# CHAPTER II

# THEORETICAL BACKGROUND AND LITERATURE REVIEW

## 2.1 Basic Principle of Photocatalysis

Heterogeneous photocatalytic was described by Palmisano and Sclafani in 1997 as "a catalytic process during, which one or more reaction steps occur by the photogeneration of electron-hole pairs on the surface of semiconductor materials, illuminated by proper energy of light" (Molinari *et al.*, 2014). From this definition, both catalyst and light are essential to induce a chemical process. When irradiation excites state of the photocatalyst, it will generate and initiate the next processes like reduction-oxidation reaction. The energy band diagrams of semiconductors is simplified and shown in Figure 2.1 (Angelo *et al.*, 2013). It consists of the highest band level (valence band $E_{VB}$) and the lowest band level (conduction band $E_{CB}$). The energy difference between conduction and valence edges is the bandgap energy of the semiconductor ($E_{BG}$).
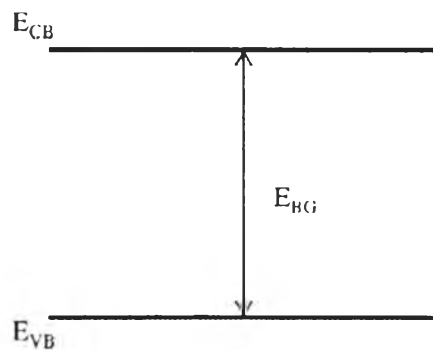


**Figure 2.1** Schematic representation of semiconductor energy band (Angelo *et al.*, 2013)

When a semiconductor absorbs photons with energy equal or higher than its band gap energy, electrons ($e^-$) are rised from the valence to the conduction band, leaving, at the same time, positively charged vacancies in the valence band, called holes ($h^+$). The photogenerated electron-hole pairs can induce redox reaction with electron donor (D) and electron acceptor (A). The electron can reduce the electron

acceptor (A⁻), whereas the hole can oxidize the electron donor ($D^+$), Figure 2.2. Normally, the hole can react easily with surface bound of water to produce hydroxyl radical (OH•) Eq. (2.1). Then, the OH• produced can react with dyes molecule to form other species and is thus responsible for the decolorization of dye (Rauf and Ashraf, 2009).

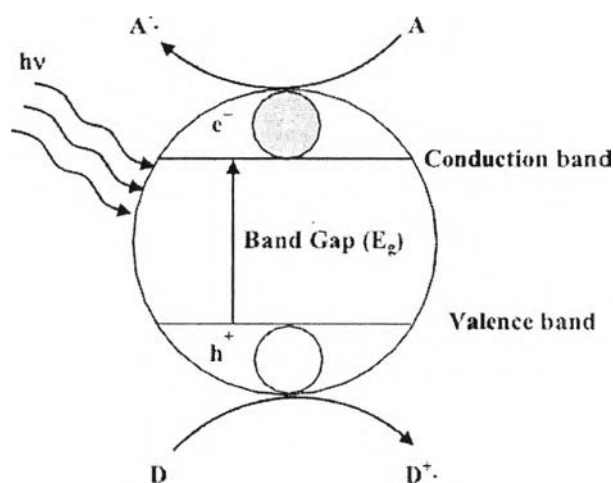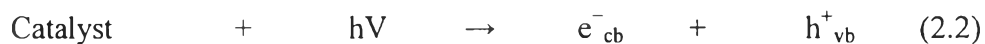$$H_2O \quad + \quad h^+_{vb} \quad \rightarrow \quad OH^\bullet \quad + \quad H^+ \quad (2.1)$$



**Figure 2.2** Simplified schematic of photocatalytic reaction (Molinari *et al.*, 2014).

### 2.1.1 Photocatalytic Degradation Mechanism

Photocatalytic degradation is a part of advanced oxidation process (AOP), which has proven to be an encouraging technology for degrading organic compounds. This technique is more effective than other AOPs because semiconductors are inexpensive and can easily mineralize various organic compounds. The photocatalytic decolorization of a dye is believed to take place according to the following mechanism. When a catalyst is exposed to UV radiation, electrons are produced from the valence band to the conduction band. As a result of this, an electron–hole pair is generated, Eq. (2.2).

$$Catalyst \quad + \quad hV \quad \rightarrow \quad e^-_{cb} \quad + \quad h^+_{vb} \quad (2.2)$$

where, $e^-_{cb}$ and $h^+_{vb}$ are the electrons in the conduction band and the positively charged vacancy in the valence band, respectively. Both these entities can migrate to the catalyst surface, where they can enter in a redox reaction with other species present on the surface. In most cases, $h^+_{vb}$ can oxidize easily with surface bound of water to produce $OH^\bullet$ radicals, Eq. (2.3), whereas $e^-_{cb}$ can reduce with $O_2$ to produce superoxide radical anion of oxygen $O_2^\bullet$.

$$H_2O \quad + \quad h^+_{vb} \quad \rightarrow \quad OH^\bullet \quad + \quad H^+ \qquad (2.3)$$

$$O_2 \quad + \quad e^-_{cb} \quad \rightarrow \quad O_2^\bullet \qquad (2.4)$$

Eq. (2.2) and Eq. (2.3) prevent the combination of the electron and the hole, which are produced in the first step. The $OH^\bullet$ and $O_2^\bullet$ produced in the above manner can then react with the dye to form other species and is thus responsible for the discoloration of the dye.

$$O_2^\bullet \quad + \quad H_2O \quad \rightarrow \quad H_2O_2 \qquad (2.5)$$

$$H_2O_2 \quad \rightarrow \quad 2OH^\bullet \qquad (2.6)$$

$$OH^\bullet \quad + \quad dye \quad \rightarrow \quad dye_{ox} \qquad (2.7)$$

$$Dye \quad + \quad e^-_{cb} \quad \rightarrow \quad dye_{red} \qquad (2.8)$$

A schematic representation of the mechanisms of generation ofoxidative species in a photocatalytic study is shown in Figure 2.3.
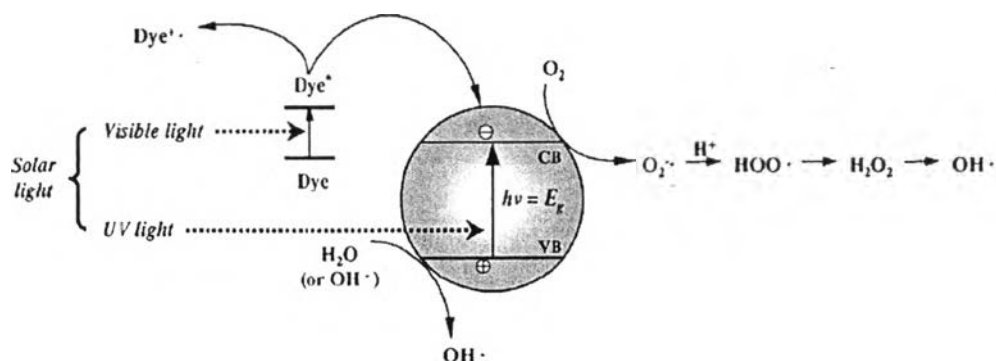


**Figure 2.3** Schematic showing the mechanisms diagram in a photocatalytic reaction (Rauf and Ashraf, 2009).

Molinari *et al.* (2014) studied the basic principle of photocatalytic hydrogen generation and focused on the photocatalytic able to work under visible light irradiation. The result showed that several methods, such as noble metal loading, ion doping, composite photocatalysts, increased the photocatalytic activity of semiconductors under visible light irradiation. That is because those methods improved the performance of semiconductor band gap on metal and also reduced the recombination charge.

Angelo *et al.* (2013) studied photocatalysis technology for $NO_x$ photo abatement. The fundamentals of photoelectrochemical devices and the photocatalysis phenomena were reviewed. The effect of operation condition was discussed and shown that photocatalysis is a green process to answer a serious environmental issue especially $NO_x$ pollution. However, the photocatalytic activity of titanium dioxide semiconductor strongly depended on several operating and process conditions when used in continuous reactors, i.e. i) inlet concentration of the pollutant, ii) air humidity, iii) light intensity and light spectrum, iv) flow rate/residence time, v) photocatalyst concentration per active area, vi) substrates, where $TiO_2$ is deposited.

Rauf and Ashraf (2009) reviewed the fundamental of heterogeneous photocatalytic dye degradation in solution using $TiO_2$ as a catalyst. They concluded that $TiO_2$ can be used as an effective catalyst for the degradation/decoloration of various dyes in solution. $TiO_2$ doped with metal ions increased its photocatalytic activity. Moreover, the degradation/decoloration rate can be influenced by operational parameters, for example, the amount of photocatalyst, pH, the type of additives, and concentration of substituent.

## 2.2 Titanium Dioxide

### 2.2.1 Structure of $TiO_2$

In generally, $TiO_2$ has three types of bulk crystalline forms, which arerutile, anatase, and brookite. Some research reviewed that the structural characteristics of both anatase and rutile materials are generally found in $TiO_2$ structure but the brookite structure is not often used for experimental investigations.

Both the rutile and anatase crystal structures are in distorted octahedron classes. In rutile, slight distortion from orthorhombic structure occurs, where the unit cell is stretched beyond a cubic shape. In anatase, the distortion of the cubic lattice is more significant, and thus the resulting symmetry is less orthorhombic. Figure 2.4 depicts the distorted octahedral symmetries characteristic of rutile and anatase (Hashimoto and Fujishima, 2005).
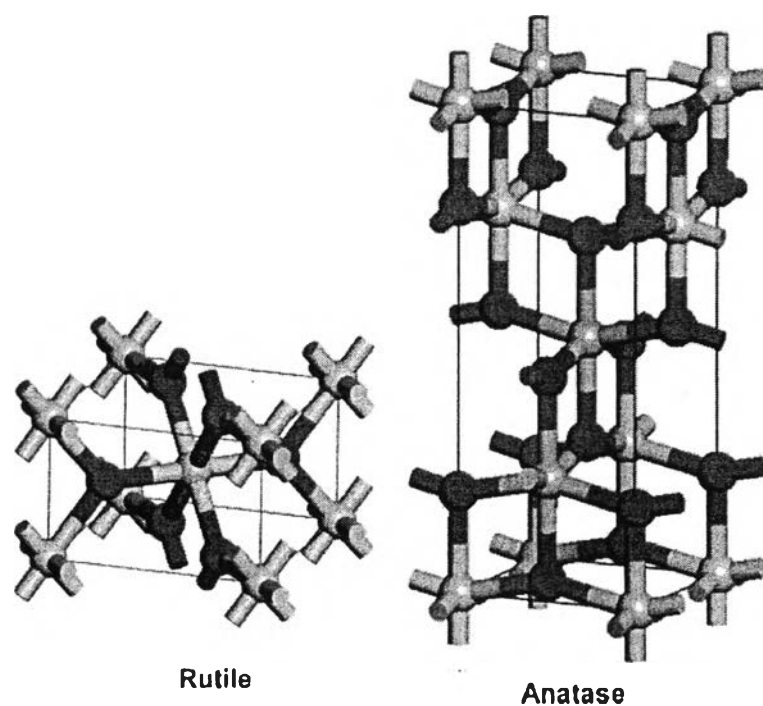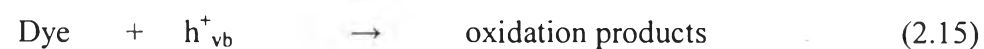


**Rutile**  **Anatase**

**Figure 2.4** Bulk crystal structures of rutile and anatase. Titanium atoms are gray, and oxygen atoms are black (Hashimoto and Fujishima, 2005).

2.2.2 Photocatalytic Mechanism of $TiO_2$

On account of high activity and stability under ultraviolent light, $TiO_2$ has been the most studied semiconductor for photocatalytic application. Several research discussed on the photocatalytic mechanism and reaction of $TiO_2$ semiconductor. When aquesous $TiO_2$ suspension is irradiated with light energy greater than its energy band gap ($E_g$ 3.2 eV), both conduction band electron ($e^-$) and valence band holes ($h^+$) are generated at the same time. The photogenerated electrons could reduce the dye or react with electron acceptors such as $O_2$ adsorbed on the

Ti(III)-surface or dissolved in water, reducing it to superoxide radical anion $O_2^{\bullet -}$. In the meantime, the photogenerated holes can oxidize the organic molecule to form $R^+$, or react with $OH^-$ or $H_2O$ oxidizing them into $OH^\bullet$ radicals. The resulting $OH^\bullet$ radical, being a very strong oxidizing agent can oxidize most of azo dyes to the mineral end-products. According to this reaction at the $TiO_2$ surface, the degradation mechanism can be shown as follows (Konstantinou and Albanis, 2004).

$$TiO_2 \quad + \quad h\nu\,(UV) \quad \rightarrow \quad TiO_2\,(e^-_{cb} + h^+_{vb}) \tag{2.9}$$

$$TiO_2\,(h^+_{vb}) \quad + \quad H_2O \quad \rightarrow \quad TiO_2 \ + \ H^+ \ + \ OH^\bullet \tag{2.10}$$

$$TiO_2\,(h^+_{vb}) \quad + \quad OH^- \quad \rightarrow \quad TiO_2 \ + \ OH^\bullet \tag{2.11}$$

$$TiO_2\,(e^-_{cb}) \quad + \quad O_2 \quad \rightarrow \quad TiO_2 \ + \ O_2^{\bullet -} \tag{2.12}$$

$$O_2^{\bullet -} \quad + \quad H^+ \quad \rightarrow \quad HO_2^\bullet \tag{2.13}$$

$$Dye \quad + \quad OH^\bullet \quad \rightarrow \quad degradation\ products \tag{2.14}$$

$$Dye \quad + \quad h^+_{vb} \quad \rightarrow \quad oxidation\ products \tag{2.15}$$

$$Dye \quad + \quad e^-_{cb} \quad \rightarrow \quad reduction\ products \tag{2.16}$$

Konstantinou and Albanis (2004) studied and reviewed the azo dye photocatalytic treatment using $TiO_2$. They concluded that azo dye degradation is possible by photocatalysis in the presence of $TiO_2$ suspension and UV, visible or solar light. The kinetics of the photocatalytic oxidation followed a Langmuir-Hinshelwood model and depended on several factors such as dye concentration, mass of catalyst, and wave length.

Xagas *et al.* (1999) studied the texture and the effect of the extension of the surface. Titanium oxide films with different surface features were prepared by sol-gel (SOL films) and sintering methods (TR films). The result showed that the properties of the photocatalytic films were strongly dependent on their synthesis and processing controls. Not only have the TR (Triton) films had higher performance than the SOL (Sol-Gel) films but also larger surface areas and smaller particle sizes. Because of the large surface areas, more light energy is absorbed higher resulting in degradation.

## 2.3 Photocatalytic Mechanism of Zinc Oxide and Vanadium Oxide

Heterogeneous photocatalytic involving titanium dioxide ($TiO_2$) appears to be the most promising technology for organic dye degradation. However, because of the relatively large band gap (3.2eV), it is necessary to extend the photo-response of $TiO_2$ by modification of its structure/composition for efficient photocatalytic activity. Doping one of various techniques to improve its response and also reduces the electrons-hole pair recombination. The main objective of doping is to decrease the band gap energy. Several transition metals, such as $Ni^{2+}$, $Zn^{2+}$, $Cr^{3+}$ and $Fe^{3+}$ can be easily incorporated into the crystal lattice of $TiO_2$. One of the most popular metals is vanadium oxide ($V_2O_5$). An advantage of vanadium oxide dopant is to improve the catalytic activity of the active metal oxide phase because the mechanical strength on surface area is increased. The most important oxidation states in aqueous solution are $V^{5+}$ and $V^{4-}$. The specific vanadium oxide species that can exist depends on the solution pH and the vanadium oxide concentration. $V^{5+}$ is known to undergo the following mechanism

$$V^{5+} + e^- \rightarrow V^{4+} \tag{2.17}$$
$$V^{4+} + O_2\,(abs) \rightarrow V^{5+} + O_2{}^{\bullet-} \tag{2.18}$$
$$V^{5+} + h^+ \rightarrow V^{6+} \tag{2.19}$$
$$V^{6+} + OH^- \rightarrow V^{5+} + OH^{\bullet} \tag{2.20}$$
$$V^{5+} + dye\,(ads) \rightarrow V^{4+} + dye^{\bullet} \tag{2.21}$$
$$V^{3+} + O_2\,(ads) \rightarrow V^{4+} + O_2{}^{\bullet-} \tag{2.22}$$

$V^{4+}$ traps holes and electrons and forms $V^{5+}$ and $V^{3+}$, respectively. Subsequently, the trapped electrons and holes are released and migrate to the surface of $TiO_2$. By accepting an electron, the adsorbed $O_2$ on the surface of $TiO_2$ is reduced to $O_2{}^{\bullet-}$, while surface hydroxyl group translates into hydroxyl radical ($OH^{\bullet}$) by accepting a hole. Both $O_2{}^{\bullet-}$ and $OH^{\bullet}$ can further degrade the dye molecule. As a result, the introduction of appropriate amount of $V^{4+}$ ions in $TiO_2$ lattice can restrain the recombination rate of photogenerated electrons and holes, enhancing the photocatalytic activity of $TiO_2$ (Rauf *et al.*, 2011).

Due to zinc oxide (ZnO) has many advantages such as high chemical stability, good electric properties, high illuminated transmittance, and good substrate adherence, ZnO is an interesting material to couple with $TiO_2$ (Ivonava *et al.*, 2011). $Zn^{2+}$ is a very important oxidation state. The presence of $Zn^{2+}$ can act as the following mechanism.

$$Zn^{2+} + e^- \rightarrow Zn^+ \tag{2.23}$$

$$Zn^+ + O_2\,(abs) \rightarrow Zn^{2+} + O_2^{\bullet-} \tag{2.24}$$

$$Zn^+ + h^+ \rightarrow Zn^{2+} \tag{2.25}$$

$$Zn^{2+} + h^+ \rightarrow Zn^{3+} \tag{2.26}$$

$$Zn^{2+} + OH^- \rightarrow Zn^{2+} + OH^{\bullet} \tag{2.27}$$

$$Zn^{3+} + e^- \rightarrow Zn^{2+} \tag{2.28}$$

$Zn^{2+}$ can generate $O_2^{\bullet-}$ and $OH^{\bullet}$ radicals, which can take place in photocatalytic reaction to effectively increase the dye degradation. Besides, in the $TiO_2$/ZnO composite, electron will transfer from the conduction band of ZnO to that of $TiO_2$, and hole can take place from the valance band of $TiO_2$ to the valance band of ZnO. This efficient charge separation causes the enhancement of photocatalytic activity and increases decolorization of dye (Rauf *et al.*, 2011).

Jaiswal *et al.* (2012) studied the preparation of V₀ and N-codoped $TiO_2$ photocatalyst powder synthesized by sol–gel method and their photocatalytic activity on rhodamine B (RhB) degradation. The effect of optimal dopant concentration for each element was discussed. The result showed that the molar ratios of 2% for V/Ti and 4% for N/Ti were suitable for the RhB degradation. The V-N codoped $TiO_2$ can increase the photocatalytic activity. In addition, the $V_2O_5$ species, on the surface of $TiO_2$, having lower energy level with respect to $TiO_2$, contributed in removing the photogenerated electrons leaving holes on the $TiO_2$.

Rauf *et al.* (2011) investigated a condense and coherent overview on the photocatalytic degradation of azo dye in the presence of $TiO_2$ doped with selective transition metals such as Cr, Cu, Fe, Mn, Zn, V, Ag, and W. The result showed that an important role in this process was played by molecular oxygen and resulting in other active species, such as $O_2^{\bullet-}$, $HO_2^{\bullet}$, $H_2O_2$, $OH^{\bullet}$, and $HO_2^{\bullet-}$. They make the

photocatalytic processes more efficient resulting in enhanced dye degradation via the formation of intermediates such as aromatic amines, phenolic compound sand several organic acids. The photocatalytic activity of vanadium doped $TiO_2$ film was estimated through degradation of Brilliant Red under visible light. Due to the narrowing band gap by vanadium doping, the degradation of dye was 60% for doped $TiO_2$. The photocatalytic degradation of dye was found 7% for undoped $TiO_2$.

Ivanova *et al.* (2011) studied the characterics of $ZnO$-$TiO_2$ films obtained by sol–gel method. The effect of calcined temperature was discussed. The result showed that the film structure had a mixture of crystalline phases and amorphous fraction at 400 °C. When increased the calcined temperature, to 750 °C, the $ZnO$-$TiO_2$ films were uniform with no defects but the surface area was decreased.

Pozan and Kambur (2014) studied the enhancement of 4-chlorophenol degradation by $ZnO$-$TiO_2$ catalyst. The catalyst was prepared by a solid-state dispersion method. The effect of weight ratio was discussed. The result showed that the photocatalytic efficiency decreased with the increase in the ZnO content increase. The optimum concentration of 20 wt% ZnO on $ZnO$-$TiO_2$ catalyst to resulted in higher reaction rate than $TiO_2$, and Degussa P-25, respectively, because the chemical interaction between ZnO and $TiO_2$ may affect the photo efficiency of oxide catalyst.

## 2.4 Acid Orange 7

Azo dyes are widely used in industry, such as textiles, papers, cosmetics, and in analytical chemistry. About a half of global production of synthetic textile dye is classified to azo compounds that have the chromophore of $-N=N-$ unit in their molecular structure. These azo dyes are known to be largely non biodegradable and also can cause cancer on human beings (Wawrzyniak *et al.*, 2006).
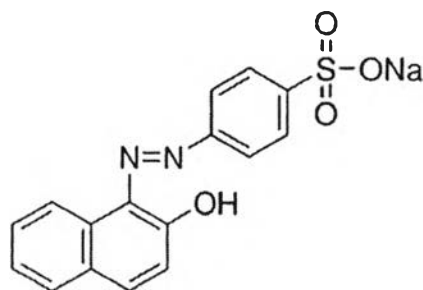
**Figure 2.5** Molecular structure of Acid Orange 7 Dye (www.lobachemie.com).

The photocatalytic degradation of an azo dye, namely acid orange 7 (AO7), has been examined with the use of TiO$_2$ catalyst. This dye mainly exists in two tautomeric forms, which is the azo form and the hydrazone form, as shown in Figure 2.6. However, the hydrazone is predominant in aqueous solution. It was found that the photocatalytic degradation of this leads to decoloration of the solution and to complete mineralization of the dye solution. AO7 adsorbs on the photocatalyst surface via the oxygen of its hydrazone form and the two oxygen atoms of the sulfonate group. Interaction with solar light results initially in cleavage of the dye molecule in the vicinity of the azo bond followed by the formation of molecules containing naphthalene and benzene-type rings. The primary reaction was the formation of aromatic acids to aliphatic acids, which caused the decrease of pH and an increase of conductivity in dye solution (Rauf and Ashraf, 2009).



**Figure 2.6** Tautomeric forms of Acid Orange 7 in aqueous solution (Stylidi*et al.*, 2003)

Stoyanova *et al.* (2014) studied the preparation of nanosized cobalt and iron-cobalt spinel oxides-bulk and supported on MgO and investigated the effect of catalyst for oxidation degradation of AO7. Furthermore, the effect of various operating parameters influencing AO7 removal such as type, catalyst loading, concentration of oxidation, and pH solution, were studied. The result showed that the nano-dimentional $Co_3O_4$ and mixed Fe-Co spinal oxides supported on MgO were proven to be a very effective heterogeneous catalyst for AO7 oxidation degradation. The AO7 degradation efficiency and rate were strongly enhanced due to several factors such as decreasing pH in acid range, increasing catalyst amount, and physical mixtures systems concentration.

Kryukona *et al.* (2007) investigated the behavior of $TiO_2$ catalyst with real structure and modified surface of $TiO_2$ with Pt. The photo decomposition of aqueous AO7 was also used as a model to characterize the photocatalytic activity of $TiO_2$. Experimental result showed that the synthesized titania possessed relatively high photocatalytic activity in the oxidation of AO7 under UV light and showed noticeable AO7 adsorption in the dark. In the $TiO_2$ calcinated at higher than 500 °C, sulfur atoms began to leave the oxide bulk and led to the highest photocatalytic degradation of AO7 equal to 66%. Moreover, the small amount of Pt added into the samples was observed to enhance the photocatalytic activity with an AO7 degradation of 97%, which was higher than that of unmodified $TiO_2$.

Muthirulan *et al.* (2014) studied the efficient route for the fabrication of $TiO_2$ decorated grapheme (GR) nanocomposites through one step route by examining the degradation of AO7 under UV/solar light irradiation. The result showed that the optimal assembly and interfacial coupling between the GR and $TiO_2$, which enhanced redox activity and electrical conductivity, had higher efficiency in the photodegradation of AO7 than $TiO_2$ alone. That was due to the electron transfer between $TiO_2$ and GR greatly retarded the recombination of photoinduced charge carriers and prolonged the electron lifetime. In addition, the UV irradiation can bring better efficiency in the degradation of AO7 than the solar light.

## 2.5 Model for the Oxidation Energy Storage of TiO₂

As the photocatalytic reactions are allowed to drive only under irradiation, the functions of the photocatalyst in the dark will be very useful. Recently, the energy storage of photocatalytic has been attrâcting and investigated by doping an active semiconductor or p-n junction semiconductor. When a p-type and n-type semiconductors are combined, the nature of p-n junction model is formed and shown on Figure 2.7. The free electrons on the n-type and the free holes on the p-type move across the junction. At the junction, the electrons and the holes tend to react with each other, creating a region depleted of any moving charges. This region is called the depletion zone (www.st-andrews.ac.uk).



Figure 2.7 General p-n junction model (www.electronics-tutorials.ws).

### 2.5.1 p-n Junction Model

Semiconductors consist of p- and n-type. The n-type has a high electron concentration, while the p-type has a high hole concentration. The connection of the two types resulting in the move of excess electrons in the n-type material to the p-type side and the excess holes from the p-type material to the n-type side. An n-type semiconductor like TiO₂ adsorbs photon having energy equal to or higher than its band gap energy. With each photon of the required energy (i.e. wavelength), that electrons rise to the unoccupied conduction band, leading to excited state conduction band electron and leaving the positive valence band holes ($h^+$) at the valence band.

Later, the electrons then transfer from the p-type (electron donor) to the valence band of the n-type (electron acceptor) semiconductor at the junction between the p- and n-type semiconductors. The holes at the p-type are not stable and need intercalation (x⁻) from an electrolyte for stabilization, as shown in Figure 2.7 The energy storage of $TiO_2$ with the p-type semiconductor takes place with the below model. The p-n heterojunction photocatalyst accelerates the separation of electron-hole pairs. Therefore, the p-n heterojunction photocatalyst has attracted much attention in recent years. (Takahashi and Tatsuma, 2005).



**Figure 2.8** p-n junction model for the oxidative energy storage photocatalyst (Takahashi and Tatsuma, 2005).

### 2.5.2 Mediation Model

The first step of the mediation model resembles the p-n junction model. That is a $TiO_2$ photocatalyst adsorbs photon having energy equal to or higher than its band gap energy. With each photon of the required energy (i.e. wavelength), electrons rise to the conduction band, leading to excited state conduction band electrons and leaving the positive valence band holes ($h^+$) at the valence band. On the other hand, unlike the p-n junction model, the electrons from the mediation ($H_2O_2$) then transfer to the valence band of $TiO_2$ for electrical neutrality, and the electrons of redox active material are transferred to mediation. As the result of the redox active

construction of the $Cu_2O$ nanowire network and the high anti photocorrosion property of the perfect crystallization of $Cu_2O/TiO_2$. In addition, the $Cu_2O/TiO_2$ network showed much higher degradation rate (1.97 µg/min $cm^2$) than the unmodified $TiO_2$ (0.85 µg/min $cm^2$). The enhanced photocatalytic activity was due to the extended absorption in the visible light resulting from the $Cu_2O$ nanowire networks, and the effective separation of photogenerated carries was driven by the photo induced potential difference generated at the $Cu_2O/TiO_2$ p-n junction interface.

Zhao *et al.* (2014) studied the preparation of the p-n heterojunction photocatalyst $CuFe_2O_4/Bi_4Ti_3O_{12}$ by ball milling with and without dispersant ($H_2O$). The effects of ball milling time and dispersant ($H_2O$) on the photocatalytic degradation of methyl orange (MO) were also investigated. The result showed that the photocatalytic performance of the sample was better than $Bi_4Ti_3O_{12}$. The heterojunction between $CuFe_2O_4$ and $Bi_4Ti_3O_{12}$ was formed during ball milling so the ball milling time strongly affected the photocatalytic activity. The enhanced photocatalytic performance can be attributed to the formation of the junction between $CuFe_2O_4$ and $Bi_4Ti_3O_{12}$, which reduced the recombination of photogenerated electro-hole pairs. Moreover, the mechanism of the photocatalytic confirmed that $O_2^{\bullet-}$ and $h^+$ were the main reactive species for the degradation of MO.

Ku *et al.* (2014) investigated the preparation of $ZnO/TiO_2$ for the photocatalytic reduction of hexavalent chromium Cr(IV). The effect of ZnO content on $ZnO/TiO_2$ photocatalyst was also studied. The result concluded that the $ZnO/TiO_2$ photocatalyst was prepared by wetness impregnation resulting in the bonds of ZnO on the surface of $TiO_2$. The containing 2.0 wt% ZnO on $ZnO/TiO_2$ exhibited the maximum photocatalytic reduction of Cr(IV) due to the enhancement of $e^-/h^+$ separation. The decrease of photocatalytic activity calcined at 700°C was attributed to the decrease of specific surface areas on $ZnO/TiO_2$.

## 2.6 Sol - Gel Method for Thin Film Preparation

Among various methods, the sol–gel method has been widely used due to the advantages of a relatively low cost and a flexible applicability to a wide range of sizes and shapes of the substrates. Sol-gel is the method involved with colloidal

suspensions that can change to viscous gels and then to solid materials during the sol–gel processing. Normally, precursors such as titanium alkoxide, titanium tetrachloride, and titanium halogenide are heated under very high calcinations temperature to obtain the desired crystal properties and a good adherence on the support. During heating, OH groups from the catalyst surface and the support can react and evaporate a molecule of water, creating an oxygen bridge, thus increasing the adherence of the catalyst to the support. In general, a dip coating apparatus equipped with an adjustable motor is used to immerse the support into a solution (gel form) and then withdrawn it at a certain speed. Therefore, this route is suitable for the production of a thin film photocatalyst. However, some drawbacks of the sol–gel method include the wide variation in the particle size distribution and the necessity of a calcination step for crystallization, which may result in the melting of the substrate. To improve the drawbacks of substrate, there are many researches that studied sol-gel with dip-coating over fiberglass, woven fiber glass, aluminum plate, and glass slide as a substrate of thin film catalyst (Shan *et al.*, 2010)
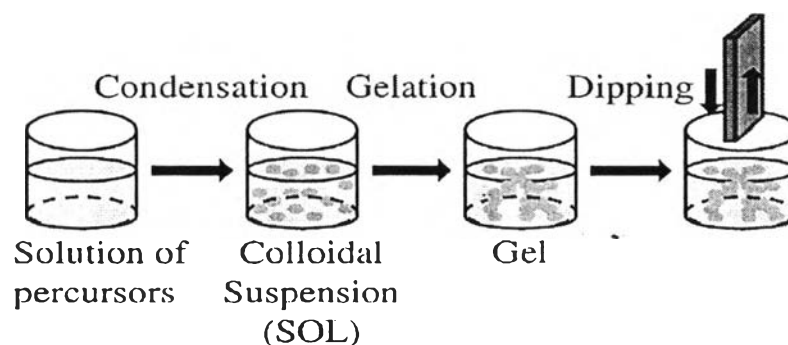


Condensation   Gelation        Dipping

Solution of     Colloidal        Gel
percursors      Suspension
                (SOL)

**Figure 2.10**  Schematic simplify diagram of sol-gel method associate with dip-coating (Angelo *et al.*, 2013).

Shan *et al.* (2010) studied the overview of the evolution in the use of different support for $TiO_2$ as a semiconductor photocatalyst. The effect of several supports such as glass, activated carbon, silica materials, polymeric materials, and the commonly techniques such as sol-gel, thermal treatment, chemical vapour deposition (CVD), electrophorectic deposition were also discussed for the removal of contaminants in wastewater. The result showed that the sol-gel method resulted in

the strong adhesion of the coating to the substrate due to chemical bonding. The research reported that the immobilised photocatalyst films were produced by the modified sol-gel method, which gave better stability and increased photocatalytic activity.

Chen and Dionysios (2006) studied the effect of Degussa P25 loading (0-100 g/L) in the precursor sol on film crystallinity, strength of adhesion, hardness, thickness, and pore structure, and also investigated the photocatalytic activity of immobilized $TiO_2$ films using the P25 powder-modified sol–gel method (PPMSGM) on stainless steel. Result showed that the photocatalytic activity can be improved by increasing P25 loading from 30 to 50 g/L. This improvement can be explained by the change in the film structure including (i) an increase in the amount of crystalline material for both anatase and rutile on the support, (ii) a decrease in the grain size, (iii) an increase in the amount of these grains, (iv) an increase in the number of pores, (v) an increase in the number of microcracks, and (vi) a decrease in the concentration of foreign metal ions (i.e., $Cr^{3+}$) on the surface of the immobilized $TiO_2$ films. On the other hand, the thickness of $TiO_2$ films does not affect directly with photocatalytic activity because the film thickness was not proportional to the amount of P25 particles in the films. In addition, the Scotch adhesion test showed that 50 g/L of P25 loading in the sol was the upper level, which could yield films with good adherence to the stainless steel support.

Lewkowicz *et al.* (2014) studied the preparation of the surface morphology and the optical properties of $TiO_2$ thin films deposited on glass with the sol-gel spin coating technique. The different temperatures of annealing (380-900 °C) were investigated. The result showed that the $TiO_2$ thin films without annealing were amorphous but their structure shifted through the anatase to rutile phases. It was clear that because the amorphous nature of $TiO_2$ was obtained using the sol-gel methods, the step of heat-treatment was required. With increasing the annealing temperature, the porosity of the $TiO_2$ thin films decreased from 67% to 15% because of shrinkage and densification of the films. The $TiO_2$ films crystallize was the anatase phase between 380-700 °C, while the rutile phase existed above 800 °C.

Hou *et al.* (2009) studied and proved the hypothesis that the application of bias potential across the photoanode can enhance the photocatalytic oxidation

process and a three-dimentional (3D) instead of a two-dimentional (2D) photoanode configuration, which would be much efficient in the electro-photocatalytic oxidation of organic compounds. The result showed that the applied bias was low but was sufficiently high enough to inhibit the recombination of electron-hole pairs efficiently and promoted acid orange II (AOII) degradation. Additionally, the 3D $TiO_2$/ACF electrode had large outer surface area along with good adsorption for organic compounds and exhibited much greater AOII degradation than the 2D $TiO_2$/ACF electrode.

## 2.7 Photocatalysis

Patel *et al.* (2014) studied the synthesis of V codoped $TiO_2$ photocatalyst in the form of thin films and studied the photocatalytic performance under visible light irradiation. The result showed that the V-N codoped $TiO_2$ thin films had maximum narrow band gap in the visible region (2.5 eV) as compared to single-element doped and undoped $TiO_2$. Moreover, the photocatalytic activity of V-N doped $TiO_2$ thin films was higher than the undoped or mono-doped films, which was attributed to both lower energy bad gap and reduced charge recombination rate.

Sun *et al.* (2008) studied the degradation of Orange G (OG) on nitrogen-doped $TiO_2$ photocatalysis under visible light and sunlight irradiation. The effect of initial solution, pH, and the dosage of hydrogen peroxide were also investigated. The result showed that not only the N-doped $TiO_2$ caused the new absorption band but also the photosensitized oxidation mechanism originated from the azo dyes themselves and contributed to the higher visible light activity. For this reason, the N-doped $TiO_2$ catalyst has higher the degradation OG than undoped $TiO_2$ catalyst under visible light. In contrast, the undoped $TiO_2$ catalyst exhibited high photocatalytic activity under sunlight irradiation. The pH result showed the optimal dosage of $H_2O_2$ was 0.5 for visible light and 15.0 mmol/l for sunlight irradiation.

Cao *et al.* (2009) studied the energy storage property of $TiO_2$-$WO_3$ powder using simple wet-chemical technique. The energy storage ability of $TiO_2$-$WO_3$ samples with different $WO_3$ crystal structures and various molar ratios of $WO_3$ to $TiO_2$ were evaluated. The result showed that the crystal structure of $WO_3$ could be

changed through the change in the heat-treatment temperature. The energy storage ability of $TiO_2$-$WO_3$ depended on the crystal structure of $WO_3$, and the molar ratio of $WO_3$/$TiO_2$ in 1:1 at heat-treated at 250 °C gave the best of energy storage ability. This ratio might help the electrons transfer during the process of photocatalytic energy storage.

Takahashi and Tatsuma (2005) studied $Ni(OH)_2$ as an energy storage material (p-type semiconductor) and coupled it with $TiO_2$ to give rise to oxidative energy by sol-gel methods. The prepared $TiO_2$-$Ni(OH)_2$ bilayer as a photochromic was estimated. The experiment result showed that the stored oxidative energy of $TiO_2$-$Ni(OH)_2$ bilayer can be discharged electrochemically or used for the chemical oxidation of various species. At pH 10 buffer, the $Ni(OH)_2$ layer was oxidized, and it turned from colorless to brown. The potential of the oxidative energy thus stored was about +0.7 V versus Ag/AgCl.

Huang *et al.* (2010) studied the photoelectrochromic properties of NiO film, which was deposited on a thin film of $TiO_{2-x}N_x$ by chemical bath deposition (CBD). $TiO_{2-x}N_x$ thin film was synthesized on the indium-tin oxide (ITO) conducing glass by sol-gel method. The result showed that the holes were generated in the $TiO_{2-x}N_x$ valence band oxidized NiO to NiOOH and the color of the $TiO_{2-x}N_x$/NiO electrode changed from colorless to brown. After 2 hr irradiation, the discharge time was about 4.2 hr at the current density of 100 $nAcm^{-2}$.

Lian *et al.* (2011) studied the effect of OH⁻ concentration in the electrolyte and surface structure in the $Ni(OH)_2$ layer on the storage of the oxidation energy of $TiO_2$ by electrodeposition method. Various current densities of porous nanostructured $TiO_2$-$Ni(OH)_2$ bilayer were discussed. The result showed that the porous $Ni(OH)_2$ layers prepared by the cathodic electrodeposition on a $TiO_2$/ITO substrate had relatively current densities (higher than 1.0 $mAcm^{-2}$). The particle size of $Ni(OH)_2$ was increased with increasing the deposition current density, which could be responsible for the enhanced oxidative energy storage of $TiO_2$-$Ni(OH)_2$ bilayer. Furthermore, the electrolytes with high OH⁻ concentration facilitated the oxidative energy storage of an UV-irradiated $TiO_2$ photocatalyst in $Ni(OH)_2$

Zhang *et al.* (2010) studied the effect of V content on the V doped $TiO_2$ nanofibers by electrospinning technique for photocatalyst applications. The result

showed that V ions could modify the electron properties of $TiO_2$ and extend its light absorption in the visible light region. It can be explained that $V^{4+}$ or $V^{5+}$ ions were successfully incorporated into the crystal lattice of anatase $TiO_2$ nanofibers. The photocatalytic results indicated that the V doped $TiO_2$ nanofibers can cause to high activity for the photodegradation of methylene blue, especially 1.0 and 5.0%wt.

Akbarzadeh *et al.* (2010) studied the photocatalytic activity of vanadia-titania thin films for the degradation of methylene blue under sunlight, and the vanadia loading was also investigated by simple sol-gel method. The result showed that the optimum concentration of vanadia in titania to obtain uniform viscous gel was found to be 0.5-4 wt%. Beyond these, the vanadia particles would block the gel network. Titania with 4 wt% vanadia was the most active catalyst for the degradation of methylene blue. Compared with pure $TiO_2$, the vanadia in $TiO_2$ increased the photodegradation rate of methylene blue by a factor of 3-6.6 times.

Wu and Chen (2004) studied the preparation of highly dispersed state of $V^{4+}$ incorporated titania photocatalyst by the sol-gel methods. The result showed that V-doped $TiO_2$ preserved its anatase phase after calcination at 400 °C. The vanadium ion in $TiO_2$ may change the band gap between the conduction and valence bands. The $0.035V/TiO_2$ can take the capability of absorbing visible light so the degradation rates of crystal violet and methylene blue on the V-doped $TiO_2$ under visible light were higher than $TiO_2$.

Chang and Liu (2011) studied the effect of both conventional bulk doping and surface doping on the photocatalytic activity under UV irradiation and the effect of the photo-generated species including trapped holes, electrons, and OH radicals. The result showed that the bulk doping by sol-gel $TiO_2$ existed mainly in $V^{3+}$ and $V^{4+}$ states. In contrast, the surface doping $V^{3+}/V^{4+}$ ions drove charge to the surface and retarded the surface recombination of electron/hole pairs. The photocatalytic activity of the doped $TiO_2$ was enhanced by 1.9 times for $3.0 \times 10^{-1}$ V/Ti molar ratio. The experimental result showed the formation of $V_2O_5$ separated the charge carriers through the formation of p-n junctions. The surface trapping and separation facilitated the interfacial charge transfer to catalyst. Therefore, surface doping metal ions improved the photocatalytic activity of $TiO_2$ to greater extent than bulk doping.