



## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Titanium (IV) Oxide

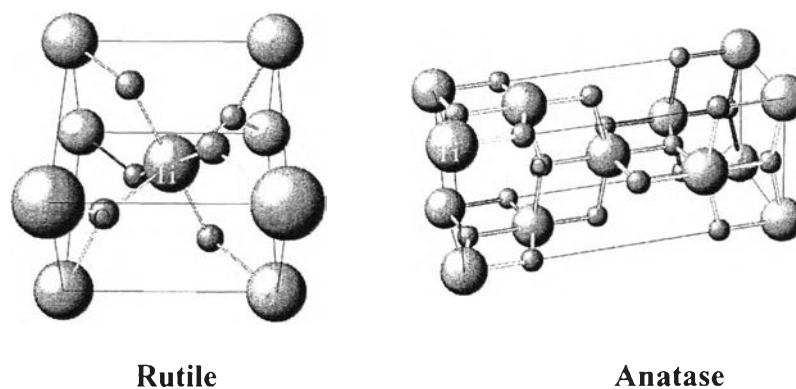
Titanium (IV) oxide is generally known as titanium dioxide or titania, appearing in white solid with the chemical formula of  $\text{TiO}_2$ . Due to its brightness and high refractive index ( $n = 2.7$ ), titania is extensively used as a white pigment, providing whiteness and opacity to products, such as paints, plastics, papers, inks, cosmetics and toothpastes. It is also used in almost every sunscreen product due to its high ultraviolet light absorptive. Fujishima *et al.* (1972) reported novel potential of titanium dioxide as photocatalyst. Recently, Kasuga *et al.* (1999) informed utilizing modified TNTs in bone regeneration material and proton conduction electrolytic film.

##### 2.1.1 Polymorphs of $\text{TiO}_2$

Three most widely known polymorphs of titanium dioxide are rutile (tetragonal), anatase (tetragonal), and brookite (rhombohedral). They exist as bulk structures and nanoparticles. Rutile has six atoms in a unit cell with each titanium atom bonded to six oxygen atoms and each oxygen atom bonded to three titanium atoms. The anatase structure is similar, but slightly more distorted than rutile. Two of the titanium-oxygen bonds are much longer than the other four bonds and the O–Ti–O bond angles deviate more than those in rutile. Brookite has an orthorhombic cell with the interatomic distances and O–Ti–O bond angles similar to those of rutile and anatase. There are six different Ti–O bonds ranging from 1.87 to 2.04 Å in length and twelve different O–Ti–O bond angles. Surprisingly, brookite and rutile are structurally similar because both phases are formed by straight polyhedron chains linked through three different corners of the unit cell, but the linking of polyhedron chains occurs through *cis*- bridges in brookite.

The polymorphs of titanium dioxide are found in different uses. For instance, the rutile phase is usually used in high-grade, corrosion-protective white coatings and paint, or in plastics, rubber, leather, sun-block lotion, and paper due to its high refractive index. The anatase phase has excellent optical and pigment

properties due to its electronic structure and it is used as an optical coating and photocatalyst. Applications of brookite are limited because it is uncommon and has historically been difficult to synthesize although it has similar general chemistry and similar physical properties (such as, color and luster) to rutile (Nie *et al.*, 2009).



**Figure 2.1** Crystalline structures of rutile and anatase.

### 2.1.2 Nanotube Structure

TiO<sub>2</sub>-based nanotubes have widely attracted attention from research communities because the nanotubes have high specific surface area, ion-changeable ability, and strong photocatalytic activity. Moreover, TiO<sub>2</sub> is useful in development in extensive applications. Currently developed methods preparing TNTs include template-assisted method (Hoyer, 1996), sol-gel process (Kasuga *et al.*, 1998), electrochemical anodic oxidation (Gong *et al.*, 2001), and hydrothermal treatment (Kasuga *et al.*, 1999).

In the template-assisted method, anodic aluminum oxide (AAO) nanoporous membrane is usually used as template. The membrane composes of an array of parallel straight nonporous material with uniform diameter and length. The size of nanotubes can be controlled by applying templates. However, the template-assisted method has several difficulties of pre-fabrication and post-removal of the templates, usually resulting in impurities.

Regarding electrochemical anodic oxidation, Gong *et al.* (2001) reported the self-assembled TNTs with highly ordered arrays. This method is based on the anodization of Ti foil to obtain a film of nanoporous titanium oxide (Zwillig

*et al.*, 1999). This group also reported the reviews associated with the fabrication factors, characterizations, formation mechanism, and the analogous applications of the TNTs arrays (Mor *et al.*, 2006).

The hydrothermal process is either suitable for large scale production or able to yield very low dimensional, well separated, crystallized nanotubes (Poudel *et al.*, 2005). Titania nanotubes produced by hydrothermal treatment show good crystallinity and give a pure-phase structure in one step in a tightly closed vessel.

As mentioned above for the approaches, electrochemical anodic oxidation and hydrothermal treatment are received wide attention among others, due to their cost-effective, easy procedure, and the feasibility/availability of widespread applications.

### 2.1.3 Microwave Irradiation

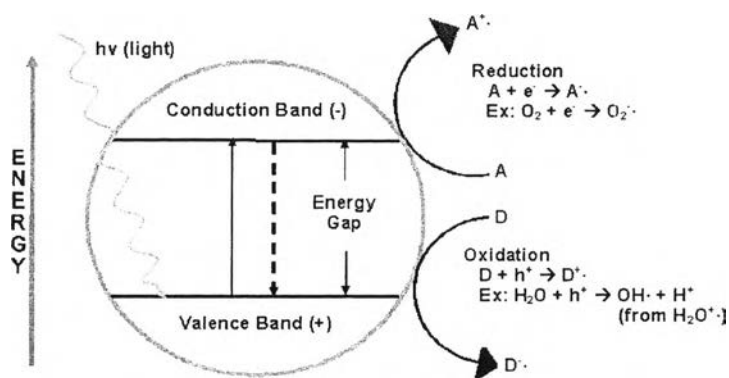
Microwave heating is a technique that has abilities to resolve the problems occurring in conventional synthesis methods (Wei *et al.*, 2009). The unique advantage of microwave irradiation is the direct energy delivering to materials through molecular-level interactions with the impinging electromagnetic field, resulting in uniform, rapid, and volumetric heating. The high reaction rates and selectivity are also obtained. Furthermore, it reduces the reaction time and gives high product yields (Liu *et al.*, 2005).

## 2.2 Photocatalytic Reactions

The photocatalytic or photochemical degradation processes are gaining importance in the area of wastewater treatment since these processes result in complete mineralization with operation at mild conditions of temperature and pressure. Many chalcogenide semiconductors, such as TiO<sub>2</sub>, ZnO, ZrO<sub>2</sub>, WO<sub>3</sub>, CdS, ZnS, and Fe<sub>2</sub>O<sub>3</sub>, have been investigated and used as photocatalyst. It should be noted that the best photocatalytic performances with maximum quantum yields have always been with TiO<sub>2</sub>. It is known as inexpensive, nontoxic, and very effective semiconductor photocatalysts (Lam *et al.*, 2008).

Photocatalytic reaction is initiated when a photoactive semiconductor is illuminated with photo of sufficient energy (band gap energy, or greater), a photon

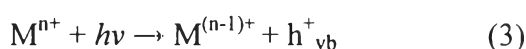
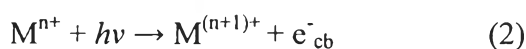
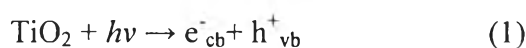
( $h\nu$ ) excites an electron from the valence band (VB), overcoming the energy band gap to the conduction band (CB) and leaves an electronic vacancy, a hole ( $h^+$ ), in the valence band, as shown in the Figure 2.2.



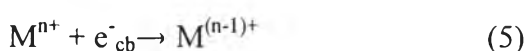
**Figure 2.2** The excitation of an electron from the valence band to the conduction band initiated by light absorption with energy equal to or greater than the band gap of the semiconductor ([http://www.cosmodec.co.za/air\\_pollution\\_control.htm](http://www.cosmodec.co.za/air_pollution_control.htm)).

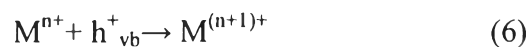
For instances, anatase and rutile are semiconductors with a band gap of 3.20 and 3.02 eV, which is equivalent to the photon energy of UV radiation with a wavelength of 387 and 410 nm, respectively. Thus, the electron and hole pair ( $e^-h^+$ ) are generated. Under proper conditions, the photo-excited electron and photo-excited hole can be made available for the redox reactions. The photo-generated hole in the VB must be sufficiently positive to carry out the oxidation of adsorbed OH<sup>-</sup> ions or H<sub>2</sub>O molecules to produce •OH radicals (the oxidative agents in the degradation of organics). A general photochemical charge-trapping, recombination, detrapping, and migration mechanism in the presence of metal ion dopants can be proposed as follows (Choi *et al.*, 1994):

Charge pair generation

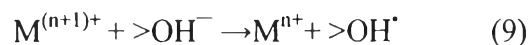
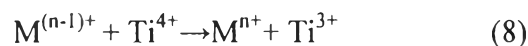


Charge trapping

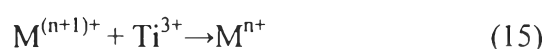
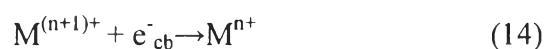
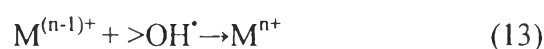
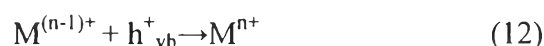
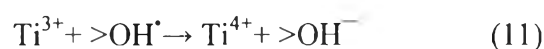




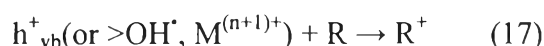
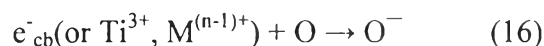
Charge release and migration



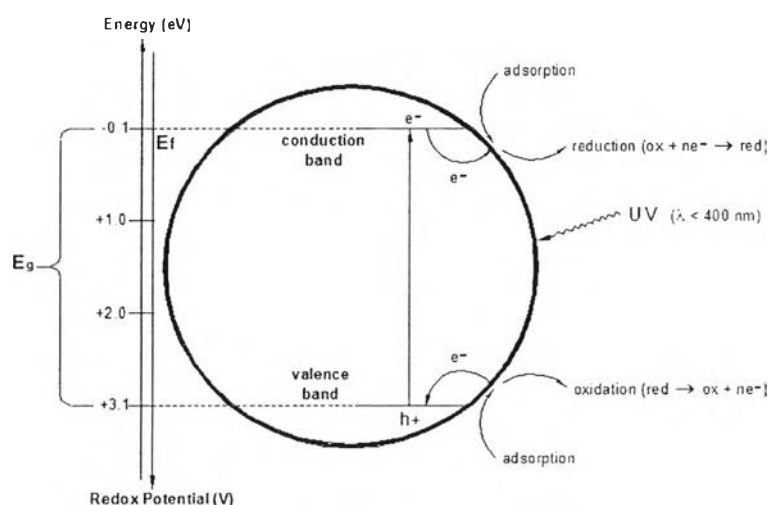
Recombination



Interfacial charge transfer



where metal ion is an dopant, O is an electron acceptor (oxidant), and R is an electron donor (reductant). The overall reaction is shown in Figure 2.3.



**Figure 2.3** Mechanism of  $TiO_2$  photocatalytic reaction

(<http://yangyang.blog.usf.edu/>).

Unfortunately,  $\text{TiO}_2$  has been limited by its wide band gap (3.2 eV), which requires ultraviolet (UV) irradiation for photocatalytic activation. On the other hand, UV light accounts for only a small fraction (5%) of the sun's energy, as compared to visible light (45%). As a result, many attempts have been made to improve the optical response of  $\text{TiO}_2$  under visible light excitation. Catalyst modification by doping with metal or transition metal ion is an approach to enhance the photocatalytic activity. Since 1980s, catalyst has been modified mainly by metal loading to achieve a better photocatalytic activity. Besides, a successful doping by transition metal ion also shows improvement in the photocatalytic system. In order to improve the effectiveness of the TNTs photocatalyst, dopant ion can modify the band gap or act as charge separators of the photoinduced electron-hole pair, thus enhancing the photocatalytic activity. Some studies have shown that metal ion doping of TNTs is effective in photocatalytic activity and better than undoped  $\text{TiO}_2$  nanotubes (Lam *et al.*, 2008).

Wong *et al.* (2004) reported that copper-doped  $\text{TiO}_2$  nanocatalysts were synthesized by photo-deposition and sol-gel methods. The results indicated that the Cu-doped  $\text{TiO}_2$  nanocatalysts with a low copper concentration prepared by the photo-deposition method showed enhanced photocatalytic activity; while catalysts synthesized by the sol-gel method did not. In particular, the  $\text{TiO}_2$  nanocatalyst doped with 1% Cu showed the best performance.  $\text{TiO}_2$  nanocatalysts doped with more than 1% Cu by the photo-deposition method showed a decrease in photocatalytic activities.

Xu *et al.* (2005) synthesized Zn ions surface-doped TNTs via an assembly process based on ligand exchange reaction and additional thermal treatment. First, the ligand exchange reaction between zinc acetyl acetonate and hydroxide radicals on  $\text{TiO}_2$  surface introduced the Zn ions onto the surface of TNTs, then the  $\text{Zn}(\text{acac})_2$  assembled TNTs were calcined at an optimal temperature (400 °C) to eliminate the organic ligands. The as-prepared Zn ions surface-doped TNTs showed a further improvement on the photocatalysis activity for degradation of methyl orange in water.

Zhang *et al.* (2008) prepared Cr-doped TNTs (Cr-TNTs) with high photocatalytic activity by the combination of sol-gel process and hydrothermal

treatment. Various techniques were employed for microstructural characterization. Transmission electron microscope (TEM) images showed that Cr-TNTs were in good tubular structure and have diameter of about 10 nm. The Cr doping induced the shift of the absorption edge to the visible light range and narrowed the band gap. The photocatalytic experiment revealed that the photocatalytic performance of TNTs could be improved by doping chromium ions.

Begum *et al.* (2008) reported that the TiO<sub>2</sub> thin films doped by Ni uniformly and non-uniformly were prepared on glass substrate from an aqueous solution of ammonium hexa-fluorotitanate and NiF<sub>2</sub> by liquid phase deposition technique. The rate of the reaction and the nature of the deposition depend on growing time and temperature. The result showed that the deposited films had amorphous background and became crystalline at 500 °C. The electron diffraction X-ray analysis (EDAX) confirmed the existence of Ni atoms in TiO<sub>2</sub> matrix. X-ray diffraction (XRD) analysis revealed the peaks corresponding to Ni but no peak of crystalline NiO was found. The transmittance spectra of Ni uniformly and non-uniformly doped TiO<sub>2</sub> thin films showed 'blue and red shifts', respectively. Ni-doped TiO<sub>2</sub> thin films could be used as photocatalyst for the photodegradation of methyl orange dye. It was found that organic dye underwent degradation efficiently in the presence of non-uniformly Ni-doped TiO<sub>2</sub> thin films when compared to uniformly doped films and pure TiO<sub>2</sub> films under visible light. The photocatalytic activity increased with an increase in the concentration of Ni in the case of non-uniformly doped thin films, but decreased with the concentration when uniformly doped thin films were used.

Hsieh *et al.* (2009) reported that a hydrothermal treatment combined with metal doping was employed to prepare highly porous Co-doped TNTs for enhancement of adsorption and visible-light-driven photocatalysis capabilities of basic violet 10 (BV10) from liquid phase. The specific surface area of the prepared TNTs reached the maximal value of  $\sim 379\text{m}^2/\text{g}$ . These tubes were hollow scrolls with typical outer and inner diameters of about 10–15 and 5–10 nm, respectively, and length of several micrometers. The anatase-type of TNTs has an average Co dopant concentration of  $5 \times 10^{20}$  ions/cm<sup>3</sup>, as determined by XRD. The hydrothermal synthesis of Co-TNTs is an efficient approach in enhancing not only specific surface area, but also photocatalysis capability under visible illumination. These novel Co-

doped TNTs are believed to be a promising candidate in a variety of photocatalysis applications because of the combination effect of a high porosity with a photocatalysis under visible illumination.

Deng *et al.* (2009) successfully synthesized Fe-doped TNTs by the combination of sol-gel process with hydrothermal treatment. After a further calcinations process, Fe-doped TNTs (Fe-TNTs) with high photocatalytic activity were obtained. The photocatalytic activity of Fe-TNTs was evaluated through the photodegradation of aqueous methyl orange. The experiments demonstrated that the 0.5% Fe-TNTs calcined at 300 °C possessed the best photocatalytic activity. Compared with pure TNTs, the doping with Fe significantly enhanced the photocatalytic efficiency.

Hussain *et al.* (2011) reported that pure TNTs and TNTs doped with iron (III) and chromium (III) were fabricated by the hydrothermal treatment in methanol and sodium hydroxide mixture. The fabricated nanotubes had high surface area, high aspect ratio, consisted of very good surface morphology and high metals dispersion. The results showed that nanotubes possessed anatase phase and are composed of up to 8–12 nm in diameter and 360–400 nm in length. The band gap of the TNTs, determined using transformed diffuse reflectance spectroscopy according to the Kubelka-Munk theory, showed a decrease in pronounced band gap on doped TNTs. The photocatalytic activity of doped nanotubes was evaluated in terms of degradation of phenol and photoreduction of carbon dioxide into methanol and ethanol under ultraviolet and infrared irradiations. It was found that iron (III) and chromium (III) doped TNTs exhibited much higher photocatalytic activity than undoped TNTs.