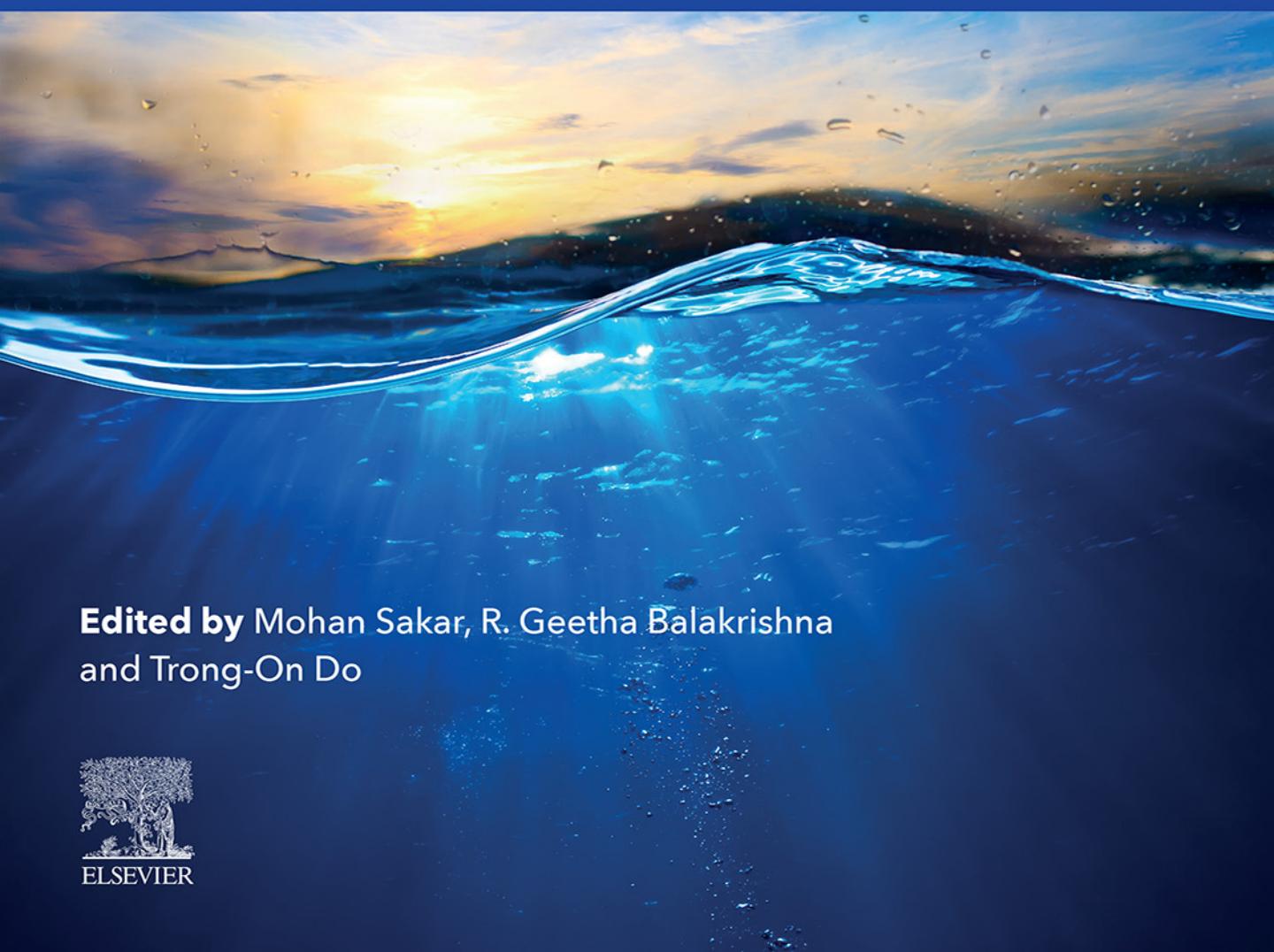


Photocatalytic Systems by Design

Materials, Mechanisms and Applications



Edited by Mohan Sakar, R. Geetha Balakrishna
and Trong-On Do



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Principles and mechanisms of photocatalysis

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1.1 Introduction and historical developments

From history, we have learned that the human race has been motivated by nature to discover intelligent answers for complicated problems in their everyday life. Similarly, natural photosynthesis drives chemical pathways using solar radiations. Hence, photocatalysis has arisen as a nature-inspired method for harvesting and converting sun energy to facilitate challenging synthetic conversions for various applications. In 1972 Fujishima and Honda (1972) first reported “photocatalysis” by water splitting under UV irradiation since then research in this field has increased many folds. Photocatalysis has been attracting extra attention as it finds applications in a variety of products across a broad range of research areas, mainly environmental and energy-related fields. Recently, metal oxides, such as TiO₂, ZnO, SnO₂, and CeO₂, have been the main choice for most studies in basic research and practical applications because of their high activity, low cost, high stability, nontoxicity, and chemical inertness, which make them suitable for applications in water and air purification, sterilization, hydrogen evolution, etc. (Albini & Fagnoni, 2008; Chen, Nanayakkara, & Grassian, 2012; Khan, Adil, & Mayouf, 2015; Ravelli, Dondi, Fagnoni, & Albini, 2009).

The “photocatalysis” shows the development of some dynamic concepts of photochemistry. The turning point that allowed photochemistry to become a science on its own was distinguishing the difference with thermal chemistry. In fact, till the beginning of the 20th century, many scientists felt that irradiation or illumination was one of the several ways existing for catalyzing a reaction, that is, making it faster, such as treating with some chemicals and heating. Giacomo Ciamician was the first scientist who put a systematic effort to understand the chemical effect of light on ascertaining whether “light and light alone,” and not, for instance, heat, caused the reactions to accelerate (Albini & Fagnoni, 2008). He properly assigned these reactions as “photochemical reaction” while the term “photocatalytic”-tagged reactions were accelerated by light, but maintaining the same

course as the thermal reactions. Later, researchers, recognized that photochemical reactions involve electronically excited states, “electronic isomers” of ground states that have a reactivity (and thermodynamics) of their own. Bodenstein in 1914 observed it, however, becomes a common concept after several years ([Albini & Fagnoni, 2008](#); [Ravelli et al., 2009](#)).

The word “photocatalysis” is of Greek origin and includes two terms (prefix “photo” derived from phos means light and “catalysis” derived from katalyo means break apart or decompose). However, there is no agreement in the scientific community as to have a proper definition of photocatalysis. It is generally used to describe a process in which light is used to trigger a substance, the photocatalyst, which modifies the rate of a chemical reaction without being involved itself in the chemical reactions. Thus, the main difference between a conventional thermal catalyst and a photocatalyst is that the latter is activated by photons of appropriate energy whereas the former is activated by heat. Photocatalytic reactions may take place homogeneously or heterogeneously. However, heterogeneous photocatalysis is more deeply studied in recent years because of its potential usage in a variety of environmental and energy-related applications as well as in organic syntheses ([Choi et al., 2016](#)). In heterogeneous photocatalysis, the reaction pathway involves the formation of an interface among photocatalysts and fluid containing the reactants and products. The processes involving irradiation adsorbate–semiconductors interfaces are generally categorized as a branch of photochemistry. Therefore, the term “heterogeneous photocatalysis” is mainly used in the cases where a light-absorbing semiconductors photocatalyst is utilized, which is in contact with either a liquid phase or a gas phase.

A material is considered to be a *catalyst* when it accelerates a chemical reaction without being consumed in a reaction, denatured or unaltered and lowers the free activation enthalpy of the reaction. *Photocatalysis* is defined as the acceleration of a reaction in the presence of light and a suitable catalyst. *Photocatalysts* are defined as a material that accelerates a chemical reaction in the presence of appropriate light and a suitable catalyst without being utilized that lowers the free activation enthalpy of a chemical reaction ([Ravelli et al., 2009](#)). *Photocatalysis* is a fast-developing field with a great possibility of a widespread range of industrial applications, such as water disinfection, air disinfection, mineralization of organic pollutants, production of renewable fuels, and organic syntheses ([Chen et al., 2012](#); [Choi et al., 2016](#); [Khan et al., 2015](#); [Ravelli et al., 2009](#)). In this chapter, the discussion will be on semiconductor-mediated photocatalysis, basic principles, classification, mechanism, limitations, and operating parameters of photocatalytic processes. This chapter also covers theory and fundamentals essential for understanding heterogeneous photocatalysis. Emphasis has been given to the electronic and optical properties of the photocatalysts. This is followed by the discussion of the principles of photocatalysis and thermodynamics as well as kinetic aspects, which determine the photocatalytic efficiency. This chapter is designed to understand fundamentals, theories, and concepts necessary for

understanding the semiconductors, such as metal oxides (TiO_2 , ZnO , SnO_2 , CeO_2 , etc.) and chalcogenides (ZnS , CdS , MoS , CdSe , CdTe , etc.) as photocatalysts (Ansari et al., 2013; Ansari, Khan, Ansari, Lee, & Cho, 2014b; Chen et al., 2012; Choi et al., 2016; Kalathil, Khan, Ansari, Lee, & Cho, 2013; Khan et al., 2015; Khan, Ansari, Pradhan, Ansari, et al., 2014; Khan, Ansari, Pradhan, Han, et al., 2014; Ravelli et al., 2009). This chapter also emphasizes the optical and electronic properties of the semiconductors, which will be described with the use of the band model, etc. Photocatalysis has been discussed in detail by giving several examples.

1.2 Semiconductors and photocatalysis

Several semiconductors are useful as photocatalysts because of the promising amalgamated light absorption properties, electronic structures, excited-state lifetimes, and charge transport characteristics. A semiconductor is nonconductive in its undoped ground state because an energy gap, that is, a wide band gap, exists between the top of the filled valence band (VB) and the bottom of the vacant conduction band (CB). Accordingly, electron transport between these bands must occur only with considerable energy change. In semiconductor photocatalysis, the excitation of an electron from the VB to CB is achieved by absorption of a photon of energy equal to or higher than the band gap energy of the semiconductor. This leads to the formation of an electron–hole pair (e^-/h^+), which is a prerequisite for all the semiconductor-assisted photocatalytic reactions. The photo-generated species formed tend to recombine and dissipate energy as heat because the kinetic barrier for the electron–hole recombination step is low. However, holes in VB and electrons in CB can be separated well in the presence of an electric field, such as the one generated spontaneously in the space charge layer of a metal–semiconductor or a fluid–semiconductor interface. Hence, the lifetime of photo generated carriers' (e^-/h^+) increases and the possibility offered to these species to exchange charge with substrates adsorbed on the photocatalyst surface and persuade primary and secondary chemical reactions.

Transfer of an electron to or from a substrate adsorbed onto the light-activated semiconductor, that is, interfacial electron transfer, is probably the most critical step in photocatalytic reactions, and its efficiency controls to a large extent the ability of the semiconductor to serve as a photocatalyst for a given redox reaction. The efficiency of electron transfer reactions is, in turn, a function of the position of the semiconductor's VB and CB edges relative to the redox potentials of the adsorbed substrates. For an anticipated electron transfer step to occur, the potential of the electron donor species should be located above (more negative than) the VB of the semiconductor, whereas the potential of the electron acceptor species should be located below (more positive than) the CB of the semiconductor. Interfacial electron transfer processes are then initiating subsequent redox reactions to form free radicals for primary and secondary reactions. The free radicals

formed, such as hydroxyl radicals ($\cdot\text{OH}$) and superoxide radicals ($\cdot\text{O}_2$), will be used as strong oxidizing agents for decomposing or degrading the organic pollutants, etc.

1.3 Fundamentals of photocatalysis

In short, photocatalysis is defined as the “acceleration of a reaction in the presence of a suitable catalyst and suitable light.” A catalyst does not change or being used up during a chemical reaction and accelerates the rate of reaction by lowering the activation energy. It includes photosensitization, which is a process by which a photochemical reaction takes place in one molecular unit as a result of the initial absorption of suitable light energy by another molecular unit, called the photosensitized. Photocatalysis assist in forming strong reducing and oxidizing agents, which help in breaking down the organic pollutants to CO_2 and H_2O in the presence of light, photocatalyst, and water (Ansari, Khan, Ansari, & Cho, 2016; Ansari, Khan, Ansari, Lee, & Cho, 2014a; Chen et al., 2012; Fujishima, Zhang, & Tryk, 2008; Khan, Ansari, Pradhan, Ansari, et al., 2014; Khan, Ansari, Pradhan, Han, et al., 2014).

1.3.1 Mechanism

When photocatalyst (such as CdS , ZnS , TiO_2 , ZnO , SnO_2 , CeO_2 , etc.) absorbs suitable light, it produces electron hole pairs (e^-/h^+) in the CB and VB respectively. The electrons in the VB of semiconductors become excited when irradiated by light. The excess energy of this excited electron promoted the electron to the CB of semiconductors, therefore, creating the positive-hole (h^+) and negative-electron (e^-) pairs. This stage is referred to as the semiconductor’s “photo-excitation” state. The energy difference between the VB and CB is known as the “band gap” energy (E_g). Fig. 1.1 shows the band gap energy of insulators, semiconductors, and conductors (Hernandez-Ramirez & Medina-Ramirez, 2015; Saravanan et al., 2016).

The photoactivation of semiconductors photocatalyst is based on its electronic excitation by photons (light) with energy ($h\nu$) greater than the band gap energy (E_g). The electrons migrate after the excitation generating vacancies in the VB (holes, h^+)

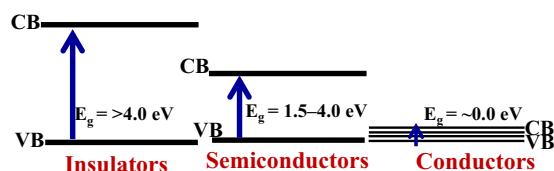


Figure 1.1
Band gap energies of the insulators, semiconductors, and conductors.

and forming regions with high electron density (e^-) in the CB (Hernandez-Ramirez & Medina-Ramirez, 2015; Hoffmann, Martin, Choi, & Bahnemann, 1995; Khataee, Zarei, & Ordikhani-Seyedlar, 2011; Kumar & Devi, 2011; Ni, Leung, Leung, & Sumathy, 2007; Nogueira & Jardim, 1998; Zioli & Jardim, 1998). These holes are pH dependent and have high positive electrochemical potentials, in the range between +2.0 and +3.5 V, measured against a saturated calomel electrode (Khataee et al., 2011). This potential is sufficiently positive to generate hydroxyl radicals ($\cdot OH$) from water molecules adsorbed on the surface of the semiconductor photocatalysts [Eqs. (1.i), (1.ii), (1.iii)]. The photocatalytic efficiency depends on the competition between the formation of e^-/h^+ pairs and the recombination of these pairs Eq. (1.iv) on the semiconductor photocatalysts surfaces (Hoffmann et al., 1995; Ni et al., 2007; Zioli & Jardim, 1998).



Though the oxidation reactions caused by the generated holes occur at the VB, the electrons transferred to the CB are responsible for reduction reactions, such as the formation of gaseous hydrogen and the generation of other important oxidizing species, such as superoxide anion radicals ($\cdot O_2$). In case of semiconductors, such as chalcogenides and metal oxides, the E_g is between 1.8–2.7 and 3.00–3.40 eV, respectively (Hernandez-Ramirez & Medina-Ramirez, 2015; Hoffmann et al., 1995; Kumar & Devi, 2011). The whole procedure is shown schematically in Fig. 1.2.

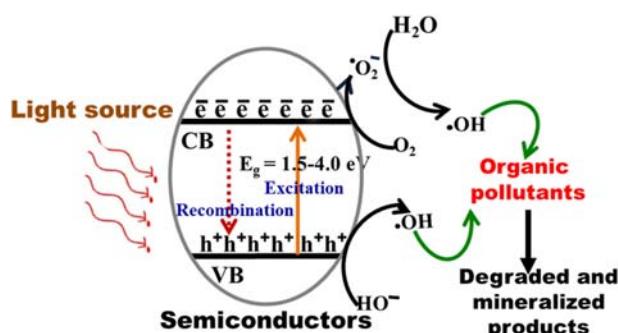


Figure 1.2

Tentative photocatalysis mechanism occurs during photocatalytic reaction at the surface of the semiconductors.

The positive hole formed in semiconductor photocatalysts dissociates the H₂O molecules to form H₂ gas and hydroxyl radicals (·OH). The negative electron reacts with adsorbed oxygen molecules to form superoxide anions (O₂^{·-}) (Ansari et al., 2016; Chen et al., 2012; Fujishima et al., 2008; Hernandez-Ramirez & Medina-Ramirez, 2015; Khan, Ansari, Pradhan, Ansari, et al., 2014; Khan, Ansari, Pradhan, Han, et al., 2014). This cycle continues till suitable light of appropriate intensity and wavelength is available. The complete mechanism of photocatalytic reaction that happens at its surface of semiconductors, in the presence of suitable light, is shown in Fig. 1.2.

The ultimate leading and advanced oxidation reactions are based on the formation of hydroxyl radicals (·OH), which are extremely powerful oxidizing agents, second only to fluorine in power (2.23 in relative oxidizing power). Through the use of the strong oxidation strength of ·OH radicals, photocatalytic oxidation can efficiently decompose, degrade, disinfect, deodorize, and purify the air, water, and different types of surfaces. Table 1.1 shows the common chemical oxidants, placed in the order of their oxidizing strength.

1.3.1.1 Photocatalysis mechanism

The photocatalysis method based on semiconductors basically involves the following stages:

- The light energy of a certain wavelength is made to fall onto a semiconductor. If the energy of incident light is equivalent to the band gap energy of the semiconductor, the electron would be excited from the VB to CB of the semiconductor.
- Holes would be left in the valance band of the semiconductor. The holes in the VB can oxidize donor molecules.

The electrons and holes could undergo subsequent reduction and oxidation reaction, respectively, with any dye molecules, which might be adsorbed on the surface of the

Table 1.1: Common chemical oxidants, placed in the order of their oxidizing strength.

Compounds/radicals	Oxidation potentials (V)	Relative oxidizing power (Cl ₂ = 1.0)
Hydroxyl radicals (·OH)	2.8	2.1
Sulfate radicals (SO ₄ ^{·-})	2.6	1.9
O ₃	2.1	1.5
H ₂ O ₂	1.8	1.3
MnO ₄ ⁻	1.7	1.2
ClO ₂	1.5	1.1
Cl ₂	1.4	1.0
O ₂	1.2	0.90
Br ₂	1.1	0.80
I ₂	0.76	0.54

semiconductor to give the degradation products. Fig. 1.2 shows the reaction mechanism of photocatalysis.

CB electrons and VB holes are generated when aqueous semiconductor suspension is irradiated with light energy greater than its band gap energy (E_g). Photo-generated electrons can react with water or OH^- and oxidize them to produce $\cdot\text{OH}$ radicals. The photo-generated electrons can react with electron acceptors, such as O_2 , adsorbed on the catalysts' surface or dissolved in water, reducing it to the superoxide radical anion $\text{O}_2^{\cdot-}$. The powerful hydroxyl radicals ($\cdot\text{OH}$) are accountable for the decomposition of organic pollutants. The excited electron and hole pairs can recombine and release the input energy as thermal energy (heat) with no chemical effect.

1.3.1.2 Oxidation mechanism

The surface of a semiconductor photocatalyst contains water, which is referred to as "adsorbed water." When this water is oxidized by positive holes, hydroxyl radicals ($\cdot\text{OH}$), which have strong oxidative decomposing power, are formed. Then, the hydroxyl radicals react with organic matter. If oxygen is present when this process takes place, the intermediate radicals in the organic compounds and oxygen molecules can undergo radical chain reactions and consume oxygen in some cases. In such case, the organic matter eventually decomposes and ultimately ends up with the end product to CO_2 and H_2O . Under some conditions, organic pollutants can directly react with the positive holes, resulting in oxidative decomposition products (Fig. 1.3) (Khan et al. 2015).

1.3.1.3 Reduction mechanism

The reduction of oxygen contained in the air occurs as a pairing reaction. As oxygen is an easily reducible substance, if oxygen is present, the reduction of oxygen takes place instead

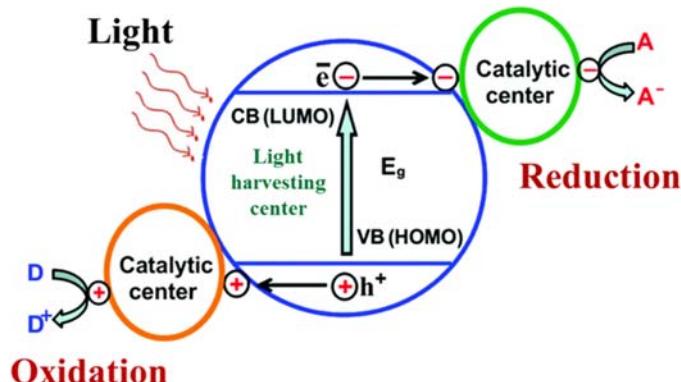


Figure 1.3
Oxidation and reduction centers at the surface of the semiconductor.

of hydrogen generation. The reduction of oxygen results in the generation of superoxide anions ($O_2^{\cdot-}$). Superoxide anions react with the intermediate in the oxidative reaction, forming peroxide or changing to H_2O_2 and then to H_2O . As reduction tends to occur more easily in organic solvent than in water, when the concentration of organic matter becomes high, the possibility of positive holes being used in the oxidative reactions with organic matter increases, thus reducing the rate of charge carrier recombination.

1.3.2 Major advantages of photocatalysis

Following are the advantages of photocatalysis:

1. Photocatalysis offers a better substitute for the energy-intensive conventional treatment methods with the capacity for using renewable and pollution-free solar energy.
2. Photocatalysis leads to the formation of harmless products, unlike conventional treatment measures that transfer pollutants from one phase to another.
3. This process can be used to destroy a variety of hazardous compounds in different wastewater streams.
4. The reaction conditions for photocatalysis are mild, the reaction time is modest, and a lesser chemical input is required.
5. Minimum secondary waste generation.
6. Photocatalysis can also be applied to the gaseous phase and aqueous treatments as well as solid-phase treatments to some extent.

1.3.3 Limitations of photocatalysis

Following are the rate-limiting steps in photocatalytic reactions, which involve:

1. interfacial charge transfer,
2. improving the charge separation, and
3. inhibition of charge carrier recombination.

These steps are important for enhancing the efficiency of the photocatalytic process.

1.3.4 Operating parameters in photocatalytic processes

The rate of photo mineralization of an organic compound by photocatalysis method depends mainly on the following parameters: reaction temperature, pH, light intensity, and effect of photocatalysts ([Pelaez et al., 2012](#)).

1. Effect of reaction temperature

Usually, photocatalysis is not temperature dependent. However, an increase in temperature can affect the amount of adsorption and enhances the recombination of

charge carriers, resulting in a decrease in the photocatalytic activity. To determine the reaction rate, the temperature depending on the kinetic parameter k_{obs} in terms of the Arrhenius equation can be expressed as follows:

$$k_{\text{obs}} = A e^{-\frac{E_a}{RT}} \quad (1.1)$$

where k_{obs} is the kinetic parameter (1/min), A is the frequency factor (1/min), E_a is the activation energy (kcal/mol), T is the temperature (K), and R is the gas constant (1.987×10^{-3} kcal/mol/K). According to this equation, the reaction rate should increase linearly with $e^{(-1/T)}$.

2. pH effect

In photocatalytic degradation reactions, the pH value is an important parameter because of the photocatalytic activity that takes place on the surface of photocatalysts. The pH of an aqueous solution affects the surface charge on the photocatalyst, the oxidation potential of the valence band, and other physiochemical properties of the system. In accordance with Nernst's law, varying the pH of the solution shifts the energies of the valence and CB edges by 0.059 V per pH unit (at ambient temperature). This results in the VB electrons becoming more potent and the CB holes becoming less potent at higher pH.

3. Effect of light intensity

The photocatalytic reaction rate largely depends on the light-harvesting ability of the photocatalyst. In general, the decomposition rate increases with increasing the light intensity during the photocatalytic reaction. Recent reports confirmed that during photocatalytic degradation reactions, increase in the degradation rate has been observed with increase in light intensity. However, excessive light intensity results in more electron–hole recombination. Another factor that limits the photonic efficiency is the thermal recombination between electrons and holes (Amani-Ghadim et al., 2019; Wang & Domen, 2020). When considering the electron–hole recombination, the appropriate light intensity I_a can be predicted by the following equation:

$$I_a = mI \quad (1.2)$$

where m is an excess coefficient and I is the light intensity. This shows that the light intensity had a great importance on the electron–hole pair's recombination.

Occasionally with the increase in light intensity, the increment in reaction rate would reduce, indicating that the utilization ratio of light energy might drop.

4. Effect of dosage of photocatalyst

The amount of photocatalyst loaded may also affect the process of photocatalytic degradation. Initially, the increase in the amount of photocatalyst increases the number of active sites on the semiconductor surface that in turn increases the number of $\cdot\text{OH}$ and $\text{O}_2^{\bullet-}$ radicals. As a result, the rate of photocatalytic degradation is increased.

In the review of TiO₂-assisted photocatalytic degradation of azo dyes in an aqueous solution, Konstantinou and Albanis reported that the initial rates are directly proportional to catalyst concentration in any reactor system. Furthermore, they observed that there is a limit of catalyst concentration, which is used for the degradation of particular organic pollutants from wastewater. Moreover, the effect of loading photocatalyst content beyond this catalyst concentration may result in the agglomeration of catalyst; hence, for photon absorption, part of the catalyst surface will be unavailable.

5. *Concentration of pollutants in wastewater*

Another main factor to determine the degradation rate is the pollutant type and its concentration. Many researchers have reported the photocatalytic activity under similar operating conditions and using similar catalysts, but the variation in the initial concentration of water contaminants results in different irradiation times necessary to achieve complete mineralization.

1.4 Semiconductors that are mainly used as photocatalysts

1.4.1 Metal oxides as photocatalysts

Photocatalysis is a promising, green, environmentally friendly method for the transformation of solar energy to chemical energy or chemical conversion using suitable semiconductor nanostructures, such as the degradation of organic and inorganic pollutants, removal of inorganic pollutants, and H₂ production. In the last three to four decades, considerable research efforts have been made to understand efficient, economical, and green sources for the treatments of organic and inorganic pollutants for environmental remediation processes, energy production, and optoelectronic devices.

Suitable semiconductor nanomaterials have played a chief role in this effort because they have an excellent combination of photochemical activity, major light-harvesting, mechanical and thermal stability. They have long been pursued photocatalytic applications, such as H₂ production through water splitting or decomposition of water pollutants. The catalytic activities of semiconductor nanomaterials are influenced significantly by the reactive sites present on the surface, due to different types of defects in the crystal structures.

Among the semiconductors, transition metal oxide nanomaterials have attracted considerable attention owing to their potential applications, such as photocatalysis, H₂ production and storage, environmental remediation, and energy. Therefore these nanomaterials are expected to be the key nanomaterials for further developments of nanoscience and nanotechnology ([Ansari et al., 2016](#); [Chen et al., 2012](#); [Fujishima et al., 2008](#); [Hernandez-Ramirez & Medina-Ramirez, 2015](#)). A large diversity of semiconducting