Chapter Three

Nanomaterial
And
Environment

3.1 History of nano materials and nanotechnology

There isn’t any accepted international definition for nano particles. But one, is the particles that have sizes below 100 nm are nano. One hundred nanometers is approximately 1/800 of the width of a human hair and 1/70 of the diameter of a red blood cell. It is not clear when humans first take advantage of nanosized materials. It is known that in the fourth-century A.D Roman glassmakers making glasses containing nanosized metals. The Lycurgus cup in British museum in London is made from soda lime glass containing silver and gold nano particles. The color of the cup changes from green to red when a light source is poured inside it (Poole, 2003). Richard Feynman used the first distinguishing concepts in nanotechnology on December 29, 1959. "There's Plenty of Room at the bottom". This is a sentence of Feyman which means nano compounds. Feynman described a process by which the ability to manipulate individual atoms and molecules and Van der Waals attraction would become more important (Feynman, 1991). The term "nanotechnology’’ was defined by Professor Norio Taniguchi at Tokyo Science University in 1974: Nano-technology mainly consists of the processing, separation, consolidation, and deformation of materials by one atom or by one molecule. Nanotechnology and nano science got started in the early 1980s with two major developments; the birth of cluster science and the invention of the scanning tunneling microscope (STM). This development led to the discovery of fullerenes in 1986 and carbon nano tubes a few years later. Nanomaterials have large surface area to mass ratio and the proportion of the total number of atoms at the surface of a structure are larger enough that surface properties become important, and this can alter chemical reactivity, thermal and electrical conductivity and mechanical properties. For instance, two or three gram nanopowder can cover an entire football field. Material reduced to nano scale can suddenly show very different properties compared to what they exhibit on a macro scale , enabling unique applications for instance , opaque substances become transparent (copper), inert material become catalyst (platinum), stable material turn combustible (aluminum), solid turns to liquids at room temperature (gold), insulator become conductors (silicon). These unique properties cause much application in science and technology. Nano particles are being used in a number of industries. Nanoscale materials are used in electronic, magnetic, biomedical, pharmaceutical, cosmetic and energy applications. They also are being used in optoelectronic industries (devices either producing light or using light in their operation, such as LEDs), catalytic applications (reducing toxic emissions from car engines) and materials applications, such as the creation of stain-resistant clothing. Nano plays key roles in many area including material processing, mechanical engineering, optics and electronics (Frank, 1987; Eric Drexer, 2004). Nanotechnology also has the potential to benefit environmental quality and sustainability detection and sensing, removal of the finest contaminants from air, water and soil, and the creation of new industrial processes to reduce waste products. Application of nano materials are summarized in different fields (Table 3.1).

3.2 Nanotechnology and the Environment:

Nanotechnology has the potential to have major consequences on the environment. Nanotechnology can benefit environmental protection by reducing use of raw and manufactured materials, minimizing or eliminating the generation of wastes and reducing toxicity (Davis, 2001; Rao et al., 2002; Salata, 2004).

Nanotechnology is used for remediation of environmental problems through control of emissions; the development of new “green” technologies that minimize the production of undesirable by-products; and the remediation of existing waste sites.

3.2.1 Energy

Nanotechnology has significant impact on energy efficiency, storage, and production. Scientists are currently finding cheap nano-enhanced photovoltaic films to generate solar power. New nanomaterials such as rechargeable batteries are more efficient and longer lasting. Nanotechnology makes more light weight and durable metals or ceramics, thus increases the energy efficiency of buildings and their heating and cooling systems.

Nanoparticle reinforced polymeric material that replace metallic components in automobiles can reduce 1.5 billion liters of gasoline consumption over the life of one year production of vehicles, and also reduce carbon dioxide emissions annually by more than 5 billion kilograms. Replacement of black carbon in tires by nanometer-scale particles of inorganic clays and polymers is a new technology that is leading to the production of environmentally friendly, wear-resistant tires. Energy saving by nanotechnology is shown in Table 3.2.

Table 3.1 Some application of nano materials in different fields

Property	**Application**
Optical	Anti-reflection coatings. Tailored refractive index of surfaces. Light based sensors for cancer diagnosis.
Magnetic	Increased density storage media. Nano magnetic particles to create improved detail and contrast in MRI images.
Thermal	Enhance heat transfer from solar collectors to storage tanks. Improve efficiency of coolants in transformers.
Mechanical	Improved wear resistance. New anti-corrosion properties. New structural materials, composites, stronger and lighter.
Electronic	High performance and smaller components, e.g., capacitors for small consumer devices such as mobile phones. Displays that are cheaper, larger, brighter, and more efficient. High conductivity materials.
Energy	High energy density and more durable batteries. Hydrogen storage applications using metal nano clusters. Electrocatalysts for high efficiency fuel cells. Renewable energy, ultra high performance solar cells. Catalysts for combustion engines to improve efficiency, hence economy.
Biomedical	Antibacterial silver coatings on wound dressings. Sensors for disease detection (quantum dots). Programmed release drug delivery systems. “Interactive” food and beverages that change color, flavor or nutrients depending on a diner’s taste or health.
Environmental	Clean up of soil contamination and pollution, e.g. oil. Biodegradable polymers. Aids for germination. Treatment of industrial emissions. More efficient and effective water filtration.
Surfaces	Dissolution rates of materials are highly size dependant. Activity of catalysts are size dependent Coatings for self cleaning surfaces,
Personal care	Effective clear inorganic sun screens.

Table 3.2 Potential of Energy saving from nanotechnology applications

Nanotechnology Application	Estimated Percent Reduction in Total Annual U.S Energy Consumption
Strong, light weight materials in transportation	6.2
Solid state lighting (such as light LED's)	3.5
Self –optimizing motor system(smart sensors)	2.1
Smart roofs (temperature –dependent reflectivity)	1.2
Novel energy –efficient separation membranes	0.8
Energy efficient distillation though supercomputing	0.3
Molecular level control Industrial catalysis	0.2
Transmission line conductance	0.2
Total	14.5

3.2.2 Water

Global population is increasing while fresh water supplies are decreasing. Water purification and desalinization are the ways of preventative defense and environmental security. Nanotechnology-based devices for water desalinization have been designed to desalt sea water using at least 10 times less energy than reverse osmosis and at least 100 times less energy than distillation and this is caused by nano carbon tubes with high surface area.

A variety of approaches are currently being explored for water purification, including the development of nanotechnology membranes for water detoxification and the use of nano magnets or charged nano materials to remove arsenic, oil, heavy metals, salt, and other pollutants from water. Many of these newly created systems use charged nano materials to adsorb pollutants, which can then be easily extracted from the water. These nano materials can later be separated from the pollutants for reuse. Advanced purification methods, such as the use of zinc sulfide or titanium dioxide nano materials as catalysts to oxidize pollutants were developed. The advantage of this process is that it breaks down pollutants into less toxic substances. The use of nano-sized particles of iron for cleaning up contaminants in groundwater, soil and sediments is one of the hottest new technologies in recent years (Toshiro, et al., 2000).

3.2.3 Remediation/Treatment

Environmental remediation includes the degradation, sequestration, or other approaches that result in reduced risks to human and environment by chemical contaminants. For example, zero-valent iron and other nanosized materials such as metalloporphyrinogens have been tested for degradation of tetra chlorethylene, trichloroethylene, and carbon tetrachloride under aerobic conditions. Enhanced solubilization of a contaminant may be helpful in a remediation setting. Nanomaterials may be useful in decreasing hydrophobic contaminants, such as polycyclic aromatic hydrocarbons (PAHs) that bound to soils and sediments by sequestration. The release of these contaminants from sediments and soils could make them more accessible to *in situ* biodegradation. For example, nanomaterials which are made from poly (ethylene) glycol modified urethane acrylate have been used to enhance the bioavailability of phenanthorene. Nanomaterials have also been studied for their ability to remove metal contaminants from air. Silica-titania nanocomposites can be used for elemental mercury removal from vapors such as those coming from combustion sources (Rickerby and Morrison, 2007).

3.3 Semiconductors:

Nowadays, environmental pollution is one of the most difficult problems in developed countries. In this field, pollution of water by factories and human activities is a big part of this problem. More than 540 million metric tons of hazardous solid and liquid wastes are generated usually by more than 14000 installations in USA, 70% of the hazard waste sites belongs to ground water, contamination solvents, volatile organics, chlorinated volatile organics, dioxins, dibenzofuraus pesticides, PCBS, chlorophenol, penta chlorophenol, heavy metal, and some specific compound such as 4-chlorophenol, trichloroethylene and perchloroethylen. Over the last 10 years, the scientist and engineers paid attention to application of semiconductor in the areas of water, air and wastewater treatment.The rate of publication exceeds 200 papers per year averaged over 10 years (Hoffman et .al., 1995).

One of the most pollutants of sea water is organotin compounds especially tributyltin compounds. The importance of degradation of organotin compounds for environment was mentioned in chapter one. There are different approaches for this problem; many methods were developed for overcoming this problem. One of the approaches is degradation of pollution by light (Hidaka, 1998). UV area of light degradates some of the chemicals, pesticides, herbicides, surfactants that are most important compounds causes problem for environment .Because UV area is small part of solar light, using UV lamps with or without catalyst was done for remediation of polluted water. Solar light usually doesn’t have enough energy for doing these reactions, because of this, normally for photoreaction semiconductor is used. Semiconductor acts as sensitizers for photoreaction, process due to electronic structure, which is characterized by a filled valence band and an empty conduction band. When a photon with an energy of (hν) matches or exceeds the band gap energy of the semiconductor (Eg), one electron is promoted from the valence band (VB) into the conduction band (CB) leaving a hole (h^+) behind. Exited state conduction band electrons (e^-) and VB holes (h^+) can recombine and dissipate the in put energy as heat, get trapped in meta stable surface states or react with electron donors and electron acceptor compounds absorbed on the semiconductors surface. In the absence of suitable electron and hole scavenger the stored energy is dissipated within a few nano seconds by recombination. If a suitable scavenger or surface defect state is available to trap the electron or hole, recombination is prevented and subsequent redox reaction may occur. The valence band holes are powerful oxidants (+1 to +3.5) volts depend on the semiconductor and pH, while the conduction band electrons are good reductants (+0.5 to –1.5) volts. Most of the organic photo degradation reactions utilize the oxidizing power of the holes either directly or indirectly. However to prevent a build up of charge one must also provide a reducible species to react with the electrons (Sobczynski and Dobosz, 2001). VB and CB and band gap of some semiconductor is shown in Figure 3.1 and Figure 3.2 (Hoffman, 1995; Mills et al., 1997).

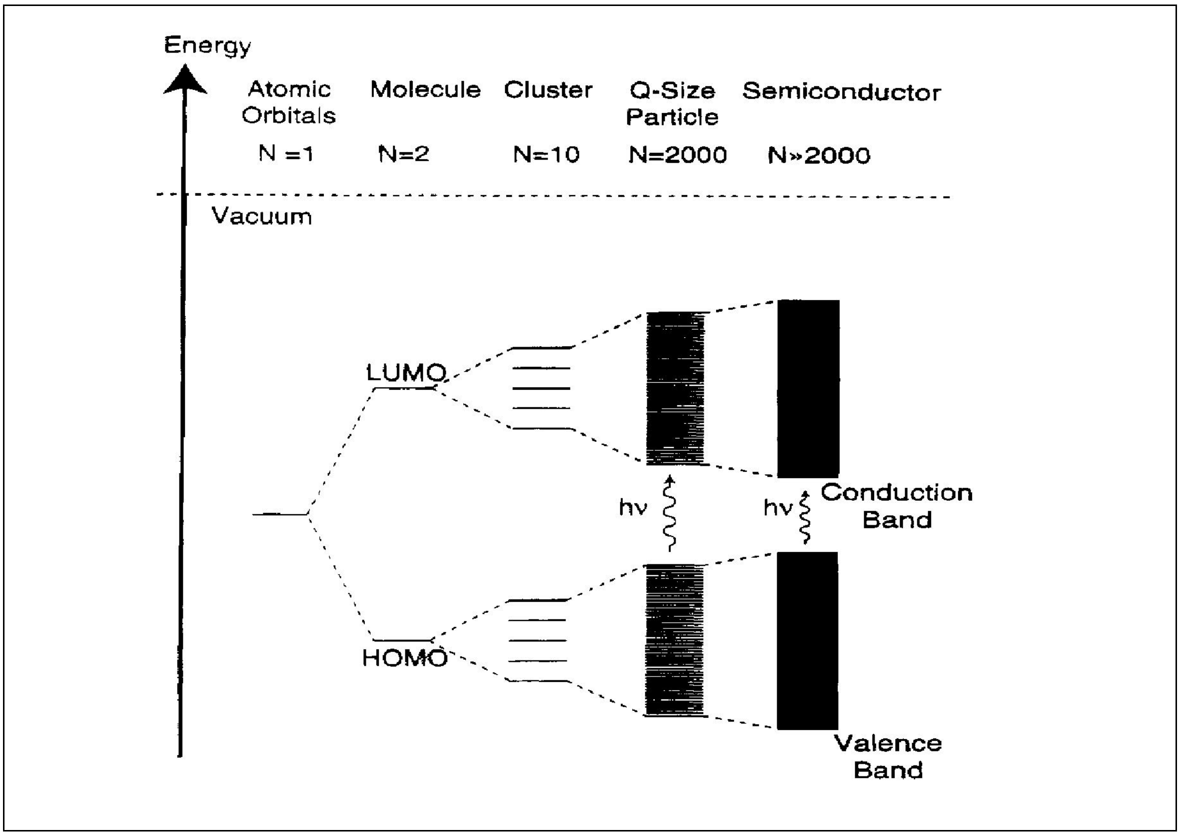

Figure3.1 Electronic structure of a semiconductor (Hoffman et al. 1995)

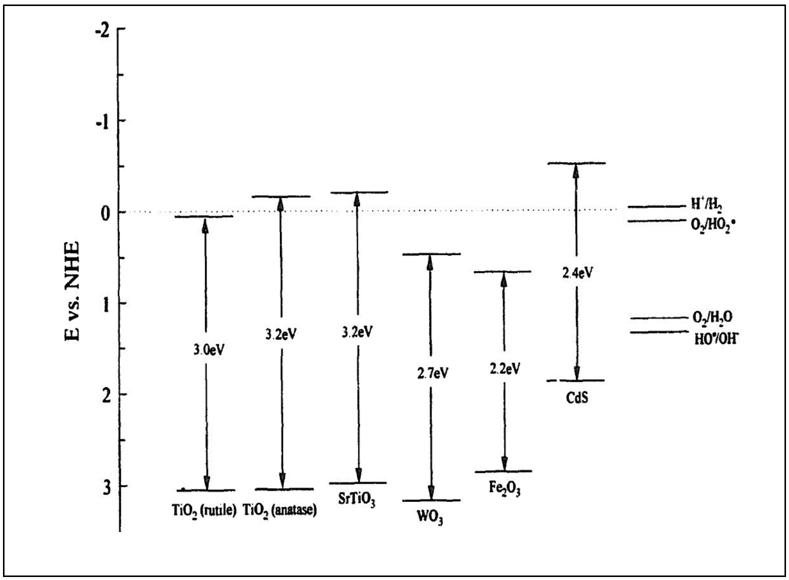

Figure3.2 Comparison of band gap of different types of semiconductor (Mills et al., 1997)

One major category of semiconductors is metal oxides such as Fe_2O_3, TiO_2, ZnO. Among various semiconductors, TiO_2 is the most used photocatalyst because of its high efficiency, nontoxicity, chemical and biological stability, and low cost. In spite of CdS has lower band gap but because this compound degradate by light, it isn't a good candidate for using in solution. Some applications of the photocatalysts are as following:

3.3.1 Some applications of semiconductors:

Some of applications of semiconductors are as following.

1. Photo- dissociation of water
2. Reduction and oxidation of water
3. Oxidation of organic compounds
4. Removal of inorganic pollutant including metal ions especially heavy metal
5. Sensitizer for photosynthesis process
6. Photo destruction of cancer cell, bacteria, viruses, photodynamic therapy
7. Degradation of pesticides, dyes and inorganic compounds

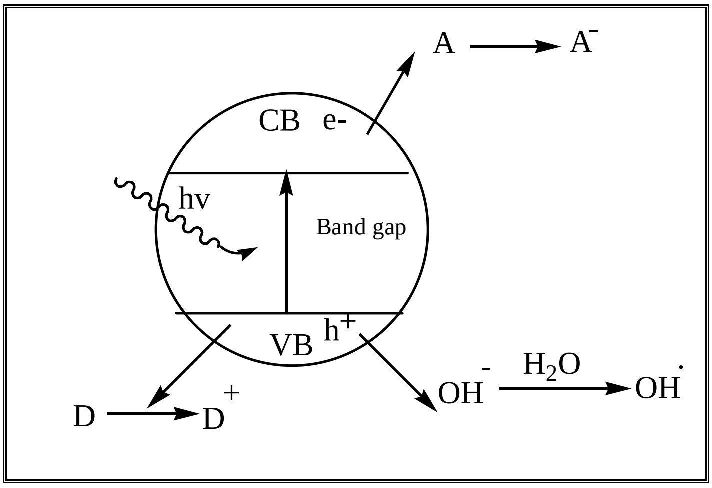

Figure 3.3 Oxidation, reduction process by photocatalyst

The semiconductor sensitizer should be 1- photoactive, 2- able to utilize visible and/or near UV, 3- biologically and chemically inert, 4- photos stable, and 5- inexpensive.

TiO_2 has these properties and is one of the best semiconductors for photo sensitizing reactions. The first clear work for mineralization by semiconductors was done by Ollis and coworkers in 1983 for photo mineralization of halogenated hydrocarbons. Oxidation- reduction process by photocatalyst is shown in Figure 3.3.

3.4 Application of nano titanium dioxide in environment:

Different environmental application of nano TiO_2 is as following:

3.4.1 Sterilizing Effect

Photocatalyst does not only kill bacteria cells, but also decompose the cell itself. The titanium dioxide photocatalyst has been found to be more effective than any other antibacterial agent, because the photocatalytic reaction works even when there are cells covering the surface and while the bacteria are actively propagating. Titanium dioxide does not deteriorate and it shows a long-term anti-bacterial effect. Disinfections by titanium oxide are three times stronger than chlorine, and 1.5 times stronger than ozone

3.4.2 Deodorizing Effect

The hydroxyl radicals accelerate the breakdown of any volatile organic **c**ompounds (VOCs) by destroying the molecular bonds. Air purifier with TiO_2 can prevent spreading smoke, soil, pollen, bacteria, virus and harmful gas.

3.4.3 Air Purifying Effect

The photo-catalytic reactivity of titanium oxides can be applied for the reduction or elimination of polluted compounds in air such as NOx, cigarette smokes, and volatile compounds arising from various construction materials. Atmospheric constituents such as chlorofluorocarbons (CFCs) and CFC substitutes, green house gases, nitrogenous and sulfurous compounds undergo photochemical reactions either directly or indirectly in the presence of sunlight. In a polluted area, these pollutants can eventually be removed (Peral et al., 1997).

3.4.4 Anti fogging, Self-Cleaning

Most of the exterior walls of buildings are polluted by automotive exhaust fumes, which contain oily components. When the original building materials are coated with a photocatalyst, a protective film of titanium oxide provides the self-cleaning building by becoming antistatic, super oxidative, and hydrophilic. The hydrocarbon from automotive exhaust is oxidized and the dirt on the walls washes away with rainfall, keeping the building exterior clean at all times (Xiao giang Wang et al., 2007).

3.4.5 Water Purification

Photocatalyst coupled with UV lights can oxidize organic pollutants into nontoxic materials, such as CO_2, and water and also can disinfect certain bacteria. This technology is very effective at removing further hazardous organic compounds and at killing a variety of bacteria and some viruses in the secondary wastewater treatment (Belapurkar et al. 2006).

One of the major applications of semiconductors is using as photo catalyst for the removal of organic and inorganic pollutants:

Nano titanium dioxide is one of the materials which have been used for removing pollution from environment as photo catalyst. Photo catalysis is a reaction which uses light to activate a substance which modifies the rate of a chemical reaction without being involved itself; the photo catalyst is the substance which can modify the rate of chemical reaction using light irradiation.

Photosystem for removal of some organic toxic material is shown in Table 3.3.

In addition to organic compounds, a wide variety of inorganic compounds are sensitive to photodegradation, examples include ammonia, azide, chromium species, copper, cyanide, iron species, mercury, nitrate and nitrite, nitic oxide, nitrogen dioxide, sulphur species. Photo mineralization of some of the inorganic compounds is shown in Table 3.4(Mills, A., and Le Huntes, 1997).

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Table 3.3 Photocalytic reaction of some organic compounds

(Mills, A., and Le Huntes, 1997)

Class	Example
Alkanes	Methane, Isobutane, Heptane, Cyclohexane
Haloalkanes	Mono, di, tri and tetrachloromethane, tribromomethane
Aliphatic alcohol	Methanol, ethanol, isopropyl alcohol
Aliphatic carboxylic acids	Formic, ethanoic, oxalic acid
Alkenes	Propene, cyclohexene
Haloalkenes	Perchloromethene,1,2 dichloromethene
Aromatics	Benzene, naphthalene
Haloaromatics	1,2 dichlorobenzebe
Nitrohaloaromatics	Dichloronitrobenzene
Phenols	Phenol, hydroquinone, catechol, o-m-p cresol
Halophenols	Pentachlorophenol
Aromatic carboxylic acids	Benzoic, phetalic, salicylic, chlorohydroxyl benzoic acid
Polymers	Polyethylene, PVC
Surfactants	Sodium dodecylsulphate, polyethylene glycole, sodium dodecyl benzene sulphonate
Herbicides	Methyl viologen, atrazine
Pesticides	DDT, parathione, lindane
Dyes	Methylene blue, rhodamine B, methyl orange,fluorescein

Table 3.4 Removal some inorganic compounds by photoreaction

(Mills, A., and Le Huntes, 1997)

$O_2 + 2NO_2 \longrightarrow 2NO_3^-$

$O_2 + 2SO_3^{2-} \longrightarrow 2SO_4^{2-}$

$2O_2 + H_2O + S_2O_3^{2-} \longrightarrow 2SO_4^{2-} + 2H^+$

$O_2 + 2CN^- \longrightarrow 2OCN^-$

$5O_2 + 4H^+ + 4CN^- \longrightarrow 2H_2O + 4CO_2 + 2N_2$

$M^{n+} + n/_2\ H_2O \longrightarrow M^0 + nH^+ + n/4\ O_2$

$M^{n+} + n/6\ CH_3OH + n/6H_2O \longrightarrow M^0 + nH^+ + n/6CO_2$

Ag>Pd>Au>Pt>>Rh>Ir>>Cu=Ni=Fe=0 using the following metal salts

$AgNO_3$, $AuCl_3$, H_2PtCl_6, $RhCl_3$, H_2IrCl_6, $Cu(NO_3)_2$, $Ni(NO_3)_2$ and $Fe(NO_3)_3$

$M^{2+} + 1/2O_2 + H_2O \rightarrow MO_2 + 2H^+$ $M^{2+} = Mn^{2+}$ and Pb^{2+} (needs Pt/TiO_2)

$O_2 + 2H_2O \longrightarrow 2H_2O_2$

$2BrO_3^- \longrightarrow 2Br^- + 3O_2$ (works best with Pt/TiO_2)

$5O_2 + 6NH_3 \longrightarrow 2N_2 + N_2O + 9H_2O$

3.5 TiO_2 photocatalytic process

Based on study by laser photolysis, mechanism of semiconductor photo catalysis by TiO_2 in heterogeneous photocatalyst is shown in Table3.5, where VB: Valence band, CB: conduction band, e^-: electron, h^+: hole, > TiOH hydrolyzed TiO_2, e-tr: trapped conduction band electron on surface, ox: electron acceptor (oxidant) $Ti^{IV}OH^{\bullet}$ Surfaced trapped, VB hole (i.e. Surface bond hydroxyl radical) and $>Ti^{III}OH$ is surface trapped CB electron. According to the mechanism there are competition between charge carrier recombination and trapping (ps) followed by the competition between trapped carrier recombination and interfacial charge transfer (micro second to mili second).

An increase in either the recombination lifetime of charge carrier or the interfacial electron-transfer rate contant is expected to result in higher quantum efficiency of photolysis.

Table 3.5 Primary processes of photosensitized (Hidaka H., 1998).

Charge transfer generation	
$TiO_2 + h\nu \longrightarrow h^+ (VB) + e^- (CB)$	fs
Charge carrier trapping	
$h^+VB + Ti^{IV}OH \longrightarrow \{>Ti^{IV}OH^{\bullet}\}^+$	fast (10 ns)
$e- CB + Ti^{IV}OH \longrightarrow \{>Ti^{III}OH\}$	shallow trap (100 ps)
$e^-CB + >Ti^{IV} \longrightarrow >Ti^{III}$	deep trap (10 ns)
Charge carrier recombination	
$e^- CB + \{>Ti^{IV}OH^{\bullet}\}^+ \longrightarrow Ti^{IV}OH$	slow 100 ns
$h^+VB + \{>Ti^{III}OH\} \longrightarrow Ti^{IV}OH$	fast 10 ns
interfacial charge transfer	
$\{>Ti^{IV}OH^{\bullet}\}^+ + Red \longrightarrow Ti^{IV}OH + Red^{\bullet +}$	slow (100 ns)
$e^-trap + Ox \longrightarrow Ti^{IV}OH+Ox^{\bullet -}$	very slow (ms)

The different recombination lifetimes and interfacial electron transfer rate constant may be due to the different preparation method of the TiO_2 and results in different crystal defects structures and surface morphology. However, oxidation may occur by either indirect oxidation via the surface bound hydroxyl radical (i.e. a trapped hole at the particle surface) or directly via the VB hole before it is trapped. In most experiments and applications of semiconductors photo-catalysis, oxygen is present to act as the primary electron acceptor.

As a consequence of the two electron reduction of oxygen, H_2O_2 is formed; the mechanism is shown as following.

$$O_2 + 2e^- (CB) + 2H^+ \longrightarrow H_2O_2$$

$$2H_2O + 2h^+ (VB) \longrightarrow H_2O_2 + 2H^+$$

Anyway hydroxyl radical has a main role in photoreaction in aqueous suspension. This radical produced by two ways:

1- Reaction of h^+ with surface water absorbed in TiO_2

$$TiO_2 + hv \longrightarrow e\text{-}(CB) + h^+ (VB)$$

$$H_2O + h^+ \longrightarrow H^+ + OH^{\bullet}$$

$$OH^- + h^+ \longrightarrow OH^{\bullet}$$

2- $OH^{\bullet}$ not only produced by h^+ of VB but also produced by H_2O_2 which produce by superoxide ion ($O_2^{\bullet -}$), O_2 reacts with e^- (CB) and prevent to recombine e^- and h^+ again.

$$O_2 + e^-(CB) \longrightarrow O2^{-\bullet}$$

H_2O_2 produced by following reaction

$$O_2^{-\bullet} + H^+ \longrightarrow HO_2^{\bullet}$$

$$2HO_2^{\bullet} \longrightarrow H_2O_2 + O_2$$

$$O_2^{-\bullet} + HO_2^{\bullet} \longrightarrow HO_2^- + O_2$$

$$HO_2^- + H^+ \longrightarrow H_2O_2$$

Breaking the band in H_2O_2 by one of the following reaction produced $OH^{\cdot}$ radical.

$$H_2O_2 + e^-CB \longrightarrow OH^{\bullet} + OH^-$$

$$H_2O_2 + O_2^{\bullet -} \longrightarrow OH^{\bullet} + OH^- + O_2$$

$$H_2O_2 \xrightarrow{h\upsilon} 2OH^{\bullet}$$

General processes for the photo oxidation mineralization of organic pollutants by TiO_2 with O_2 are shown in Figure 3.4.

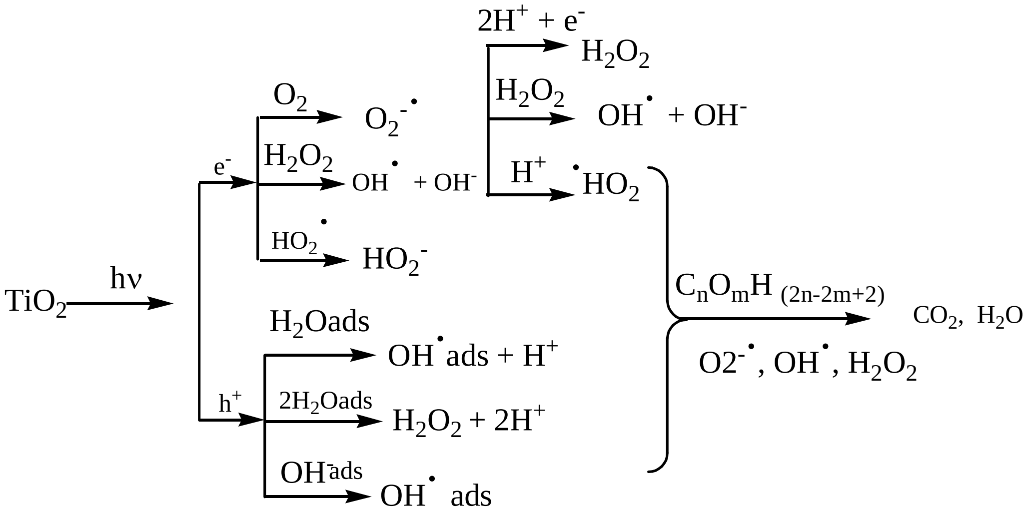

Figure 3.4 general processes for the photo oxidation mineralization of organic pollutants by TiO_2+O_2 (Banerjee et al., 2006)

Electron hole recombination on most semiconductors material is usually very fast (<10 ns for TiO_2) because of this, for better efficiency scavenger is used. The most commonly used electron scavenger is dissolved oxygen, and most commonly used hole scavenger is PVA (polyvinyl alcohol) or thiocyanate. The yield of reaction affected by morphology, crystal phase, specific surface area, particle aggregate size and surface density of OH groups in the TiO_2 samples and because of this, researches usually uses TiO_2 P_{25} Degussa which is produced through the high temperature (greater than 1200 ^{o}C) flame hydrolysis of $TiCl_4$ in the precense of hydrogen and oxygen. The TiO_2 is heated with steam to remove HCl which is also produced as part of the reaction the product is 99.5% pure TiO_2 (anatase, rutile ratio 70: 30) which is non porous, cubic particles with rounded edge. The P_{25} TiO_2 powder has a surface area of 50 ± 15 m^2/g and an average particle diameter by number, of 21 nm, 90% of the particles fall in the size rang 9-38 nm (Mills et al., 1997).

However it may be considered surprising that a TiO_2 photo catalyst which is good at destroying of one organic substrate may be ineffective at destroying another, and for a different sample of TiO_2 the situation can be reversed.

Many researches claim that rutile is a catalytically inactive or much less active form of TiO_2 while others find that rutile has selective activity toward certain substrates. In the case of 4-cholorophenod oxidation highly annylated (T>800˚C) rutile appears to be photo inactive. It was shown that TiO_2 in the rutile form is substantially better photo catalyst for the oxidation of CN^- than the anatase, on the other hand the Degussa P_{25} TiO_2 is a better catalyst than rutile for photoreductive of $HCrO_4^-$. For finding reproducible results using standard TiO_2 the same as TiO_2 P_{25} Degussa is unavoidable. Use of size quantized semiconductor to increase photo-efficiencies is supported by several studies. Photocatalytic oxidation of organic compounds is of considerable interest for environmental applications and in particular for control of eventual destruction (i.e. elimination) of hazardous wastes. The complete mineralizaton is oxidation of organic compounds to CO_2 and inorganic compounds such as SO_4^{2-}, NO_3^-, ammonia, and H_2O. Degradation a variety of aliphatic and aromatic chlorinated hydrocarbons via heterogeneous photo oxidation on TiO_2 has been reported. The general classes of compounds have been degradated are alkanes, haloalkanes , alcohol , carboxylic acid, alkenes, aromatics, haloaromotics, polymers, surfactants, herbicides, pesticides and dyes

(Habibbi and Nasre Esfahani, 2006; Hidaka and Zhao, 1998; Hideo, 2004; Hisao, 1992; Guo Min Zuo et al., 2006).

3.5.1 Structures of different forms of TiO_2:

Among various semiconductors, TiO_2 is the most used photocatalyst because of its high efficiency, nontoxicity,chemical and biological stability, and low cost. TiO_2 exists in three different crystalline habits: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). The Structures of different kinds of TiO_2 is shown in Figure 3.5.

All three crystalline structures consist of deformed TiO_6 octahedra connected differently by corners and edges. In rutile, two octahedra edge shared to form linear chains along the [001] direction and the TiO_6 chains are linked to each other through corner-shared bondings. In anatase, each octahedron shares four edges with other four octahedra, resulting in a zigzag structure. In brookite, each octahedron shares three edges and the octahedra arrangement produces a crystalline structure with tunnels along the *c*-axis. Rutile is the stable form, whereas anatase and brookite are metastable and are readily transformed to rutile when heated. Anatase is the phase normally found in the sol–gel syntheses of TiO_2 but brookite is often observed as a by-product when the precipitation is carried out in an acidic medium at low temperature. Pure brookite without rutile or anatase is rather difficult to be prepared (Dongliang Liao, 2007; Mills and Le Hunte, 1997; Wen-zhen Zhang, et al., 2007; Xianfeng et al., 2005).

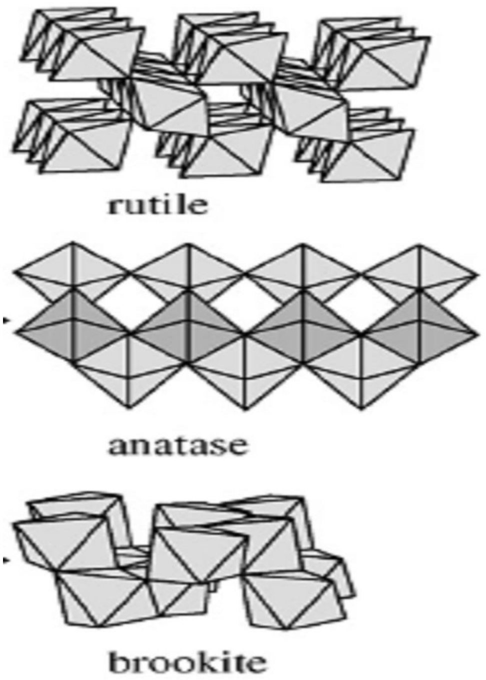

Figure 3.5 Structures of different kinds of TiO_2

3.6 Modification and improvement of photocatalytic activity:

Because of some limitation such as recombination electron and hole, and for broadening the band gap of semiconductor for using in visible light, improvement of semiconductors sometimes is necessary: There are several methods for improvement semiconductor activity.

3.6.1 Scavengers:

Because the rates of recombination electron and hole are very high, recombination is occurred, because of this using scavenger to prevent recombination is necessary, O_2 is the most famous scavenger. As already mentioned O_2 react with e^-(CB) and produce $O_2^{\cdot -}$ and hydroxyl radical which enhance the rate of photodegradation, other compounds the same as H_2O_2, acetone, and peroxydisulphate should be used as scavenger (Mills and Valenzuela, 2004).

3.6.2 Doping of metals and metal ions:

For the time it was found that with doping of Pt on TiO_2 the photocatalytic activity increases. Based on Schotky, at interface of TiO_2 with metal, electron is trapped and prevents to recombine with hole. Doping of Fe^{III} on TiO_2 has been shown to increase the quantum yield efficiency for the photoreaction of N_2 and of the methyl-viologen and to inhibit electron–hole recombination. Doping metal on semiconductor for photooxidation reduction reaction is shown in Figure 3.6.

Bahneman et al. have studied the photodegradation of dichloroacetic acid using Ti/Fe mixed oxide and found the rate almost four times of pure TiO_2. This doping provides a broad range of wavelength suitable for band gap excitation than pure TiO_2 (Sclatani and Palmisano, 1999; Shah et al., 2002; Terry and Mattinson, 2008).

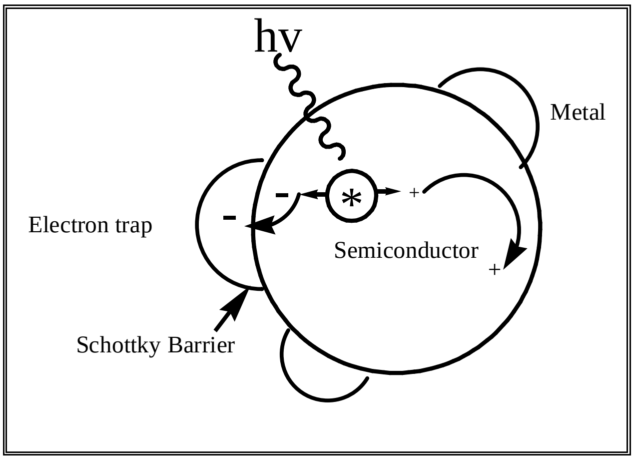

Figure 3.6 Doping metal on semiconductor for photooxidation reduction reaction

3.6.3 Coupling different kinds of semiconductor

For increasing quantum yield, simultaneous increasing energy domain, coupling technique should be used, for example, we can couple CdS and TiO_2. After irradiation to semiconductor, electron transfer from VB to CB (CdS) and then e^- transfers to CB (TiO_2) and cause charge separation and increasing yield of photoreaction (Mills and Valenzuela, 2004). Coupling of two semiconductors is shown in Figure 3.7.

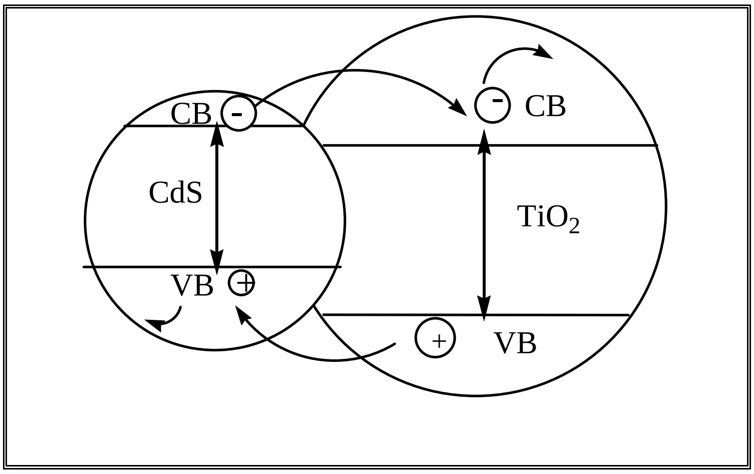

Figure 3.7 Coupling two semiconductors

3.6.4 Dye sensitizer:

Deposition organic dye such as Rose Bengal and Rodamine B on semiconductor cause broadening the wavelength of band gap and increase quantum yield. Organic dyes have high absorption in visible region. TiO_2 absorbs the light at

$\lambda < 355$ nm, but with using organic dyes visible area of light should be absorbed. After irradiation, dye is exited, the electron from excited state of dye transfers to semiconductor and the photoreaction is done. Dye sensitizing mechanism of semiconductor (TiO_2) is shown in Figure 3.8. We can use antracene, porphyrin, and phthalocyanine that absorb visible light as photosensitizes (Vesely et al., 2005; .Hideo, 2004).

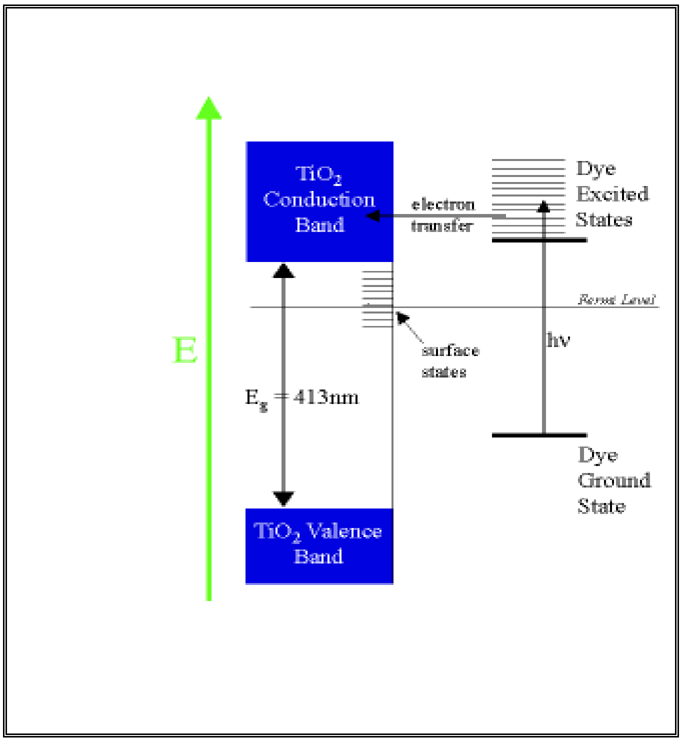

Figure 3.8 Dye sensitizing of semiconductor (TiO_2)

3.6.7 Polyoxometallate:

Polyoxometallate compounds are metal–oxygen clusters mainly of molybdenum and tungsten. The best-known typical categories of Polyoxometallates (POMs) are (a) isopoly compounds with the general molecular structure $[M_mO_\Psi]^{p-}$, such as $(W_{10}O_{32})^{4-}$and (b) hetopoly compounds with the general molecular structure $[X\chi M_mO\psi]^{q-}$, where χ can be one of about 60 elements of various groups of the periodic table except the noble gases and $\chi < m < \psi$, e.g. $(PW_{12}O_{40})^{3-}$. The ψ/m ratio can take various values, for example 1:12 or 2:18 for the Keggin and Dawson structure, respectively. POMs are generally prepared by the condensation reaction occurring upon acidification of solutions of MoO_4^{2-} or WO_4^{3-}. POMs have characteristic properties that render them interesting substances for catalysis and photocatalysis. These properties can be summarized:(a) Solubility in water and organic solvents, (b) Thermal stability, (c) Low toxicity, (d) Ability to serve as electron and oxygen relays, (e) Strong absorption in the near UV–VIS light (<400 nm), (f) Reduction of POMs leaving their structure intact, and (g) The reduced form can be re-oxidized by various oxidizing reagents (i.e. O_2, H^+, Mn^{+2}).

Irradiating with visible and near-UV light makes POMs powerful oxidizing reagents capable of destroying a great variety of organic compounds. The photocatalytic oxidation of many organic pollutants has been demonstrated using POMs. The reduced form of POMs was re-oxidized by O_2. Recently, the re-oxidation of POM reduced forms by metal cations, which are precipitated as metal particles of zero valences has been reported. In this way, metal ions are removed from the solution, and purification of waste waters from both organic and inorganic pollutants can be achieved in principle. Until now, the decontamination process has been studied separately in terms of organic and inorganic pollutants accordingly. Process, focus on the photocatalytic degradation of organics in the presence of POMs, using metal cations (inorganic pollutants) for the regeneration of the photocatalyst and, at the same time, for reduction and removal from aqueous solution. Irradiation of the POMs with λ <400 nm results in the formation of the excited state see (equation 1). The excited state of POMs is a strong oxidant able to oxidize and, most often, mineralize organic substrates, including organic pollutants. POMs are reduced to colored, generally blue species (equations 2 and 3), the reduced form of POMs can be easily monitored owing to their characteristic spectra in the visible. At the same time, organic compounds, after oxidation to intermediate products, are generally mineralized to CO_2, H_2O, and inorganic anions (equation 4).

Concerning the mechanism of the photo-oxidation reactions, it seems that there are two general pathways through which the excited POMs reacts with organic substrates in aqueous solution: (a) direct reaction (equation 3) and (b) indirect reaction (equation 4) through formation of OH^o radicals from the reaction of the excited POM with H_2O (equation 2). There are evidences for the generation of OH^o radicals that can be summarized as follows: (a) determination of hydroxylation products prior to mineralization (b) ESR experimental data and (c) high excited state potentials for the oxidation of H_2O to OH^o radicals. Recently, more experimental data have been reported, in agreement with the formation of OH radicals, based on the comparison of photo-degradation of chlorophenols with POMs and H_2O_2. However, the formation of OH^o radicals by POMs cannot be generalized. Few studies tend to exclude the possibility of these reactions occurring via OH^o radicals, giving rise to a mechanism of direct reaction. The reduced POMs can be re-oxidized by dioxygen, which undergoes reductive activation through the formation of O_2^- species (equation 5). These species area strong oxidants capable of initiating further oxidation (equation 6)

(Hoffman et al., 1998; Hiskia et al., 2006).

$$\text{POM} \longrightarrow \text{POM*} \qquad (1)$$

$$\text{POM*} + H_2O \longrightarrow \text{POM}^- + OH^\bullet + H^+ \qquad (2)$$

$$\text{POM} + \text{org}^\bullet \longrightarrow \text{POM}^- + \text{org}^+ \qquad (3)$$

$$OH^\bullet + \text{organic compounds} \;. \longrightarrow H_2O + CO_2 \text{ and inorganic compound} \qquad (4)$$

$$\text{POM}^- + O_2 \longrightarrow \text{POM} + O_2^- \qquad (5)$$

$$O_2^- + \text{org}^\bullet \longrightarrow \text{oxidation product} \qquad (6)$$