules and forms intermediate like Hydroxyle radicals, hydrated electrons and hydrogen atoms. These intermediate reacts with organics to form byproducts.</th>
<th>• No potential for bormate formation.</th>
<th>• Public perception may prove to be significant obstacle to drinking water implementation.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cavitation</td>
<td>This process induce the formation of cavitation microbubbles. These bubbles implode violently after reaching a critical resonance size</td>
<td>• Simple design resulting in minimum maintenance cost.</td>
<td>• No full scale application exists.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Energy usage compared to AOP’s</td>
<td>• Supplement oxidants are required like O₃ and H₂O₂ to achieve</td>
</tr>
<tr>
<td>H₂O₂/UV</td>
<td>As in O₃ and UV process several synergistic mechanism results in the destruction of organics. The OH Route is the predominate removal mechanism. For H₂O₂ greater number of radicals is formed when MP-UV lamps are used compared to LP- UV lamps.</td>
<td>• No potential for bormate formation.</td>
<td>• Turbidity can interfere with UV light penetration.</td>
</tr>
<tr>
<td></td>
<td>• No off gas treatment is required.</td>
<td>• MP- UV and pulsed UV can serve as disinfectant.</td>
<td>• Less stoichiometrically efficient at producing OH than O₃/UV process.</td>
</tr>
<tr>
<td></td>
<td>• No limition by mass transfer relative to O₃ process.</td>
<td>• Full scale drinking water system exists in Salt Lake City.</td>
<td>• Interfering compound (eg: nitrate) can absorb UV light.</td>
</tr>
<tr>
<td></td>
<td>• No potential for potentional for bormate formation.</td>
<td>• No off gas treatment is required.</td>
<td>• Public perception may prove to be significant obstacle to drinking water implementation.</td>
</tr>
<tr>
<td></td>
<td>• MP- UV and pulsed UV can serve as disinfectant.</td>
<td>• No off gas treatment is required.</td>
<td>• No full scale application exists.</td>
</tr>
<tr>
<td></td>
<td>• Full scale drinking water system exists in Salt Lake City.</td>
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</tr>
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</tr>
<tr>
<td></td>
<td>• No potential for bormate formation.</td>
<td>• No off gas treatment is required.</td>
<td>• Supplement oxidants are required like O₃ and H₂O₂ to achieve</td>
</tr>
</tbody>
</table>
and generate high temperature nad high reactive radicals. Removal of organics occurs by thermal decomposition at the bubble water interface and by reaction with the radicals. Oxidation and cavitation is enhanced by addition of O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> using UV.

<table>
<thead>
<tr>
<th>TiO&lt;sub&gt;2&lt;/sub&gt; catalyst UV oxidation</th>
<th>Fentons reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>When TiO&lt;sub&gt;2&lt;/sub&gt; is illuminated by UV light valence band electrons excites towards the conduction band resulting in the formation of holes. These holes react with the water molecules that in turn produce hydroxyl and other radicals that oxidize the organic compounds. Formation of H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt; intermediate can also assist the overall oxidation process.</td>
<td>Radicals induced OH are produced when Fe(II) react with H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;. Destruction of organic matters occure by reaction with these radicals. Iron acts as a catalyst for this reaction.</td>
</tr>
<tr>
<td>No potentional for bormate formation.</td>
<td>No potentioal for bormate formation.</td>
</tr>
<tr>
<td>Can perform at higher wavelength than other UV oxidation process.</td>
<td>Not an energy intensive process compared to AOP’s that utilize O&lt;sub&gt;3&lt;/sub&gt; or UV.</td>
</tr>
<tr>
<td>No off gas treatment is required.</td>
<td>No off gas treatment is required.</td>
</tr>
<tr>
<td>No full scale application exists.</td>
<td>No full scale application exists.</td>
</tr>
<tr>
<td>Pre treatment is required to avoid fouling of TiO&lt;sub&gt;2&lt;/sub&gt;.</td>
<td>Iron extraction system is required.</td>
</tr>
<tr>
<td>If TiO&lt;sub&gt;2&lt;/sub&gt; is added as slurry then separation step is required.</td>
<td>Very less pH (&lt;2.5) is required to keep iron as solution.</td>
</tr>
<tr>
<td>Potentional for rapid loss of TiO&lt;sub&gt;2&lt;/sub&gt; activity, requiring catalyst onsite storage or regeneration method.</td>
<td>pH adjustment will increase operating and maintenance cost.</td>
</tr>
<tr>
<td>May require oxyger sparging.</td>
<td></td>
</tr>
</tbody>
</table>

Reaction mechanism is highly pH dependant, requires close monitoring and control.
2.14 Various Materials Employed in the Preparation of Photocatalytic materials

Titanium dioxide TiO$_2$, and ZnO, have been considered as promising materials for use in dynamic random access memories, dye sensitized solar cells, photocatalysts for environmental remediation and water splitting, coating materials to obtain superhydrophilic surfaces, and optical devices. One promising approach to develop new photocatalysts is the tuning of the optical properties of UV- light active catalysts by substitutional doping. There are too many materials which have been used as a support and as a dopant to enhance the efficiency of photocatalyst. A brief detail of some of the compounds which is been used as support and the details of the doping materials employed in the present work to increase the efficiency of photocatalyst is summerised below.

2.14.1 Carbon Nanomaterials

Natural carbon can exist in several forms. Most people know about graphite and diamond, but there is a third type- fullerene or carbon nanotube. By far the most common fullerene is C$_{60}$. It is also called a "buckyball". But there are some other relatively common fullerenes such as C$_{70}$, C$_{76}$, and C$_{84}$ [63, 64]. Figure 2.7 shows structure of various carbon polymorphs.

![Figure 2.7 Structures of Various carbon compounds](image)

Carbon Nanotubes, discovered in 1991 by Iijima of NEC Corporation [66], belong to the fullerene family, a molecular form of carbon, quite distinct from diamond and graphite. The easiest way to visualize how nanotubes are built up is to start with graphite, the most stable form of crystalline carbon. Graphite consists of layers of carbon atoms. Within the layers the atoms are arranged at the corners
of hexagons, which fill the whole plane (in the idealized case without defects). The carbon atoms are strongly (covalently) bound to each other (carbon-carbon distance $\sim 0.14$ nm), leading to a very large in-plane value for Young's modulus. The layers themselves are rather weakly bound to each other (weak long range van de Walls type interaction, interlayer distance of $\sim 0.34$ nm). Starting with only one layer of 2-dimensional graphite we end up with a cylinder with only one wall, a single wall carbon nanotube (SWNT). If more layers are taken, cylinders with multiple walls may result, a multi wall nanotube (MWNT) [56]. Figure 2.8 illustrates the formation of SWNT from graphite sheet.

![Figure 2.8 Illustration of Formation of a single walled carbon nanotube from a simple graphite sheet][67]

Thus cylindrical structures of carbon atoms take two forms: single-walled nanotubes (SWNTs) and multiwalled nanotubes (MWNTs), each of which has its advantages and disadvantages for different applications. SWNTs are essentially single layers of pure-carbon atoms rolled into a seamless tube capped at each end by half-spherical fullerene structures. They measure about 1 nm or $10^{-9}$m in diameter, and differ from MWNTs in that all of their atoms form a single covalently bound network. This gives SWNTs more distinctive electronic and optical properties. SWNTs tend to aggregate in bundles that are bound by van der Waals attraction. SWNT can be close-end and open-end. In close-end SWNT, the both ends have fullerene structure, i.e. consisting of hexagon and pentagon [68]. The structure of SWNT is given in figure 2.9.

![Figure 2.9 Bonding structure of a single walled nanotube (closed end)][67]
2.14.2 Titanium Dioxide

Titanium dioxide was first produced commercially in 1923 and accounts for approximately 70% of the total volume of pigment production. Relatively small quantities of titanium dioxide are used for non-pigmentary purposes. In 2004, worldwide production of titanium dioxide was 4.4 million tons.

Titanium is obtained from a variety of ores that contain ilmenite, rutile, anatase and leucoxene, which are mined from deposits located throughout the world. Most titanium dioxide pigment is produced from titanium mineral concentrates by the chloride or sulfate process, either as the rutile or the anatase form. Titanium dioxide occurs in nature as the well-known naturally occurring minerals rutile, anatase and brookite, additionally two high pressure forms, the monoclinic baddeleyite form and the orthorhombic $\alpha$-PbO$_2$ form have been found at the Ries crater in Bavaria. The most common form is rutile, which is also the most stable form. Anatase and brookite both convert to rutile upon heating [69]. Rutile, anatase and brookite all contain six coordinate titanium. The primary particles are typically between 0.2 and 0.3 μm in diameter, although larger aggregates and agglomerates are formed. Ultrafine grades of titanium dioxide have a primary particle size of 10–50 nm and are used predominantly as ultraviolet blockers in sunscreens and plastics, and in catalysts. Most commercial titanium dioxide products are coated with inorganic (e.g. alumina, zirconia, silica) and organic (e.g. polyols, esters, siloxanes, silanes) compounds to control and improve surface properties. Titanium dioxide has been used as been used as white paint and pigment due to its high refractive index and contrast ratio and it is also used in dye sensitized solar cells. Since discover of water splitting on TiO$_2$ electrode by Honda and Fugishima TiO$_2$ has become the most photocatalytic material [70-72]

2.14.3 Zinc Oxide

Zinc oxide is an inorganic compound with the formula ZnO. It usually appears as a white powder, nearly insoluble in water. The powder is widely used as an additive into numerous materials and products including plastics, ceramics, glass, cement, rubber (e.g. car tires), lubricants [73], paints, ointments, adhesives, sealants, pigments, foods (source of Zn nutrient), batteries, ferrites, fire retardants, etc. ZnO is present in the Earth crust as a mineral zincite; however, most ZnO
used commercially is produced synthetically. The mineral usually contains a certain amount of manganese and other elements and is of yellow to red color [74]. Crystalline zinc oxide is thermochromic, changing from white to yellow when heated. In recent years, ZnO has been widely studied due to its intrinsic properties suitable for optoelectronic applications. With a wide direct bandgap of 3.37 eV at room temperature, ZnO has been regarded as an excellent semiconductor material for UV detection [75].

In materials science, ZnO is often called an II-VI semiconductor because zinc and oxygen belong to the 2nd and 6th groups in the periodic table, respectively. This semiconductor has several favorable properties: good transparency, high electron mobility, wide bandgap, strong room-temperature luminescence, etc. Due to these properties ZnO has wide application in transparent conducting films, optical devices, photocatalysis sensors, solar cells, cosmetics, nanostructure, varistors, UV observers industrial additives and micro wave dielectrics [76-80]. These properties are already used in emerging applications for transparent electrodes in liquid crystal displays and in energy-saving or heat-protecting windows and electronic applications of ZnO as thin-film transistor and light-emitting diode.

2.14.4 Tungsten

Tungsten also known as wolfram is a chemical element that has the symbol W and atomic number 74. A steel-gray metal, tungsten is found in several ores, including wolframite and scheelite. It is remarkable for its robust physical properties, especially the fact that it has the highest melting point (3,422°C, 6,192°F), lowest vapor pressure and (at temperatures above 1,650°C) the highest tensile strength [81] of all the non-alloyed metals and the second highest of all the elements after carbon [82]. Tungsten is often brittle and hard to work in its raw state; however, if pure, it can be cut with a hacksaw [83]. Tungsten has the lowest coefficient of thermal expansion of any pure metal. The most common formal oxidation state of tungsten is +6, but it exhibits all oxidation states from -1 to +6 [84]. The pure form is used mainly in electrical applications, but its many compounds and alloys are used in many applications, most notably in light bulb filaments, X-ray tubes (as both the filament and target), and super alloys. Tungsten is also the only metal from the third transition series that is known to
occur in biomolecules [85, 86]. Tungsten compounds are used in catalysts, inorganic pigments (e.g. tungsten oxides), and also as high-temperature lubricants (tungsten disulfide).

### 2.14.5 Molybdenum

Molybdenum was discovered in 1778 by Carl Wilhelm Scheele and first isolated in 1781 by Peter Jacob Hjelm. Molybdenum is a Group VI chemical element with the symbol Mo and atomic number 42. It has the eighth-highest melting point of any element. Molybdenum is a transition metal with an electronegativity of 1.8 on the Pauling scale and an atomic mass of 95.9 g/mole [87]. It does not react with oxygen or water at room temperature. At elevated temperatures, molybdenum trioxide is formed in the reaction $2\text{Mo} + 3\text{O}_2 \rightarrow 2\text{MoO}_3$ [88]. Because of its lower density and more stable price, molybdenum is implemented in the place of tungsten [89]. Molybdenum rapidly oxidizes at temperatures above 760 °C (1,400 °F), making it better-suited for use in vacuum environments [90].

### 2.14.6 Cadmium

Cadmium is a chemical element with the symbol Cd and atomic number 48. It is soft, bluish-white, transition metal; cadmium is known to cause cancer and occurs with zinc ores. Cadmium is used largely in batteries and pigments. The most common oxidation state of cadmium is +2, though rare examples of +1 can be found. Cadmium is a soft, malleable, ductile, toxic, bluish-white bivalent metal. It is similar in many respects to zinc but reacts to form more complex compounds. In some semiconductors such as cadmium sulfide, cadmium selenide, and cadmium telluride, this can be used for light detection or solar cells. HgCdTe is sensitive to infrared. In molecular biology, it is used to block voltage-dependent calcium channels from fluxing calcium ions.

### 2.14.7 Chromium

Chromium is a chemical element which has the symbol Cr and atomic number 24. It was discovered by Louis Nicolas Vauquelin in the mineral Crocoite (lead chromate) in 1797. Chromium is mined as chromite (FeCr$_2$O$_4$) ore [91]. Chromium is a member of the transition metals, in group VI. The most common oxidation states of chromium are +2, +3, and +6, with +3 being the most stable.
+1, +4 and +5 are rare. Chromium compounds of oxidation state +6 are powerful oxidants. It is used as a catalyst, metal polish known as green rouge, in synthetic ruby, as a cleaning agent in magnetic tapes etc.

2.14.8 Neodymium

Neodymium was discovered by Carl F. Auer von Welsbach, a German chemist, in 1885. Neodymium, a rare earth metal, is present in Mischmetal to the extent of about 18%. The metal has a bright, silvery metallic luster; however, as one of the more reactive rare earth (Lanthanide) metals, it quickly oxidizes in air. Didymium, of which neodymium is a component, is used for coloring glass to make welder's goggles. Neodymium colors glass delicate shades ranging from pure violet through wine-red and warm gray. Light transmitted through such glass shows unusually sharp absorption bands. Glass containing neodymium can be used as a laser material to produce coherent light.

2.14.9 Manganese

Manganese is a chemical element, designated by the symbol Mn. It has the atomic number 25. Manganese is a gray-white metal, resembling iron. It is a hard metal and is very brittle, fusible with difficulty, but easily oxidized. Manganese metal and its common ions are paramagnetic. The most common oxidation states of manganese are +2, +3, +4, +6 and +7, though oxidation states from +1 to +7 are observed. Mn$^{2+}$ often competes with Mg$^{2+}$ in biological systems, and manganese compounds where manganese is in oxidation state +7 are powerful oxidizing agents. Manganese dioxide has been used since antiquity to oxidatively neutralize the greenish tinge in glass caused by trace amounts of iron contamination. MnO$_2$ is also used in the manufacture of oxygen and chlorine, and in drying black paints. In some preparations it is a brown pigment that can be used to make paint and is a constituent of natural umber.

2.14.10 Indium

Indium is a soft, ductile, malleable with metallic luster. Its colour is silvery white and it has a face-centered tetragonal structure with atomic number 49. The oxidation state of indium is 3. It was discovered by Reich and Richter, who later isolated the metal. Indium is most frequently associated with zinc materials, and it is from these that most commercial indium is now obtained; however, it is also
found in iron, lead, and copper ores. The first large-scale application for indium was as a coating for bearings in high-performance aircraft engines during World War II. Afterwards, production gradually increased as new uses were found in fusible alloys, solders, and electronics. In the 1950s, tiny beads of it were used for the emitters and collectors of PNP alloy junction transistors. In the middle and late 1980s, the development of indium phosphide semiconductors and indium tin oxide thin films for liquid crystal displays (LCD) aroused much interest. By 1992, the thin-film application had become the largest end use [92, 93].

2.14.11 Tin

The word "tin" is cognate with the German "Zinn," describing a soft, white metal with a low melting point. Its two main uses, both past and present, have been the coating of other metals, and in alloys. Tin (Sn), atomic number 50, atomic weight 118.70, is a member of column IVA of the periodic table, five elements whose outer electron configuration is $s^2p^2$. It easily combines with carbon (C), silicon (Si), germanium (Ge) and lead (Pb). Tin has the unusually low melting point of 231.85°C, and the unusually high boiling point of 2260, 2270 or 2687°C, according to different authorities. This great range makes it easy to form alloys without loss in vaporization. Tin exhibits the oxidation states +2 and +4, like lead. In the +2 state, it is basic and behaves like a metal. In the +4 state, it is amphoteric and can behave in an acidic manner in alkaline solution. The oxidation state +2 is called stannous, and the +4 state is called stannic. In foil was once a common wrapping material for foods and drugs; replaced in the early 20th century by the use of aluminium foil, which is now commonly referred to as tin foil. Tin becomes a superconductor below 3.72 K. In fact, tin was one of the first superconductors to be studied; the Meissner effect, one of the characteristic features of superconductors, was first discovered in superconducting tin crystals.

2.14.12 Silver

Silver is a precious metal and (like gold and copper) is classified as a coinage metal. The date of its discovery is not known, but it has been identified in jewelry, coins, and religious ornaments dating to more than 2,000 years ago from ancient civilizations in South America, Egypt, Mesopotamia, and China. The chemistry of silver was not well-known before 1880, although silver nitrate was used
medicinally in the 1800s. Recent research has recognized the highly reactive nature of the silver ion and its ability to form numerous inorganic and organic complexes. **Silver** is a chemical element with the chemical symbol **Ag** and atomic number 47. A soft, white, lustrous transition metal, it has the highest electrical conductivity of any element and the highest thermal conductivity of any metal. The metal naturally occurs in its pure, free form (native silver) and as an alloy with gold, as well as in various minerals, such as argentite and chlorargyrite. Silver's catalytic properties make it ideal for use as a catalyst in oxidation reactions, for example, the production of formaldehyde from methanol and air by means of silver screens or crystallites containing a minimum 99.95 weight-percent silver. Silver (upon some suitable support) is probably the only catalyst available today to convert ethylene to ethylene oxide (later hydrolyzed to ethylene glycol, used for making polyesters)—a very important industrial reaction.

Oxygen dissolves in silver relatively easily compared to other gases present in air. Attempts have been made to construct silver membranes of only a few monolayers thickness. Such a membrane could be used to filter pure oxygen from air and water.

### 2.14.13 Iron

Iron is a chemical element with the symbol **Fe** and atomic number 26. Iron is a group 8 and period 4 elements. The melting point of iron is 1535°C, boiling point is 2750°C, specific gravity is 7.874 (20°C), with a valence of 2, 3, 4, or 6. Pure iron is chemically reactive and corrodes rapidly, especially in moist air or at elevated temperatures. Four allotropic forms, or ferrites, are known: a, b, g, and d, with transition points at 770, 928, and 1530°C. The ‘a’ form is magnetic, but when iron is transformed into the b form, the magnetism disappears, although the lattice remains unchanged.

### 2.15 Different Techniques used for the Preparation of Photocatalytic Materials

There are too many techniques which are in use for the synthesis of photocatalytic materials. The properties of the semiconductor dependent on their sizes, morphologies, degree of crystallinity and crystallographic structures [94-98]. Therefore controlled preparation of nanoparticles is of great interest and importance in the field of chemistry and Material Science [99] for the preparation
of the photocatalyst. Several methods such as hydrolysis (chemical precipitation) [100], reverse micelles (microemulsion) [101-103], sol-gel [103, 104], and hydrothermal crystallization [104-113], have been used to prepare TiO$_2$ nanoparticulates. All these methods have been briefly discussed with respect to the synthesis of TiO$_2$.

2.15.1 Chemical Precipitation

Precipitation is a unit process in which a settleable and/or filterable solid is formed by the chemical joining of two or more inorganic dissolved chemical species. This is the most widely used method in the synthesis of TiO$_2$. The aqueous titanium dioxide precipitate prepared by the addition of titanium (IV) chloride in aqueous hydrochloric acid with ammonia solution at 0°C. The precipitate obtained is recovered and washed with deionised distilled water to remove residual amounts of acid. The product is then ultrasonicated to obtain a stable titanium dioxide solution. The solvent is removed by rotary evaporation at room temperature. The product obtained is white powder which is finally calcined between 200 and 600°C. After thermal treatment, the titanium dioxide powder becomes insoluble in colloidal form in water, but their adsorption capability is retained. Various workers have modified this technique in order to obtain desired morphology of the nanoparticulates [114, 115].

2.15.2 Reverse Micelles

Reverse micelles have attracted significant attention in the recent past. Their utility has been demonstrated in various chemical systems. Reverse micelles are used as size-controlling microreactors for a variety of aqueous chemical reactions. [116-118] this method of preparing mesoporous TiO$_2$ has been reported by Stathatos [119]. Nanosized pure TiO$_2$ particles of high crystallinity and high surface area can be prepared by hydrolysis of metal alcoxide in TX-100/isoctane reverse micellar solutions as reaction media. The size of the ultrafine particle will be controlled by changing the water content of the reverse micellar solution and 4-10nm particles were prepared. The solution will appear turbid, however, it clears by the addition of titanium isopropoxide. The resultant alkoxide solution is kept stirring at room temperature for hydrolysis reaction resulting in the TiO$_2$ sol. After the solvent is removed the TiO$_2$ powder is heat treated or sintered in air up to 500°C.
2.15.3 Sol Gel Technique

The sol-gel process is a versatile solution process for making ceramic and glass materials. In general, the sol-gel process involves the transition of a system from a liquid "sol" (mostly colloidal) into a solid "gel" phase. A sol is a dispersion of the solid particles (~ 0.1-1 mm) in a liquid where only the Brownian motions suspend the particles. A gel is a state where both liquid and solid are dispersed in each other, which presents a solid network containing liquid components. The sol-gel coating process usually consists of 4 steps:

- The desired colloidal particles once dispersed in a liquid to form a sol.
- The deposition of sol solution produces the coatings on the substrates by spraying, dipping or spinning.
- The particles in sol are polymerized through the removal of the stabilizing components and produce a gel in a state of a continuous network.
- The final heat treatments pyrolyze the remaining organic or inorganic components and form an amorphous or crystalline coating [120-123].

When the principle of Sol-Gel method is applied to the production of the titanium alkoxide of titanium, that is the organic compound of titanium are used in the presence of alcohol or some other chelating agents such as dihydric alcohol, carboxylic acid and β-diketonates to control hydrolysis [103, 104, 124-126]. Titanium solution is produced through the process of the hydrolysis that dispersed the small particles of hydroxide of titanium. The sol is sintered along with the substrate to be crystallized, and thus the titanium dioxide is formed.

2.15.4 Hydrothermal Technique

The word hydrothermal deriver from a Greek word “hydros” meaning water and “thermos” means heat. This is one of the oldest techniques of growing crystals. Sir Roderick Murchison (1792-1871), a British Geologist, was the first to use the term hydrothermal in the mid 19th century to describe the action of water at elevated temperature and pressure in bringing about changes in the earth’s crust leading to the formation of various rocks and minerals [127]. Hydrothermal technique is a soft chemistry or soft solution processing, in a single-step process that is more environmentally friendly than vacuum or chemical vapor deposition.
In a typical hydrothermal run, the starting precursors for the synthesis of TiO$_2$ are taken in the Teflon liner in a definite molar proportion. The liner is tightly closed and placed inside the respective autoclave. A stainless steel washer is placed on the upper portion of the liner and then the cap of the autoclave provided with a spring system inside (to hold the liner tightly) is used to close the autoclave tightly. Finally the autoclave assembly is placed inside the oven at a desired temperature over a definite experimental duration.

After the treatment, the products are removed and rinsed with mild acid when alkaline solvents are used in the hydrothermal experiment and mild base when acidic solvents are used to remove any residual alkalinity/acidity in the product and then thoroughly washed with double distilled water to remove any persisting acid or alkali till the pH of the wash becomes neutral. The product obtained is ultrasonicated for two to three cycles of 5 minutes each to disperse the particulates or to make them unagglomerated. And finally the obtained particulates are dried at very low temperature such as 30$^\circ$C to 40$^\circ$C.

The major advantages of the use of hydrothermal technology in material synthesis are as follows:

- High quality and purity of the products
- Low temperature processing in a closed system
- Decrease in agglomeration between particles
- Control of size and morphology (monodispersed particulates)
- Uniformed composition and purity of the products
- The hydrothermal run products do not require further high temperature treatments like calcinations or pyrolysis.
- Does not require complicated and expensive experimental setup
- Environmentally benign.

2.16 Motivation for the Present Work

The fast pace of industrialization, galloping demand for energy and reckless exploitation of natural resources during the last century have been mainly responsible for aggravating the problem of environmental pollution, which is now
set to pose serious threat to biodiversity and ecosystem processes. Water pollution has many sources. The most polluting of them are the city sewage and industrial waste discharged into the rivers.

Waste water from manufacturing or chemical processes in industries contributes to water pollution. Industrial waste water usually contains specific and readily identifiable chemical compounds. During the last fifty years, the number of industries in India has grown rapidly. However water pollution is concentrated within a few subsectors, mainly in the form of toxic wastes and organic pollutants.

The immediate removal of such hazardous pollutants from its sources of generation, followed by treatment, reuse, or dispersal into the environment is necessary to protect public health and environment. If contaminants are removed from the aqueous phase to render water safe for discharge or useable for recycle, an early question is into what phase are they delivered? Conventional microbiological degradation desperately needs the assistance of new technologies, like for instance advanced oxidation processes, to degrade hazardous persistent materials by chemical oxidation. The central attraction of advanced oxidation processes (AOP) is that organic contaminants are commonly oxidized to CO₂. The relatively small amounts of organic matter, and the ultimate fate that organic matter might experience under other treatment regimes, does not imply a significant contribution to greenhouse gases. Thus, the AOPs offer an attractive option to use the gas phase as the carbon sink. Heterogeneous photocatalysis in the presence of semiconductor materials is an AOPs developed recently. This new method has shown to be effective for the oxidation of a lot of organic compounds under mild temperature and pressure conditions with a measurable rate up to negligible concentration level. The interest in heterogeneous photocatalysis is shown by the increase in number of publications. Over 2000 papers have been published on this topic since 1981 to 1997 [129] and it continues to dominate the research today. The output of such an intensive research is a large number of publications [130 - 171]. The visible light photocatalysis is an interesting topic where the tuning of the band gap of the semiconductor photocatalyst is done. This is because the band gap of TiO₂ is 3.03 eV for rutile and 3.18 for anatase and three different values (3.1, 3.2, and 3.3 eV) have been reported for the optical band gap of zinc oxide and only UV light can be utilized for the photodegradation at this range. Since the UV
light only accounts for about 4% of the solar radiation energy while the visible light contributes about 50%, the inability to utilize visible light limits the efficiency of solar photocatalyst for the degradation process. In order to resolve the above listed problems and enhance the photodegradation property of the photocatalyst, continuous efforts are being made to promote the photocatalytic activity and enhance the visible light response. Addition of electron donors (hole scavengers), addition of carbonate salts, noble metal loading, metal ion doping, anion doping, dye sensitization, composite semiconductors, metal ion implantation etc, were investigated and some of them have been proven to be useful to enhance photocatalytic property.

2.17 Objectives of the Present Work

The objectives of the present work are as follows

- Literature survey on the photocatalytic material, their preparation techniques, characterization techniques and their application in different field.
- Preparation of highly designer photocatalytic compounds under hydrothermal conditions.
- Hydrothermal preparation of photocatalytic compounds under mild pressure and temperature conditions. Preparation of designer photocatalytic particulates like (1:1) TiO$_2$: CNT, ZnO: CNT, TiO$_2$: MoO$_3$, ZnO: MoO$_3$ composites and metal oxide doped ZnO compounds, W$^{+6}$:TiO$_2$, Ti$^{+4}$: AlPO$_4$ etc., composites. Preparation of metal oxide doped ZnO compounds thereby reducing the band gap of the ZnO which can act as a visible light photocatalyst.
- The effect of pressure and temperature conditions, pH of the starting media, type of solvent, metal oxide source, experiment duration, etc are studied in detail.
- Characterization of the prepared photocatalytic materials using powder X-ray diffractometer, fourier transform IR spectrometer, scanning electron microscope, photoluminescence spectroscopy, dynamic light scattering and photoabsorption studies.
• To study the photodegradation efficiency of photocatalyst prepared using some commercial dyes and to study the applicability of these prepared photocatalytic compounds in the treatment of real time industrial effluents.

• To study the effect of these prepared photocatalytic compounds under various rate determining parameters like initial dye concentration, amount and type of the catalyst, pH of the aqueous medium, intensity and type of the illuminating light and the solution temperature on the degradation.

• To propose the degradation mechanism for some of the commercial dyes employed in the degradation studies.

• To highlight the efficiency of this technology and the photocatalytic compounds prepared in the degradation of industrial effluent and organics.
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