

CHAPTER II

BACKGROUNDS AND LITERATURE REVIEW

2.1 Principle of photocatalytic reactions

The photocatalytic process has drawn a great deal of attention in many works in the field of treatment and purification of air and water due to its ability to complete the oxidation of organic substances and the reduction of metal ions.

The basic principles of this method are the adsorption of substrates on catalytic surfaces and the irradiation process. A photocatalyst or semiconductor (SC) is characterized by an electronic band where the highest occupied energy band, called valence band (vb), and the lowest unoccupied band, called conduction band (cb). These two bands are separated by the energy gap called the band gap (E_{bg}). When the semiconductor is illuminated with light that has energy higher or equal to the band gap, electrons (e^-) in the valence band are activated to the conduction band, creating holes (h^+) in the valence band as illustrated in Figure 2.1

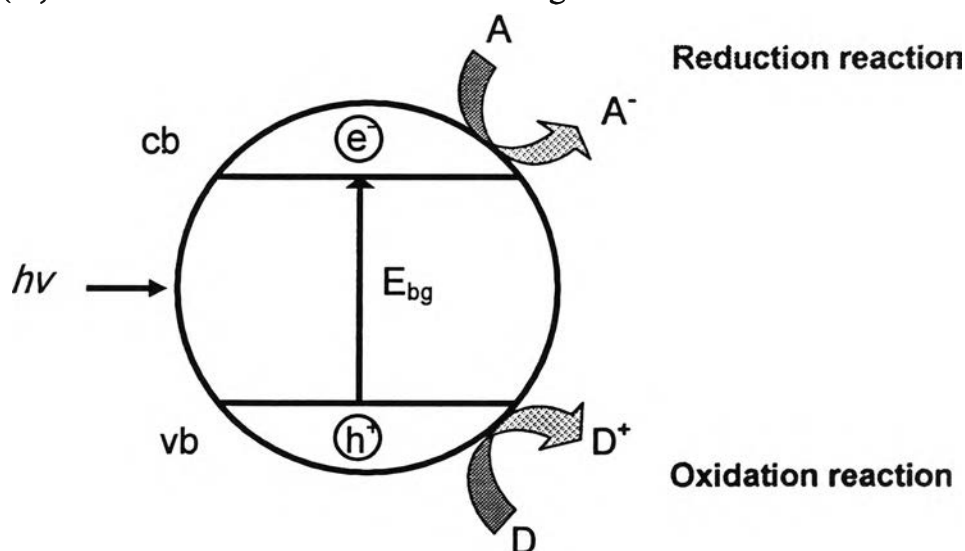


Figure 2.1 Scheme of the photocatalytic process over photocatalyst

The energy level at the bottom of the conduction band is the reduction potential of photoelectrons and the energy level at the top of the valence band determines the oxidizing ability of photoholes, each value reflecting the ability of the system to promote reductions and oxidations. From a thermodynamic point of view, adsorbed species can be reduced by conduction band electrons if they have redox potentials more positive than the flat band of the conduction band. In addition, they can be oxidized by valence band holes if they have redox potentials more negative than the flat band of the valence band (Litter, 1999). The band edge positions of several semiconductors are presented in Figure 2.2.

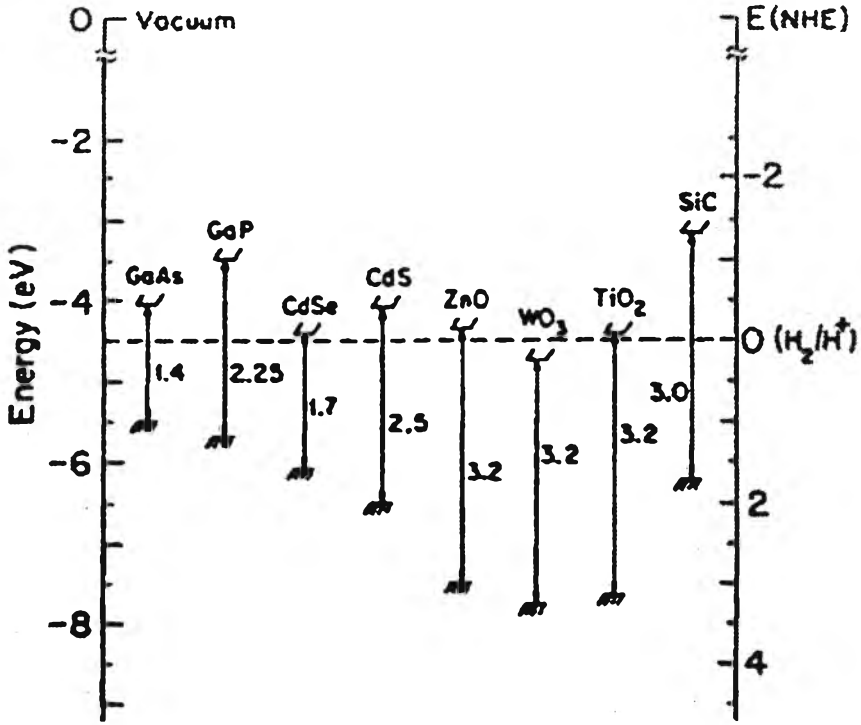


Figure 2.2 Energy band gap for various semiconductors at pH 1 (Linsebigler et al., 1995)

2.2 Titanium dioxide (TiO₂)

A semiconductor using in photocatalysis could be an oxide or sulfide of metals such as TiO₂, CdS, ZnO and WO₃. Titanium dioxide (TiO₂) is one of the most widely used as a semiconductor in photocatalysis due to its high activity, non-toxicity, corrosion stability, environmental friendly and low cost. In nature, there are three different crystal structures of TiO₂: brookite, rutile and anatase. Both rutile and anatase are often used in photocatalysis (Linsebigler et al., 1995). Their structures are illustrated in Figure 2.3 and their properties are shown in Table 2.1.

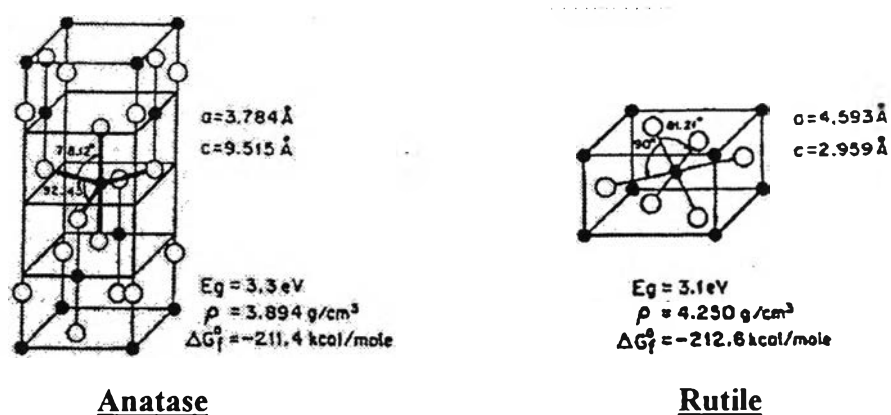
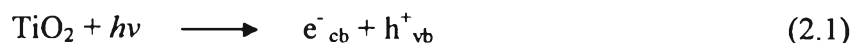


Figure 2.3 Structure of anatase and rutile (Linsebigler et al., 1995)

Table 2.1 Properties of anatase and rutile (Linsebigler et al., 1995; Fujishima et al., 1999; Litter, 1999)

Properties	Anatase	Rutile
Crystalline form	Orthorhombic	Orthorhombic
Band gap energy (eV)	3.200	3.030
Band gap wavelength (nm)	384	411
Hardness (Mohs)	5.5-6.0	6.0-7.0
Density (g/cm ³)	3.894	4.250
Gibbs free energy, ΔG_f° (kcal/mole)	-211.4	-212.6
Lattice constant, a (Å)	3.784	4.593
Lattice constant, c (Å)	9.515	2.959
Melting point	Changes to rutile at high temperature ~800°C	1858°C

When TiO_2 is irradiated by ultraviolet (UV) or light that the energy equals to or higher than the band gap (>3.2 eV), a reaction can be expressed by the following equation:



This process is followed by the formation of extremely reactive radicals (like OH^\bullet) at TiO_2 surface, and/or by a direct oxidation of the polluting species (R) as shown below:



From these equations, organic contaminants can undergo mineralization process to carbon dioxide and water such as phenol, 2,3,4-chlorophenol, benzene, parathion and dyes (Herrmann, 1999). In addition, organic compounds containing phosphorus, sulfur, and halogen may be oxidized quantitatively yielding phosphate (PO_4^{3-}), sulfate (SO_4^{2-}), and halide (X^-), respectively (Matthews, 1987).

Sobczyński et al. (2004) studied the mechanism of phenol decomposition and its intermediates in the presence of illuminated TiO_2 . They found that while TiO_2 was illuminated, the major intermediates were hydroquinone, p-benzoquinone and catechol. After completion of the reaction, only four compounds, carbondioxide, water, formic acid and acetic acid, were identified.

In the presence of metal ions, electrons from conduction band can be captured by these electron acceptors. The original oxidation state of the metal ions can be reduced to a different oxidation state (less harmful) as follow:



where M is metal ion such as Cr, Hg, Pb, Cu and Cd.

One of the most important parameters that affects the efficiency of this process is the standard redox potential of the involved metallic couple (M^{n+}/M) related to the flatband potential because only those species with reduction potential much more positive than the conduction band edge can be photoreduced, as shown in Figure 2.4.

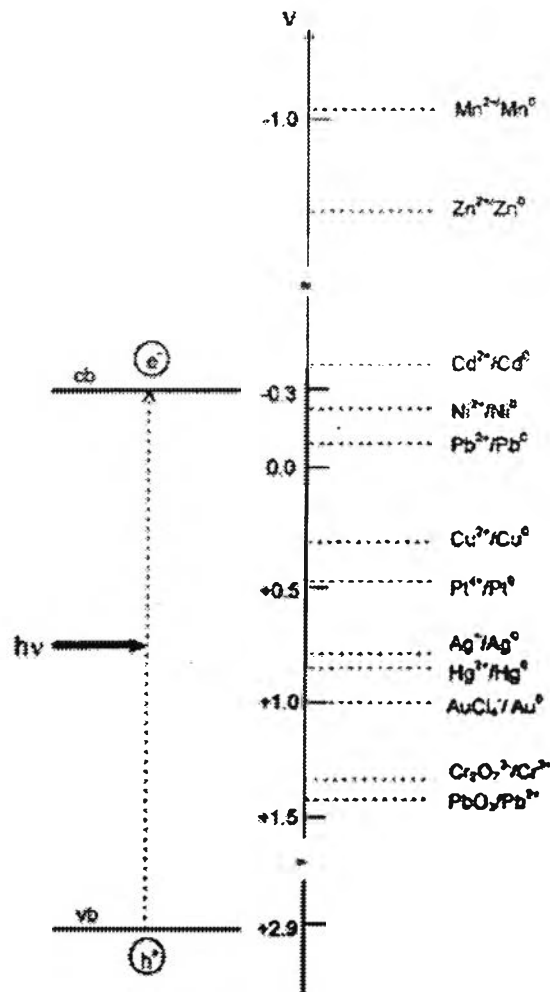


Figure 2.4 Position of the redox potentials of various metallic couples related to the energy levels of the conduction band and valence band of TiO_2 Degussa P-25 at pH 0 (Litter, 1999)

According to figure 2.4, it can be seen that metallic couple from $\text{PbO}_2/\text{Pb}^{2+}$ to $\text{Ni}^{2+}/\text{Ni}^0$ can be reduced by TiO_2 conduction band electrons, while the reduction reaction cannot occur with the metallic couple from $\text{Cd}^{2+}/\text{Cd}^0$ to $\text{Mn}^{2+}/\text{Mn}^0$.

TiO₂ can be used in two forms: suspended and immobilized. The former is not practical for industrial application because it requires stirring during the reaction and filtration after the reaction. These problems can be overcome by using the latter which is generally immobilized on inert substrates (Matthews, 1987; Pozzo et al, 1997; Hilmi et al, 1999)

2.3 Sol-gel process (Brinker and Scherer, 1990; Pierre, 1998)

The sol-gel process is a method used to synthesize ceramics and glass of several metal oxides through hydrolysis of metal alkoxide and polycondensation (Dislich, 1988). In fact, this method is not only designate as a unique technique, but also a very board type of procedures that centralized around a single scheme as presented in Figure 2.5. The application of sol-gel process is widely used in coating devices. These include optical coating, electronic coating, abrasion coating, barrier coating and protective coating (Klein, 1991)

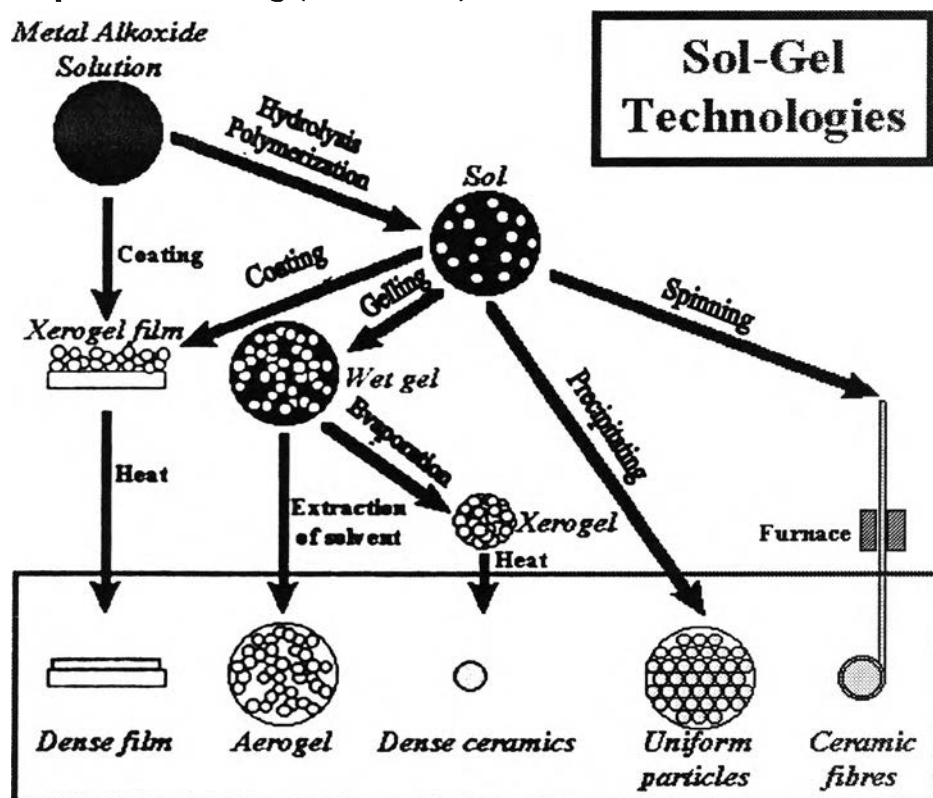


Figure 2.5 Diagram of sol-gel process (Casalboni, M)

2.3.1 Definition of sol and gel

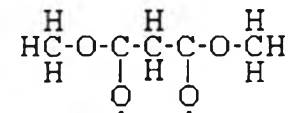
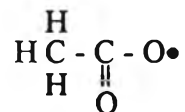
Sol is a colloidal suspension of solid particles within a liquid phase. The solid particles, denser than the surrounding liquid, must be small enough for the forces responsible of dispersion.

Gel is a substance which contains a porous three-dimensionally interconnected solid network throughout a liquid phase and it is only limited by the size of the container. If the solid network is made of colloidal sol particles, the gel is said to be colloidal. If the solid network is made of sub-colloidal chemical units, then the gel is polymeric. The nature of gels depends on the coexistence between the solid network and the liquid medium. If the liquid is mostly composed of water, and if that aqueous phase is the one presenting in greatest proportion, then the gel is an aqua gel. If the liquid phase is largely composed of an alcohol, then the gel is an alcogel. The gel can be formed by polycondensation or by rapid evaporation of the solvent during film or fiber preparation to obtain xerogel, which is dried under normal conditions, and aerogel, which is dried under supercritical conditions such as in an autoclave.

2.3.2 Type of precursors

In the sol-gel process, the precursors (starting compounds) for preparation of a colloid are composed of a metal or metalloid element surrounded by various ligands. A list of the most commonly used ligands is presented in Table 2.2. An alkyl is a ligand formed by removing one hydrogen (proton) from an alkane molecule. An alkoxy is a ligand formed by removing a proton from the hydroxyl on an alcohol.

Table 2.2 Commonly used ligands. (Brinker and Scherer, 1990)

<i>Alkyl</i>		<i>Alkoxy</i>	
methyl	•CH ₃	methoxy	•OCH ₃
ethyl	•CH ₂ CH ₃	ethoxy	•OCH ₂ CH ₃
<i>n</i> -propyl	•CH ₂ CH ₂ CH ₃	<i>n</i> -propoxy	•O(CH ₂) ₂ CH ₃
<i>iso</i> -propyl	H ₃ C(•C)HCH	<i>iso</i> -propoxy	H ₃ C(•O)CHCH
<i>n</i> -butyl	•CH ₂ (CH ₂) ₂ CH ₃	<i>n</i> -butoxy	•O(CH ₂) ₃ CH ₃
<i>sec</i> -butyl	H ₃ C(•C)HCH ₂ CH ₃	<i>sec</i> -butoxy	H ₃ C(•O)CHCH ₂ CH ₃
<i>iso</i> -butyl	•CH ₂ CH(CH ₃) ₂	<i>iso</i> -butoxy	•OCH ₂ CH(CH ₃) ₂
<i>tert</i> -butyl	•C(CH ₃) ₃	<i>tert</i> -butoxy	•OC(CH ₃) ₃
Other			
Acetylacetonate	$\text{H}_3\text{COC}(\bullet\text{O})\text{CH}_2(\text{O}\bullet)\text{COCH}_3$ 		
Acetate	$\bullet\text{OOCCH}_3$ 		

Remark: Dot(•) indicates bonding site, Parentheses indicate atom with available bond.
n = normal (meaning a linear chain), *sec* = secondary, *tert* = tertiary.

Metal alkoxides are popular precursors because they react readily with water, called hydrolysis, as in the following reaction:



The M represents a metal, such as Si, Ti and Al, and R is an alkyl group then OR is an alkoxy group and ROH is an alcohol. This reaction may go to completion or be only partially hydrolyzed depending on the amount of water and the presence of a catalyst. The desired rate of the hydrolysis reaction is obtained by controlling various factors. The most important factors are water and the alkyl group. For a slow reaction, hydrolysis must be carried out in dry environment or adding only small amount of water. As for the alkyl group, the longer it is, the harder it is to break the O-R bond and the slower the reaction.

Two partially hydrolyzed molecules can link together in a condensation reaction to give a bridging oxygen or metaloxane group, M-O-M:



or



This reaction can continue to build larger metal-containing molecules by the process of polymerization. The rate of hydrolysis has to be slower than that of condensation in order to obtain homogeneous gels rather than precipitates.

The sol-gel process involved initially a homogeneous solution of one or more selected alkoxides. Examples of metal alkoxides commonly used in sol-gel process are listed in Table 2.3. These alkoxides react at different rates according to the electronegativity of the cation.

Table 2.3 Common alkoxide for sol-gel process (Klein, 1997)

Name	Formula	Formula weight (g)	Density at 20°C (g/cm ³)
Tetraethyl orthosilicate	Si(OC ₂ H ₅) ₄	208	0.936
Trimethyl borate	B(OCH ₃) ₃	104	0.915
Aluminum <i>sec</i> -butoxide	Al(OC ₄ H ₉) ₃	246	0.967
Titanium isopropoxide	Ti(OC ₃ H ₇) ₄	284	0.955
Zirconium isopropoxide	Zr(OC ₃ H ₇) ₄	327	1.05

2.3.3 Advantages and limitations of sol-gel process

The pros and cons of sol-gel method can be concluded in Table 2.4.

Table 2.4 Advantages and limitations of sol-gel method (Pierre, 1998)

Advantages	Limitations
1. New hybrid organic-inorganic materials which do not exist naturally can be produced. 2. Very pure products are obtained. 3. Chemical processes or the first step are always carried out at low temperature.	1. Cost of precursors. 2. Some precursors and organic solvents are toxic.

2.4 Thin film formation (Dislich, 1988; Klein, 1991)

After the sol preparation, the solution is applied to a substrate by dip coating, spin coating or spray deposition. The former is the most widely used for film deposition since it can produce samples with a high degree of uniformity and simple thickness control. In addition, it can be reproduced and can coat on any size and shape of substrate. An additional advantage is the ability to produce multi-layer coating. Dip coating can be achieved either by batch (Figure 2.6) or continuous process (Figure 2.7).

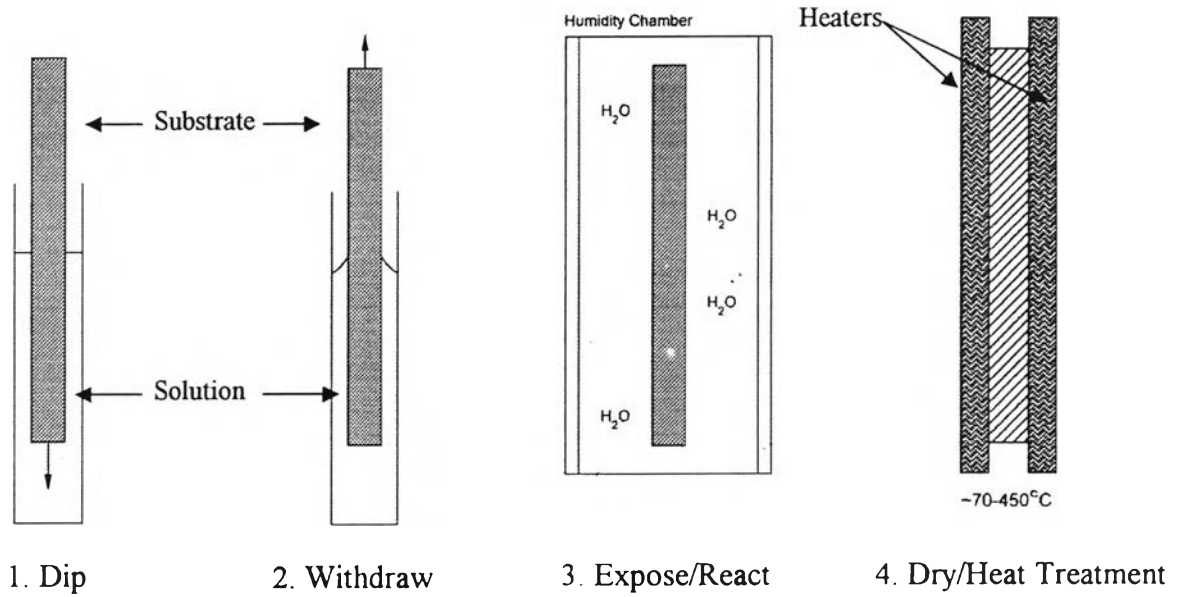


Figure 2.6 Schematic diagrams of a batch process for dipping (Klein, 1991)

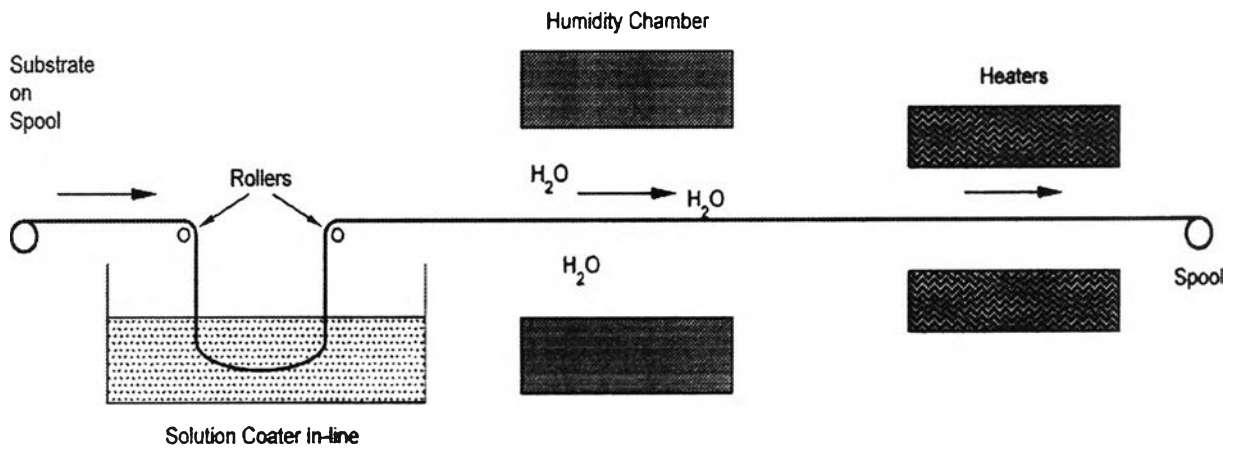


Figure 2.7 Schematic diagrams of a continuous process for dipping (Klein, 1991)

In this process, the substrate is lowered into a vessel containing the sol-gel solution and withdrawn at a constant speed that generates a continuous film on the substrate. The liquid film run-off the substrate adheres to the surface and solidifies

rapidly through the evaporation of solvent. At this stage, the chemical formation of the coating layer begins by evaporation of solvent, hydrolysis and condensation.

The thickness of the coating layer can be controlled by speed of withdrawal from the solution, concentration of the solution, solution viscosity and the angle of withdrawal. Besides, the surface tension of the solution, vapor pressure, and relative humidity above the coating bath are also affected the film thickness (Dislich, 1988). Vicente et al. (2001) showed that the film thickness increased with increasing withdrawal rate and increasing in oxide content.

2.5 Drying and heat treatment

After finishing the deposition, the film must be dried and required further heat treatment for crystallization as most gels are amorphous. The chemical formation of the oxide layer continues during this step. During the layer formation, water vapor diffuses from the tightly controlled atmosphere into the deposited layer and keeps the hydrolysis going. At the same time, the polycondensation process continues until the pure oxide layer has been formed at higher temperature.

2.6 Factors influencing on TiO₂ thin film activity

There are many parameters affecting TiO₂ thin film activity, such as calcination temperature, film thickness, as well as supporting material.

Regarding the TiO₂ thin film, the crystalline forms can be affected by temperature in heat treatment. It is due to anatase induced to rutile at high temperature that influence on the photocatalytic activity. Yu, Zhao and Zhao (2001) found that the photocatalytic activity of TiO₂ films coated on soda-lime glass was enhanced with the increase of the heat treatment temperature, being ascribed to the crystalline

transformation of TiO₂ film from amorphous to anatase phase. Moreover, the film showed the maximum photoactivity when it was fired at 500°C.

Liqiang et al. (2003) reported that the phase transformations of TiO₂ thin film, coated on titanium plate, from amorphous to anatase was completed at the temperature range from 450 to 550°C, and amount of anatase increased with the increasing calcinations temperature (Liu et al., 2003). The film which was calcined at 600°C showed the highest activity for phenol degradation. Furthermore, the photocatalytic activity of nanoparticle TiO₂/Ti film increased with increasing coating time and the crystallite size of anatase increased with the increasing calcinations temperature as well (Pecchi et al., 2001; Kim, Hahn et al., 2002)

Ha and Anderson (1996) tested the photocatalytic degradation of formic acid by TiO₂ supported on stainless steel plate. The coated film was calcined at temperatures between 300 and 600°C in order to study the effect of the firing temperature on crystal size and reaction rate. The X-ray diffraction showed that all of the TiO₂ films which were fired at temperature up to 600°C had only anatase structure, and particle size increased as the calcination temperature increased. They also stated that the retardation effect of phase transformation depended on the type of the supporting material. For example, TiO₂ film coated on quartz persisted in anatase form even after annealing at 1000°C (Kim, Hahn et al., 2002). TiO₂ films prepared on SnO₂-covered glass, rutile began to appear between 500°C and 550°C. In unsupported TiO₂, rutile began to form between 400°C and 500°C (Kim, Anderson and Zeltner, 1995) While in TiO₂ supported on titanium plate, the phase transformation from anatase to rutile began to appear at 600°C (Liqiang et al., 2003). For TiO₂ film coated on NiTi alloy, anatase phase was the main form when heat treatment temperature was in the region of 400-500°C. At temperature of 600-750°C, anatase and rutile existed simultaneously. Above 800°C, there was the only rutile presented (Liu et al., 2003).

From a coating point of view, ideally the supporting material for titanium as a photocatalyst should adhere well with the catalyst and should not degrade the catalyst activity through attachment processes. Various types of catalyst support are used, for

example glass plates, glass beads, fiber optics, quartz, sand, silica gel, stainless steel (Pozzo et al., 1997).

According to the previous studies, Ha and Anderson (1996) reported that stainless steel plate had potential as a supporting material for a TiO₂ photocatalyst used for the photocatalytic degradation of formic acid. Besides, preparation of TiO₂ film coated on stainless steel webnet exhibited high photocatalytic activity for the degradation of formaldehyde (Shang et al., 2003).

Supported catalysts are more likely to be used in commercial systems because they eliminate the need for filtration or the settling and resuspension of the photocatalyst. However, there is inherently decrease in the surface area available for reaction. In order to improve the surface area, the film has been prepared by incorporating some organic polymers with precursor solution. The chemical additives used in this work are polyethylene glycol with molecular weight 600 (PEG600) and diethylene glycol. Their properties are illustrated in Table 2.5.

Table 2.5 Physical properties of polyethylene glycol with molecular weight 600 (PEG600) and diethylene glycol (DEG)

Properties	PEG600 ^(a)	DEG ^(b)
Formular	H(OCH ₂ CH ₂) _n OH (n varies from 12.5 to 13.9)	O(CH ₂ CH ₂ OH) ₂
Molecular weight (g)	570-630	106.12
Apperence (25°C)	Colorless to light yellow transparent liquid	Clear liquid
Specific gravity (g/cm ³)	1.1265	1.1197
Boiling point	250	246

Remark:

^(a)http://www.ilo.org/public/english/protection/safework/cis/products/icsc/dtasht/_icsc15/icsc1517.htm

^(b)http://www.ilo.org/public/english/protection/safework/cis/products/icsc/dtasht/_icsc06/icsc0619.htm

Generally, the application of PEG for industry includes emulsifying agent, plasticizer, humectant, and water-soluble lubricant for rubber molds and textiles, in food and food packaging, detergents, softeners and ointments, pharmaceuticals, hair preparations and cosmetics. Roles of PEG were confirmed by Kato, Tsuge and Niihara (1996), and Kato and Niihara (1997). They reported that adding of PEG affected the crystallization by controlling hydrolysis and polycondensation reaction. PEG remained in the coating heated at a temperature as high as 400°C and decomposed to carbon dioxide at the temperature before the crystallization of the coating. As soon as the gas phase left from the coating film, the nano-sized space remained, and the fine crystallites with preferred orientation generated simultaneously. Moreover, the larger the amount and molecular weight of PEG (compared between PEG with molecular weight 2000 and 4000) are, the larger the size and numbers of pores are produced in the resultant coating film on the decomposition of PEG during heat treatment (Yu, Zhao, Zhao and Wang, 2001). In addition, the film surface morphology was smooth at lower molecular weight of PEG due to the good solubility of PEG, while the suppressed polycondensation enhanced the formation of macroscopic cracks at higher molecular weight (Kajihara and Yao, 2000).

Zhang, Au et al. (2004) reported that doping PEG in indium tin oxide thin film was resulted in the crack-free films with improved surface roughness, optical transmittance rate and the decreased electrical resistance. But the thickness of the films was hardly influenced by the addition of PEG when the molecular weight was not too high.

Srikanth et al. (2001) investigated the effect of the amount of PEG on film thickness and surface morphology. From scanning electron microscope (SEM) photographs, the film which was prepared from the sol without PEG appeared to have a heavily cracked formation. With the addition of 40% (w/t) of PEG, a smooth film surface was obtained. Further increasing the amount of PEG caused re-formation of the cracking with increasing both in size and number. In contrast, the film thickness was increased with increasing PEG content.

DEG is also used as an organic additive. It is expected to play an important role in stabilizing the dipping solution. Negishi et al. (1995) found that solutions

without DEG were unstable. TiO_2 particles were formed spontaneously after the solution was mixed for several minutes. Rao A.P. and Rao A.V. (2003) prepared rhodamine 6G (R6G) laser dye doped silica xerogel by sol-gel method using various organic additives. It was reported that DEG was a good additive to get highly fluorescent, monolithic and transparent R6G doped silica xerogels and it can reduce the percentage volume shrinkage of the sample as well.

Generally, TiO_2 can be used in two forms: suspended and immobilized. The former is not practical for use because it requires stirring during the reaction and filtration after the reaction, thus these problems can be overcome by using the latter which supports the catalyst on inert substrates as a film. To obtain the thin film, there are many techniques have been used such as chemical vapor deposition, sputtering, electron-beam evaporation and the sol-gel method (Pozzo et al., 1997; Sonawane et al., 2002). Among these techniques, the sol-gel process is accepted as the most practical ways to prepare TiO_2 thin film.

From previous works, the TiO_2 thin films can be prepared by various conditions. Negishi et al. (1995) prepared TiO_2 thin films on glass substrate by sol-gel dip coating. Titanium tetraisopropoxide ($\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$, TTiP) was used as a precursor, ethanol as solvent, and polyethylene glycol with a molecular weight of 600 (PEG600) and diethylene glycol (DEG) as organic/polymer additive. The solution contained 10 g of TTiP, 80 mL of ethanol and 10 g of the additives. PEG600 and DEG amounts were varied; 10 g of DEG, 7.5 g of DEG and 2.5 g of PEG600, 5 g of DEG and 5 g of PEG600, 2.5 g of DEG and 7.5 g of PEG600, and 10 g of PEG600. **Glass plates were dipped into the sol, and then calcined at 450°C for 1 h after every ten dipping.**

Ha and Anderson (1996) prepared TiO_2 film by supporting on stainless steel plate using the sol-gel technique. TTiP, water and nitric acid were used as chemical precursors at a ratio of mL at TTiP: H_2O : HNO_3 = 30:300:2. The sol was deposited on the substrate by spinning. The coated gel was dried at room temperature and then calcined at temperatures between 300 and 600°C for 2 h. Multi-coating was used in order to achieve a desired film thickness, 1-4 coating cycle.

Ao et al. (2001) synthesized TiO_2 using the sol-gel method. The synthetic photocatalyst was prepared from TTiP, ethanol and PEG600 in the mole ratio of TTiP: ethanol: PEG600 at 1:15:10. The catalyst was immobilized on glass fiber by dip-coating. Next, the glass fiber was dried at 100°C for 2 h and then calcined at 450°C for 2 h.

Fretwell and Douglas (2001) prepared a thin film of TiO_2 using the sol-gel method by dip coating and spin coating. The sol contained 5 g of TTiP, 40 mL of ethanol, 2.5 g of PEG600 and 2.5g of DEG. Films from dip-coated and spin-coated were calcined at 450°C for 30 min in furnace. Photocatalytic activities of both films were not different.

2.7 Chromium

2.7.1 Properties of chromium

Chromium is a transition element in Group VIB of the periodic table. It exhibits oxidation states from chromium(-II) to chromium(+VI). The most common forms are chromium(0), trivalent (or chromium(III)), and hexavalent (or chromium(VI)). Chromium(III) occurs naturally in the environment and is an essential nutrient required by the human body to promote the action of insulin in body tissues so that sugar, protein, and fat can be used by the body. Chromium(VI) and chromium(III) are generally produced by industrial processes. The metal chromium, which is the chromium(0) form, is a steel-gray solid with a high melting point. It is used mainly for making steel and other alloys. The most important industrial uses of chromium are in electroplating and chromium pigments. Leather tanning is another significant use, followed by wood preservation, catalysts and commercial electronic equipment (Richard, 1998; Schrank et al., 2002). Chromium(VI) is thermodynamically stable as the chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) anions which are soluble in aqueous solutions. Chromium(III) is insoluble in water, therefore, treatment of aqueous waste streams usually involves reduction of Cr^{6+} to Cr^{3+} prior to

precipitation and sedimentation. Common methods used for dealing with heavy metal containing in wastewater are precipitation, activated carbon adsorption, ion exchange and membrane separation (Schrank et al., 2002). However, they require either high energy or large quantities of chemical. Besides, these treatments pose a problem since their sludge is considered as hazardous waste that needs to be disposed (Khalil et al., 1998; Ku and Jung, 2001).

2.7.2 Health effects of chromium (Toxicological review)

Chromium(III) is an essential nutrient for humans. The shortages may cause heart conditions, disruptions of metabolism and diabetes. But the uptake of too much chromium(III) can cause health effects as well, for instance skin rashes.

Chromium(VI) is more toxic than chromium(III). It is known to cause various health effects such as skin rashes, upset stomachs and ulcers, respiratory problems, weakened immune systems, kidney and liver damage, alteration of genetic material, lung cancer and death. Adverse effects of the hexavalent form on the skin include ulceration, dermatitis, and allergic skin reactions. Inhalation of hexavalent chromium compounds can result in ulceration and perforation of the mucous membrane of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch.

2.7.3 Photocatalytic reduction of chromium (VI)

Parameters influenced the photocatalytic removal of chromium (VI) in the presences of TiO₂ have been studied. For example, Ku and Jung (2001) investigated the reduction of Cr(VI) under various solution pH value, TiO₂ dosages, light intensities, dissolved oxygen levels and other operating condition. The reduction rates of Cr(VI) by photocatalysis were significantly higher for acidic solutions than alkali solutions. Increasing the light intensity would drastically increase the reduction rate of Cr(VI) which, however, was ultimately influenced by the amount of TiO₂ present in

solution. The presence of dissolved oxygen had minimum effect on the reduction of Cr(VI) in acidic condition. The presence of ethanol might act as scavenger for holes and promoting the photocatalytic reduction of Cr(VI) by electrons.

Watcharenwong (2003) investigated the effects of pH, TiO₂ dosage, type of organic and inorganic additives on the photocatalysis of Cr(VI) from synthetic wastewater. The results showed that the optimum pH for Cr(VI) removal under UV-irradiation was at pH 3 with 59.40% Cr(VI) removal efficiency. In the presence of formate ions, the efficiency was enhanced to 82.46%.

The synergistic effect of photoreduction between two metal ions [Cu(II) and Cr(VI)] was found by Goeringer et al. (2001). In the absence of Cu(II), 800 μM Cr(VI) was not completely converted to Cr(III), even after 4 h irradiation. While the presence of 800 μM Cu(II) resulted in complete Cr(VI) reduction within 20 min. Similarly, the half-life for the photoreduction of 600 μM Cu(II) decreased from 1 h without Cr(VI) to 5 min in the presence of 1.6 mM Cr(VI).

Since metal ions can use electrons in the reduction process, they are able to prevent the electron-hole recombination resulting in the increase of oxidation efficiency. From a synergistic point of view, photocatalytic decontamination is also more useful when applied to wastewater containing mixtures of hazardous organic and inorganic species. Fu et al. (1998) reported that the promoting effect of 4-chlorophenol (4CP) on photocatalytic Cr(VI) reduction was distinguished and confirmed in the condition of excluding homogeneous reaction in Cr(VI)-4CP-TiO₂ system.

Schrank et al. (2002) studied photocatalytic reactions using Cr(VI) and dye in single and mixed systems. In the single system, both Cr(VI) and dye were degraded in acidic pH. In neutral pH, Cr(VI) was not reduced, while dye was almost completely oxidized by both acidic and neutral conditions. The reduction of Cr(VI) in the mixed system was faster than that in the single system, as dye was oxidized by photo-excited holes that prevented electron-hole recombination and promoted photoreduction of Cr(VI) on TiO₂. On the other hand, the oxidation of dye was also faster in the mixed system than in the single system as a result of the prevention of electron-hole recombination by Cr(VI).