CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Hydrogen: Fuel of the Future

Hydrogen is now being considered as an ideal fuel for the future. Hydrogen fuel can be produced from clean and renewable energy sources and, thus, its life cycle is clean and renewable. Solar and wind are the two major sources of renewable energy, and they are also the promising sources for renewable hydrogen production. However, presently, renewable energy contributes only about 5% of the commercial hydrogen production primarily via water electrolysis, while other 95% hydrogen is mainly derived from fossil fuels (Bak *et al.*, 2002). Renewable hydrogen production is not popular yet because the cost is still high. Photovoltaic water electrolysis may become more competitive as the cost continues to decrease with the technology advancement, however the considerable use of small band gap semiconducting materials may cause serious life cycle environmental impacts. Alternatively, photocatalytic water splitting using TiO_2 for hydrogen production offers a promising way for clean, low-cost, and environmentally friendly production of hydrogen by solar energy.

Hydrogen has many potential applications, including the powering of non-polluting vehicles, domestic heating, and aircraft. Therefore, hydrogen, as an energy carrier, is anticipated to join photovoltaic electricity as the foundation of sustainable energy system. Recent efforts in the development of vehicles fuelled by hydrogen, either directly or through hydrogen fuel cells, may serve as examples of how close is the hydrogen age. The diagram in Figure 2.1 shows that, while the introduction of fuel cell technology will lead to a substantial reduction in the emissions of greenhouse gases (expressed in carbon units per kilometer), the use of fuel cells powered by hydrogen obtained from solar energy will reduce the emissions to nearly zero. Hydrogen is not present in nature in a gaseous form. However, it is abundantly available in plants, as well as in several compounds, such as methane, methanol, and higher hydrocarbons. Most importantly, it is available in water. Therefore, hydrogen must be extracted from these compounds.
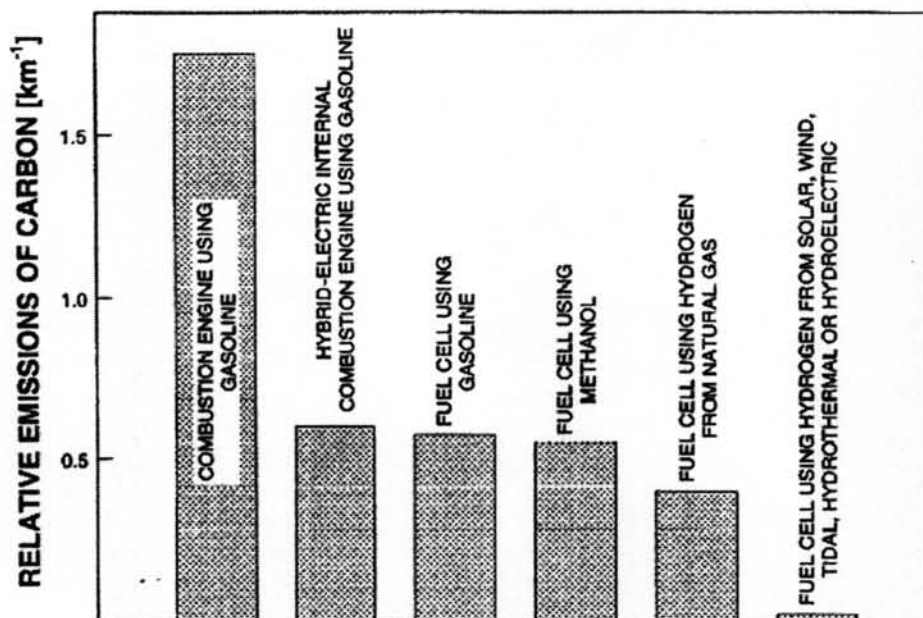
Figure 2.1 Relative emissions of greenhouse gases (expressed in carbon units per km) for vehicles powered by today's internal combustion engine using gasoline compared to vehicles powered by fuel cells (Bak *et al.*, 2002).

2.2 Semiconductor

A semiconductor is a material with an electrical conductivity that is intermediate between that of an insulator and a conductor. Like other solids, semiconductor materials have electronic band structure determined by the crystal properties of the material. The actual energy distribution among electrons is described by the Fermi level and temperature of the electrons. At absolute zero temperature, all of the electrons have energy below the Fermi energy, but at non-zero temperature, the energy levels are randomized, and some electrons have energy above the Fermi level.

Among the bands filled with electrons, the one with the highest energy level is referred to as the valence band, and the band outside of this is referred to as the conduction band. The energy width of the forbidden band between the valence

band and the conduction band is referred to as the band gap (E_g). The overall structure of band gap energy is shown in Figure 2.2.

The band gap can be considered as a wall that electrons must jump over in order to become free. The amount of energy required to jump over the wall is referred to as the band gap energy. Only electrons that jump over the wall and enter the conduction band (CB, which are referred to as conduction electrons) can move around freely. When light is illuminated at appropriate wavelengths with energy equal or more than band gap energy, valence band (VB) electrons can move up to the conduction band (CB). At the same time, as many positive holes as the number of electrons that have jumped to the conduction band (CB) are created.
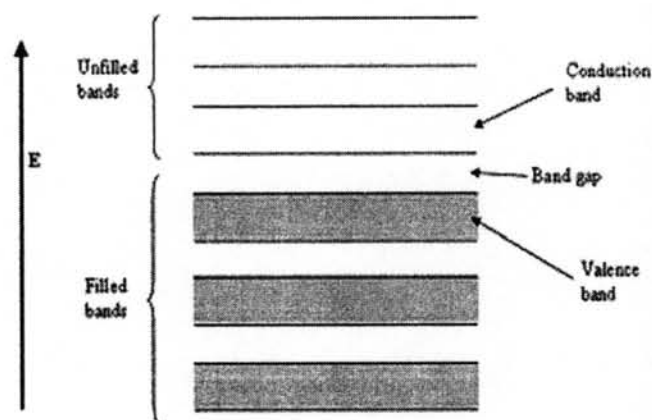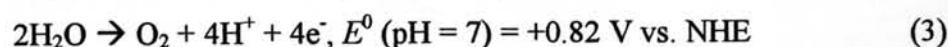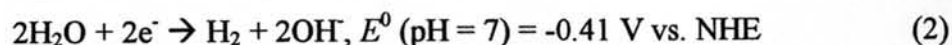

Figure 2.2 The structure of band gap energy.

2.3 Water Splitting: Hydrogen Generation Using Solar Energy

The general enthusiasm for the use of hydrogen as an environmentally friendly fuel has been encouraged by the fact that the combustion of hydrogen results in the generation of water, which neither causes air pollution nor leads to the emission of greenhouse gases. This consideration is correct, assuming that hydrogen is generated using a source of renewable energy, such as solar, wind, hydroelectric, or hydrothermal energy. To date, the technologies for hydrogen generation using sources of renewable energy are in the incubation stage. The growing interest in
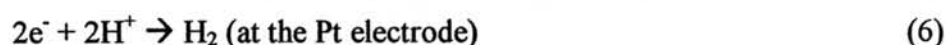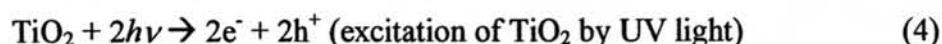
hydrogen has resulted from the increasing need to develop hydrogen technologies that are based on the utilization of renewable sources of energy. There is a large body of literatures indicating that the most promising method of hydrogen generation using a source of renewable energy is that based on photoelectrochemical water decomposition using solar energy (Archer *et al.*, 1990). Since the first report of this method proposed by Fujishima and Honda (Fujishima *et al.*, 1972) almost 35 years ago, there have been many literatures published on the impact of different structures and materials on the performance of photoelectrochemical cells. The energy conversion efficiency of water photoelectrolysis is primarily determined by the properties of materials used for the photoelectrodes.

For photoelectrolysis of water, a potential difference of more than 1.23 eV is necessary between cathodic and anodic electrodes (Eq. (1)), where the following anodic and cathodic reactions take place simultaneously (Eq. (2) and (3)).

$$H_2O \rightarrow H_2 + 1/2O_2, E = 1.23 \text{ eV} \tag{1}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-, E^0 (pH = 7) = -0.41 \text{ V vs. NHE} \tag{2}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-, E^0 (pH = 7) = +0.82 \text{ V vs. NHE} \tag{3}$$

This potential difference is equivalent to the energy of a wavelength of approximately 1008 nm. Therefore, if the energy of light is used effectively in an electrochemical system, it should be possible to decompose water with visible light of wavelength shorter than 1008 nm.

Although water splitting by solar light irradiation has been investigated by many researchers, any useful and applicable method has not been developed yet. Because water is transparent to visible light, it cannot be decomposed by visible light alone. It can be split by irradiation alone only with ultraviolet light shorter than 190 nm. Fujishima and Honda were the first to study photodecomposition of water over semiconductor photoelectrolysis cells using light of wavelength $\lambda < 400$ nm. From Fujishima and Honda's results, it was suggested that water could be decomposed by light into oxygen and hydrogen according to the following Eq. (4)-(6):

$$TiO_2 + 2h\nu \rightarrow 2e^- + 2h^+ \text{ (excitation of TiO}_2 \text{ by UV light)} \tag{4}$$

$$2h^+ + H_2O \rightarrow 1/2O_2 + 2H^+ \text{ (at the TiO}_2 \text{ electrode)} \tag{5}$$

$$2e^- + 2H^+ \rightarrow H_2 \text{ (at the Pt electrode)} \tag{6}$$

The overall reaction can be expressed as Eq. (7):

$$H_2O + h\nu \rightarrow 1/2O_2 + H_2 \tag{7}$$

Despite the success of Fujishima-Honda, use of a photoelectrochemical cells involves the difficulty of constructing the oxide semiconductor photoelectrode. Therefore, applications of the principle of water photodecomposition using semiconductor to heterogeneous photocatalytic systems using powdered semiconductors instead of photoelectrodes have been actively studied by reason of their advantages over photoelectrochemical cells, i.e. low cost to construct, chemical stability under the light, and large surface area. Such attempts have been supported by two experimental advances. One is accumulation of data on photocatalytic reactions over powdered semiconductors, while the other is Bard's concept that can be pictured as a ''short-circuited'' photoelectrochemical cell where semiconductor electrode and metal counter electrode have been brought into contact in single particle. The history and development of the briefly mentioned progress about water splitting can be traced as follows (Bard *et al.*, 1995).

2.3.1 Efficiency

The free energy change for water splitting reaction is $\Delta G° = 237.2$ kJ/mol or 2.46 eV/molecule of H_2O. Since two electrons are involved in the reaction, this corresponds to 1.23 eV/e, which is also the standard emf for the reaction. The photons in the solar spectrum provide sufficient energy to drive this reaction, but the efficiency of the reaction depends upon how the reaction is carried out. It is possible to cause water splitting thermally with light via concentrators and a solar furnace by heating water to 1500-2500 K. However, the efficiency of this process is typically below 2%, and the cost of the capital equipment and material stability problems suggest that this approach for water splitting is not a promising one.

Since water itself does not absorb appreciable ration within the solar spectrum, one or more light-absorbing species, i.e. semiconductors as the photoconverters, must be used to transform the radiant energy to chemical (or electrical) energy in the form of electron/hole pairs, i.e. to the oxidizing and reducing potentials needed to drive the reaction. The maximum efficiency for photochemical

water splitting has been considered in a number of papers and depends upon the band gap (or threshold energy), E_g, of the semiconductor. Radiation of energy below E_g is not absorbed while that above E_g is partly lost as heat by internal conversion or intraband thermalization processes. Additional thermodynamic losses occur because the excited state concentration is only a fraction of that of the ground state and because some excited states are lost through radiative decay (Archer *et al.*, 1990).

2.3.2 Semiconductor Solid State Photovoltaic Based Systems

A number of different approaches are possible with semiconductors. The most direct approach employs a solid state photovoltaic solar cell to generate electricity that is then passed into a commercial-type water electrolyzer, as shown in Figure 2.3(a). The electrolysis of water at a reasonable rate in a practical cell requires applied voltages significantly larger than the theoretical value (1.23 V at 25°C). Moreover, the components are rugged and should be long-lived. The problem with such a system is its cost. Solar photovoltaics cannot currently produce electricity at competitive prices, and hydrogen from water electrolyzers is significantly more expensive than that produced chemically from coal or natural gas.
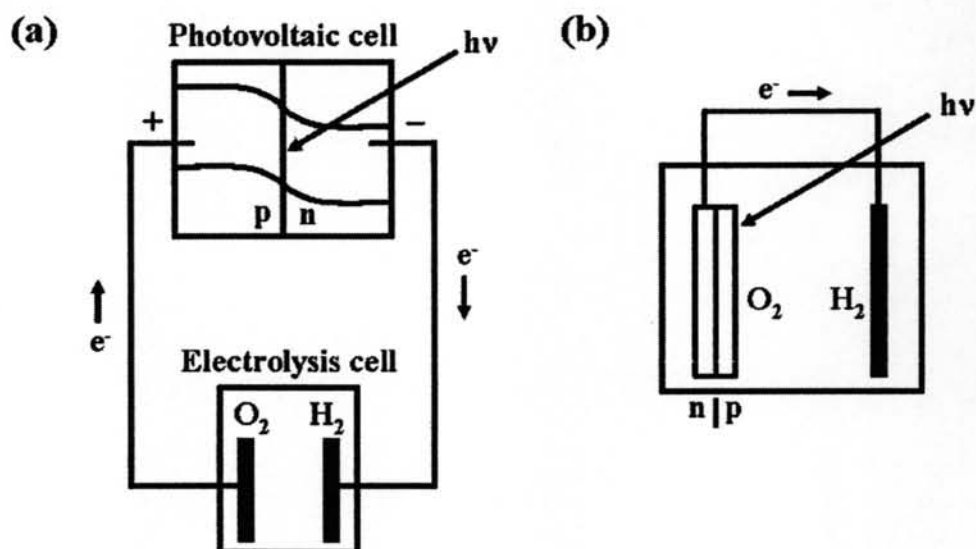

Figure 2.3 Schematic of (a) solid state photovoltaic cell driving a water electrolyzer and (b) cell with immersed semiconductor p/n junction (or metal/semiconductor Schottky junction) as one electrode.

An alternative system involves the semiconductor photovoltaic cell immersed directly in aqueous system, as illustrated in Figure 2.3(b). At the least, this eliminates the costs and mechanical difficulties associated with separate construction and interconnection of solar and electrochemical cells. In one such system, the electrodes are composed of single or multiple semiconductor p/n junctions that are irradiated while they are within the cell. This simpler apparatus is attained at the cost of encapsulating and coating the semiconductors to protect them from the liquid environment and probably with a more limited choice of electrocatalyst for H_2 or O_2 evolution. Note that, in addition to p/n semiconductor junctions, those between a metal and semiconductor (Schottky barriers) can also be used to produce a photopotential.

2.3.3 Semiconductor Electrode (Liquid Junction) Systems

Of more interest are systems, in which the photopotential to drive the water splitting reaction is generated directly at the semiconductor/liquid interface, as shown in Figure 2.4. Rather extensive research was carried out on various metal electrodes, sometimes covered with oxide or other films, and immersed in a variety of solutions, including some containing fluorescent dyes. The discovery of the transistor and interest in semiconductor materials led to more extensive electrochemical and photoelectrochemical studies, usually with the goal of characterizing the semiconductor.
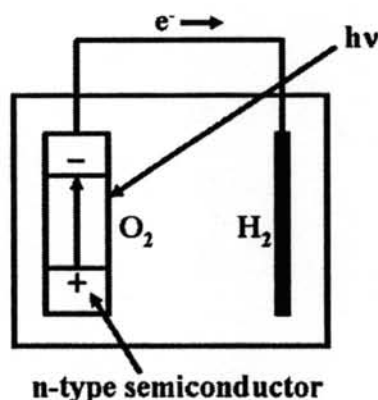

Figure 2.4 Schematic of liquid junction semiconductor electrode cell.

The modern era of semiconductor electrodes and interest in these in photoelectrochemical devices for energy conversion, especially via the water splitting reaction, can be cited to the work of Fujishima and Honda on single-crystal TiO_2 electrodes (Fujishima *et al.*, 1972). Indeed, water splitting in TiO_2-based cells can be accomplished, but only with an additional electrical bias. The problem with TiO_2 is that the conduction band is too low, i.e. at an insufficiently negative potential, to generate hydrogen at a useful rate. Moreover, because the TiO_2 band gap is too large (3.2 eV for anatase and 3.0 eV for rutile), only a small fraction of the solar light is absorbed. Cells with TiO_2 electrodes of various types, e.g. single crystal, polycrystal, and thin film, have nevertheless been heavily investigated, largely because TiO_2 is very stable and is a good model for understanding the semiconductor/liquid interface.

2.3.4 Semiconductor Particle Systems

A considerable simplification of the apparatus is possible if the electrochemical cell can be replaced by simple dispersions of semiconductor particles. In such dispersions, the semiconductor particles can be coated with islands of metals or metal oxides that behave as catalytic sites, with each particle behaving as a microelectrochemical cell. TiO_2 has been a favorite material, although other compounds, such as CdS and ZnO, have also been studied. While a number of interesting photoreactions have been carried out, including the use of particles to destroy organics and to plate metals from waste water (Ollis *et al.*, 1993) and for synthetic purposes (Serpone *et al.*, 1989), reports on the use of particulate systems for water splitting remain controversial. An extension of this approach is the use of colloidal-sized particles down to nanoparticles. Such small particles also have very high surface areas that, in principle, allow faster capture of the photogenerated charges by solution species and with less bulk recombination.

Recently, several researchers have focused on either hydrogen generation in the presence of a sacrificial electron donor or oxygen production in the presence of a sacrificial electron acceptor. Including a sacrificial reagent also often completely reverses the net thermodynamics, converting an inherently up-hill (photosynthetic) reaction such as water splitting into a net energetically down-hill

(photocatalytic) transformation by coupling the endothermic steps with other highly exothermic ones. For efficient hydrogen evolution, several features are necessary: (1) a robust photocatalyst for efficient evolution of hydrogen must be effective in trapping the reduced relay, (2) the sacrificial donor must be inexpensive and readily available, and (3) each of the components must be both chemically and optically compatible.

2.4 Photocatalysis and Photocatalysts for Hydrogen Generation

2.4.1 Background on Photocatalysis

Photocatalytic reactions have been extensively studied. Photocatalytic reactions are classified into two categories: "down-hill" and "up-hill" reactions. Degradation such as photo-oxidation of organic compounds using oxygen molecules is generally a down-hill reaction, of which the reaction proceeds irreversibly. In this reaction, a photocatalyst works as a trigger to produce O_2^-, HO_2, $OH\bullet$, and H^+ as active species for oxidation at the initial stage. This type of reaction is regarded as a photo-induced reaction, as depicted in Figure 2.5(a), and has been extensively studied using titanium dioxide photocatalyst (Fujishima et al., 2000). On the other hand, water splitting reaction is accompanied by a largely positive change in the Gibbs free energy (ΔG^0 = 237 kJ/mol) and is an up-hill reaction. In this reaction, photon energy is converted into chemical energy, as also shown in Figure 2.5(b), similar to photosynthesis by green plants. Therefore, this type of reaction is called artificial photosynthesis.
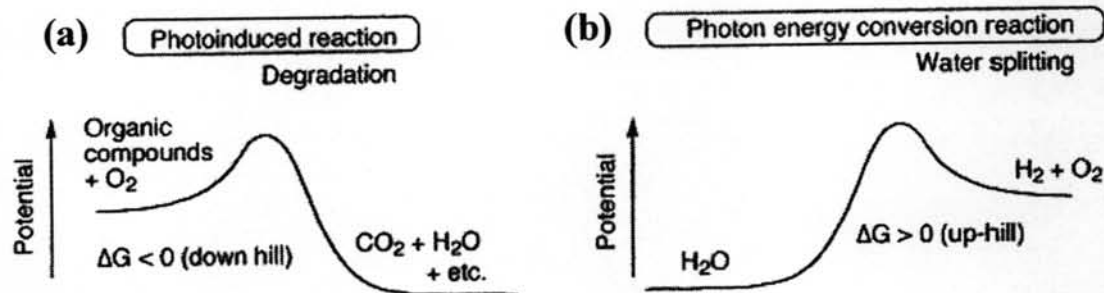
Figure 2.5 Types of photocatalytic reactions: (a) photoinduced reaction and (b) photon energy conversion reaction.

The importance of hydrogen energy has recently been recognized again, especially for use in fuel cells with due concern for environmental issues. However, hydrogen is industrially produced by steam reforming of hydrocarbons such as methane, generating a large amount of CO_2, a greenhouse gas. Hydrogen has to be produced from water using natural energy if one is concerned about environmental issues. Therefore, water splitting using a photocatalyst is a challenging reaction because it is one of the most important reactions for solving energy and environmental problems.

2.4.2 Photocatalytic Water Splitting Process

During photocatalytic process, the illumination of a semiconductor photocatalyst with light radiation activates the catalyst, establishing a redox environment in the aqueous solution. Semiconductors act as sensitizers for light-induced redox processes due to their electronic structure, which is characterized by a filled valence band (VB) and an empty conduction band (CB) (Hoffmann *et al.*, 1995). The energy difference between the valence and conduction bands is called the band gap (E_g).

The principle of water splitting using a semiconductor photocatalyst is shown in Figure 2.6. The semiconductor photocatalyst absorbs impinging photons with energies equal to or higher than its band gap or threshold energy. Each photon of the required energy (i.e. wavelength) that strikes an electron in the occupied valence band (VB) of the semiconductor atom can elevate that electron to the

unoccupied conduction band (CB), leading to excited state conduction band electrons and positive valence band holes (Serpone *et al.*, 1989). The photogenerated electrons and holes cause redox reactions similar to electrolysis. Water molecules are reduced by the electrons to form H_2 and oxidized by the holes to form O_2, leading to overall water splitting. The width of the band gap and the potentials of the conduction and valence bands are important for the semiconductor photocatalyst material. The bottom level of the conduction band (CB) has to be more negative than the reduction potential of H^+/H_2 (0 V vs NHE), while the top level of the valence band (VB) has to be more positive than the oxidation potential of O_2/H_2O (1.23 V).
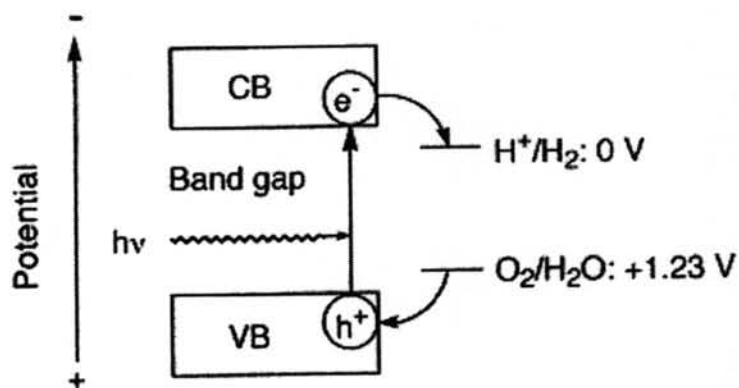

Figure 2.6 Reaction schematic for water spitting reaction over semiconductor photocatalysts.

The competition between charge carrier recombination and charge carrier trapping followed by the competition between recombination of trapped carriers and interfacial charge transfer are what determine the overall quantum efficiency for interfacial charge transfer. Also of great importance are the band positions or flat band potentials of the semiconductor material. These indicate the thermodynamic limitations for the photoreactions that can take place.

However, the potential of the band structure is just the thermodynamic requirement. Other factors such as chare separation, mobility, and lifetime of photogenerated electrons and holes also affect the photocatalytic properties, as shown in Figure 2.7, in which the fate of these charge carriers may take different paths. Firstly, they can get trapped in the bulk either in shallow or in deep traps.

Secondly, they can recombine, non-radiatively or radiatively, dissipating the input energy as heat. Finally, they can react with electron donors or acceptors adsorbed on the surface of the photocatalyst (Hoffmann *et al.*, 1995). These properties are strongly influenced by bulk properties of the material such as crystallinity. Surface properties such as surface area and active reaction sites are also imperative. Cocatalysts such as Pt and NiO are often loaded on the surface in order to introduce active sites for H_2 evolution. Thus, suitable bulk and surface properties and energy structure are demanded for photocatalysts. So, one can state that the photocatalyst is a highly functional material.
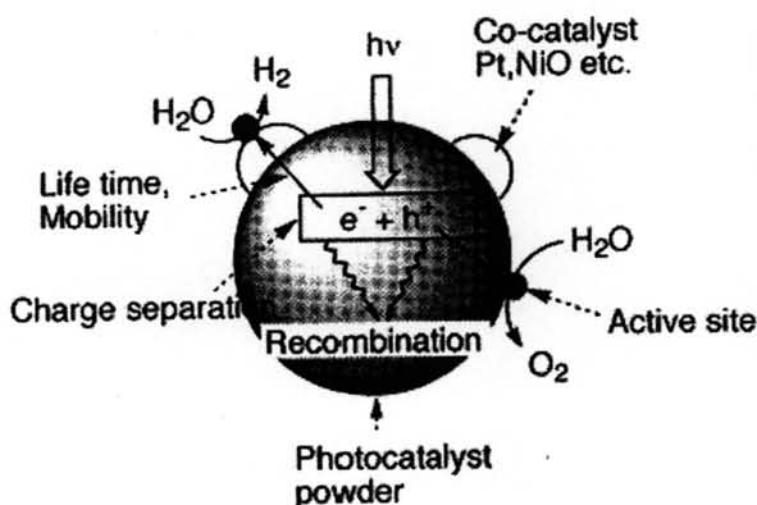

Figure 2.7 Processes occurring in semiconductor photocatalyst under photoexcitation for water splitting reaction.

2.4.3 Photocatalysts

Since water is transparent to solar radiation, direct decomposition of water by solar light is not viable. Energetically, it seems relatively easy to photocatalyze water, since the theoretical minimum photovoltage required for this process is only 1.23 eV. Semiconductors, in the presence of light energy, are capable of decomposing water into hydrogen and oxygen depending upon energy levels of their conduction and valence bands. In an ideal system, conduction band level should be well above (more negative than) the hydrogen reduction level, and valence band edge should be well below (more positive than) the water oxidation level for an

efficient production of hydrogen and oxygen from water by photolysis. Thus depending upon the relative positions of the energy levels of conduction and valence bands with respect to H^+/H_2 and O_2/H_2O levels, semiconductors can be used to decompose water using solar energy. Some of the semiconductors satisfying both conditions are TiO_2, Ta_2O_5, $SrTiO_3$, α-Fe_2O_3, ZnO, ZnS, CdS, PbS, etc. However, most of these materials could not potentially used due to either wide band gap energy or photocorrosive nature, since a semiconductor photocatalyst should ideally be chemically and biologically inert, photocatalytically stable, easy to produce and to use, efficiently activated by sunlight, able to efficiently catalyze the reaction, inexpensive, and without risks for both the environment and human beings.

TiO_2, the semiconductor most thoroughly investigated in the literature, seems to be the most promising for photocatalytic water splitting. This semiconductor provides the best compromise between photocatalytic performance and stability in aqueous media. On the other hand, binary metal sulfide semiconductors such as CdS and PbS are regarded as insufficiently stable for photocatalysis, at least in aqueous media as they readily undergo photocorrosion. These materials are also known to be toxic. Fe_2O_3 is not suitable semiconductors as they readily undergo photocorrosion, as well (Hoffmann et al., 1995). Moreover, the band gap of ZnO (3.2 eV) is equal to that TiO_2, however ZnO is also unstable in water with $Zn(OH)_2$ being formed on the particle surface. This results in photocatalyst deactivation (Howe, 1998).

As mentioned, TiO_2 has been most widely used for studies of photocatalytic decomposition of water, because of its high stability against photocorrosion and its favorable band-gap energy. However, most of studies concluded that in aqueous suspension systems, TiO_2 could not decompose water stoichiometrically, and the photocatalytic activities dropped rapidly with reaction time. On the other hand, high activities in the photocatalytic decomposition of water are often obtained by addition of so-called "sacrificial reagents", which are generally carbon-containing molecules, especially alcohols such as methanol and ethanol due to the presence of polarity and its ability to donate the lone electron pair acting as hole scavenger and subsequently preventing electron-hole recombination. This suggests that photoexcited electrons and holes can be efficiently separated in a

small semiconductor particle and that they are available for an irreversible chemical reaction, oxidization of sacrificial reagent. It is, therefore, inferred that a low efficiency of photodecomposition of water into H_2 and O_2 is mainly due to a rapid reverse reaction between produced H_2 and O_2. Thus, a critical problem to be resolved for realizing the up-hill reaction efficiently is how to prevent such thermodynamically favored reverse reaction.

2.5 Titanium Oxide Photocatalyst

2.5.1 General Remarks

Titanium dioxide (TiO_2) belongs to the family of transition metal oxides TiO_2 has received a great deal of attention due to its chemical stability, non-toxicity, low cost, and other advantageous properties. Particularly, TiO_2 is extensively utilized in solar energy conversion, i.e. solar cell, and photocatalysis applications (Hoffmann et al., 1995). As a result of its high refractive index, it is used as anti-reflection coating in silicon solar cells and in many thin film optical devices. TiO_2 is successfully used as gas sensor (due to the dependence of the electric conductivity on the ambient gas composition and is utilized in the determination of oxygen and carbon monoxide concentrations at high temperatures (> 600°C), and simultaneously determining CO/O_2 and CO/CH_4 (Savage et al., 2001) concentrations. Due to its hemocompatibility with the human body, TiO_2 is also used as a biomaterial (as bone substituent and reinforcing mechanical supports).

2.5.2 Crystal Structure and Properties

The main four polymorphs of TiO_2 found in nature are anatase (tetragonal), brookite (orthorhombic), rutile (tetragonal), and TiO_2 (B) (monoclinic). The structures of rutile, anatase, and brookite can be discussed in terms of (TiO_2^{6-}) octahedrals. The three crystal structures differ by the distortion of each octahedral and by the assembly patterns of the octahedral chains. Anatase can be regarded to be builtup from octahedrals that are connected by their vertices, in rutile, the edges are connected, and in brookite, both vertices and edges are connected, as shown in Figure 2.8 (Carp et al., 2004).
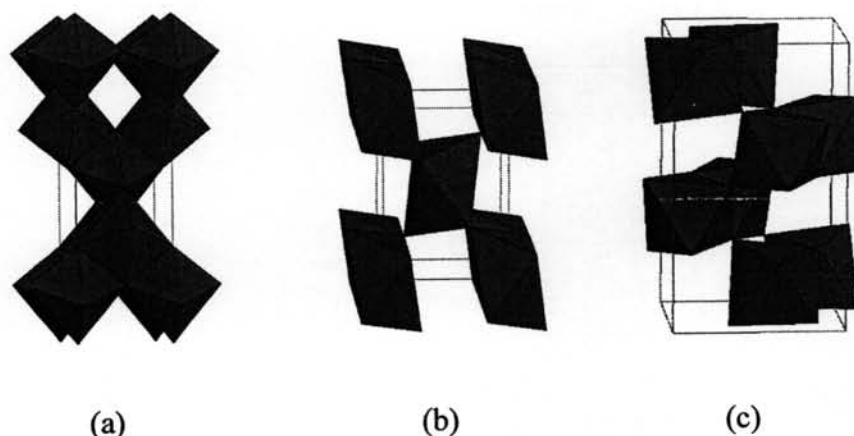
(a)	(b)	(c)

Figure 2.8 Crystal structures of (a) anatase, (b) rutile, and (c) brookite.

Thermodynamic calculations based on calorimetric data predict that rutile is the most stable phase at all temperatures and pressures up to 60 kBar. The small differences in the Gibbs free energy (4-20 kJ/mol) among the three phases suggest that the metastable polymorphs are almost as stable as rutile at normal pressures and temperatures. Particle size experiments affirm that the relative phase stability may reverse when particle sizes decrease to sufficiently low values due to surface energy effects (surface free energy and surface stress, which depend on particle size). If the particle sizes of the three crystalline phases are equal, anatase is the most thermodynamically stable at sizes less than 11 nm, brookite is the most stable between 11 and 35 nm, and rutile is the most stable at sizes greater than 35 nm (Zhang *et al.*, 2000).

The enthalpy of the anatase-rutile phase transformation is low. However, there are widespread disagreement in the value, which ranges from -1.3 to -6.0 ± 0.8 kJ/mol. Kinetically, anatase is stable, i.e. its transformation into rutile at room temperature is so slow that the transformation practically does not occur. At macroscopic scale, the transformation reaches a measurable speed for bulk TiO_2 at temperature greater than 600°C. During the transformation, anatase pseudoclose-packed planes of oxygen are retained as rutile close-packed planes, and a co-operative rearrangement of titanium and oxygen ions occurs within this configuration. The proposed mechanism implies at least spatial disturbance of the

oxygen ion framework and a minimum breaking of Ti–O bonds as a result of surface nucleation and growth. The nucleation process is very much affected by the interfacial contact in nanocrystalline solids, and once initiated, it quickly spreads out and grain growth occurs (Ding *et al.*, 1998).

The anatase-rutile transformation has been studied for both mechanistic and application-driven reasons, because the TiO_2 phase (i.e. anatase or rutile) is one of the most critical parameters determining the use as a photocatalyst, catalyst, or as ceramic membrane material. This transformation, achieved by increased temperature or pressure, is influenced by several factors such as concentration of lattice and surface defects, particle size, and applied temperature and pressure.

In photocatalysis applications, both crystal structures, i.e. anatase and rutile, are commonly used, with anatase showing a greater photocatalytic activity for most reactions. It has been suggested that this increased photoreactivity is due to anatase's slightly higher Fermi level, lower capacity to adsorb oxygen, and higher degree of hydroxylation (i.e. number of hydroxyl groups on the surface). Reactions, in which both crystalline phases have the same photoreactivity (Deng *et al.*, 2002) or rutile a higher one, (Mills *et al.*, 2003) are also reported. Furthermore, there are also studies, which claim that a mixture of anatase (70-75%) and rutile (30-25%) is more active than pure anatase (Mugglie *et al.*, 2001). The disagreement of the results may lie in the intervening effect of various coexisting factors, such as specific surface area, pore size distribution, crystal size, and preparation methods, or in the way the activity is expressed. The behavior of Degussa P-25 commercial TiO_2 photocatalyst, consisting of a mixture of anatase and rutile in an approximate proportion of 80/20, is for many reactions more active than both the pure crystalline phases. The enhanced activity arises from the increased efficiency of the e^-/h^+ separation due to the multiphase nature of the particles. Water splitting reaction is a special case because band bending is necessary in order to reduce and oxidize water.

2.5.3 Semiconductor Characteristic and Photocatalytic Activity

Due to oxygen vacancies, TiO_2 is an n-type semiconductor. A semiconductor photocatalyst is characterized by its capability to adsorb simultaneously two reactants, which can be reduced and oxidized by a photonic activation through an efficient absorption ($h\nu \geq E_g$). The ability of a semiconductor to undergo photoinduced electron transfer to an adsorbed particle is governed by the band energy positions of the semiconductor and the redox potential of the adsorbates. The energy level at the bottom of conduction band is actually the reduction potential of photoelectrons. The energy level at the top of valence band determines the oxidizing ability of photogenerated holes, each value reflecting the ability of the system to promote reductions and oxidations. The flat band potential (V_{fb}) locates the energy of both charge carriers at the semiconductor-electrolyte interface, depending on the nature of the material and system equilibrium. From the thermodynamic point of view, adsorbed couples can be reduced photocatalytically by conduction band electrons if they have more positive redox potentials than V_{fb} of the conduction band, and can be oxidized by valence band holes if they have more negative redox potentials than V_{fb} of the valence band (Rajeshwar, 1995).

Unlike metals, semiconductors lack a continuum of interband states to assist the recombination of electron-hole (e^-/h^+) pairs, which assure a sufficiently long life time of the pairs to diffuse to the photocatalyst surface and initiate a redox reduction. The differences in lattice structures of anatase and rutile TiO_2 cause different densities and electronic band structures, leading to different band gaps (for bulk materials: anatase 3.20 eV and rutile 3.02 eV). Therefore, the absorption thresholds correspond to wavelengths of 384 and 410 nm for the two TiO_2 forms, respectively. The mentioned values concern single crystals or well-crystallized samples. Higher values are usually obtained for weakly crystallized thin films or nanosized materials. The blue shift of the fundamental absorption edge in TiO_2 nanosized materials has been observed amounting to 0.2 eV for crystallite sizes in the range of 5-10 nm.

2.6 Nano-Photocatalysts

2.6.1 General remarks

Nanocrystalline photocatalysts are ultras-mall semiconductor particles, which are few nanometers in size. During the past decade, the photochemistry of nanosized semiconductor particles has been one of the fastest growing research areas in physical chemistry. The interest in these small semiconductor particles originates from their unique photophysical and photocatalytic properties. Several review articles have been published concerning the photophysical properties of nanocrystalline semiconductors. Such studies have demonstrated that some properties of nanocrystalline semiconductor particles are in fact different from those of bulk materials.

Nanosized particles possess properties with fall into the region of transition between the molecular and bulk phases. In the bulk material, the electron excited by light absorption funds a high density of states in the conduction band, where it can exist with different kinetics energies. In the case of nanoparticles, however the particle size is the same as or smaller than the size of the first excited state. Thus, the electrons and holes generated upon illumination cannot suit into such a particle, unless they assume a state of higher kinetics energy.

Hence, as the size of the semiconductor particle is reduced below a critical diameter, the spatial confinement of the charge carriers within a potential well, like "a particle in a box", causes them to mechanically behave quantum. In solid state terminology, this means that the bands split into discrete electronic states (quantized levels) in the valence and conduction bands, and the nanoparticle progressively behaves similar to a giant atom. Nanosized semiconductor particles, which exhibit size-dependent optical and electronic properties, are called quantized particles or quantum dots (Kamat, 1995).

2.6.2 Activity of Nano-Photocatalysts

One of the main advantages of the application of nanosized particles is the increase in the band gap energy with decreasing particle size. As the size of a semiconductor particle falls below the critical radius, the charge carriers begin to

behave mechanically quantum, and the charge confinement leads to a series of discrete electronic states. As a result, there is an increase in the effective band gap and a shift of the band edges. Thus by varying the size of the semiconductor particles, it is possible to enhance the redox potential of the valence band holes and the conduction band electrons.

However, the solvent reorganizational free energy for charge transfer to a substrate remains unchanged. The increasing driving force and the unchanged solvent reorganizational free energy are expected to lead to an increase in the rate constants for charge transfer at the surface. The use of nanosized semiconductor particles may result in increased photocatalytic activity for systems, in which the rate-limiting step is interfacial charge transfer. Hence, nanosized semiconductor particles can possess enhanced photoredox chemistry with reduction reactions, which might not otherwise proceed in bulk materials, being able to occur readily using sufficiently small particles. Another factor, which could be advantageous, is the fact that the fraction of atoms that are located at the surface of a nanoparticle is very large. Nanosized particles also have high surface area to volume ratios, which further enhances their catalytic activity. One disadvantage of nanosized particles is the need for light with a shorter wavelength for photocatalyst activation. Thus, a smaller percentage of a polychromatic light source will be useful for photocatalysis.

In large TiO_2 particles (Zhang et al., 1998) volume recombination of the charge carriers is the dominant process and can be reduced by a decrease in particle size. This decrease also leads to an increase in the surface area, which can be translated as an increase in the available surface active sites. Thus, a decrease in particle size should also result in higher photonic efficiencies due to an increase in the interfacial charge carrier transfer rates. However, as the particle size is lowered below a certain limit, surface recombination processes become dominant, since firstly most of the electrons and holes are generated close to the surface, and secondly surface recombination is faster than interfacial charge carrier transfer processes. This is the reason why there exists an optimum particle size for maximum photocatalytic efficiency.

2.7 Photocatalyst Modification Techniques to Enhance H_2 Production

2.7.1 Noble Metal Loading

Noble metals, including Pt, Au, Pd, Rh, Ni, Cu, and Ag, have been reported to be very effective for enhancement of TiO_2 photocatalysis. As the Fermi levels of these noble metals are lower than that of TiO_2, photo-excited electrons can be transferred from conduction band to metal particles deposited on the surface of TiO_2, while photo-generated valence band holes remain on the TiO_2. These activities greatly reduce the possibility of electron-hole recombination, resulting in efficient separation and stronger photocatalytic reactions. As electrons accumulate on the noble metal particles, their Fermi levels shift closer to the conduction band of TiO_2, resulting in more negative energy levels. This is beneficial for water splitting for hydrogen production. Furthermore, smaller metal particles deposited on TiO_2 surface exhibit more negative Fermi level shift. Accumulated electrons on metal particles can then be transferred to protons adsorbed on the surface and further reduce the protons to hydrogen molecules. Therefore, noble metals with suitable work function can help electron transfer, leading to higher photocatalytic activity. Bamwenda *et al.* (1995) compared hydrogen production from water-ethanol solution using Au-loaded TiO_2 and Pt-loaded TiO_2 as photocatalysts. It was found that loading of Pt worked better than loading of Au. Sakthivel *et al.* (2004) investigated photooxidation of Acid Green 16 using Pt, Au, and Pd-loaded TiO_2 as photocatalysts. Optimal loading was observed in their experiments. Too much metal particle deposition might reduce photon absorption by TiO_2 and might also become electron-hole recombination centers, resulting in lower efficiency. Loadings of Pt and Au were more effective than loading of Pd because of suitable electron affinity and work function of Pt and Au. It should be noted that although the loading of noble metal can reduce recombination to some extent, hydrogen production from pure water-splitting is difficult to achieve, because: (i) recombination cannot be completely eliminated; and (ii) backward reaction of H_2 and O_2 to form H_2O is thermodynamically favorable. Therefore, as discussed in the previous sections, electron donors or carbonate salts, as well as other mediators, are required to avoid the above listed problems. Since Pt is very expensive, more research is needed to identify low-cost metals with

acceptable enhancement of photocatalytic activity. For example, Dhanalakshimi *et al.* (2001) investigated dye-sensitized hydrogen production. When Pt/TiO_2 and Cu/TiO_2 were used as photocatalysts, enhanced hydrogen production was observed, and the effect of Cu loading was almost comparable to Pt loading. Unlike dye sensitization, Wu and Lee (2004) deposited Cu particles on TiO_2 surface for hydrogen production from methanol solution. At the optimal loading of Cu, hydrogen production rate was enhanced as much as 10 times higher. Other low-cost metals, such as Ni and Ag, were also found to be effective for photocatalytic activity enhancement. These low-cost but effective metals are expected to be promising materials to improve photocatalytic activities of TiO_2 for practical applications. For photocatalytic hydrogen production, Pt is mostly considered by several researchers to be the most effective cocatalyst and is widely used, resulting in considerably high H_2 evolution efficiency.
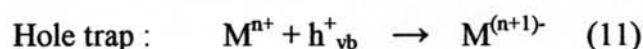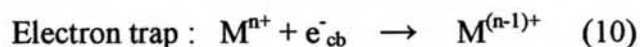
2.7.2 Ion Doping

2.7.2.1 Metal Ion Doping

Transitional metal ion doping and rare earth metal ion doping have been extensively investigated for enhancing the TiO_2 photocatalytic activities. Choi *et al.* (1994) carried out a systematic investigation to study the photoreactivity of 21 metal ions doped into TiO_2. It was found that doping of metal ions could expand the photo-response of TiO_2 into visible spectrum. As metal ions are incorporated into the TiO_2 lattice, impurity energy levels in the band gap of TiO_2 are formed, as indicated below:

$$M^{n+} + h\nu \quad \longrightarrow \quad M^{(n+1)+} + e^-_{cb} \qquad (8)$$

$$M^{n+} + h\nu \quad \longrightarrow \quad M^{(n-1)+} + h^+_{vb} \qquad (9)$$

where M and M^{n+} represent metal and the metal ion dopant, respectively. Furthermore, electron (hole) transfer between metal ions and TiO_2 can alter electron hole recombination as:

$$\text{Electron trap}: \quad M^{n+} + e^-_{cb} \quad \longrightarrow \quad M^{(n-1)+} \qquad (10)$$

$$\text{Hole trap}: \quad M^{n+} + h^+_{vb} \quad \longrightarrow \quad M^{(n+1)-} \qquad (11)$$

The energy level of $M^{n+}/M^{(n-1)+}$ should be less negative than that of the conduction (CB) edge of TiO_2, while the energy level of $M^{n+}/M^{(n+1)+}$ should be less positive than that of the valance band (VB) edge of TiO_2. For photocatalytic reactions, carrier transferring is as important as carrier trapping. Only if the trapped electron and hole are transferred to the surface, photocatalytic reactions can occur. Therefore, metal ions should be doped near the surface of TiO_2 particles for a better charge transferring. In case of deep doping, metal ions likely behave as recombination centers, since electron/hole transferring to the interface is more difficult. Furthermore, there exists an optimum concentration of doped metal ion, above which the photocatalytic activity decreases due to the increase in recombination. Among the 21 metal ions studied, Fe, Mo, Ru, Os, Re, V, and Rh ions can increase photocatalytic activity, while dopants Co and Al ions cause detrimental effects. The different effects of metal ions result from their abilities to trap and transfer electrons/holes. For example, Cu and Fe ions can trap not only electrons but also holes, and the impurity energy levels introduced are near to conduction band, as well as valance band edges of TiO_2. Therefore, doping of either Cu or Fe ions could be recommended for enhancement of photocatalytic activity.

Peng *et al.* (2004) investigated the effect of Be ion-doped TiO_2 on photocatalytic hydrogen production in the presence of electron donors (ethanol). It was found that doping the metal ions near the surface was beneficial for charge carrier transferring, while deep doping led to poor performance. Furthermore, doping content and preparation methods could also affect photocatalytic hydrogen production. Under optimal condition of Be ion doping into TiO_2, hydrogen production was found to be 75% higher than that of un-doped TiO_2. Extensive research on metal ion doping method for enhancement of TiO_2 photocatalytic activities has been carried out, especially for water/air cleaning applications. Organic compounds adsorbed by the photocatalysts are decomposed mainly by the valence band holes and radicals induced by holes. Therefore, the mechanism involved in transferring these photo-generated holes to the interface is of paramount importance. On the other hand, for photocatalytic hydrogen production, the transfer of conduction band electrons to the interface and their energy levels are the most important factors that affect the hydrogen production rate. Hence, the results based on water/air

cleaning applications cannot be directly applied to hydrogen production. Besides, the TiO_2 photocatalytic effect is very sensitive to the metal ion doping methods, doping content, and doping depth. Therefore, a systematically, comparative investigation is needed in order to characterize photocatalytic hydrogen production enhanced by metal ion doping.

2.7.2.2 Anion Doping

The use of anion doping to improve hydrogen production under visible light is rather a new method with few investigations reported in open literature. Doping of anions (N, F, C, S etc.) in TiO_2 crystalline could shift its photo-response into visible spectrum. Unlike metal ions (cations), anions less likely form recombination centers and, therefore, are more effective to enhance the photocatalytic activity. Asahi et al. (2001) determined the substitutional doping contents of C, N, F, P, and S for O in anatase TiO_2. It was found that mixing of p states of N with 2p of O could shifts VB edge upwards to narrow down the band gap of TiO_2. Although doping of S had resulted in a similar band gap narrowing, the ionic radius of S was reported to be too large to be incorporated into the lattice of TiO_2. Dopants C and P were found to be less effective as the introduced states were so deep that photo-generated charge carriers were difficult to be transferred to the surface of the catalyst.

The nitrogen doped TiO_2 thin film was prepared by sputtering TiO_2 in an N_2 (40%)/Ar gas mixture, followed by annealing at 550°C in N_2 for about 4 h. Nitrogen doped TiO_2 powder was also prepared by treating TiO_2 in NH_3 (67%)/Ar at 600°C for 3 h. The N-doped TiO_2 was reported to be effective for methylene blue decomposition under visible light ($\lambda > 400$ nm). Additionally, it was reported by Umebayashi et al. (2002) that S-doped TiO_2 could be prepared by oxidation annealing of TiS_2. Annealed at 600°C, TiS_2 was partly changed to anatase TiO_2. The residual S atoms in the anatase TiO_2 formed S-doped TiO_2 by Ti–S bonds. Band structures of the S-doped TiO_2 were calculated using the super cell approach. It was found that when TiO_2 was doped with S, the mixing of S3p states with the valance band of TiO_2 increased the width of valence band, resulting in band gap narrowing. Since the band gap narrowing was caused by valence band upward shifting, the conduction band remained unchanged. Therefore, the S-doped TiO_2

should be able to reduce protons for hydrogen production under visible light. On the other hand, the upward shift of valence band may reduce the oxidation ability under visible light. Ohno *et al.* (2004) developed a new method to prepare S-doped TiO_2 powder. Titanium isopropoxide was mixed with thiourea in ethanol and stirred. After subsequent evaporation, aging, and calcination, S-doped TiO_2 powder was obtained. The S ions were incorporated to replace some of the Ti atoms in the form of S^{4+}. The photocatalytic activity of S-doped TiO_2 was then evaluated by photodecomposition of 2-propanol and methylene blue. It was reported that S-doped TiO_2 worked better than pure TiO_2 under visible light irradiation. Although the valence band was shifted upwards, the oxidation ability was found to be still high. Other anions, such as C and F ion have also been investigated and found to be able to expand photo-response in visible spectrum.

Reddy *et al.* (2005) investigated the absorption of TiO_2 extended into the visible light region by doping with anion S, N, and C. The results showed that all anions could improve absorption of TiO_2 by reducing the band gap energy. The feature was more evident in N-doped TiO_2 compared to C and S, because N-doped TiO_2 showed two band gap transitions. The first one was in the UV region (385 nm), which is accounted for the fundamental band transition of TiO_2, and the second in the visible region (495 nm), as a result of nitrogen doping. The distinction between two surface states was reflected as individualistic redox peaks. In contrast, the C- and S-doped samples did not show a sharp absorption edge as observed for pure TiO_2. This would imply that the doping introduces electronic states in the band gap that are spread across the band gap, resulting in a diffused absorption spectrum.

N-doped TiO_2 has been the most extensively investigated. The reported methods to dope N are heating of titanium hydroxide and urea, reactive DC magnetron sputtering, nitriding of anatase TiO_2 with alkylammonium salts, and treating TiO_2 powder in NH_3 (80%)/Ar gas flow at 550°C. Similar to S-doping, N-doping also caused a valence band upward shift, resulting in a narrow band gap and less oxidating holes. Mrowetz *et al.* (2004) reported that N-doped TiO_2 was unable to oxidize $HCOO^-$. However, for hydrogen production, electrons are responsible for reducing protons, and the ability of oxidation does not affect the performance

because the valence level of TiO_2 is far more positive than oxygen evolution energy level, and the conduction band remains almost unchanged after N-doping, being at a more negative than hydrogen production energy level. This throws a possibility that N-doped TiO_2 should be able to reduce protons for hydrogen production, although intensive researches have not been investigated. Under visible light irradiation, electrons can be promoted from energy levels in the band gap formed by nitrogen doping to conduction band. However, electron-hole recombination possibility of N-doped TiO_2 was reported to be higher than undoped TiO_2 (Torres et al., 2004). For efficient photocatalytic reaction, coupling with other technologies, such as noble metal loading or electron donor addition, is necessary.

2.8 Porous Materials

The classification of pores according to size has been under discussion for many years, but in the past, the terms "micropore" and "macropore" have been applied in different ways by physical chemists and some other scientists. In an attempt to clarify this situation, the limits of size of the different categories of pores included in Table 2.1 have been proposed by the International Union of Pure and Applied Chemistry (IUPAC), (Rouquerol et al., 1999), (Ishizaki et al., 1988) As indicated, the "pore size" is generally specified as the "pore width", i.e. the available distance between the two opposite walls. Obviously, pore size has a precise meaning when the geometrical shape is well defined. Nevertheless, for most purposes, the limiting size is that of the smallest dimension, and this is generally taken to represent the effective pore size. Micropores and mesopores are especially important in the context of adsorption.

Table 2.1 Definitions about porous solids

Term	Definition
Porous solid	Solid with cavities or channels which are deeper than they are wide
Micropore	Pore of internal width less than 2 nm
Mesopore	Pore of internal width between 2 and 50 nm
Macropore	Pore of internal width greater than 50 nm
Pore size	Pore width (diameter of cylindrical pore or distance between opposite walls of slit)
Pore volume	Volume of pores determined by stated method
Surface area	Extent of total surface area determined by given method under stated conditions

According to the IUPAC classification, porous materials are regularly organized into three categories on a basis of predominant pore size as follows:

-Microporous materials (pore size < 2 nm) include amorphous silica and inorganic gel to crystalline materials, such as zeolites, aluminophosphates, gallophosphates, and related materials.

-Mesoporous materials (2 nm ≤ pore size ≤ 50 nm) include the M41S family (e.g. MCM-41, MCM-48, MCM-50, and etc.) and other non-silica materials synthesized via intercalation of layered materials, such as double hydroxides, metal (titanium, zirconium) phosphates, and clays.

-Macroporous materials (pore size > 50 nm) include glass-related materials, aerogels, and xerogels.

Nowadays, micro- and mesoporous materials are generally called "nanoporous materials". Particularly, mesoporous materials are remarkably very suitable for catalysis applications, whereas the pores of microporous materials may become easily plugged during catalyst preparation if high loading is sought.