

CHAPTER III

THEORY

It is known that titanium (Ti) can form a large number of addition compounds by coordination with other substances such as hydrogen, nitrogen, boron, carbon, oxygen, and other systems. Titanium dioxide (titania) is a titanium compound that is the most important commercial form. Physical and chemical properties of titania have been studied to include preparation procedure and its advantages.

3.1 Titanium (Ti) (Sornnarong Theinkeaw, 2000)

Titanium (atomic number 22; ionization potentials: first 6.83 eV, second 13.67 eV, third 27.47 eV, fourth 43.24 eV) is the first member of Group IVB of the periodic chart. It has four valence electrons, and Ti (IV) is its most stable valence state. The lower valence states Ti (II) and Ti (III) exist, but these are readily oxidized to the tetravalent state by air, water, and other oxidizing agents. The ionization potentials indicate that the Ti^{4++} ion would not be expected to exist and, indeed, Ti (IV) compounds are generally covalent. Titanium is able to expand its outer group of electrons and can form a large number of addition compounds by coordination with other substances having donor atoms, e.g., oxygen or sulfur. The most important commercial forms are titanium (IV) oxide and titanium metal.

Thermochemical data

Thermochemical data of titanium (IV) oxide and other titanium compounds are described. Data relating to changes of state of selected titanium compounds are listed in Table 3.1.

Table 3.1 Thermal data for changes of state of titanium compounds

Compound	Properties	Temperature,K	$\Delta H, \text{kJ/mol}$
TiCl ₄	melting point	249.05	9.966
	Boiling point	409	35.77
TiCl ₃	sublimation temperature	1104.1	166.15
TiCl ₂	sublimation temperature	1591.5	248.5
TiI ₄	melting point	428	19.23±0.63
	Boiling point	652.6	56.48±2.09
TiF ₄	sublimation temperature	558.6	97.78±0.42
TiBr ₄	melting point	311.4	12.89
	Boiling point	504.1	45.19
TiO ₂	phase change (anatase to rutile)		ca-12.6

3.2 Titanium (IV) oxide (Sornnarong Theinkeaw, 2000 and Fujishima *et al.*, 1999)

Physical and chemical properties

Titanium dioxide may take on any of the following three crystal structures: rutile, which tends to be more stable at high temperatures and thus is sometimes found in igneous rocks, anatase, which tends to be more stable at lower temperatures (both belonging to the tetragonal crystal system), and brookite, which is usually found only in minerals and has a structure belonging to the orthorhombic crystal system. The titanium dioxide use in industrial products, such as paint, is almost a rutile type. These crystals are substantially pure titanium dioxide but usually amount of impurities, e.g., iron, chromium, or vanadium, which darken them. A summary of the crystallographic properties of the three varieties is given in Table 3.2.

Although anatase and rutile are both tetragonal, they are not isomorphous (Figure 3.1). The two tetragonal crystal types are more common because they are easy to make. Anatase occurs usually in near-regular octahedral, and rutile forms slender prismatic crystal, which are frequently twinned. Rutile is the thermally stable form and is one of the two most important ores of titanium.

The three allotropic forms of titanium dioxide have been prepared artificially but only rutile, the thermally stable form, has been obtained in the form of transparent large single crystal. The transformation from anatase to rutile is accompanied by the evolution of ca. 12.6 kJ/mol (3.01 kcal/mol), but the rate of transformation is greatly affected by temperature and by the presence of other substance which may either catalyze or inhibit the reaction. The lowest temperature at which conversion of anatase to rutile takes place at a measurable rate is ca. 700°C, but this is not a transition temperature. The change is not reversible; ΔG for the change from anatase to rutile is always negative (see Table 3.1 and 3.2 for thermodynamic data)

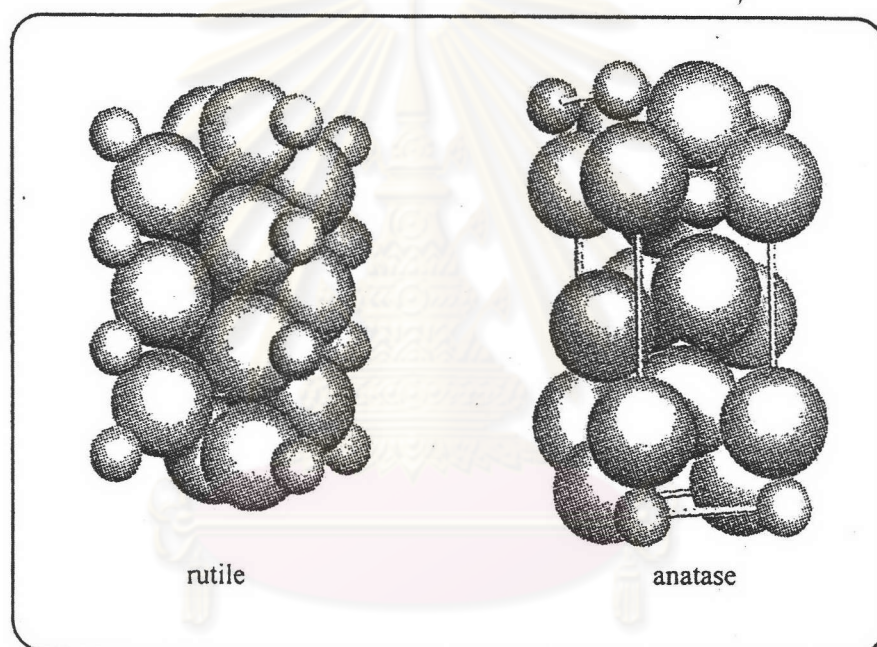


Figure 3.1 Crystal structure of TiO_2 . (Fujishima *et al.*, 1999)

Heating amorphous titanium (IV) oxide, prepared from alkyl titanates of sodium titanate with sodium or potassium hydroxide in an autoclave at 200 to 600°C for several days has produced brookite. The important commercial forms of titanium dioxide are anatase and rutile, and these can readily be distinguished by X-ray diffraction spectrometry.

Since both anatase and rutile are tetragonal, they are both anisotropic, and their physical properties, e.g. refractive index, vary according to the direction relative to the crystal axes. In most applications of these substances, the distinction between

crystallographic direction is lost because of the random orientation of large numbers of small particles, and it is mean value of the property that is significant.

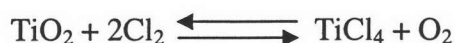
Table 3.2 Crystallographic properties of anatase, brookite, and rutile.

<i>Properties</i>	Anatase	Brookite	Rutile
Crystal structure	Tetragonal	Orthorhombic	Tetragonal
Optical	Uniaxial, negative	Biaxial, positive	Uniaxial, negative
Density, g/cm ³	3.9	4.0	4.23
Harness, Mohs scale	5 ^{1/2} – 6	5 ^{1/2} – 6	7 – 7 ^{1/2}
Unit cell	D _{4a} ¹⁹ .4TiO ₂	D _{2h} ¹⁵ .8TiO ₂	D _{4h} ¹² .3TiO ₂
Dimension, nm			
a	0.3758	0.9166	0.4584
b		0.5436	
c	0.9514	0.5135	2.953

Measurement of physical properties, in which the crystallographic directions are taken into account, may be made of both natural and synthetic rutile, natural anatase crystals, and natural brookite crystals. Measurements of the refractive index of titanium dioxide must be made by using a crystal that is suitably orientated with respect to the crystallographic axis as a prism in a spectrometer. Crystals of suitable size of all three modifications occur naturally and have been studied. However, rutile is the only form that can be obtained in large artificial crystals from melts. The refractive index of rutile is 2.75. The dielectric constant of rutile varies with direction in the crystal and with any variation from the stoichiometric formula, TiO₂; an average value for rutile in powder form is 114. The dielectric constant of anatase powder is 48.

Titanium dioxide is thermally stable (mp 1855°C) and very resistant to chemical attack. When it is heated strongly under vacuum, there is a slight loss of oxygen corresponding to a change in composition to TiO_{1.97}. The product is dark blue but reverts to the original white color when it is heated in air.

Hydrogen and carbon monoxide reduce it only partially at high temperatures, yielding lower oxides or mixtures of carbide and lower oxides. At ca. 2000°C and under vacuum, carbon reduces it to titanium carbide. Reduction by metal, e.g., Na, K, Ca, and Mg, is not complete. Chlorination is only possible if a reducing agent is present; the position of equilibrium in the system is



The reactivity of titanium dioxide towards acids is very dependent on the temperature to which it has been heated. For example, titanium dioxide that has been prepared by precipitation from a titanium (IV) solution and gently heated to remove water is soluble in concentrated hydrochloric acid. If the titanium dioxide is heated to ca. 900°C, then its solubility in acids is considerably reduced. It is slowly dissolved by hot concentrate sulfuric acid, the rate of salvation being increased by the addition of ammonium sulfate, which raises the boiling point of the acid. The only other acid in which it is soluble is hydrofluoric acid, which is used extensively in the analysis of titanium dioxide for trace elements. Aqueous alkalis have virtually no effect, but molten sodium and potassium hydroxides, carbonates, and borates dissolve titanium dioxide readily. An equimolar molten mixture of sodium carbonate and sodium borate is particularly effective as is molten potassium pyrosulfate.

3.3 Preparation procedure

Large surface area titanium dioxide powders have been prepared by several methods. The physical and chemical properties of titanium dioxides are quite different by the process of preparation.

3.3.1 Precipitation method

Precipitation method involves the growth of crystals from a solvent of different composition to the crystal. The solvent may be one of the constituents of the desired crystals, e.g., crystallization of salt hydrate crystals using water as the solvent, or the solvent may be entirely separate liquid element or compound in which the crystals of interest are partially soluble, e.g., SiO₂ and various high melting silicates

may be precipitated from low melting borate or halide melts. In these cases, the solvent melts are sometimes referred to as fluxed since they effectively reduce the melting point of the crystals by a considerable amount.

The method has recently been used to grow crystals of titanium (IV) oxide using titanium tetrachloride as starting material. Titanium (IV) oxide which, after washing and drying at 110°C, can be calcined at 800°C to remove combined water and chloride, according to the stoichiometric relation as follows:



This method used involves precipitation from titanium tetrachloride as hydrated titanium (IV) oxide conversion of the precipitate to the double oxalate, recrystallization of this from methanol and subsequent calcinations.

3.3.2 Sol-gel method

To prepare a solid using the sol-gel method, a sol is first prepared from suitable reactants in a suitable liquid. Sol preparation can either be simply the dispersal of an insoluble solid or addition of a precursor which reacts with the solvent to form a colloid product. A typical example of the first is the dispersal of oxides or hydroxides in water with the pH adjusted so that the solid particles remain in suspension rather than precipitate out. A typical example of the second method is the addition of metal alkoxides to water. The alkoxides are hydrolyzed giving the oxide as a colloidal product. The sol is then either treated or simply left to form a gel. To obtain a final product, the gel is heated. This heating serves several purposes—it removes the solvent, it decomposes anions such as alkoxides or carbonates to give oxides, it allows rearrangement of the structure of the solid and it allows crystallization to occur.

3.3.3 Hydrothermal method (West, 1997)

The method involves heating the reactants in water/steam at high pressures and temperatures. The water performs two roles, as a pressure-transmitting medium and as a solvent, in which the solubility of the reactants is P, T-dependent. In addition, some or all of the reactance are partially soluble in the water under pressure and this enables reaction to take place in, or with the aid of, liquid and/or vapor phases. Under these conditions, reactions may occur that, in the absence of water, would occur only at much high temperatures. The method is therefore particularly suited for the synthesis of phases that are unstable at higher temperatures. It is also a useful technique for growth of single crystals; by arranging for a suitable temperature gradient to be present in the reaction vessel, dissolution of the starting material may occur at the hot end and reprecipitation at the cooler end.

The design of hydrothermal equipment is basically a tube, usually of steel, closed at one end. The other end has a screw cap with a gasket of soft copper to provide a seal. Alternatively, the 'bomb' may be connected directly to an independent pressure source, such as a hydraulic ram; this is known as the 'cold seal' method. The reaction mixture and an appropriate amount of water are placed inside the bomb, which then sealed and placed inside an oven at the required temperature, usually at a temperature in the range 100-500°C. Pressure is controlled either externally or by the degree of filling in a sealed bomb. By making use of the P/T 'phase diagram', Figure 3.3(a); curve AB is the saturated steam curve and separates water (above) from steam (below); at temperatures above 374°C, point B, the water is in the supercritical condition and there is no distinction between liquid and vapor states.

The applications of the hydrothermal method is:

(a) *Synthesis of new phases: calcium silicate hydrate.*

Hydrothermal methods have been used successfully for the synthesis of many materials. A good example is the family of calcium silicate hydrates, many of which are important components of set cement and concrete. Typically, lime, CaO and quartz, SiO₂, are heated with water at temperatures in the range 150 to 500°C and

pressure of 0.1 to 2 kbar. Each calcium silicate hydrate has, for its synthesis, optimum preferred conditions of composition of starting mix, temperature, pressure and time. For example, xonolite, $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$, may be prepared by heating equimolar mixtures of CaO and SiO_2 at saturated steam pressures in the range 150 to 350°C.

(b) Growth of single crystals.

For the growth of single crystals by hydrothermal methods it is often necessary to add a mineralizer. A mineralizer is any compound added to the aqueous solution that speeds up its crystallization. It usually operates by increasing the solubility of the solute through the formation of soluble species that would not usually be present in the water. For instance, the solubility of quartz in water at 400°C and 2 kbar is too small to permit the recrystallization of quartz, in a temperature gradient, within a reasonable space of time. On addition of NaOH as a mineralizer, however, large quartz crystals may be readily grown. Using the following conditions, crystals of kilogram size have been grown: quartz and 1.0 M NaOH solution are held at 400°C and 1.7 kbar; at this temperature some of the quartz dissolves. A temperature gradient is arranged to exist in the reaction vessel and at 360°C the solution is supersaturated with respect to quartz, which precipitates onto a seed crystal. In summary, therefore, quartz dissolves in the hottest part of the reaction vessel, is transported throughout the vessel via convection currents and is precipitated in cooler parts of the vessel where its solubility in water is lower. Quartz single crystals are used in many devices in radar and sonar, as piezoelectric transducers, as monochromators in X-ray diffraction, etc. Annual world production of quartz single crystals, using hydrothermal and other methods, is currently a staggering 600 tons.

Using similar methods, many substances have been prepared as high quality single crystals, e.g. corundum (Al_2O_3) and ruby (Al_2O_3 doped with Cr^{3+}).

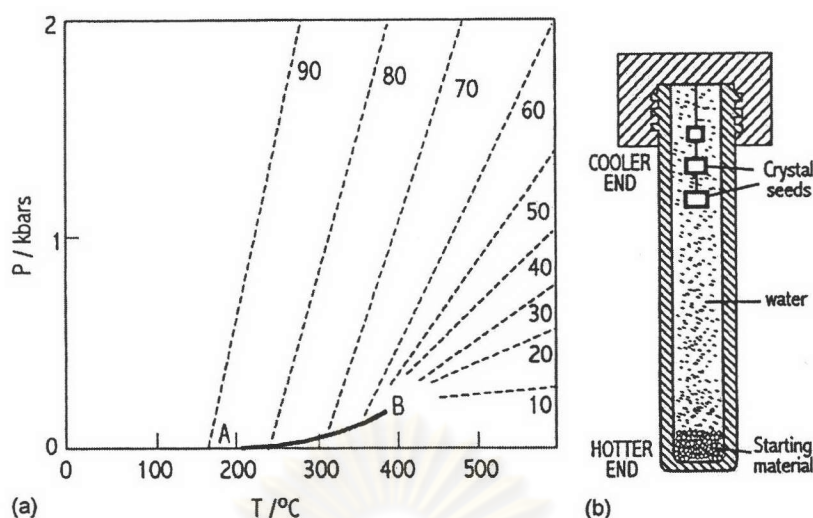


Figure 3.2 (a) Pressure-temperature relations for water at constant volume, dashed curves represent pressures developed inside a close vessel; numbers represent the percentage degree of filling of the vessel by water at ordinary P, T. (b) Schematic hydrothermal bomb used for crystal growth.

3.3.4 Glycothermal and solvothermal method

Glycothermal method and solvothermal method have been developed for synthesis of metal oxide and binary metal oxide by using glycol and solvent as the reaction medium, respectively. The use of glycol or solvent instead of water in the hydrothermal method produced the different form of intermediate phase and the stability of such intermediate phase was not strong. Instability of the intermediate phase gives a large driving force to the formation of product under quite mild condition. The preparation method is described in the experimental section, Chapter IV.

3.4 Single crystal (McGraw-Hill encyclopedia of science & technology, 1997)

In crystalline solids the atoms or molecules are stacked in a regular manner, forming a three-dimensional pattern, which may be obtained by a three-dimensional repetition of a certain pattern unit called a unit cell. When the periodicity of the pattern extends throughout the certain piece of material, one speaks of a single crystal.

A single crystal is formed by the growth of a crystal nucleus without secondary nucleation or impingement on other crystal.

3.4.1 Growth techniques

Among the most common methods of growing single crystals are those of P. Bridgeman and J. Czochralski. In the Bridgeman method the material is melted in a vertical cylindrical vessel, which tapers conically to a point at the bottom. The vessel then is lowered slowly into a cold zone. Crystallization begins in the tip and continues usually by growth from the first formed nucleus. In the Czochralski method a small single crystal (seed) is introduced into the surface of the melt and then drawn slowly upward into a cold zone. Single crystals of ultrahigh purity have been grown by zone melting. Single crystals are also often grown by bathing a seed with a supersaturated solution, the supersaturation being kept lower than necessary for sensible nucleation.

When grown from a melt, single crystals usually take the form of their container. Crystals grown from solution (gas, liquid, or solid) often have a well-defined form, which reflects the symmetry of the unit cell. For example, rock salt or ammonium chloride crystals often grow from solutions in the form of cubes with faces parallel to the 100 planes of the crystal, or in the form of octahedrons with faces parallel to the 111 planes. The growth form of crystals is usually dictated by kinetic factors and does not correspond necessarily to the equilibrium form.

3.4.2 Physical properties

Ideally, single crystals are free from internal boundaries. They give rise to a characteristic x-ray diffraction pattern. For example, the Laue pattern of a single crystal consists of a single characteristic set of sharp intensity maxima.

Many types of single crystal exhibit anisotropy, that is, a variation of some of their physical properties according to the direction along which they are measured. For example, the electrical resistivity of a randomly oriented aggregate of graphite crystallites is the same in all directions. The resistivity of a graphite single crystal is different, however, when measured along crystal axes. This anisotropy exist both for structure-sensitive properties, which are strongly affected by crystal imperfections

(such as cleavage and crystal growth rate), and structure-insensitive properties, which are not affected by imperfections (such as elastic coefficients).

Anisotropy of a structure-insensitive property is described by a characteristic set of coefficients, which can be combined to give the macroscopic property along any particular direction in the crystal. The number of necessary coefficients can often be reduced substantially by consideration of the crystal symmetry, whether anisotropy, with respect to a given property, exists depends on crystal symmetry. The structure-sensitive properties of crystals (for example, strength and diffusion coefficients) seem governed by internal defects, often on an atomic scale.

3.5 Photocatalytic process [Fujishima *et al.* (1999)]

The primary photocatalytic process occurring upon irradiation of a semiconductor catalyst. A semiconductor (SC) is characterized by an electronic band structure in which the highest occupied energy band, called valence band (VB), and the lower empty band called conduction band (CB), are separated by a band gap. The magnitude of the fixed energy gap between the electronically populated valence band and the largely vacant conduction band governs the extent of thermal population of the conduction band in its intrinsic state. The band gap also defines the wavelength sensitivity of the semiconductor to irradiation [Fox and Dulay (1993)]. When a photon of energy higher or equal to the band gap energy is absorbed by a semiconductor particle, an electron from the valence band is promoted to the conduction band with simultaneous generation of an electronic vacancy or "hole" (h^+) in the valence band. Figure 3.3 shows the photocatalytic process occurring on an illuminated semiconductor particle.

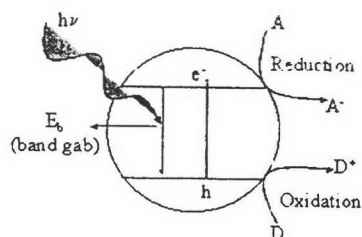
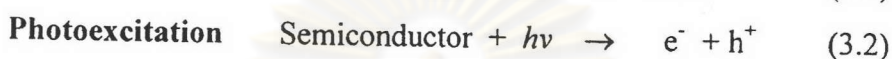
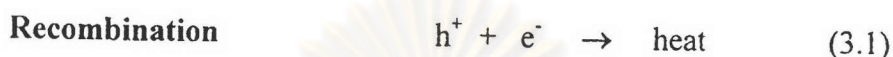


Figure 3.3 The photocatalytic process occurring on an illuminated semiconductor particle [Litter (1999)].

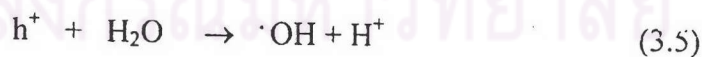
In most materials that are electrically conductive, i.e. metals, two types of carriers - electrons (e^-) and holes (h^+) - immediately recombine on the surface or the bulk of particle in a few nanoseconds and the energy dissipated as heat (equation (3.1)). On semiconductor such as titanium dioxide, however, they survive for longer periods of time to allow these carriers can be trapped in surface states where they can react with donor (D) or acceptor (A) species adsorbed or close to the surface of the particle (equations (3.2), (3.3), (3.4)) [Litter (1999)].



Thereby, subsequent oxidation and reduction can be initiated.

In aqueous solution, hydroxyl radicals ($\cdot\text{OH}$) production is favored because of the abundance of hydroxyl groups and water molecules on the surface of catalyst. However, in the gas phase, organic substrates can themselves act as adsorbed traps for the photogenerated hole since in the gas phase, water molecules are not the predominant species in contact with the catalyst. Although in the presence of water vapor, OH groups are presented on the catalyst surface and their contribution to photooxidation can not be discarded [Alberici *et al.* (1997)].

When adsorbed water molecules are oxidized by holes, hydroxyl radicals, which have strong oxidizing power are formed (equations (3.5), (3.6)).



The hydroxyl radicals can then react with organic components, initially producing free radicals (unstable molecules that have one unpaired electron). When molecular oxygen is present (reactions always occur in the presence of oxygen from the air in the use of the photocatalyst for environment), because it also has unpaired electrons, it likes to react with these free radicals producing organic peroxy

radicals, which, in addition to containing an unpaired electron, also now contain two oxygens. These radicals can then take part in chain reactions. In a short time, organic compounds are completely degraded, i.e. converted into carbon dioxide and water.

Meanwhile, the electrons that are produced in the electron-hole pairs are also put to work. These electrons are used to reduce (i.e., add electrons) to oxygen in air. Because oxygen is easier to reduce than water, it will tend to be reduced, producing the superoxide radical anion ($O_2^{\cdot-}$) (equation 3.7).



The superoxide anion attaches itself to the peroxy radicals mentioned in the previous paragraph. The resulting unstable product now contains at least four oxygens and can decompose to produce a carbondioxide molecule. On the molecular scale, superoxide acts like a "supercharge", greatly increasing the oxidation process, which is in fact a form of combustion. In addition to this mechanism, another interpretation proposed recently is that the formation in air of so-called atomic oxygen (O^{\cdot}), which is extremely reactive, directly acts on the carbon bonds in organic material

3.6 The main factors involved in photocatalytic process

There are two main factors involved in photocatalytic process. Photocatalysis is the combination of photochemistry and catalysis, it implies that light and catalyst are the main factors, which initiate the chemical transformation, oxidation and reduction reaction. Light is not only one, which can work effectively, but it, can work effectively when teamed up with catalyst especially titanium dioxide catalyst.

3.6.1 Photocatalyst [Fujishima *et al.* (1999)]

Catalyst that used in photocatalytic process usually called "photocatalyst". In the previous section, photochemical process involves in electronic structure of photocatalyst.

Atoms have discrete energy levels for their electrons. Molecules often contain like atoms but the Pauli exclusion principle forbids identical quantum numbers in all respects, resulting in the "splitting" of a given atomic energy level into a set of closely spaced levels typically of order of the numbers of atoms involves energy levels split so finely that a so-called "band" structure of allowed energies (quantum states) emerges, with infinitesimal or virtually continual distribution of energy levels within a given "orbital". For a semiconductor such as titanium dioxide (TiO_2), the highest filled band is termed the valence band, and the lowest unoccupied level is the conduction band. The separation of the valence band top from the conduction band bottom is termed the band gap [Ollis (1998)].

As already mentioned, the reaction starts with the exposure of photocatalyst to light. After light is absorbed by photocatalyst, two types of carriers - electron (e^-) and holes (h^+) - are generated. Unlike metals oxide, a semiconductor oxide is good photocatalyst because of the long live both of these carriers. For this reason semiconductor oxides are used in photocatalytic process such as TiO_2 , ZnO , SrTiO_3 , K_4NbO_2 , Fe_2O_3 and SnO_2 .

Especially titanium dioxide (TiO_2), titanium dioxide is one of the most basic materials in our daily life. It also has been used widely in photocatalytic process because of its radiation stability, non-toxicity and good reactivity [Alberici (1997)]. Naturally, the type of titanium dioxide that used as a pigment is different from that used as a photocatalyst. Might say that titanium dioxide has two aspects but one set of properties. Titanium dioxide is a semiconductor and is chemically activated by light energy. Its photoactivity tends to decompose organic materials that come in contact with it.

One of the reasons for the anatase type titanium dioxide is more photoactive than the rutile type may lie in the differences in their so-called energy band structures.

The band gap energy of a semiconductor is the minimum energy of light required to make the material electrically conductive or in the other words, to get the electrons excited enough to get moving. For anatase -type titanium dioxide this energy is 3.2 electron volts (eV), which corresponds to UV light (388 nanometers), while the band gap energy for the rutile type is 3.0 eV, corresponding to violet light (413 nanometers). In more technical terminology, the band gap energy for a semiconductor indicates the minimum energy of light necessary to produce conduction band (CB) electrons, which, for example, can give rise to electrical conductivity (photoconductivity) and valence band (VB) "holes," which are actually the absence of electron. These holes can react with water to produce the highly reactivity hydroxyl radical (OH \cdot). Both the holes and the hydroxyl radicals are very powerful oxidants, which can be used to oxidize most organic materials. The level of the CB for anatase turns out to be 0.2 eV higher than that for rutile (figure 3.4).

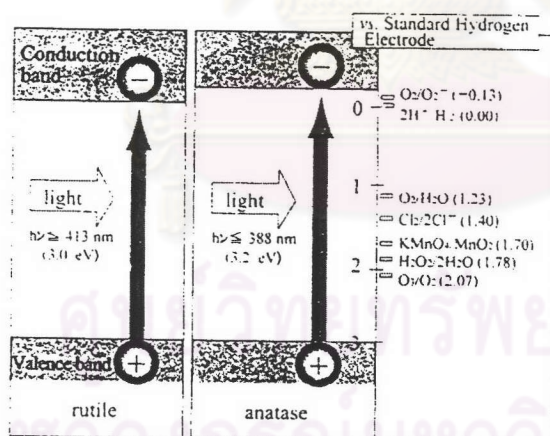


Figure 3.4 Energy diagram for TiO₂ and relevant redox potentials [Fujishima *et al.* (1999)].

The VB energies for anatase and rutile are both similar, which is very low in the energy diagram, meaning that, for both materials, the VB holes (and the hydroxyl radicals) have great oxidizing power. The CB energy for rutile is close to the potential required to electrolytically reduce water to hydrogen gas, but that for anatase is higher

in the energy diagram, meaning that it has higher reducing power. This means that it can drive the very important reaction involving the electrolytic reduction of molecular oxygen (O_2) to superoxide (O_2^-). Superoxide is found that it's almost as important as the holes and hydroxyl radicals in breaking down organic compounds.

3.6.2 Light [Fujishima *et al.* (1999)]

Light is a form of energy characterized by waves, can be classified by wavelength, which is the distance between wave crests as indicated in figure 3.5. The light visible to eyes is only small part of total light spectrum, these range from about 400-700 nanometers (Note: one nanometer is one per million of a centimeter). But the visible light is not usually used for the photocatalytic process because the most active and usually used catalyst for this process is titanium dioxide which has band gap energy is about 3.0 eV or 400 nanometer, which falls in the near ultraviolet (figure 3.6). Photoexcitation of photocatalyst molecule involving absorption of energy equal to the energy difference between electron states using. so near UV or UV light (300-400 nanometer) is used for photocatalytic process.

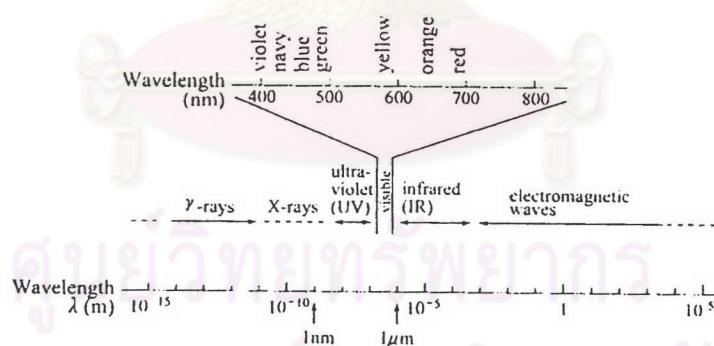


Figure 3.5 The spectrum of light [Fujishima *et al.* (1999)].

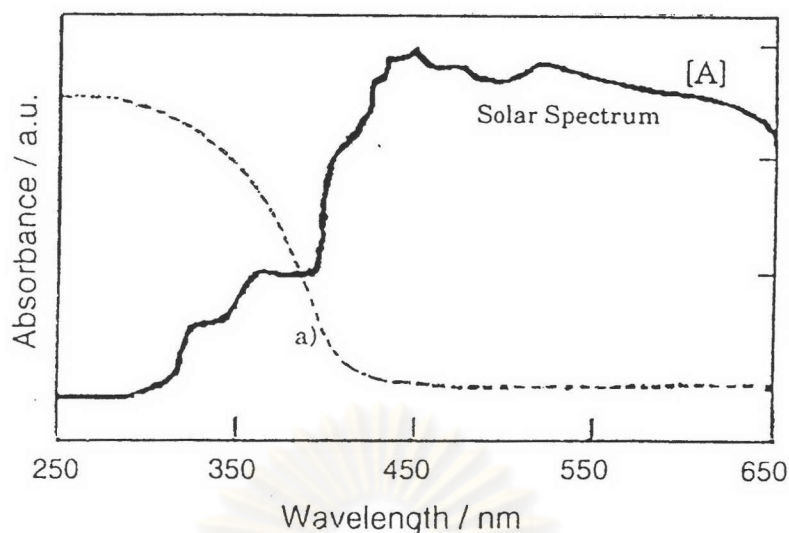


Figure 3.6 The absorption band of the TiO_2 photocatalyst to solar spectrum [Anpo *et al.* (1998)].

Ultraviolet light (UV), which includes wavelengths shorter than 400 nanometers. Although UV light is a part of solar light and even interior lighting, it is only limited part. Even in the outdoors, during daytime, UV light constitutes only about 1 mWcm^{-2} at the most. UV light, however, can work effectively when teamed up with titanium dioxide.

3.7 Inhibition of electron-hole recombination by oxygen [Fox and Dulay (1993)]

The rates and efficiencies of photoassisted degradation of organic substrates are significantly improved in the presence of oxygen or by the addition of several inorganic oxidizing species, such as peroxydisulfate, periodate, and peroxides. The effect of molecular oxygen is primarily as an efficient conduction band electron trap, suppressing electron-hole recombination.

Electron trapping similarly suppresses electron-hole recombination. Because the conduction band of TiO_2 is nearly isoenergetic with the reduction band potential of oxygen inert solvents, adsorbed oxygen serves as a trap for the photogenerated conduction band electron in many heterogeneous photocatalytic reactions. It is often found that photocatalytic activity is nearly completely suppressed in the absence of oxygen, possibly because of back interfacial electron transfer from active species

present on the photocatalyst surface, and the steady-state concentration of oxygen has a profound effect on the relative rate of photo catalyzed decontamination occurring under ambient conditions. The resulting species, superoxide O_2^- , is highly active and can attack either organic molecules or adsorbed intermediates or, after protonation, can provides another source for surface-bound hydroxy radicals. Its precise role has yet to be established unambiguously.

Oxygen concentration dependence has been explained as involving O_2 adsorption and depletion, both in the dark and during illumination, at the photocatalyst surface. That rutile possesses much lower photoactivity than anatase (despite the fact that both forms of TiO_2 are thermodynamically capable of reducing O_2) has been explained by the higher rate of electron-hole recombination on rutile because of its lower capacity to adsorb O_2 .

The superoxide (O_2^-) thus formed is an effective oxygenation agent, attacking both neutral substrates and surface-adsorbed radicals and/or radical ions. This attack occurs before desorption from the surface since the presence of dissolved superoxide traps in solution does not inhibit photocatalytic reduction-protonation sequence generates hydrogen peroxide, which can be decomposed on the photocatalyst surface to form hydroxy radical, which can also initiate oxidative functional group interconversions.

Always exist structural defects on the surface and inside the titania particles. These structural defects are related with the destiny of photoexcited electrons. Surface defects are good for high photoactivity because they are used as an active site on which the electron donor or acceptor is adsorbed. However, the bulk defect lowers the photoactivity because they provide sites for the recombination of the photogenerated electrons.