2.1 Introduction

Photocatalytic oxidation is a process where semiconductor, upon absorption of a photons, act as catalyst producing highly reactive radicals. These are mainly hydroxyl radicals, which can oxidize organic compounds and inactivate microorganisms. Thus organic molecules/microorganisms are decomposed to form carbon dioxide, water and mineral acids as final products. A variety of organic compounds/microorganisms can be photocatalytically oxidized and eventually mineralized according to the following general reaction [1-9]:

\[ \text{Organic compound / Microorganism} + O_2 \rightarrow (\text{ZnO} + h\nu) \rightarrow CO_2 + H_2O + \text{Mineral Acids} \]

This chapter describes the theoretical aspects of various semiconductor terminologies, processes and degradation mechanisms related to purification of water.

2.2 Some important terminologies

In this section, some important terminologies are defined for the convenience to discuss experimental results.

i) Band Model

In order to describe electron transfer to or from a semiconductor, it is desirable to utilize the concept of band model. The band model of a solid stems directly from the statistic distribution of atomic energy levels. According to Pauli exclusion principle, the energy levels of identical overlapping electronic orbitals cannot be equal. Analysis shows that the discrete energy levels of the atoms forming the solid broaden when the orbitals overlap; forming bands of energy levels with about \( 2 \times 10^{22} \) levels in each band when there is the order of \( 10^{22} \) atoms in the crystal. Bands are large number of orbitals with different energy levels. These bands are again divided into two types i.e. valence band and conduction band. The aggregate of orbitals occupied by valence electrons is called the valence band (VB) of the solid. The band associated with the first excited state, normally unoccupied by electrons, is called the conduction band (CB) of the solid. The energy gap between conduction and valence band of a solid is called the bandgap energy. One important property of semiconductor is that, when a photon of energy greater than or equal to the band gap of semiconductor is incident on it, the electron and hole pairs are generated.
ii) **Fermi level** \( (E_f) \)

The Fermi Level and the Fermi distribution describe the distribution of electrons and holes among the available energy levels in the solid. According to first order approximation, all the energy levels below the Fermi level are occupied by electrons, while all the energy levels above Fermi level are unoccupied by electrons. From a statistical point of view, Fermi level is the average energy of electrons and electrons moving from the solid to ions in solution originate with a free energy of \( E_f \). From a chemical point of view, the Fermi level is the electrochemical potential of electrons in the solid.

iii) **Photoelectrochemical (PEC) solar cell**

There are several methods of collecting and converting solar energy viz. photovoltaic, photoelectrochemical, photothermal and photosynthetic. Out of these routes the photoelectrochemical system is easiest one. A PEC effect is defined as one in which irradiation of electrode/electrolyte system produce a change in electric potential \((E_{oc})\) or in the current flowing in external circuit \((I_{sc})\) \([10]\)

Early semiconductor electrochemistry studies \([11]\) have shown that the distribution of potential at the semiconductor – electrolyte interface is almost similar to that at a simple p-n junction. A direct conversion of solar energy into electrical energy using a semiconductor electrolyte interface was demonstrated by Gerischer \([12]\). These are generally known as photoelectrochemical solar cells.

**Semiconductor-electrolyte (S-E) interface**

When an appropriate semiconductor is immersed in an appropriate electrolyte the excess charge residing on the electrode surface must be exactly balanced by an equal charge of opposite sign on the solution side. This can happen by charge transfer across the electrode – electrolyte system.

When semiconductors are brought into contact with liquid, due to the difference in Fermi levels of the two phases, charged planes or space charge layer almost inevitably form at the interface to reach an equilibrium. A schematic diagram of this interface is shown in Fig. 2.1.

**Space charge region in the semiconductor**

When a semiconductor is dipped into an electrolyte, the junction is characterized by the presence of a space charge layer in the semiconductor adjacent to the interface.
with the electrolyte. For semiconductors, the chemical potential of electrons is given by the Fermi level in the semiconductor. For liquid electrolytes, the chemical potential of electrons is determined by the redox potential of redox couples present in the electrolyte. If the initial Fermi level in n-type semiconductor is above the initial Fermi level in the electrolyte, then equilibration of the two Fermi levels occurs by transfer of electrons from semiconductor to the electrolyte. This produces a positive space charge layer in the semiconductor. As a result, the conduction and valence band edges are bent upwards, establishing a potential barrier against further electron transfer into the electrolyte. A reverse effect will occur with p-type semiconductors having an initial Fermi level below that of the redox potential.

**Figure 2.1 Schematic diagram of semiconductor liquid interface**

Fermi levels, $E_{f,\text{semi}}$ and $E_{f,\text{redox}}$ are at different levels resulting in electron transfer from semiconductor to electrolyte which establishes the equilibrium. This flow of electrons results in the accumulation of ions in the semiconductors to form the space charge region near the interface in the semiconductors. A strong local electric field is developed and band bending takes place. The potential drop in the semiconductor space charge layer depends on the difference between the Fermi levels of semiconductor and the redox electrolyte, if the former is free from excess charge.

**Helmholtz double layer**

Helmholtz double layer is a dense layer of ions stuck to the electrode. In this region, the potential varies linearly with distance. This dense layer is divided into inner and outer Helmholtz planes. The inner Helmholtz plane (IHP) is adjacent to the
electrode surface and consists of completely oriented water dipoles and specifically adsorbed (or contact-adsorbed) ions. The orientation of water dipoles depends on the specific interaction with the electrode surface as well as the electric field. Large ions with negative free energy of contact adsorption are expected to be contact-adsorbed. In aqueous system, the cations react rather strongly with the water molecule and their inner hydration sphere is retained. This limits their closest distance of approach to the electrode. They are thus separated from the electrode by approximately one or two water molecules. On the other hand, anions interact weakly with water; hence hydration sheath is not covered on them. Thus the closest distance of approach could correspond to direct contact; they can be a part of IHP. The outer Helmholtz plane (OHP) consists of solvated ions (usually cations) at the closest distance approach from the electrode interface. The OHP thus consists of partly ionized water dipole layers. Bockris et al. [13] developed a model of electrode-electrolyte interface and is shown in Fig. 2.2 (a). In absence of contact adsorbed ions the potential distribution is as shown in Fig. 2.2 (b). In presence of contact adsorbed ions, it can be seen from Fig. 2.2(c) that the potential distribution changes across the double layer. OHP (X=X_2) is the site at which non-specifically adsorbed ions arrive to take part in the charge transfer processes.

Gouy-Chapman diffuse layer

The size of the ions forming the outer Helmholtz plane (OHP) is such that the sufficient number of them cannot neutralize the charge on the electrode. Therefore, the remaining charges are held with increasing disorder as the distance from the electrode surface increases and the electrostatic forces become weaker and dispersion by thermal motion is more effective. These less ordered charges forcing opposite to that on the electrode constitute the diffuse part of double layer. Thus all the charges, which neutralize that on the electrode, are held in a region between OHP and the bulk of the electrolyte. The additional charges required to neutralize the total charge on the electrode forms the Gouy-Chapman layer or diffuse layer.

The region of the photo-potential can now be understood by considering the changes that occur at such an interface by the absorption of band gap radiation. Irradiation of the semiconductor electrolyte interface is produces electron hole pairs, the electrons being promoted to the conduction band. The potential difference across the space charge layer causes the electrons to move towards the bulk of the semiconductor at this is downhill path for the electrons in a n-type semiconductor.
Fig. 2.2 (a) Electrode Electrolyte Interface, (b) Potential Distribution across the double layer & (c) The schematic of electrodes immersed in electrolyte.

Photoinduced charge transfer across S-E junction

The minority carriers h+ moves towards the surface of the electrolyte. This movement of the charge carriers in the field of the space charge layer counteracts the band bending, causing as partial return to the charge carrier distribution as before band bending and is shown in Fig. 2.3.
The result is the development of a Fermi level in the semiconductor called the photon Fermi level which is no longer equal to the redox potential of the electrolyte \( E_{F(Photo)} - E_{F(redox)} \) goes up as the photo-potential on illuminating the interface with light \((hv \geq Eg)\). A photocurrent can now the observed by connecting the photoanode to a suitable counter electrode. The photocurrent depends on the absorption coefficient of the semiconductor, width of the space charge region, hole diffusion length, area of illuminated electrode, photon energy and radiation intensity. Under short circuit conditions the Fermi levels of the semiconductor and the potential of the redox couple of the solution are equalized and a net charge flows during the illumination.

\[
\begin{align*}
\text{Semiconductor} & \quad \text{Electrolyte} \\
\text{(In dark)} & \quad \text{(In dark)} \\
E_c & \quad E_{c^*} \\
E_f & \quad E_{f^*} \\
E_v & \quad E_{v^*} \\
W_{Ox} & \quad E_{f, \text{redox}} \\
W_{Red} & \\
h^+ & \quad e^- \\
h_v &
\end{align*}
\]

**Fig. 2.3** The position of bands under illumination responsible for photo induced charge transfer

**iv) Flat band potential**

The Fermi level of a semiconductor can be controlled by an applied external potential bias. The flat band potential is the applied potential, when the bands of the semiconductor are flat. In other words, there is no band bending on the semiconductor side of the interface. By measuring the flat band potential, the band edge of semiconductor can be determined. For most oxide semiconductors their flat band potentials have a Nernstian-type pH dependence in aqueous media.
v) On-set potential

For a n-type semiconductor electrode, when the applied potential is below the conduction band edge (or below the flat band potential), there would be no electrons withdrawn from the semiconductor. As a result, there is no anodic current observed even if there are large amount of electrons under illumination. The on-set potential refers to the potential at which anodic photocurrent starts to be measured. In ideal cases, the on-set potential approximates the flat band potential.

2.3 Classification of photon/semiconductor systems

In semiconductors, the valence electrons have little chance of being thermally excited and only a small portion of electrons with high kinetic energy can reach the conduction band resulting in low electrical conductivity. When the two bands of a solid material are further separated to larger than 3 eV, similarly the free electron concentration is further lowered and such material is regarded as insulator. However, this definition is not rigid, since, for example ZnO is still considered to be semiconductor even though it has a band gap of 3.2 eV. Light excitation of a semiconductor promotes electrons from the valence band to the conduction band. In metals, where there is a continuum of energy states, the light generated electrons deactivates easily and the lifetime of the electron/hole pair is so short that they cannot be harvested. The existence of band gap in semiconductors prevents rapid deactivation of the excited electron/hole pairs, which can be deactivated only by recombination. This assures that an electron/hole pair lifetime is sufficiently long to participate in interfacial electron transfer [14].

Depending on the methods of harnessing the light generated electron/hole pairs and the purpose of the applications, few areas of studies have emerged from photon/semiconductor interactions. According to the types of semiconductors involved, the areas of studies can be classified in to bulk semiconductor systems and particulate semiconductor systems (Fig. 2.4). When the size of semiconductors is down to nanometer scale or sub-micrometer scale, they display a number of different properties to those of the macro-size semiconductors. The former systems are defined as particulate semiconductor systems and the latter are defined as bulk (thick or thin film) semiconductor systems. In history, the early research focused mainly on the bulk semiconductors. The bulk semiconductor theory has been well established and various applications have been extensively studied [15].
The particulate semiconductors refer to semiconductor with particle sizes ranging from nanometer to sub-micrometer. The ZnO nanoparticles photocatalysis in visible light has become one of the most active research areas in the past two decades. Since the successful application of nanoparticle ZnO film electrode as photocatalyst in water purification. Moreover it can be used for the total destruction of organic compounds in wastewater [16].

### 2.4 Energetics and redox power of semiconductors

Semiconductor can absorb light with energy higher than certain energy thresholds that is determined by the bandgaps \( E_g \) of semiconductors. Once photons are absorbed, photoelectrons and photoholes are formed. The photogenerated electrons and holes quickly relax to the bottom of the conduction band and the top of the valence band respectively by dissipating their kinetic energy. These electrons and holes can be used to drive a redox reaction. Thermodynamically, the energy level of the conduction band edge \( E_{cs} \) is a measure of the reduction strength of electrons in the semiconductor, whereas that of valence band edge \( E_{vs} \) is a measure of the oxidation power of holes in the semiconductor.

Different semiconductors possess different band edge energies. The higher the valence band edge potential, the higher oxidizing power its holes. For a semiconductor to have ‘universal’ photocatalytic reactivity toward different organic compounds,
thermodynamically its valence band edge must sit at a relatively high potential. Small band-gap semiconductors have a better absorption spectrum match with solar emission spectrum. From an utilization of solar energy point of view, the small band gap semiconductors would be a better choice. However, small band gap semiconductors normally do not have high valence band potential. Compounding this problem is that many semiconductors, particularly, the small band gap semiconductors suffer from serious chemical corrosion and photocorrosion when used as photocatalysts [17-18]. Therefore, the selection of semiconductor photocatalysts, depending on the application, often involves the compromise between a number of factors, such as high oxidizing power, good solar spectrum coverage and chemical/photochemical stability.

2.5 Fundamentals of photocatalysis

Principle of photocatalysis

The band gap is characteristic for the electronic structure of a semiconductor and is defined as the energy interval (ΔEg) between the valence band (VB) and the conduction band (CB). According to the band gap model [19], as shown in Fig 2.5, VB electrons are transferred to the CB, when the semiconductor is illuminated with photons having energy content equal to or higher than the band gap, creating electron–hole pairs (1). After migration to the semiconductor surface (2), electron–hole pairs may induce redox reactions with adsorbates having suitable redox potentials (3). From a thermodynamic point of view, VB holes can oxidize adsorbed compounds if the redox potential of the VB is more positive than that of the adsorbates. Similarly, CB electrons can reduce adsorbed species, if they have a more negative redox potential than the adsorbates. In the absence of suitable adsorbates, electron–hole pair recombination occurs with release of thermal energy and/or light (4). The rate of a photocatalytic reaction especially depends on the type of the photo catalytic semiconductor and on the light radiation that is used in its initiation [20]. Further factors that influence a photocatalytic reaction are:

- pH of the medium with which the semiconductor surface is in contact;
- Amount of the photocatalyst/area of the thin film influencing the reaction kinetics;
- Stream of photons, as oversupply of light accelerates electron–hole recombination;
• Temperature, higher temperatures cause frequent collision between the semiconductor and the substrate

![Diagram of band gap model]

**Figure 2.5 Schematic representation of the “band gap model.”** (1) Photo induced electron–hole pair creation; (2) charge migration to the surface; (3) redox reactions; (4) recombination. VB and CB represent valence band and conduction band, respectively.

Simply speaking, the photocatalyst is a semiconductor that on surface of which a strong oxidation occurs by the energy in light. ZnO irradiated with near ultraviolet light below λ < 385 nm, which are generated by UV-lamps and even common fluorescent lamps, free hydroxyl radicals can be generated. The oxidation can oxidize most organic and inorganic pollutants and therefore can perform functions such as anti-bacteria/anti-virus, deodorization, exhaust gases removal and self-cleaning.

Photocatalysis has great potential as an alternative water treatment method due to the possibility to remove by-product precursors. This process also ensures the public health safety of drinking water due to its ability to inactivate micro-organisms. Photocatalytic processes for water treatment are divided into two groups:

**a) Homogeneous photocatalytic oxidation**

In the homogeneous system, photocatalysis of either hydrogen peroxide or ozone under UV illumination supplies hydroxyl radicals. During this process continual consumption of oxidant occurs, e.g. UV/hydrogen peroxide.

**b) Heterogeneous photocatalytic oxidation**

Comparatively, in the heterogeneous process, hydroxyl radicals are produced from the redox reaction between photo-excited electrons and electron acceptors on the surface of the semiconductor photocatalyst. The process is catalytic and allows the
semiconductor to remain active for long periods of time. Therefore, heterogeneous photocatalysis is advantageous, e.g. such as UV/semiconductor photocatalysis.

2.6 Photoelectrocatalysis

Photocatalysis can be further enhanced by applying a potential to the ZnO film. This induces an electric field within the particles increasing charge separation. If one can remove the photogenerated electrons from the semiconductor particle (e.g. by application of an electric field), it is possible to increase the efficiency of oxidation at the semiconductor electrolyte interface.

Photoelectrocatalysis on ZnO represents a promising alternative technology for degradation of organic pollutants and inactivation of microorganisms in water. It is based on the photogeneration of separated electrons and positive holes. These charge carriers either recombine or move to its surface where they can react with adsorbed molecules. Positive holes typically oxidize organic compounds, inducing their oxidative degradation, while electrons mainly reduce molecular oxygen to superoxide radical anions. Recombination of photogenerated positive holes and electrons is responsible for the relatively low quantum yield of photocatalytic degradation.

![Figure 2.6 Potential distribution for a semiconductor-electrolyte interface](image)

Upon application of an electrical bias to the ZnO film, CB electrons are removed to the back contact. This promotes charge separation and increases charge transfer through the film. As electrons are removed, hydroxyl radical production is increased therefore reducing the electrostatic repulsion of negatively charged particles. This is known as the electrical double layer effect, whereby the electrode becomes positively charged relative to the solution nearby, decreasing the local cation concentration within the Helmholtz layer. The potential varies with distance from the electrode surface and the electrolyte solution without a change in applied potential as shown in Fig. 2.6.
2.7 Mechanism and Reaction Kinetics

2.7.1 Mechanism of photocatalysis on a ZnO thin film

ZnO is the last member of the 3d –transition metal oxide series with Zn having completely filled 3d orbitals (3d<sup>10</sup>). The valence band of ZnO consists of only d states and the conduction band consists of s-p hybridized orbitals. When ZnO is exposed to near UVA light, electrons in the valence band are excited to the conduction band leaving behind holes. These excited electrons in the conduction band are now in an s-p hybridized state. Thus holes are in a pure 3d state (VB) and excited electrons are in a s-p hybridized state. Hence nature of valance and conduction band is completely different, this is called dissimilar parity. Under such dissimilar parity, transition probability of electron to the valence band reduces hence reduction of e<sup>-</e<sup>-h<sup>+ recombination. Such condition for the other 3d transition metal oxide members does not occur since 3d – states are present in both the valence as well as conduction bands. The photoexcited e<sup>-</e<sup>-h<sup>+ pair has similar parity and hence recombination is faster. Thus TiO<sub>2</sub> and ZnO are only two among the 3d transition metal oxide semiconductors which remain stable on photo-oxidation [21].

Figure 2.7 Schematic representation of some of the main processes occurring on a semiconductor particle. (a) Absorption of photon and electron–hole pair formation and migration of electron and hole: arrows marked (1) and (2) show electron–hole recombination at surface and bulk respectively, and those marked (3) reduction of acceptor and (4) oxidation of donor. (b) On absorption of photon of energy hn, electrons are excited from valence band (VB) to conduction band (CB). There is transfer of electron to oxygen molecule to form superoxide ion radical (·O<sub>2</sub>–2) and transfer of electron from water molecule to VB hole to form hydroxyl radical (·OH)[ 17].
The band gap value of ZnO is 3.2 eV. Back side illumination with UVA light (λ < 385 nm), will excite electrons from valence band to the conduction band, producing an e−-h+ pair. Photocatalyst is characterized by its ability to absorb simultaneously two reactants, which can be reduced and oxidized by efficiently absorbing light (\( hν ≥ E_g \)) and ability to transfer electron from conduction band to the adsorbed particle (acceptor), which is governed by band gap position of the semiconductor and redox potential of the adsorbate. From the thermodynamic point of view, the redox potential of the adsorbate (acceptor) should be below the CB of the semiconductor. If the adsorbate is donor, then the potential level of the adsorbate (donor) should be above the VB position of the semiconductor in order to donate an electron to hole in the VB. The process of transfer of electron from the semiconductor to the adsorbate is called the reduction mechanism and the process of transfer of electron from the adsorbate to the semiconductor is called oxidation mechanism. Thus, the energy level at the bottom of CB determines the reduction ability of photolecetrons and the energy level at the top of VB determines the oxidation ability of photoholes. If the adsorbed couples are considered to be water and dissolved oxygen, then water gets oxidized by positive holes and it splits into •HO and H+. As oxygen is easily reducible, reduction of oxygen by photoelectrons of the conduction band results in generation of superoxide radical anions (•O−2), which in turn reacts with H+ to generate •HO2. On subsequent reaction with electron to produce hydrogen peroxide (HO−2), and then with hydrogen ion, a molecule of H2O2 is produced [22].

Possible photocatalytic process in photodegradation phenomenon can be written as follows. Photocatalytic process begins with absorption of photon (hν)

\[
ZnO + hν \rightarrow ZnO(e^- + h^+) \tag{2.2}
\]

Reactions involving conduction band e−

\[
ZnO(e^-) + O_2 \rightarrow ZnO + O^2^- \tag{2.3}
\]

\[
ZnO(e^-)^+ + O^2^- + 2H^+ \rightarrow ZnO + H_2O_2 \tag{2.4}
\]
\[
\text{ZnO}(e^-) + H_2O_2 \rightarrow \text{ZnO} + \cdot \text{OH} + OH^- \quad (2.5)
\]

\[
\cdot O^- + H_2O_2 \rightarrow \cdot \text{OH} + O^- + O_2 \quad (2.6)
\]

\[
\cdot O^- + H^+ \rightarrow \text{ZnO} + \cdot \text{HO}_2 \quad (2.7)
\]

\[
\text{ZnO}(e^-) + \cdot \text{HO}_2 \rightarrow \text{ZnO} + \text{HO}_2^- \quad (2.8)
\]

\[
\text{HO}_2^- + H^+ \rightarrow H_2O_2 \quad (2.9)
\]

\[
2\cdot \text{HO}_2 \rightarrow O_2 + H_2O_2 \quad (2.10)
\]

Reactions involving valence band h+

\[
\text{ZnO}(h^+) + H_2O_{\text{ads}} \rightarrow \text{ZnO} + \cdot \text{OH}_{\text{ads}} + H^+ \quad (2.11)
\]

\[
\text{ZnO}(h^+) + 2H_2O_{\text{ads}} \rightarrow \text{ZnO} + 2H^+ + H_2O_2 \quad (2.12)
\]

\[
\text{ZnO}(h^+) + \text{OH}^+_{\text{ads}} \rightarrow \text{ZnO} + \cdot \text{OH}_{\text{ads}} \quad (2.13)
\]

Reactive oxygen species such as H$_2$O$_2$, $\cdot$O$_2$ (ROS) and hydroxyl radicals ($\cdot$OH) cause damage to various cell components leading to biocidal activity induced by photocatalysis. Subsequently, termination reactions also take place during the above process:

\[
\cdot \text{OH} + H^+ + 2e^- \rightarrow H_2O \quad (2.14)
\]

\[
\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad (2.15)
\]
Figure 2.8 Chain of reactions involved in the production of reactive oxygen species such as \( \text{H}_2\text{O}_2, \text{•O}_2^- \) and hydroxyl radical \( \text{•OH} \)

The hydroxyl free radical \( \text{•OH} \) is highly reactive, short lived and detrimental. It can break organic host compound. The superoxide anion \( \text{•O}_2^- \) is long lived and cannot destroy the bounds due to its negative charge where as hydrogen peroxide can destroy. The above chain of reaction is shown illustratively in Fig.2.8.

2.7.2 Mechanism of photoelectrocatalytic inactivation bacteria

To date, numerous studies have been carried out to demonstrate the germicidal effects of semiconductor photocatalysis [23-28]. The vast majority of thesis focus on the destruction of bacterial pathogens in particular *Escherichia coli* (*E.coli*), most likely due to the fact that coliforms are traditionally used as indicators of faecal contamination in water supplies. Coliform bacteria may not necessarily cause disease, but can be indicators of pathogenic organisms that do. The latter could cause intestinal infections, dysentery, hepatitis, typhoid fever, cholera and other illnesses. Intestinal infections and dysentery are generally considered as minor health problems. They can, however, prove fatal to infants, the elderly, and those who are ill.
Matsunaga et al. [29] were the first to report on the “novel concept of photochemical sterilisation”. They looked at the destruction of *Lactobacillus acidophilus*, *Saccharomyces cerevisiae* and *E.coli* (10^3 cells/mL) using platinum-loaded titanium dioxide and showed that cell death occurred following incubation with TiO_2/Pt particles under metal halide lamp irradiation for 60–120 min. The several parameters affects photocatalysis process such as concentration of catalyst, UV light intensity, microbial starting concentration, temperature, pH and aeration on experimental outcome. The photocatalyst may be used in the form of an aqueous suspension or on a solid support. The schematics of photoelectrochemical inactivation of bacteria process is shown in Fig 2.9.

The hydroxyl-free radical •OH is highly reactive, short-lived and it can penetrate cell walls and break DNA strands. Superoxide anion •O_2^- is more long-lived and cannot
penetrate the cell walls due to its negative charge whereas hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) can penetrate the cell walls. Superoxide anion and hydrogen peroxide are both highly reactive to biological macromolecules and also act precursors for the hydroxyl radical (\cdotOH). After penetrating the cell wall, H\textsubscript{2}O\textsubscript{2} gets activated by ferrous (Fe\textsuperscript{2+}) ion present in the cell via the Fenton reaction:

\[
Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdotOH + OH^-
\] (2.16)

Thus, when ZnO is illuminated to produce H\textsubscript{2}O\textsubscript{2}, the Fenton reaction may take place in vivo and produce more hydroxyl radicals. Outside the cell wall, where both H\textsubscript{2}O\textsubscript{2} and \cdotO\textsuperscript{2} are present, additional hydroxyl radical \cdotOH is produced via and the Fenton reaction (2.16)

\[
Fe^{3+} + ZnO(e^-) \rightarrow Fe^{2+} + O_2
\] (2.17)

\[
Fe^{3+} + \cdotO_2^- \rightarrow Fe^{2+} + O_2
\] (2.18)

\[
Bacteria + (H^+, \cdotOH, H_2O_2) \rightarrow CO_2
\] (2.19)

The above chemical process can be extended to any organic and bio-microorganisms, including cancer cells. The bacterial inactivation efficiency can follow first order kinetics with respect to bacterial colony count (N\textsubscript{t}), which is shown by Eq. (2.20) [30].

\[
\ln\left(\frac{N_t}{N_0}\right) = -kt
\] (2.20)

where, N\textsubscript{t} is the number of colony forming unit (CFU) after irradiation for t min; N\textsubscript{0} the number of CFU at 0 min; k the inactivation rate constant; N\textsubscript{t}/N\textsubscript{0} the survival ratio. The schematic of the process of E.coli photokilling on semiconductor film is shown in fig. 2.10. The E. coli is a Gram-negative bacterium and has a membrane structure as shown in Fig. 2.11[31]. E. coli cells have a rod-like morphology with a length of approximately 1–3 \( \mu \)m and a diameter of 0.5–1 \( \mu \)m. The cell envelope of E.coli consists of an inner membrane (~ 8 nm thick), a periplasm containing the peptidoglycan (cell wall) and an outer membrane (~ 10–15 nm thick). The inner and outer membranes have a lipid bilayer structure.
Figure 2.10 Schematic illustration (a–c) of the process of *E. coli* photokilling on semiconductor film. In the lower row, the part of the cell envelope is magnified [18]

The outer layer of the outer membrane (OM) bilayer consists of lipopolysaccharide (LPS) and the inner layer of the OM bilayer consists of phospholipids. The OM also contains proteins such as porins that act as passive diffusion channels for hydrophilic molecules. The inner membrane consists of ~ 40% phospholipids and ~ 60% protein.

Figure 2.11 Cell envelope of gram-negative bacteria
It has become apparent that the primary target for photocatalytic attack is the cell wall. This fact goes some way towards explaining the observed differences in susceptibility of particular microbes to photocatalytic attack. The Gram positive cell wall while structurally less complex than that of the Gram negative cell wall, is surrounded a thick peptidoglycan layer and fungi, which were shown to be much less susceptible to photocatalytic attack than bacteria [32]. Once the integrity of the cell wall has been destroyed, leakage of intracellular contents takes place which ultimately results in cell death.

2.8 Parameters influencing the photocatalytic process

2.8.1 Effect of light intensity

The incident light intensity determines the rate of photoelectron and photohole generation and consequently the photoelectron/hole concentrations in an illuminated semiconductor. It influences not only the rate of photocatalytic degradation of organic matter, but also the rate of photoelectron and photohole recombination [33]. In this regard, the light intensity affects the overall quantum efficiency of photocatalytic degradation. With slurry system, at very low light intensity, photocatalytic degradation rates (or quantum efficiency) usually increase linearly with the light intensity. Nevertheless, at high light intensity, a non-linear dependence for many degradation reactions has been observed [34]. The square root dependence of the reaction rate on the light intensity is often attributed to the enhanced recombination of photoelectrons and photoholes at higher light intensities [35]. An alternative explanation attributes this to the inhibition of active surface sites and competition for photoholes by reaction intermediates [36]. The cause for this kind of rate/light intensity dependence is still unclear. Partly, it may be attributed to the way such experiments were carried out, where reduction and oxidation reaction take place on the same particles and the reduction reaction could be the control step of the overall photocatalytic process. Partly, it may be caused by the way that the photocatalytic degradation rates are expressed. In such studies, usually, the reaction rates are expressed by the disappearance rates of original substrates. Due to the uncertainty of their degradation degree and the competition for photoholes by intermediates or other photohole acceptors, only considering the part of photoholes consumed by a specific assumed reaction would be impossible to elucidate the underlining cause for this lowered quantum efficiency at
higher light intensities. Photocurrent directly reflects the photohole capture rate by various photohole acceptors including intermediates. A study of photocurrent dependence on light intensity at different potential bias would offer an insight into the reason for the lowered quantum efficiency of overall photocatalytic process at higher light intensities.

2.8.2 Effect of pH

The pH of the solution is an important parameter in the photocatalyzed degradation of organic wastes as it is known to influence the surface charge of the semiconductor thereby affecting the interfacial electron transfer and the photoredox process [37]. The effect of pH on the degradation of phenol in presence of both ZnO and TiO$_2$ reveal that, in the case of TiO$_2$, maximum degradation is observed at pH 4 and 10, with the degradation almost complete in the alkaline region. In the case of ZnO, the degradation is not varying much in the pH range of 4-7, even though in this case also, the maximum is observed in the alkaline pH range [38]. The low reactivity on ZnO, under acidic conditions can also be due to the photo-corrosion of ZnO in acidic aqueous suspensions. Significant amounts of Zn$^{2+}$ have been detected in ZnO suspensions [39]. In this regard, the pH would greatly influence the photocatalytic oxidation kinetics of strong adsorbates.

However, at high pH, surface -OH groups on oxide semiconductors will dissociate into -O$^-$ + H$^+$. At low pH, surface -OH groups on oxide semiconductors will be protonated: -OH + H$^+$ $\rightarrow$ -OH$^{2+}$. At some pH in between, neither the first nor the second reaction occurs. Therefore, the surface is not charged (if no other strong electrolyte is present, whose ions may adsorb). This can be called the point of zero charge. The influence of supporting electrolyte on impurities like AO7 degradation has been noted previously and can be ascribed to pH. The point of zero charge of ZnO is reported to be 5.8. Below this pH, ZnO is positively charged, which seems to enhance interaction with AO7 and ZnO, i.e. AO7 is adsorbed, leading to an increased probability of direct hole transfer, down to low concentrations. This directly reflects in the kinetic parameter and in the reaction decay rate.

2.8.3 Effect of initial solute concentration

Using low concentrations of pollutants is beneficial since the catalyst surface active sites may be saturated at high concentrations. According to the Langmuir-Hinshelwood reaction kinetics, for dilute solution ($C_0 < 10^{-3}$ M), the reaction is of the
apparent first order, whereas the reaction is reduced to the zero order at high concentration ($C_0 > 5 \times 10^{-3} \text{ M}$) [40].

### 2.8.4 Effect of electrode (photocatalyst) material

The choice of electrode material is also important for its use in photodegradation of organic impurities in water. There are many ways as to how organic impurities can be removed. In most of the cases, the material is used in nanoparticulates or slurry forms. There are however, several drawbacks of these systems. Therefore, now research is moving towards using the photoelectrodes in the form of adherent thin film.

#### 2.8.5 Effect of potential bias

There is another factor, which is responsible for facilitating the degradation reactions i.e. application of suitable potential bias to the photoelectrode. Suitable electrical bias to the photoelectrode, promotes the separation of charge carriers within the semiconductor electrode and avoids the recombination of electron-holes thereby moving the electrons towards the counter electrode. Hence, the photocatalytic action of the electrode can be boosted [41].

At a given light intensity and electrolyte composition, the photohole removal rate is constant, which is equivalent to the saturation photocurrent obtained upon illumination. At the same time, the overall photohole capture rate is also related to the removal rate of electrons, which is dependent on the applied potential bias [42]. If there is electron build-up at the surface of electrode, it will suppress the photohole capture rate and facilitate the photoelectron-hole recombination. As a result, the overall photocatalytic oxidation rate will be decreased. The applied potential bias, in effect, acts as an external force to remove the photoelectron by drawing the electron through the external circuit to the auxiliary electrode. This is, in turn, minimizes the build-up of electrons on electrode. In the low potential range, the removal rate of the available photoelectron is proportional to the electric field across the film. The degree of the electron build-up decreases with an increase in the potential bias. Therefore, the overall photocatalytic oxidation rate (photocurrent) increases with potential bias. Under these conditions, the overall process is controlled by electron migration in the semiconductor film. When the applied potential bias is sufficiently high, there is no electron build-up and the overall photocatalytic oxidation rate is solely reliant on the photohole capture rate at ZnO surface. Hence, the photohole capture rate at the electrode surface controls the overall photocatalytic oxidation process.
2.8.6 Effect of temperature

Since, photocatalysis is activated by photons; photocatalytic reactions can operate at room temperature and are relatively insensitive to temperature changes. The peer-reviewed literature reports that reaction rates are typically the highest for reactor temperatures between 20 to 80 °C, with reaction rates generally decreases for temperatures above 80 °C. Water adsorbed on the photocatalyst has been reported extensively to play a critical role in the surface-mediated photocatalytic reactions, trapping valance band holes and forming hydroxyl radicals. As reactor temperatures exceeds 80 °C and approach the boiling point of water, the loss of water on the surface may limit the photocatalytic reaction. Likewise, the surface adsorption-desorption equilibrium of target compounds and intermediates may shift towards the gas phase at elevated temperatures thereby reducing the interaction of gas molecules with photocatalytic surface. On the other hand, the change in surface coverage of the reactants and intermediates at elevated temperatures may make more surface sites available for desired reactions. Furthermore, conventional hetererogenous catalytic reactions may occur at elevated temperatures depending on the reacting species and the catalyst [43].

Thus the effect of temperature on a given photocatalytic reaction will be highly dependent on the contaminant, catalyst and other compounds present at the catalyst surface (e.g. water, intermediates or end reaction products).

2.8.7 Effect of dopant

Doping of noble metal ions in semiconductor may lead to an enhanced efficiency of the photocatalyst [44]. The photo-physical mechanism of doped semiconductor is not fully understood. This method of improving photocatalytic activity is mainly used in aqueous media. ZnO particles can be simply substitutionally of interstially doped with different cations, can formed mixed oxides or a mixture of oxides. The dopant parameters include the concentration of dopants and the applied thermal treatment [40]. The total induced alteration of the photocatalytic activity is made up from the the sum of changes which occurs in:

i. The light absorption capacity of the ZnO photocatalyst;
ii. Adsorption capacity of the substrate molecules at the catalysts surface;
iii. Interfacial charge transfer rate;
iv. Physical contact with microorganisms.
2.8.8 Effect of heterojunction (ZnO/TiO₂)

Photoelectrocatalytic system has received a great deal of attention due to drastically enhanced quantum efficiency. By applying external bias or by doping noble metal ions recombination of generated electron–hole pairs is retarded. ZnO and TiO₂ has been widely used as photoelectrocatalyst for water and air purification because of high surface activity and absence of toxicity. However, the intrinsic semiconducting characteristics of ZnO and that of TiO₂ are different. The heterojunction films composed of ZnO and TiO₂ layers were provided to improve photoelectrocatalytic properties [45]. The heterojunction that influence the photocatalytic properties are: (a) surface recombination due to surface characteristics of each material and (b) interface recombination between TiO₂ and ZnO. The photocatalysis is mainly determined by the surface characteristics of the films. It is found that the surface recombination occurs more easily in ZnO. Therefore, surface recombination is fast for TiO₂/ZnO system, compared to ZnO/TiO₂ system. The photocatalytic properties for heterojunction are determined by the combination of surface and interface recombination. In addition, it is possible to increase the photocatalytic properties under applied bias. From these effects, with the ZnO film with thin TiO₂ layer the most organic matter and microorganisms are decomposed under applied bias.

2.9 Strategies for photocatalytic enhancement

2.9.1 Quantum efficiency and visible light absorption

Various methods and modifications are attempted to enhance the overall efficiency of the photocatalytic process. The most important modification to date is the reduction of the TiO₂ particle size within the nanometer range which has been shown to significantly increase its catalytic activity [46]. This is due to the higher surface-to-volume ratio, and as such, it is routine to use nanometer-sized particles. Reactor performance is enhanced by dispersing the TiO₂ nanoparticles in water, because of higher surface contact of the nanoparticles with the target compounds. However, the difficulty in separating unsupported particles from water for reuse is limiting commercially viable industrial reactors. Therefore, a need to employ supported catalysts is realized where a thin layer of nanometer-sized TiO₂ particles can be formed on a supporting surface. These can be particle or fixed supports, with the majority of research performed in the former case. TiO₂, for example, has been fixed onto tubes,
glass plates, fibres, membranes, or photoreactor walls [47]. However, catalytic activity approximately five to six times lower is usually seen (compared with the powdered form). This is due to reduced surface-to-volume ratio (from binding with the supporting surface); catalyst agglomeration (surface clumping) during fixation; and the mass transfer limit for the organic compounds [48]. Film thickness is also of great importance: if the film is too thin, not enough light will be absorbed and if too thick, the holes are generated too deep in the catalyst layer [49]. These problems can overcome by employing a nanoporous film to ensure maximum light absorption and also by bringing the pollutant close to the film surface.

2.9.2 Sensitization of photocatalyst: composite semiconductor

In electronic applications, the exact electrical response exhibited by a metal oxide film depends strongly on composition and on microstructural characteristics, such as particle size, shape, crystallinity, and defect structure [50]. It is also well-known that intimate contacts between one nanoscale semiconducting oxide and another with different electronic properties can result in hybrid properties, including electronic rectification [51]. An additional advantage that heterostructures may have over single-component materials is the ability to shield a photochemically unstable material from the surrounding electrolyte with a corrosion-resistant outer layer allowing some narrower band gap materials to be used. There have been many reports of the improved photoelectrochemical activity that can be achieved using such coupled semiconductor systems [52-53]. In some of these studies, one semiconductor acts as a sensitizer for another, whereas in others, it is the modification of surface properties that appears to play a greater role in the enhancement of photoelectrochemical activity.
References


