CHAPTER 2

THEORETICAL BACKGROUND

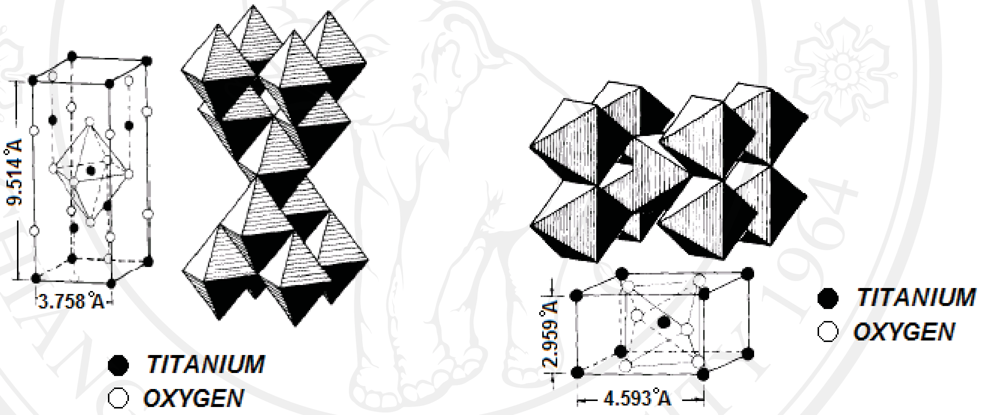
This chapter provides the relevant background on TiO_2, Fe_2O_3 and their properties such as hydrophilic, photocatalytic properties including the practical applications. Moreover, the literature of preparation of TiO_2 NPs and Fe_2O_3 NPs which were used in this work will be described.

2.1 Titanium dioxide (TiO_2)

TiO_2 is one of the basic materials which have been widely used for many applications, such as self cleaning surface, anti-fogging surface, solar cell, water purification, white pigment in paints, organic decomposition, air purification, cosmetics, food stuffs and anti-bacterial applications [1-11]. TiO_2 exists in three crystalline modifications: anatase, rutile, and brookite [12,13]. Generally, TiO_2 is a semiconducting material with the band gap energy of about 3.2 eV (for bulk materials) which can be chemically activated by light, especially in the UV range. The photoactivity of TiO_2 which is known for approximately 60 years is investigated extensively [14]. For a long time, there was a considerable problem especially what its application as pigment concerns. Under the influence of light the material tends to decompose organic materials. This effect leads to the well-known phenomenon of "paint chalking" where the organic components of the paint are decomposed as result of photocatalytic processes. In recent years semiconductor photocatalysis using TiO_2

has been applied to important problems of environmental interest like detoxification of water and of air.

TiO_2 is commercially available in two crystal structures which are anatase and rutile phases. In comparison, anatase shows higher photoactivity. Rutile has a density of 4.2 g/cc, while anatase has a density of 3.9 g/cc. This difference is explained by their different crystal structures [12,13,15]. The Rutile modification is more closely packed than the anatase crystal, as shown in Figure 2.1.



(a) (b)

Figure 2.1 Crystal structures of (a) anatase and (b) rutile TiO_2 [16,17].

Although TiO_2 absorbs only approximately 5 % of the solar light reaching the surface of the earth, it is the best investigated semiconductor in the field of chemical conversion and storage of solar energy [18,19]. Rutile TiO_2 pigments scatters light more efficiently and more stable and durable than anatase pigments. TiO_2 is unique in that it combines high refractive index with a high degree of transparency in the visible region of the spectrum, as shown in Figure 2.2 and Table 2.1. This combination affords the coatings formulator a route to highly opaque and bright whites or tints at minimum film thicknesses.

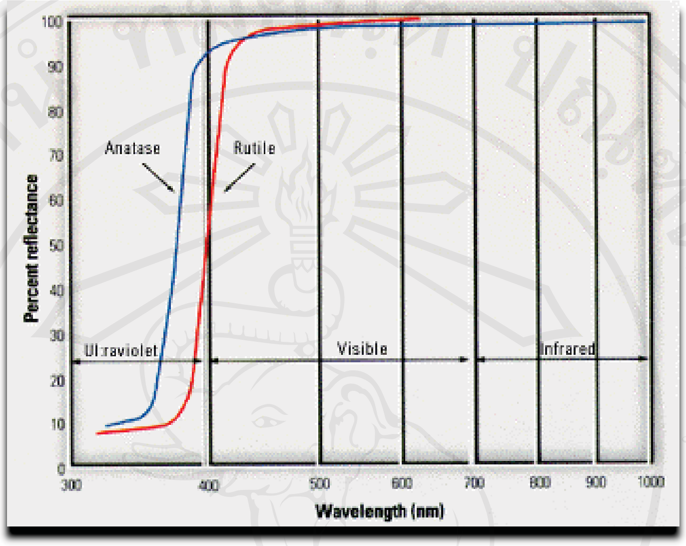


Figure 2.2 Percent reflectance of anatase and rutile at various wavelength [20].

Table 2.1 Refractive index of rutile and anatase TiO_2

Material	Refractive Index
Rutile TiO_2	2.76
Anatase TiO_2	2.52

Refractive index calculated by:

$$\boldsymbol{Refractive\ Index} = \frac{Speed\ of\ light\ in\ vacuum}{Speed\ of\ light\ on\ substance}$$

2.2 Properties of TiO_2

TiO_2 especially that in anatase phase has emerged as an excellent photocatalytic material and most recently the interest is shifted to the area of photoinduced hydrophilicity which involves not only self cleaning surfaces but also anti-fogging ones. One of the most interesting aspects of TiO_2 is the types of photochemistry responsible for photocatalysis and hydrophilicity which are completely different, even though both can occur simultaneously on the same surface. Glass coated with a thin film of TiO_2 exhibits these two intriguing properties when illuminated with UV light. Thus, we can summarize the unique properties of TiO_2 as follows:

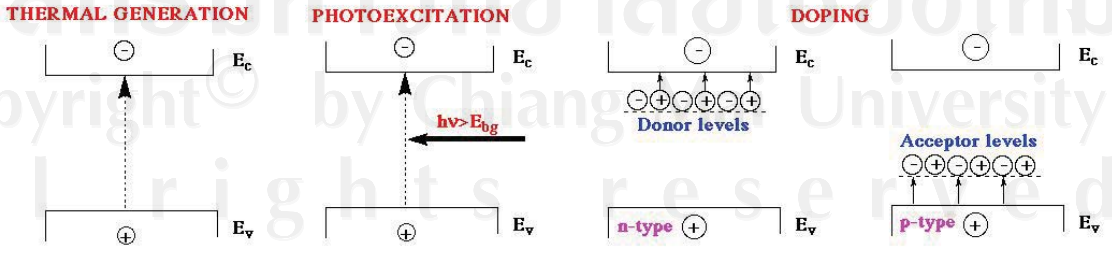
- Photocatalytic (light-induced) breakdown of organic compounds that come into contact with TiO_2, making it self-degreasing
- TiO_2 has a very high affinity for water (hydroplilic properties), so that water does not bead up but forms a continuous sheet.
- TiO_2 is semiconductive and transparent in the visible region of the spectrum
- TiO_2 is a highly porous material that provides strong enhancement of the surface area (~1000) times
- High affinity of TiO_2 surface too many types molecules leads to easy surface modification
- TiO_2 is a low cost material, easy to produce in large quantities, chemically inert, non-toxic and also biocompatible

2.2.1 Photocatalysis

It is well known that the photocatalysis is the first unique property of TiO_2. Thus, in this section we will describe the basic principle of the photocatalysis which are shown below.

Basic principle of heterogeneous photocatalysis

In general, mobile charges carriers which can be generated by three different mechanisms are thermal excitation, photo-excitation and doping, as shown in Figure 2.3. If the band gap energy is sufficiently small (less than half an electron volt) thermal excitation can promote an electron from the valence band (V_B) to the conduction band (C_B). In a similar manner, an electron can be promoted from V_B to C_B upon the absorption of a photon of light, photo-excitation, provided that give up energy (hv) > band gap energy (E_{bg}). The third mechanism of generating mobile charge carriers is doping. This charge transfer introduces conditions of non-balance, which leads to the reduction or to the oxidation of the species absorbed on the surface of the semiconductor.



(a) (b) (c)

Figure 2.3 Mobile charge carriers by (a) thermal generation (b) photo-excitation and (c) doping [20].

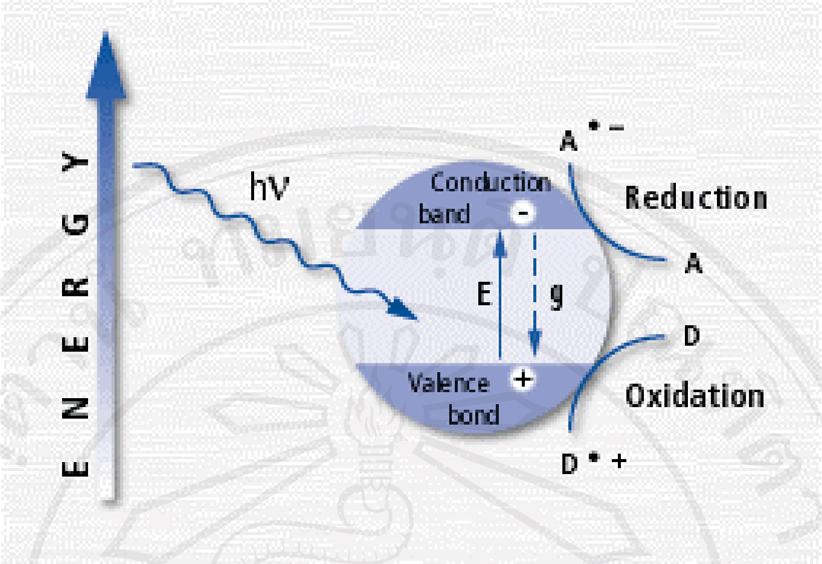


Figure 2.4 Operation of a photochemical excited semiconductor particle [21].

From Figure 2.4, when a photon with energy of *hv* exceeds the energy of the band gap, an electron (e^-) is promoted from the V_B to the C_B leaving a hole (h^+) behind. In electrically conducting materials, i.e. metals, the produced charge carriers are immediately recombined. In semiconductors, a portion of this photo-excited electron-hole pairs diffuse to the surface of the catalytic particles (electron hole pairs are trapped at the surface) and take part in the chemical reaction with the adsorbed donor (D) or acceptor (A) molecules. The holes can oxidize donor molecules (2.1) whereas the conduction band electrons can reduce appropriate electron acceptor molecules (2.2).

$$D + h^+ \rightarrow D\bullet^+ \qquad (2.1)$$

$$A + e^- \rightarrow A\bullet^- \qquad (2.2)$$

A characteristic feature of semiconducting metal oxides is the strong oxidation power of their holes h^+. They can react in a one-electron oxidation step with water (2.3) to produce the highly reactive hydroxyl radical (•OH). Both the holes and the hydroxyl radicals are very powerful oxidants which can be used to oxidize most organic contaminants.

$$H_2O + h^+ \rightarrow \bullet OH + H^+ \qquad (2.3)$$

In general, air oxygen acts as electron acceptor (2.4) by forming the super-oxide ion $\bullet O_2^-$

$$O_2 + e^- \rightarrow \bullet O_2^- \qquad (2.4)$$

Super-oxide ions are also highly reactive particles which are able to oxidize organic materials.

TiO_2 as photocatalyst

In recent years, semiconductor photocatalysis using TiO_2 has been applied to important problems of environmental interest like detoxification of water and of air. TiO_2 is a semiconductor with $E_{bg} = 3.2$ eV. If this material is irradiated with photons of the energy > 3.2 eV (wavelength < 388 nm), the band gap is exceeded and an electron is promoted from V_B to C_B. Consequently, the primary process is the charge-carrier generation (2.5).

$$\mathrm{TiO_2} + h\nu \rightarrow h^{+} + e^{-} \tag{2.5}$$

The ability of a semiconductor to undergo photoinduced electron transfer to adsorbed particles is governed by the band energy positions of the semiconductor and the redox potentials of the adsorbates. The relevant potential level of the acceptor species is thermodynamically required to be below the C_B of the semiconductor. Otherwise, the potential level of the donor is required to be above the V_B position of the semiconductor in order to donate an electron to the empty hole. The band-edge positions of several semiconductors are presented in Figure 2.5.

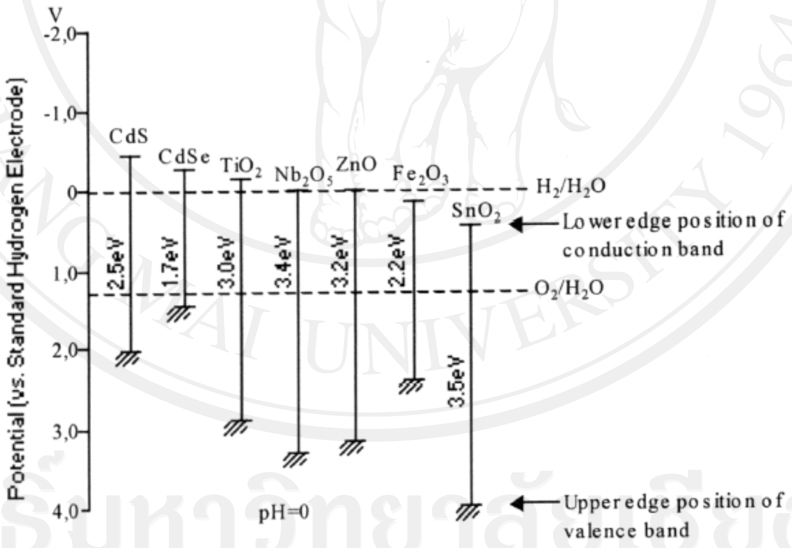


Figure 2.5 Band-edge energies of typical semiconductors [22].

Reaction of oxidation-reduction may possibly occur as shown in Figure 2.6. There is a 3.2 eV of band gap between conductive and charging zones, when electrons (e^-) and holes (h^+) are irradiated by applying light. In general, the electrons and the holes recombine immediately and do not originate photocatalyst reaction, but they carry on through for a while and move up to the surface of the particles and react as shown below.

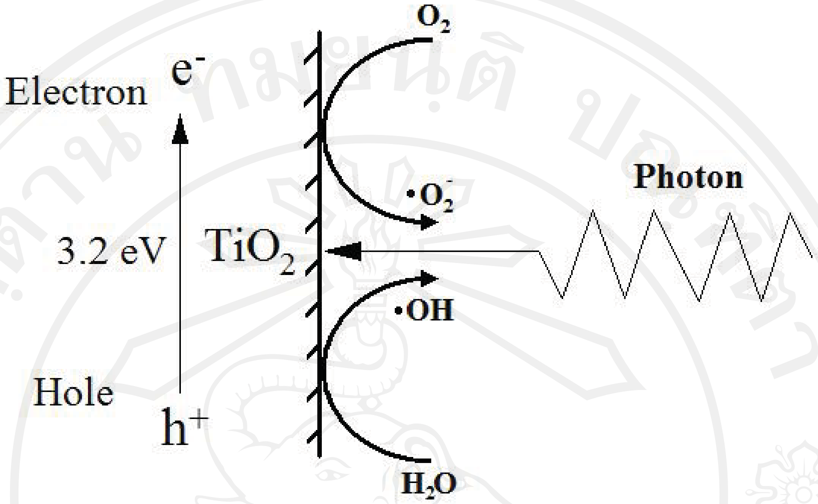


Figure 2.6 Oxidation-reduction reaction on the surface of TiO_2 [23].

Absorbed water on the surface of TiO_2 is oxidized by the holes and then originates oxidative hydroxyl radical (•OH). Then the hydroxyl radical reacts to organic matters. If oxygen exists in this reaction process, radicals which are intermediates of organic compounds and oxygen molecules start off a radical chain reaction [(2.1) to (2.5)]. Eventually, the organic matters break down into carbon dioxide and water. On the other hand, the electron deoxidize and generate super oxide ion ($\bullet O_2^-$) (2.4). It is conceivable that the superoxide ion produce peroxide which comes to the intermediates of oxidative reaction, or generates water through hydrogen peroxide.

$$H_2O + h^+ \rightarrow \bullet OH$$

$$O_2 + e^- \rightarrow \bullet O_2^-$$

Semiconductors are usually covered with hydroxyl groups on their surfaces as well as physisorbed water molecules. We know that the surface of TiO_2 is promptly hydroxylated when the TiO_2 is contact with water. On the other hand, when water dissociates on a pure TiO_2 surface two distinctive hydroxyl groups are formed. Assuming that anatase particles consists of a mixture of these surface planes, complete surface coverage by OH^- should be around 5-15 OH^-/nm^2 on room temperature.

2.2.2 Hydrophilicity and super-hydrophilicity

Exposing UV light to a surface of TiO_2 gives very high hydrophilic (water loving) properties when the contact angle of water is five degrees or below. This status remains for a few hours to a week and then involutes slowly. This phenomenon is likely to be understood as having hydrophilic properties by breaking down due to photocatalyst reaction where absorbed dirt of organic matter on a surface of TiO_2 becomes hydrophobic (water hating). However, a whole new phenomenon taking place on the surface of TiO_2 can be presumed according to several experiments. Moreover, we found that the surface after exposing also has super lipophilicity that has a high affinity to oil. Both water-based and oil-based dirt hardly adhere on such amphipathic surface and even if it does, dirt can easily be rinsed off with water. In addition to self-cleaning effects, anti-clouding effects for windows and glass clouded over with condensation have been considered as applications of super hydrophilic properties. Such applications include bathroom mirrors, car windows and fender mirrors.

For a given droplet on a solid surface, the contact angle is a measurement of the angle formed between the surface of a solid and the line tangent to the droplet radius from the point of contact with the solid. The contact angle is related to the surface tension by the Young's equation through which the behavior of specific liquid-solid interactions can be calculated. A contact angle of zero results in wetting (super-hydrophilic), while an angle between 0° and 90° results in spreading of the drop (due to molecular attraction). Angles greater than 90° indicate the liquid tends to bead or shrink away from the solid surface. (see Figure 2.7)

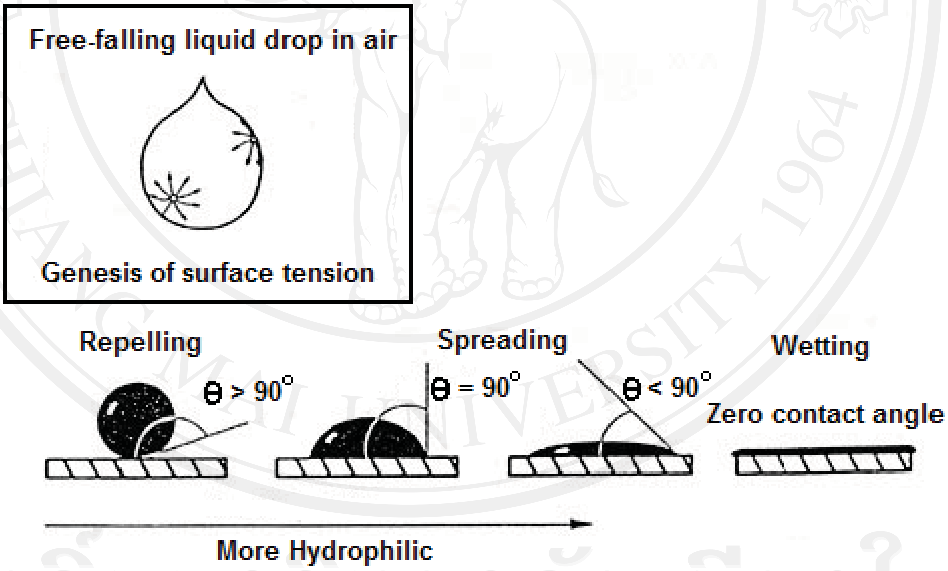


Figure 2.7 Droplet on the solid surface [24].

Also called hydrophilic, is a characteristic of materials exhibiting an affinity for water. Hydrophilic literally means "water-loving" and such materials readily adsorb water. The surface chemistry allows these materials to be wetted forming a water film or coating on their surface. Hydrophilic materials also possess a high surface tension value and have the ability to form "hydrogen-bonds" with water. TiO_2 acquires super-hydrophilic properties after UV illumination. In this case, electrons and holes are still produced, but they react in a different way. The electrons tend to reduce the Ti (IV) cations to the Ti (III) state, and the holes oxidize the O_2^- anions. In the process, oxygen atoms are ejected, creating oxygen vacancies (Figure 2.8). Water molecules can then occupy these oxygen vacancies, producing adsorbed OH groups, which tend to make the surface hydrophilic. The longer the surface is illuminated with UV light, the smaller the contact angle for water becomes; after about 30° min or so under a moderate intensity UV light source, the contact angle approaches zero, meaning that water has a tendency to spread perfectly across the surface.

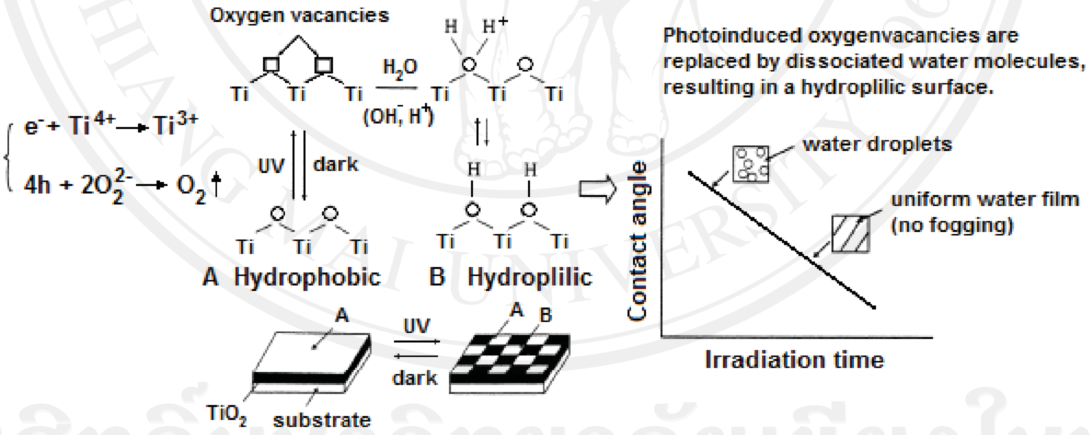


Figure 2.8 Mechanism of photo-induced hydrophilicity [25,26].

In the usual environment, a surface of material repels the water to a certain extent. Figure 2.9 shows the shape of the water drops on the surfaces of glass, resin and hydrophobic resin.

Figure 2.9 Shape of water drops on the surface of glass, resin and hydrophobic resin [27].

Hydrophilicity of a material can be represented with a contact angle of water with the material. The contact angles of water with inorganic materials, such as glass are 20°-30°. Also, the contact angles of water with usual resins and hydrophobic resins, such as silicone resin or fluorocarbon polymer, are 70°-90° and more than 90°, respectively. Until now, there are few materials that have the contact angle of water less than 10°, except water absorptional materials or activated surface using interface activator. However, these materials have little durability and the low contact angle values do not last for a long time. Our modified TiO_2 photocatalyst thin film has interesting property of super-hydrophilicity. At first, the contact angle of water with the TiO_2 thin film is several tens degrees. Then, by the irradiation of UV light, the contact angle decreases gradually, and at last, it reaches 0°. After that, the contact angle remains only several degrees for scores of hours without the irradiation of UV light. Besides, even if the contact angle increases, it easily decreases again only by the irradiation of UV light. Therefore, the modified TiO_2 thin film is the first truly practical material that realizes the super-hydrophilicity. Figure 2.10 shows the change of the contact angle of water with a TiO_2-silicone thin film by UV irradiation. Before UV irradiation, the contact angle with the film is more than 90°, and then it gradually decreases to 0° with UV irradiation and the film never repels water. Now, we are theoretically studying the rationale of this phenomenon.

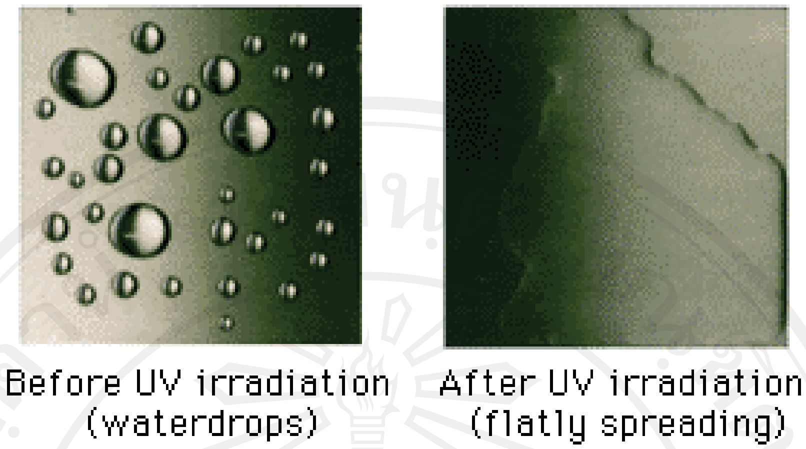


Figure 2.10 Change of the contact angle of water with TiO_2-silicone thin film by UV irradiation [28].

The super-hydrophilicity should be caused by the function of photocatalyst. As TiO_2 photocatalyst decomposes hydrophobic molecules those originally existing on the surface of material, very thin film of physisorbed water forms on the surface. We presume that the water thin film is the origin of the super-hydrophilicity. Belove the schematic diagram of presumed super-hydrophilicizing mechanism is showed:

STEP 1: Chemisorbed water on the surface of TiO_2 is so unstable that it is stabilized with an adsorption of hydrophobic molecule (Figure 2.11).

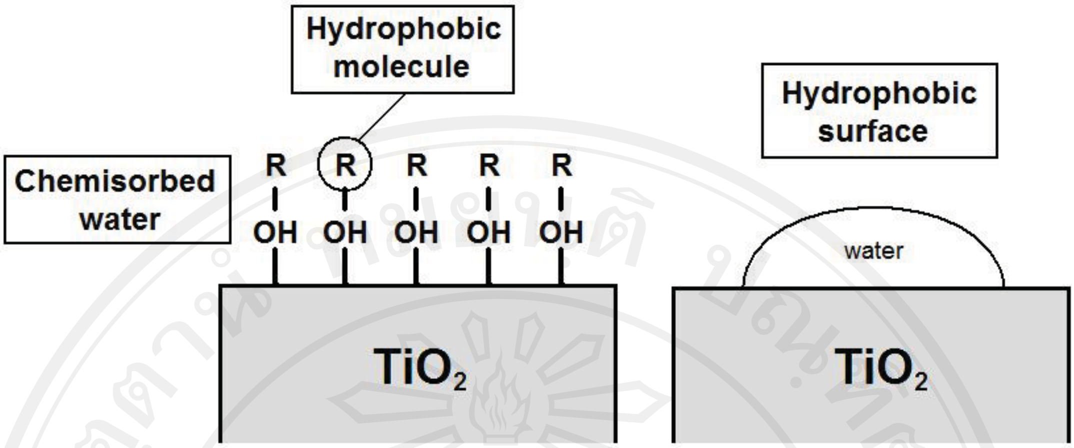


Figure 2.11 Chemisorbed water on the TiO$_2$ surface [29].

STEP 2: With irradiation of light, photocatalyst decomposes hydrophobic molecule and chemisorbed water is exposed to the surface (Figure 2.12).

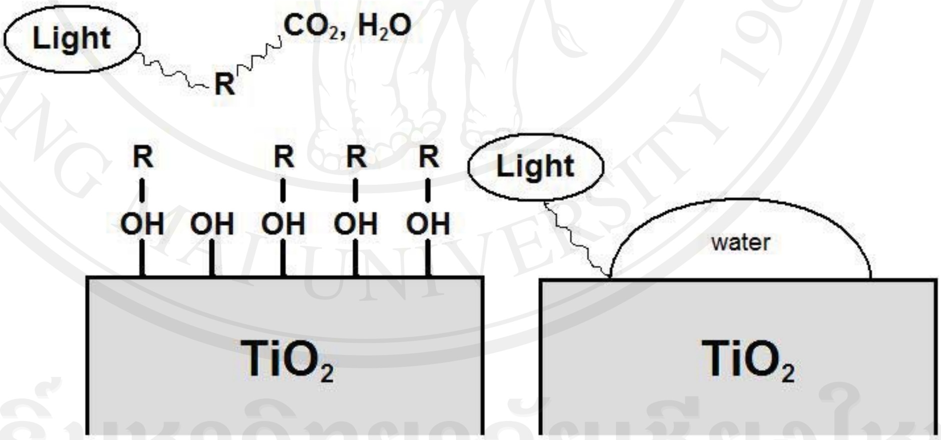


Figure 2.12 irradiation of light on the TiO$_2$ surface [29].

STEP 3: Exposed chemisorbed water physisorbs and bonds with another water (Figure 2.13).

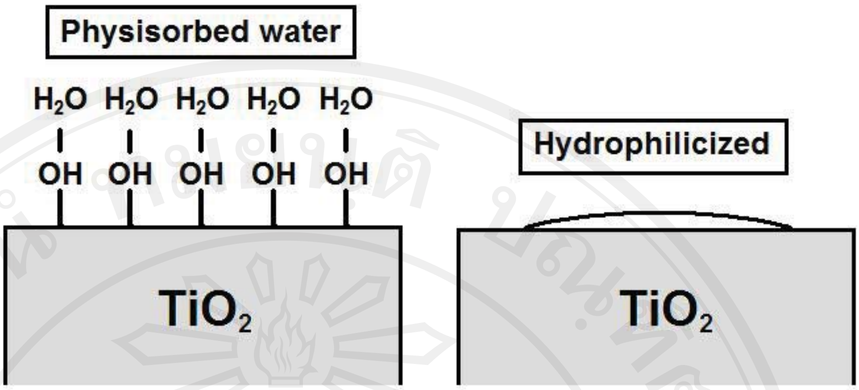


Figure 2.13 Exposed chemisorbed water physisorbs and bonds with another water on the TiO_2 surface [29]

STEP 4: Physisorbed water is taken in the structure by the surface diffusion and stabilized (Figure 2.14).

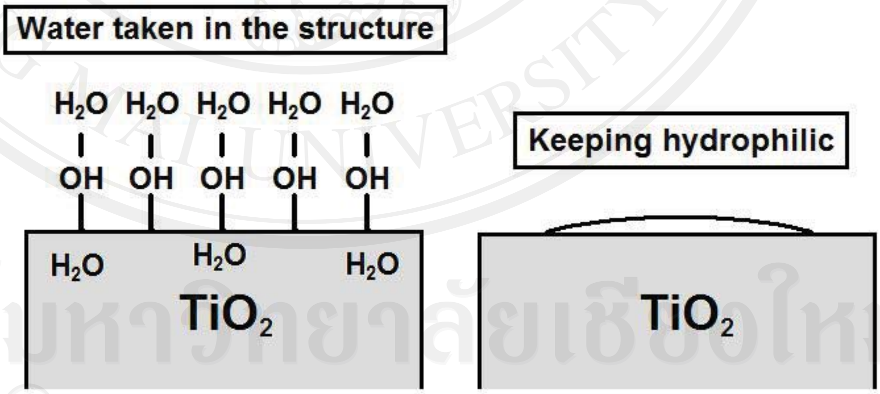


Figure 2.14 Physisorbed water on the TiO_2 surface [29].

2.3 Practical applications

The main areas of activity in TiO_2 photocatalysis are shown in Figure 2.15. As already mentioned, in the last 10 years photocatalysis has become more and more attractive for the industry regarding the development of technologies for purification of water and air. Compared with traditional advanced oxidation processes the technology of photocatalysis is known to have some advantages such as ease of setup and operation at ambient temperatures, no need for post processes, low consumption of energy and consequently low costs.

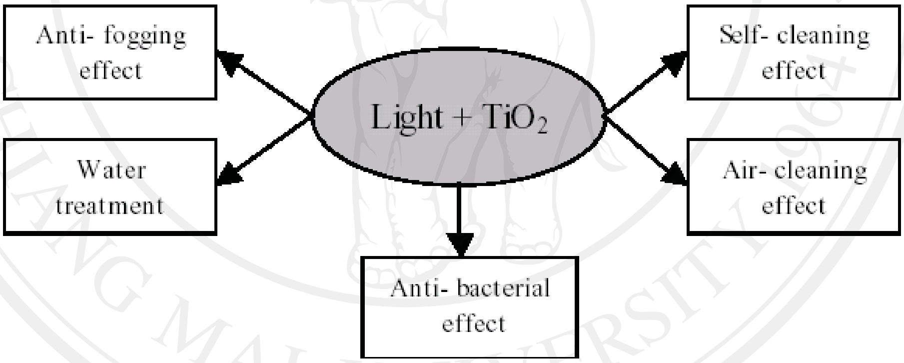


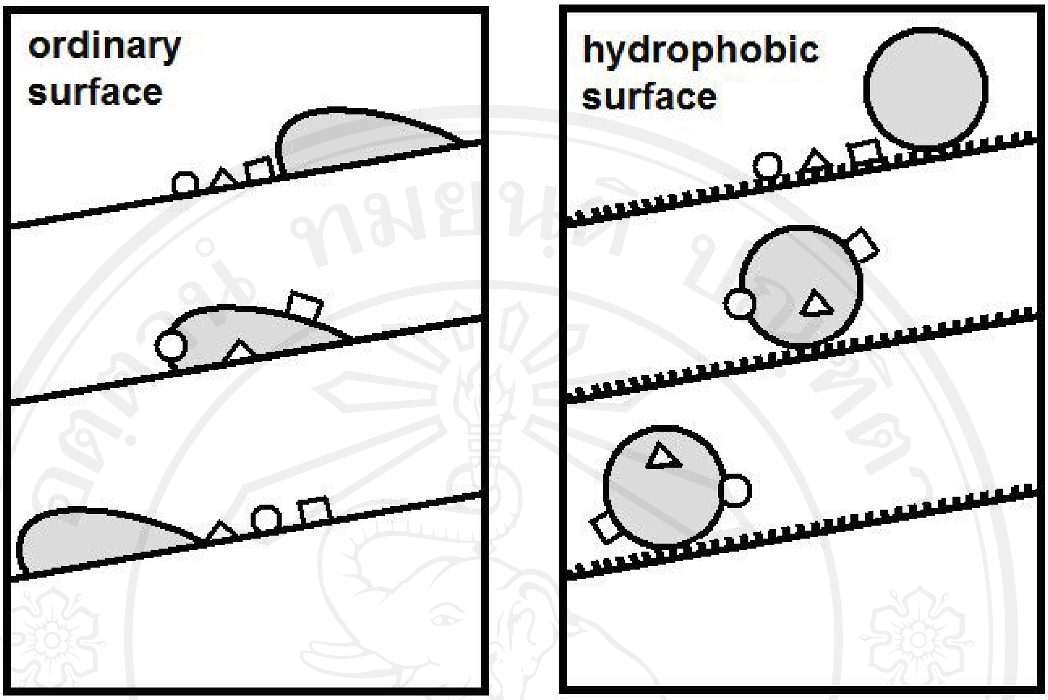
Figure 2.15 Major areas of activity in TiO_2 photocatalysis.

2.3.1 Self cleaning surface

In practical, surface cleaning of building materials such as tiles, facades and glass panes causes considerable trouble, high consumption of energy and chemical detergents and consequently, high costs. To realize self-cleaning material surfaces there are two principal ways: the development of so-called super-hydrophobic or super-hydrophilic surfaces. In the term of hydrophobic, materials possessing this characteristic have the opposite response to water interaction compared to hydrophilic materials. Hydrophobic materials (water hating) have little or no tendency to absorb water and water tends to "bead" on their surfaces (i.e. discrete droplets). Hydrophobic materials possess low surface tension values and lack active groups in their surface chemistry for formation of "hydrogen-bonds" with water.

The wetting of a solid with water where air is the surrounding medium is dependent on the relation between the interfacial tensions (water/air, water/solid and solid/air). The ratio between these tensions determines the contact angle between water droplets on a given surface. A contact angle of 0° means complete wetting and a contact angle of 180° corresponds to complete non-wetting. Hydrophobic surfaces with low wettability and contact angles more than 100° are known for a long time. The higher this angle the lower is the value of the adhesion work. Decreasing of the contact angle leads to enlarged values of the adhesion work (hydrophilic surfaces).

By transferring the microstructure of selected plant surfaces to practical materials, superhydrophobic surfaces could be developed. The water repellency of plant surfaces has been known for many years. That water-repellent surfaces also indicate self-cleaning properties has been completely overlooked. Recently, Barthlott et al. investigated and proved the correlation between the microstructure, wettability and contaminants in detail using lotus leaves [30]. This was called the *Lotus Effect* because it can be demonstrated beautifully with the great leaves of the lotus plant. The microrough surfaces show contact angles higher than 130°. That means, the adhesion of water, as well as particles is extremely reduced. Water which contacts such surfaces will be immediately contracted to droplets. The particles of contaminants adhere to the droplet surfaces and are removed from the rough surface when the droplets roll of (see Figure 2.16).



(a) (b)

Figure 2.16 (a) Ordinary surface and (b) hydrophobic surface (Lotus effect) [30].

If TiO_2 of the anatase type is exposed to UV light very low contact angles are obtained (<1°). These materials have the unique property of "attracting" rather than repelling water *(super-hydrophilicity).* The water lies flat on the surface in sheets instead of forming droplets. If the illumination is stopped, the super-hydrophilic behaviour of the TiO_2 surface is retained for approximately two days. Furthermore, UV illumination of TiO_2 leads to the formation of powerful agents with the ability to oxidize and decompose many types of bacteria, organic and inorganic materials. In the following, the principles and potential applications of TiO_2 photocatalysis were discussed.

2.3.2 Anti-fogging surface

The steam fogs a mirror and a glass easily, because moisture in the air is cooled down and numerous water drops form on the surface of the usual materials. However, utilizing the super-hydrophilic coating, the water cannot exist in the shape of a drop, but spreads flatly on the super-hydrophilic surface. Figure 2.17 shows the dependence of the anti-fogging ability on the contact angle of water.

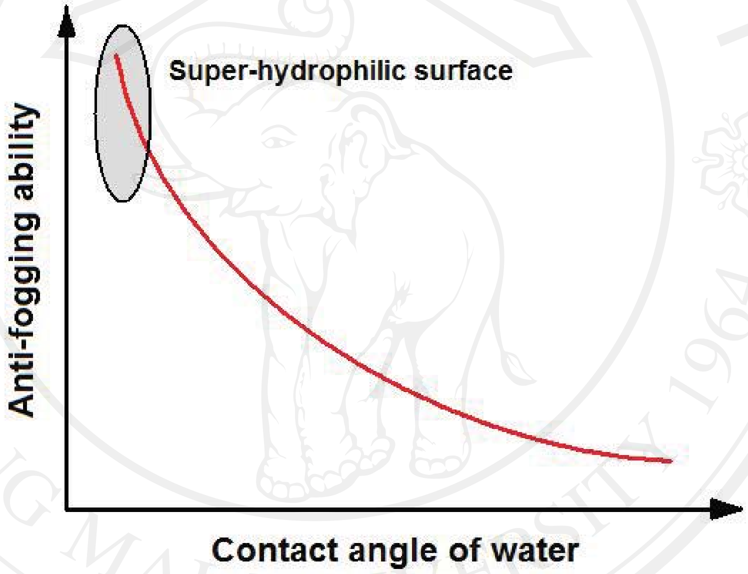


Figure 2.17 Dependence of the anti-fogging ability on the contact angle of water [31].

Recently, the opposite way to remove water drops from the surface of material has been proposed. For example, super-hydrophobic coating is applied for windshield to remove the water drops easily. However, super-hydrophobic surface cannot stop fogging of the windshield unless the water drops is removed with wind power or vibration. On the contrary, the super-hydrophilic surface never fogs on condition of no wind nor vibration. Applying the super-hydrophilic photocatalyst for a surface of a mirror or a glass, they remain the clear surface without fogging semi permanently.

Figure 2.18 shows the difference of the fogging with steam between normal glass and the photocatalyst coated glass.

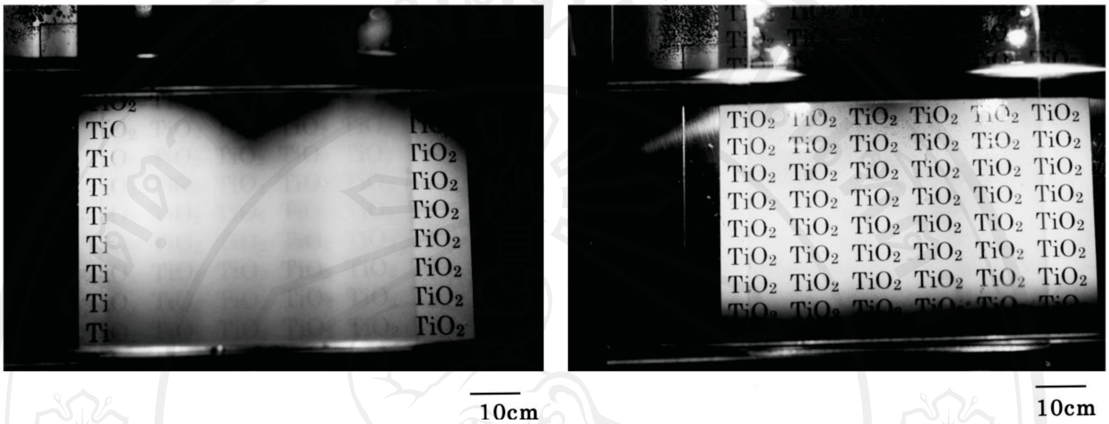


Figure 2.18 The difference of the fogging with steam between normal glass and the photocatalyst coated glass [32].

Though the normal glass fogs with steam, the super-hydrophilic glass remains transparent. In this way, the super-hydrophilic technology easily realizes the anti-fogging glass products and mirrors with low costs.

Contact angle measurements were performed to examine the surface wettability change of the Anatase polycrystalline sample upon UV illumination. Figure 2.19 shows time dependence of the water contact angle upon UV illumination ; Figure 2.19(a) and in the dark Figure 2.19(b). As shown in the figure, water contact angle decreases with illumination time when is irradiated by UV. Three hours are sufficient to give rise to a highly hydrophilic surface. The final contact angle with water was almost zero. When the contact angle becomes lower than 58, the antifogging property is observed on the steamed surface. Figure 2.19(b) shows the time dependence of the water contact angle of the sample in the dark. The initial contact angle was almost zero after complete hydrophilization by enough UV illumination. The surface reconverted the hydrophobic state gradually. We reported previously that the conversion from hydrophobic to hydrophilic is explained by assuming that the surface Ti_4^+ sites are photoreduced to the Ti_3^+ state accompanying oxygen vacancy and dissociative water adsorption on the vacancy site. This process is considered to be substantially the same as the surface reduction processes of Ti_4^+ to Ti_3^+ induced by Ar ion sputtering, electron beam exposure and high energy UV light.

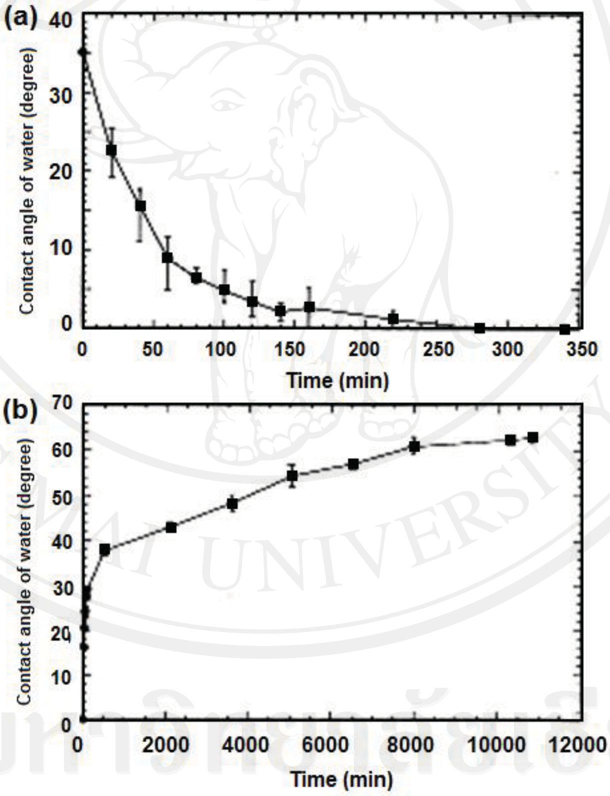


Figure 2.19 Time dependence of the water contact angle in ambient atmosphere: (a) Upon UV illumination and (b) in the dark [32].

If a TiO_2 film coated on the surface of common soda-lime glass (SLG) shows a high photocatalytic activity. It is known, however, that the diffusion of Na^+ ions into the nascent TiO_2 film from the SLG substrates during heat treatment process significantly deteriorates the photocatalytic activity Fujishima and Narasinga have prepared TiO_2 thin films on different substrates such as quartz, SLG, and SiO_2-precoated SLG (SiO_2/SLG) substrates via the spray pyrolysis method, and showed that the TiO_2 coated on SiO_2/SLG had much higher catalytic activity than that of TiO_2 films coated on bare SLG.

2.3.3 Antibacterial activity

Photocatalyst is not adequate to break down large quantities of a substance at once, but it is highly effective in breaking break down growing substances, which initially have a small quantity, such as bacteria and virus. The differences from a silver antibacterial agent are that an antibacterial agent can break down dead bacteria and toxin called endotoxic which is released after killing bacteria. Also, some dirt can be broken down by photocatalyst reaction so that it brings certain advantages of maintaining antibacterial spectrum without cleaning.

Photocatalysis has an advantage over other sterilization techniques in that illuminated titania can not only disinfect but also detoxify. For example, while UV illumination by itself is partially effective in killing *Escherichia coli* (*E. coli)*, this merely results in the release of endotoxin, a pyrogenic constituent of the bacteria, from the dead cells. But illuminated TiO_2 can rapidly inactivate the bacteria while simultaneously destroying the endotoxin.

2.3.4 Air purification

Elimination of NO_x by coating wall surfaces of express highways with TiO_2 has been started in Osaka. Such an approach is not necessarily effective when used in open air, and a key point is riding on how NO_x is added to TiO_2 coatings. A grand project of air purification coating all large constructions and exterior walls with TiO_2 has also been considered. Also, advanced implements for air purification and odor elimination by applying UV light to a TiO_2 treated filter of air purification equipment used indoors have been considered. Dirt, which is stuck on a filter, can be broken down by photocatalyst, so that filter replacement is not required.

2.3.5 Water treatment

TiO_2 photocatalysis is becoming an increasingly interesting oxidation process for the air cleaning as well as water treatment. The advantage of photocatalysis in water purification is the complete mineralization of organics caused by the photogeneration of OH radicals originating from water via the OH groups of theTiO_2 surface.

2.4 Iron Oxide

In general, magnetic NPs have many unique magnetic properties, such as superparamagnetic, high coercivity, low Curie temperature, high magnetic susceptibility, etc. Moreover, magnetic NPs have been investigated for magnetic fluids, data storage, catalysis and also bio-applications [33-37]. Especially, magnetic fluids and data storage are extensively use for commercial applications. In the last decade, the several types of magnetic iron oxides have been carried out in the field of magnetic NPs (mostly includes the Fe_3O_4 magnetite, $Fe^{II}Fe^{III}{}_2O_4$, ferromagnetic, supperparamagnetic when the size is less than 15 nm), α-Fe_2O_3 (hematite, weakly ferromagnetic or antiferromagnetic), γ-Fe_2O_3 (maghemite, ferromagnetic), FeO (wustite, antiferromagnetic), ε-Fe_2O_3 and β-Fe_2O_3 [38]. Among this, magnetite and maghemite are very interesting in biocompatibility because it have already proven. However, it is a technological challenge to control size, shape, stability, and dispersibility of NPs in desired solvents. Magnetic iron oxide NPs have a large surface-to-volume ratio and therefore possess high surface energies. Consequently, they tend to aggregate so as to minimize the surface energies. Moreover, the naked iron oxide NPs have high chemical activity, and are easily oxidized in air (especially magnetite), generally resulting in loss of magnetism and dispersibility. Therefore, providing proper surface coating and developing some effective protection strategies to keep the stability of magnetic iron oxide NPs is very important.

2.5 Properties of iron oxide

In general, magnetic iron oxides composed of 3 structures are iron (II) oxide (FeO), iron (III) oxide; diiron trioxide (Fe_2O_3) and triiron tetraoxide; iron (II, III) oxide, magnetite (Fe_3O_4). The structure and its magnetic properties can be described as bellowed.

2.5.1 Iron (II) oxide (FeO)

Iron (II) oxide, also known as ferrous oxide, iron oxide/oxidized iron or more commonly rusted iron is one of the iron oxides. It is a black-colored powder with the chemical formula of FeO. It consists of the chemical element iron in the oxidation state of 2 bonded to oxygen and its mineral form is known as wüstite. The chemical structure of iron (III) was showed in Figure 2.20. Iron (II) oxide should not be confused with rust which usually consists of hydrated iron (III) oxide (ferric oxide). Iron (II) oxide is an example of a non-stoichiometric compound and the ratio of the elements iron and oxygen can vary, samples are typically iron deficient with a compositions ranging from $Fe_{0.84}O$ to $Fe_{0.95}O$ [39].

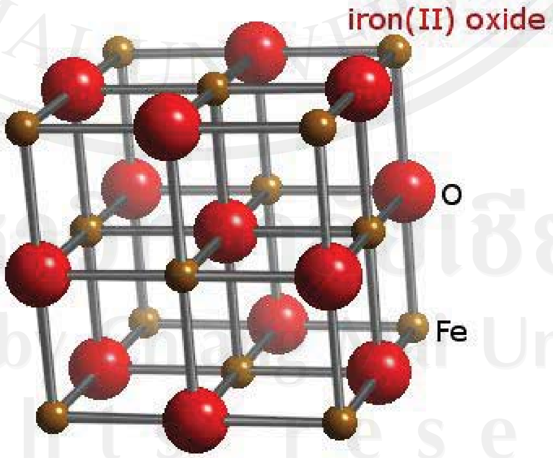


Figure 2.20 Chemical structure of iron (II) oxide.

Iron(II) oxide adopts the cubic, rock salt structure, where iron atoms are octahedrally coordinated by oxygen atoms and the oxygen atoms octahedrally coordinated by iron atoms. The non-stoichiometry occurs because of the ease of oxidation of Fe^{II} to Fe^{III} effectively replacing a small portion of Fe^{II} with two thirds their number of Fe^{III} which take up tetrahedral positions in the close packed oxide lattice [40]. Below 200 K there is a minor change to the structure which changes the symmetry to rhombohedral and samples become antiferromagnetic.

2.5.2 Iron (III) oxide (Fe_2O_3)

Iron (III) oxide is the inorganic compound with the formula Fe_2O_3. It is of one of the three main oxides of iron, the other two being FeO which is rare and Fe_3O_4 which also occurs naturally as the mineral magnetite. The chemical structure of Fe_2O_3 is shown in Figure 2.21.

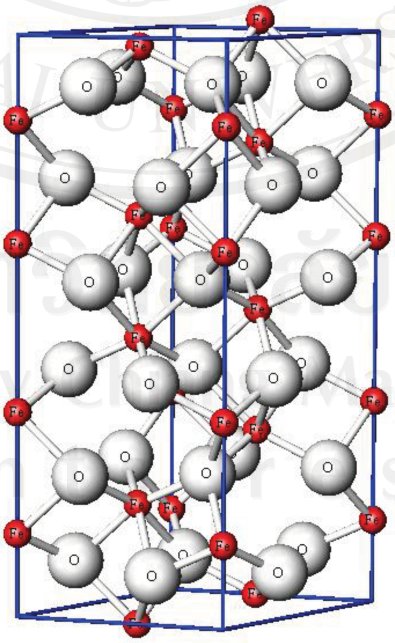


Figure 2.21 Chemical structure of Fe_2O_3.

As the mineral known as hematite, Fe_2O_3 is the main source of the iron for the steel industry. Fe_2O_3 is paramagnetic reddish brown and readily attacked by acids. Rust is often called iron (III) oxide and to some extent this label is useful because rust shares several properties and has a similar composition. To a chemist, rust is considered an ill-defined material, described as hydrated ferric oxide.

Different forms

Alpha phase (α)

α-Fe_2O_3 has the rhombohedral, corundum (α-Al_2O_3) structure and is the most common form. It occurs naturally as the mineral hematite which is mined as the main ore of iron. It is antiferromagnetic below ~260 K (Morin transition temperature), and weak ferromagnetic between 260 K and 950 K (Neel temperature) [41]. It is easy to prepare using both thermal decomposition and precipitation in the liquid phase. Its magnetic properties are dependent on many factors, e.g. pressure, particle size, and magnetic field intensity.

Beta phase (β)

Cubic face centered, metastable, at temperatures above 500 °C converts to alpha phase. It can be prepared by reduction of hematite by carbon, pyrolysis of iron (III) chloride solution, or thermal decomposition of iron (III) sulfate.

Gamma phase (γ)

Cubic, metastable, converts to the alpha phase at high temperatures. It occurs naturally as the mineral maghemite ferrimagnetic. Ultrafine particles which were smaller than 10 nm are superparamagnetic. Can be prepared by thermal dehydratation of gamma iron (III) oxide-hydroxide, careful oxidation of iron (II,III) oxide. The ultrafine particles can be prepared by thermal decomposition of iron (III) oxalate.

Epsilon phase (ε)

Rhombic, shows properties intermediate between alpha and gamma. So far has not been prepared in pure form; it is always mixed with the alpha phase or gamma phases. Material with a high proportion of epsilon phase can be prepared by thermal transformation of the gamma phase. The epsilon phase is metastable, transforming to the alpha phase at between 500 and 750 °C. It can also be prepared by oxidation of iron in an electric arc or by sol-gel precipitation from iron (III) nitrate.

2.5.3 Iron (II, III) oxide (Fe_3O_4)

Iron (II, III) oxide; (Fe_3O_4) or Magnetite is a ferrimagnetic mineral with chemical formula Fe_3O_4, one of several iron oxides and a member of the spinel group. The chemical structure of Fe_3O_4 is shown in Figure 2.22. The chemical IUPAC name is iron (II,III) oxide and the common chemical name ferrous-ferric oxide. The formula for magnetite may also be written as $FeO{\cdot}Fe_2O_3$, which is one part wüstite (FeO) and one part hematite (Fe_2O_3). This refers to the different oxidation states of the iron in one structure, not a solid solution. The Curie temperature of magnetite is 858 K (585 °C; 1,085 °F).

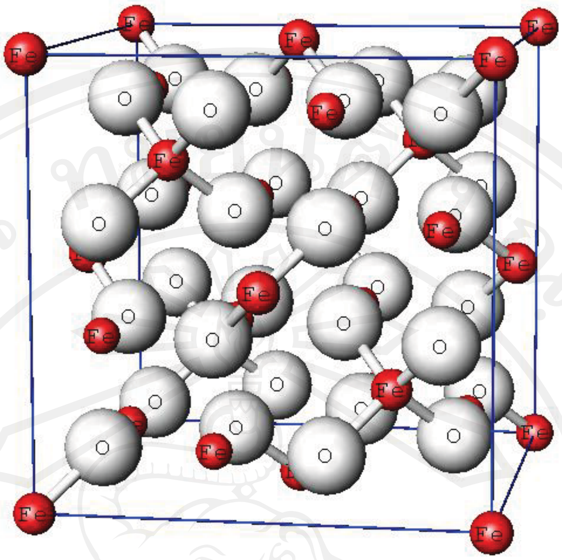


Figure 2.22 Chemical structure of Fe_3O_4

Properties

Magnetite is the most magnetic of all the naturally occurring minerals on Earth [42]. Naturally magnetized pieces of magnetite, called lodestone, will attract small pieces of iron, and this was how ancient man first discovered the property of magnetism. Lodestone was used as an early form of magnetic compass. Magnetite typically carries the dominant magnetic signature in rocks, and so it has been a critical tool in paleomagnetism, a science important in discovering and understanding plate tectonics and as historic data for magnetohydrodynamics and other scientific fields. The relationships between magnetite and other iron-rich oxide minerals such as ilmenite, hematite, and ulvospinel have been much studied, as the complicated reactions between these minerals and oxygen influence how and when magnetite preserves records of the Earth's magnetic field.

Magnetite has been very important in understanding the conditions under which rocks form and evolve. Magnetite reacts with oxygen to produce hematite, and the mineral pair forms a buffer that can control oxygen fugacity. Commonly igneous rocks contain grains of two solid solutions, one between magnetite and ulvospinel and the other between ilmenite and hematite. Compositions of the mineral pairs are used to calculate how oxidizing was the magma (i.e., the oxygen fugacity of the magma). A range of oxidizing conditions is found in magmas and the oxidation state helps to determine how the magmas might evolve by fractional crystallization.

Small grains of magnetite occur in almost all igneous rocks and metamorphic rocks. Magnetite also occurs in many sedimentary rocks, including banded iron formations. In many igneous rocks, magnetite-rich and ilmenite-rich grains occur that precipitated together from magma. Magnetite also is produced from peridotites and dunites by serpentinization. Magnetite is a valuable source of iron ore. It dissolves slowly in hydrochloric acid.

2.6 Practical applications of iron oxide

Some iron oxides are widely used in ceramic applications, particularly in glazing. Many metal oxides provide the colors in glazes after being fired at high temperatures. Iron oxides yield pigments (see iron oxide pigments). Natural iron oxides pigments are called ochres. Many classic paint colors, such as raw and burnt siennas and umbers, are iron-oxide pigments. These pigments have been used in art since the earliest prehistoric art known, the cave paintings at Lascaux and nearby sites. Iron (III) oxide is typically used.

Iron pigments are also widely used in the cosmetic field. They are considered to be nontoxic, moisture resistant, and non-bleeding. Iron oxides graded safe for cosmetic use are produced synthetically in order to avoid the inclusion of ferrous or ferric oxides, and impurities normally found in naturally occurring iron oxides. Typically, the iron (II) oxide pigment is black, while the iron (III) oxide is red or rust-colored. (Iron compounds other than oxides can have other colors.)

Black oxide converts ferrous materials into magnetite for corrosion resistance purposes. A grade of hematite called MIO (micaceous iron oxide) is used as anti-corrosion paint (many bridges, Eiffel tower).

Iron oxide is used in magnetic recording, recording sound, pictures, video and computer data on plastic tape or floppy disks.

Iron oxides are used as contrast agent in Magnetic Resonance Imaging, to shorten proton relaxation times, (T1, T2 and T2*). The superparamagnetic contrast agents are composed of a water insoluble crystalline magnetic core, usually magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3). The mean core diameter ranges from 4 to 10 nm. This crystalline core is often surrounded by a layer of dextran or starch derivatives. The total size of the particle is expressed as the mean hydrated particle diameter. USPIO, Ultrasmall Superparamagnetic Iron Oxide nanoparticles, which usually have single crystal cores, have a mean hydrated particle diameter less than 50 nm.

They may also be used in electrochromic paints. Combined with aluminium powder, iron oxide forms thermite, which is used in demolition and bomb building. The iron oxide cycle (Fe_3O_4/FeO) is a two-step thermochemical process used for hydrogen production.

2.7 Synthesis of colloidal NPs

Generally, initial development of new crystalline materials in colloidal NPs form has been generated by many techniques such as, combustion flame, plasma, laser ablation, chemical vapour condensation, plasma spray, spray pyrolysis including hydrolysis sol-gel. In this thesis, a novel and simple technique as so called "a sparking process" and pyrosol method are presented for use to synthesis of NPs.

2.7.1 Synthesis of colloidal TiO_2 NPs by sparking process

The sparking is electrical mechanism which occurred from the sparking off two metallic sharp tips by a high DC voltage. Detailed insights into the nucleation mechanism were shown in Figure 2.23. From the figure, the high temperature and pressure on molten metallic at the two tip surfaces were generated by the bombardment of electrons and ions, ionized during the spark. Thus, metallic nanodroplets were generated and moved towards the substrate (in this case is an aqueous solution) by the high kinetic energy. The particle size can be described thermodynamically with the Young-Laplace equation, i.e. $\Delta P = 2\gamma / r$ where r is the radius of curvature, γ is surface free energy of the molten metal and ΔP is the pressure difference between inside (P_{in}) and outside (P_{out}) the droplet [43].

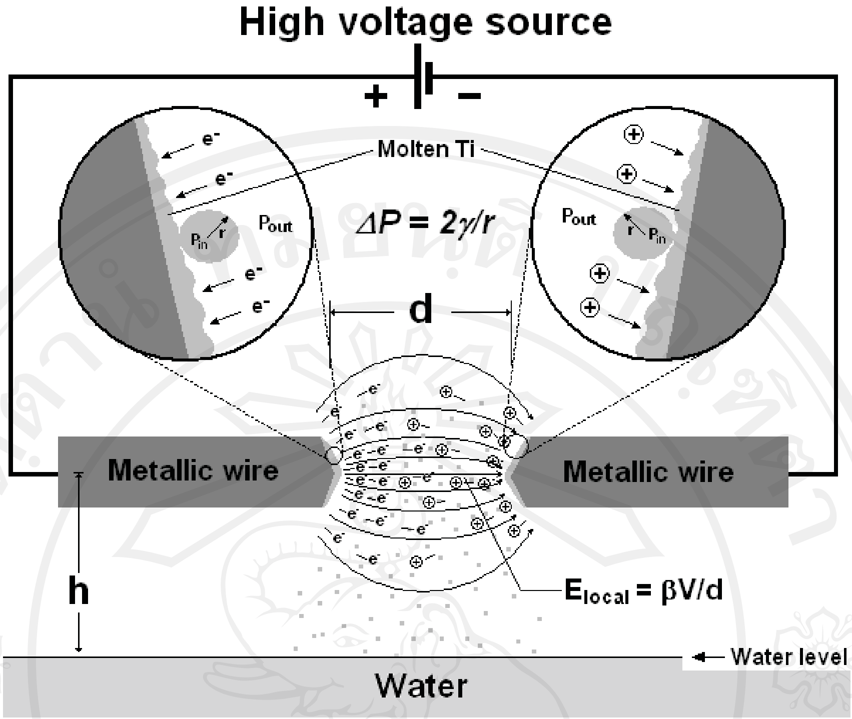


Figure 2.23 Schematic diagram of the nucleation mechanism of colloidal NPs deposited by the sparking off two metallic sharp tips.

2.7.2 Synthesis of Fe_2O_3 nanoparticles by pyrosol method

Recently, the study of nanoparticles (NPs) have received increasing attention [44,45]. Iron oxide NPs are well known catalysts for carbon nanotube fabrication [46,47]. However, the catalyst is costly and will not bring the price of carbon nanotube down at the mass production scale. Although many techniques are available to produce the NPs such as the citrate pyrolysis [48], a low-temperature hydrothermal method [49,50], flow injection synthesis [51], chemical vapor deposition [52], sol–gel processes [53], pulsed laser evaporation [54], sputtering[55] and spray pyrolysis [56-59]. In this work, we have developed an alternative configuration of the pyrosol method which is a very simple and low-cost scheme to produce iron oxide NPs. The schematic diagram of the pyrosol apparatus was showed in figure 2.24

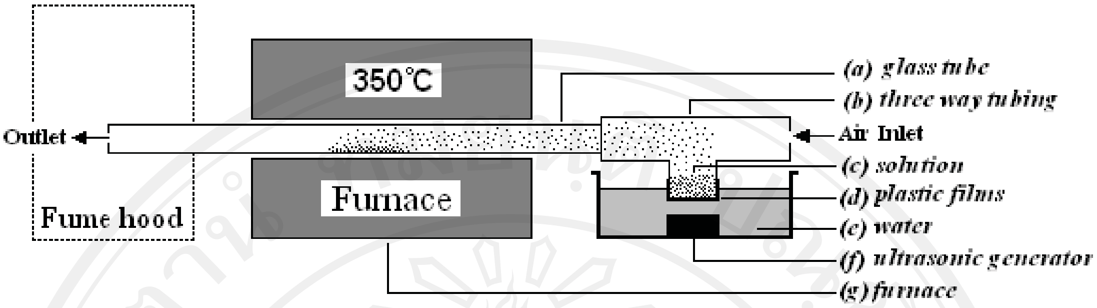


Figure 2.24 Schematic diagrams of the pyrosol apparatus.

The process was started in a tube furnace (a) which was connected to a three way tube (b) containing an aqueous iron (III) nitrate ($Fe(NO_3)_3.9H_2O$) solution (c). A mist generator (f) was immerged in water (e) and placed under the solution, which was separated from water using a plastic film (d). The process starts from aerosol generation of precursor solution which containing Fe^+ ions was then atomized by the mist generator. The aerosol was subsequently brought into the tube furnace (g) by a controlled flowing air stream.

When mixed iron (III) nitrate with ultra pure water and atomized by a mist generator, the misted droplet was generated and iron oxide was formed to the following reaction.

$$2Fe(NO_3)_3 \bullet 9H_2O \Rightarrow 2Fe^{3+} + 6(NO_3)^- + 18H^+ + 18(OH)^-$$

$$\Rightarrow 2Fe(OH)_3 + 6H(NO_3) + 12H_2O$$

$$\Rightarrow Fe_2O_3 + 6H(NO_3) + 15H_2O$$

At that time the average diameter of the misted droplets can be approximately calculated according to Lang [60]

$$Dd = 0.34\left(\frac{8\pi\gamma}{\rho f^2}\right)^{1/3} \tag{2.6}$$

where Dd is the droplet diameter, γ is the solution surface tension ($72.9\text{x}10^{-3}$ N/m; surface tension of pure water), ρ is the solution density and f is the applied ultrasonic frequency (1.7 MHz). The diameter of the misted droplets was calculated using the above parameters and were showed in Table 1. The mean diameter of the particles (Dp) formed from the misted droplet was theoretically calculated using the following equation [61]

$$Dp = Dd\left(\frac{C_{pr} M_{FO}}{\rho_{FO} M_{pr}}\right)^{1/3} \tag{2.7}$$

where Dp is the mean diameter of the particles (Fe_2O_3) fabricated through pyrolysis reaction, C_{pr} is the precursor concentration, M_{FO} is the molecular mass of the Fe_2O_3 (159.7 mol); M_{pr} is the molecular mass of the precursor (404 mol), and ρ_{FO} is the theoretical density of the Fe_2O_3 (5.25 g/cm^3).