SYNTHESIS AND CHARACTERIZATION OF CARBON COATED AND NITROGEN DOPED TiO_2 FOR ENHANCED PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTANTS UNDER UV-VIS AND VISIBLE LIGHT IRRADIATION

by

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IN THE NAME OF ALLAH, THE MOST GRACIOUS AND MOST MERCIFUL

Thanks to Allah S.W.T for giving me the opportunity to do and complete this thesis successfully. A journey is easier when you travel together. Interdependence is certainly is more valuable than independence. This thesis is the results of five years of works whereby I have been accompanied and supported by many people. It is a pleasant aspect that I have now opportunity to express my gratitude to all of them.

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LIST OF ABBREVIATIONS

a.u	Arbitrary units
AOPs	Advance oxidation processes
CHN	Carbon, Hydrogen, Nitrogen
COD	Chemical Oxygen Demand
CB	Conduction Band
e^-	Negative electron
E_{bg}	Energy band gap
h^+	Positive hole
hv	Photonic energy
LUMO	Lowest unoccupied molecular orbital
MB	Methylene Blue dye
HUMO	Highest unoccupied molecular orbital
HRTEM	High Resolution Transmission Electron Microscopy
PL	Photoluminescence
RR4	Reactive Red 4 dye
SEM	Scanning Electron Microscopy
TOC	Total Organic Compounds
UV	Ultraviolet
UV-VIS DRS	UV-Visible diffuse reflectance spectroscopy
VB	Valence band

SINTESIS DAN PENCIRIAN TiO_2 TERSALUT KARBON DAN TERDOP NITROGEN BAGI PENINGKATAN PENGURAIAN PEMFOTOMANGKINAN KE ATAS BAHAN CEMAR ORGANIK DI BAWAH SINARAN CAHAYA UV-VIS DAN NAMPAK

ABSTRAK

TiO_2 komersial yang murah dan sedia ada dipasaran iaitu TiO_2 (99% anatase) dan TiO_2-P25 (80% anatase dan 20% rutile) telah diubahsuai untuk menghasilkan TiO_2 tergabung karbon (C) dan nitrogen (N) bagi meningkatkan fotoaktiviti bahan tersebut dibawah sinaran cahaya UV dan cahaya nampak. Modifikasi fotopemangkin ini jalankan dengan menggunakan polimer semulajadi iaitu ENR-50 dan penggumpal tanah gambut (peat) sebagai prekursor karbon sementara urea digunakan sebagai prekursor nitrogen dan karbon. TiO_2 terubahsuai dengan menggunakan ENR-50 menghasilkan TiO_2 tersalut C. Keadaan optimum bagi C adalah 1 g larutan ENR-50 dan 560°C bagi suhu kalsinasi untuk menghasilkan sampel optimum tersalut C yang mengandungi sebanyak 0.25% C dengan lapisan ketebalan 0.68 nm. Dengan menggunakan pencelup reaktif merah 4 (RR4) sebagai model bahan cemar, kadar penguraian foto bagi C tersalut TiO_2 optimum menjadi 3.7 dan 5.5 kali ganda lebih cepat berbanding TiO_2 asal masing- masing di bawah sinaran 45 W lampu kalimantang dan solar. Lapisan C yang terdapat pada TiO_2 adalah penyebab meningkatnya kadar penguraian foto kerana ia bertindak sebagai pengaut elektron. Walaubagaimanapun,tiada kesan penguraian pemfotomangkinan dapat dilihat di bawah cahaya nampak disebabkan tenaga luang jalur yang melebihi 3.0 eV.

TiO_2-P25 terubahsuai dengan penggumpal tanah gambut menghasilkan lapisan C berketebalan 0.34 nm dimana kandungan N yang sedikit juga dikesan. Keadaan optimum untuk TiO_2-P25 tersalut C adalah sebanyak 0.4 g larutan penggumpal tanah gambut pada kalsinasi suhu 450 °C. TiO_2-P25 tersalut karbon yang optimum telah meningkatkan fotoaktiviti penguraian pencelup RR4 dengan ketara berbanding TiO_2-P25 asal di bawah sinaran 45 W lampu kalimantang dan solar dan ia juga menunjukkan sedikit respon fotoaktiviti terhadap sinaran cahaya nampak.

TiO_2-P25 terubahsuai menggunakan urea menghasilkan TiO_2-P25 tersalut C dengan lapisan C berketebalan 2.04 nm sementara N terdop sebagai Ti-N bagi menukarganti tempat oksigen dalam pemangkin. Keadaan optimum bagi modifikasi fotopemangkin ini adalah 1 g urea dan 350°C pada suhu kalsinasi. Fotoaktiviti yang baik dapat diperhatikan dengan sebanyak 90% pengelup RR4 dapat disingkirkan dengan hanya 5 minit diiradiasikan dibawah 45 W lampu kalimantang. C tersalut N terdop TiO_2-P25 menunjukkan respon yang sangat bagus dibawah sinaran cahaya nampak dengan menyelesaikan tugasan kurang dari 120 minit penguraian terhadap pencelup RR4, sementara tiada kesan penguraian pemfotomangkinan yang dapat dilihat dengan menggunakan TiO_2-P25 asal dibawah kondisi yang sama. Kesan sinergi bagi setiap modifikasi fotopemangkin diterokai dengan menggunakan SEM, HRTEM, XPS, BET, UV-Vis-DRS, CHN dan spektroskopi fotopendarcahaya. Penilaian terhadap fotopemangkin bagi sampel juga dijalankan dengan menggunakan metilena biru (MB) dan fenol sebagai bahan cemar kedua dan ketiga. Kesan terhadap parameter operasi seperti kesan muatan pemangkin, kadar aliran udara dan pH awal adalah masing –masing 0.02 g, 25 mL min^{-1} dan pH 7. Kesemua fotopemangkin terubahsuai adalah stabil terhadap sinaran yang lama dan aktiviti foto juga konsisten sehingga 5 kitaran ulang guna.

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ABSTRACT

A commercially available and relatively cheap TiO_2 (99% anatase) and TiO_2-P25 (80% anatase and 20% rutile) were modified to produce carbon (C) and nitrogen (N) incorporated TiO_2 to improve its photoactivity under UV-Vis and visible light regions. Both the TiO_2 and TiO_2-P25 were modified using natural polymers of ENR-50 and peat coagulant (peat) as carbon precursor while urea was used as N and C precursor. TiO_2 modified with ENR-50 produced a C coated TiO_2. The optimum condition for C coating was 1.0 g ENR-50 solution and 560 °C of calcination temperature to yield the optimum C coated sample containing 0.25 % C with a C layer thickness of 0.68 nm. By using Reactive Red 4 dye (RR4) as model pollutant, the photocatalytic degradation rate of the optimum C coated TiO_2 was 3.7 and 5.5 times faster than that of the pristine TiO_2 under 45 W fluorescent lamp and solar irradiations respectively. The C layer present in TiO_2 was responsible for increasing its photoactivity by acting as an electron scavenger. However, no photocatalytic degradation was observed under visible light irradiation for all C coated TiO_2 due to their bandgap energy (E_g) values higher than 3.0 eV.

TiO_2-P25 modified with peat coagulant produced a 0.34 nm thickness of C layer coated on its surface where a low amount of N was also detected. The optimum condition for C coated TiO_2-P25 was at 0.4 g of peat coagulant solution

loading using 450°C of calcination temperature. The optimum C coated TiO_2-P25 significantly increased the photocatalytic degradation of RR4 dye as compared with pristine TiO_2-P25 under a 45-W fluorescent lamp and solar light and also indicates low photocatalytic activity under visible light irradiation.

TiO_2-P25 modified with urea produced a photocatalyst coated with 2.04 nm C thickness while N was doped as Ti-N where it substituted the site of oxygen atom of the catalyst. The optimum preparation for this modified photocatalyst was at 1 g of urea and 350°C of calcination temperature. A good photocatalytic activity was observed where 90% of RR4 dye was removed by the optimum C coated N doped TiO_2-P25 in only 5 minutes of irradiation under a 45 W fluorescent lamp. The bandgap energy for C coated N doped P25 was reduced to 2.6 eV. It demonstrated impressive photocatalytic activity under visible light irradiation by degrading the RR4 dye entirely in less than 120 minutes. Meanwhile, no photocatalytic degradation was observed using pristine P25 under the same condition. The synergistic effects of each modified photocatalysts were examined using SEM, HRTEM, XPS, BET, UV-Vis-DRS, CHNS and photoluminescent analyses. The photocatalytic evaluation of the samples was also carried out using methylene blue (MB) and phenol as the second and third pollutants. The operational parameters for all modified photocatalysts such as effect of catalyst loading, aeration flow rate and initial pH were found to be optimum at 0.02 g, 25 mL min^{-1} and pH 7 respectively. All the modified photocatalysts were stable upon exposure to the long duration of irradiation and their photoactivity activities were consistent up to the 5^{th} cycle of reuse.

CHAPTER 1

INTRODUCTION

1.1 Environmental Problems

Environmental pollution, such as contaminated water or polluted air, has become a global issue threatening the health of mankind. Typical polluting sources are toxic organic molecules or hazardous gas compounds which are released from household waste, livestock waste and local industries. Science is thus involved in searching for new alternatives and ecologically sustainable techniques for cleaning up the environmental contamination [1]. Different solutions for solving these problems have already been proposed such as air scrubbing, adsorption etc., but some of them only remove the pollutant from one phase to another and then require additional processes to eliminate the toxic compounds [2].

1.2 Advance Oxidation Process (AOP)

Advanced oxidation processes (AOPs) are efficient novel methods for water treatment that have produced very good results in industrialized countries and are beginning to be employed in the developing regions [3-5]. AOPs are based on physicochemical processes that produce profound changes in the structure of chemical species. The concept was initially established by Glaze et al. [4], who defined AOPs processes as those involving generation and use of powerful transitory species especially hydroxyl radical ($HO^{\bullet}$). This species can be generated by photochemical process (solar light) or by other forms of energy, and has a high efficiency for organic matter oxidation [5]. Some AOPs, such as heterogeneous photocatalysis, radiolysis and others, can also produce reducing agents, allowing the transformation of pollutants that are difficult to oxidize such as some metal ions or

halogenated compounds into safer species. AOPs are usually divided into non-photochemical and photochemical processes, as listed in Table 1.1.

Table 1.1: Advanced Oxidation Technologies and other related processes [6].

Non-photochemical processes	Photochemical processes
Alkaline ozonation (O_3/OH^-)	Water photolysis in vacuum ultraviolet (VUV)
Ozonation with hydrogen peroxide (O_3/H_2O_2)	UV/ hydrogen peroxide
Fenton and related processes (Fe^2+/H_2O_2)	UV/O_3
Electrochemical oxidation processes	Photo-Fenton
γ -Radiolysis and electron-beam treatment	UV/periodate
Non-thermal plasma	Heterogeneous photocatalysis
Electrohydraulic discharge—ultrasound	
Oxidation in sub/and supercritical water	
Zero-valent iron	
Ferrate (K_2FeO_4, Fe(VI))	

The high efficiency of AOPs is supported on thermodynamic and kinetic grounds, due to the participation of radicals. The hydroxyl radical can attack virtually all organic compounds and it reacts 106–1012 times more rapidly than alternative oxidants such as ozone (O_3) [5]. From Table 1.2, it can be observed that, after fluorine, hydroxyl radical ($OH^{\bullet}$) is the most energetic oxidant due to its high redox potential (high redox potential means strong oxidant agent species).

Table 1.3 shows that the reaction rate constant of different compounds with $OH^{\bullet}$ are several orders of magnitude higher than those with O_3. Another active oxygen species is the superoxide radical ($O_2^{\bullet -}$) and its conjugate acid from the hydroperoxyl radical ($HO_2^{\bullet}$). These radicals are also produced in many AOPs, but they are far less active than $OH^{\bullet}$ since as indicated in Table 1.2, their redox potentials are lower than that of $OH^{\bullet}$ radical.

Table 1.2: Redox potentials (E^0) of some oxidants [7].

Species	E^0(V, 25 °C)[1]
Fluorine	3.03
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.78
Perhydroxyl radical/ Hydroperoxyl radical	1.70
Permanganate	1.68
Chlorine dioxide	1.57
Hypochlorous acid	1.49
Chlorine	1.36
Bromine	1.09
Superoxide radical	0.59
Iodine	0.54

[1] : Redox potentials referred to normal hydrogen electrode (NHE)

Table 1.3: Rate constants (k in M^{-1} s^{-1}) for some organic compounds with hydroxyl radical and ozone [8].

Compound	Rate constant (M^{-1} s^{-1})	
	$OH^{\bullet}$	O_3
Chlorinated alkenes	$10^9 – 10^{11}$	$10^{-1} – 10^3$
Phenols	$10^9 – 10^{10}$	10^3
Aromatics	$10^8 – 10^{10}$	$1 – 10^2$
Ketones	$10^9 – 10^{10}$	1
Alcohols	$10^8 – 10^9$	$10^{-2} – 1$
Alkanes	$10^6 – 10^9$	10^{-2}

When a target pollutant compound is attacked by $OH^{\bullet}$, three main mechanisms may be involved in the degradation of organics: hydrogen abstraction, $OH^{\bullet}$ addition or substitution and electron transfer. Hydrogen abstraction is generally the first step in many acid compounds [5, 7, 8]:

$$RH + OH^{\bullet} \rightarrow H_2O + R^{\bullet} \rightarrow \text{further oxidation reactions} \quad (1.1)$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \rightarrow \text{further oxidation reactions} \quad (1.2)$$

AOPs are developed and commercialized to a variable degree and are undergoing constant change as technological advances take place. At present, UV/H_2O_2, UV/O_3, $UV/H_2O_2/O_3$, photo fenton and heterogeneous photocatalysis (UV/TiO_2) are commercialized [6].

1.3 Heterogeneous Photocatalysis

The words “photocatalyst” is Greek origin and composed from two parts: the “photo” (light) and the word “catalysis” (decomposed). Although there was no consensus in the scientific community as to proper definition of photocatalyst, the term generally can be used to describe the active substance under light irradiation [9]. The photocatalysis is the process to enhance the rate of a chemical reaction in the presence of light without being involved itself in the chemical transformation. Thus, the main difference between a conventional thermal catalyst and photocatalyst is that the former is activated by the heat whereas the latter is activated by photons from the light to appropriate energy. Photocatalytic reactions may occur homogeneously or heterogeneously, but heterogeneous photocatalysts is more intensively studied in

recent years because of its potential use in a variety of environmental and energy-related applications as well as organic synthesis [10].

Heterogeneous photocatalysis is a potential process that has been focused since the early 1970s, when Fujishima and Honda discovered the photocatalytic splitting of water on TiO_2 electrodes [11]. This technique is considered to be one of the most promising Advanced Oxidation Process (AOPs) because of its specific advantages. Heterogeneous photocatalysis is based on the interaction between semiconductor materials and photon from light. By considering that we can get 'free' light from the sun, the idea of using solar light energy as a resource to clean up the environment is an ideal and extremely promising approach. Sun light is a clean and renewable energy source that is readily available. Before reaching the Earth's surface, a part of the solar energy is absorbed by the stratosphere, ozonosphere and other atmospheric layers [12].

Solar radiation reaching the Earth with 5 and 43% of UV and visible light respectively, with the remaining part (52%) is composed of infrared and longer wavelengths radiation (Figure 1.1). Approximately 40% of the total amount of radiation arriving on Earth is mainly composed of visible, infrared, and radio energies. In case of ultraviolet (UV) light, it is generally divided into three regions namely UV-A (315 – 400 nm), UV-B (280 – 315 nm) and UV-C (100 – 280 nm) [13], which is responsible for most of the photochemical processes occurring in the atmosphere. UV-C radiance is mostly filtered by Earth's ozone layer, UV-A and UV-B radiations still pass and have the potential to generate photochemical processes such as the synthesis of vitamin D. However, long term exposure to UV light is very dangerous to human body since it probably can cause skin damage and cancer [14]. The development of photocatalytic technology under different application is

illustrated in Table 1.4. In its early age, a revolutionary idea of cleanliness was suggested by the great Japanese 'fathers' of this field [15]. In the past, 'light cleaning' means 'a fast job (a quick wipe-up or dusting)', but in the future it will mean 'cleaning with light'. The representation of a city with complete self cleaning technology is depicted in Figure 1.2.

Table 1.4: Different applications of photocatalysis technology [16].

Property	**Category**	**Application**
Self-cleaning	Material for residential and office buildings	Exterior tiles, kitchen bathroom components, interior furnishing, plastic surface, building stone
	Indoor and Outdoor lamps and related systems	Translucent paper for indoor lamp covers, coating on fluorescent lamp and highway tunnel lamp cover glass
	Materials for roads	Tunnel wall, sound proofed wall, traffic sings and reflactors
	Others	Tent material, clothes for hospital garments and uniforms and spray coating for cars
Air- cleaning	Indoor air cleaners	Room air cleaner, photocatalyst-equipped air conditioners and interior air cleaner for factories
	Outdoor air purifiers	Concrete for highways, roadways and building
Water purification	Drinking water	River water, groundwater, lakes and water storage tanks
	Others	Fish feeding tanks, drainage water and industrial wastewater
Antitumor activity Cancer therapy		Endoscopic-like instruments
Self-sterilizing	Hospital	Tiles to cover the floor walls of operating rooms, silicone rubber for medical catheters and hospital garments and uniforms
	Others	Public rest rooms, bathrooms

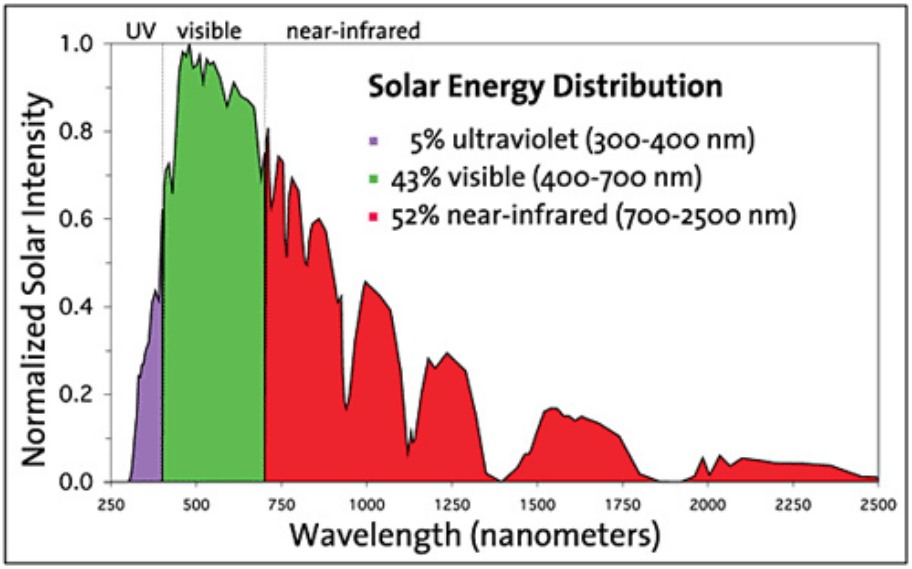

Figure 1.1: Earth's light environment (solar spectrum) [17].

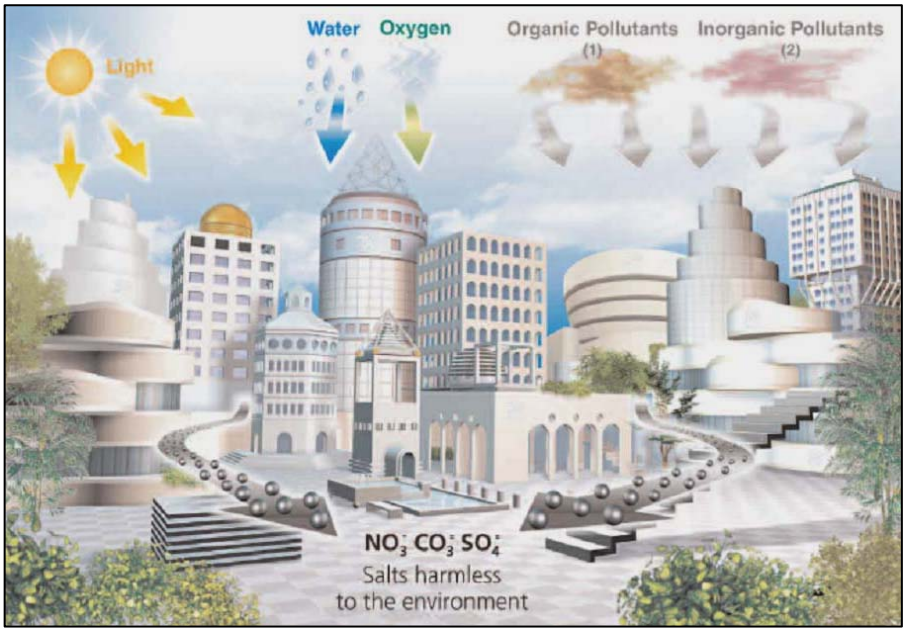

Figure 1.2: Representation of a city governed by urban photocatalysis, proposed by Italcementi group [18].

1.4 Principles of semiconductor photocatalysis

Semiconductors are particularly useful as photocatalyst because of a favorable combination of electron structure, light absorption properties, charge transport characteristics and excited state lifetime [19]. The electron characteristics of conductors, semiconductors and insulators can be described accordingly via the band theory. The corresponding energy levels are so closely spaced that they form bands because of the large number of atoms interact in a solid material. Each band has a different energy and the electrons fill from the lowest to the highest energy and it is similar to the way that electrons occupy the orbitals in a single atom. The highest energy filled band, which is analogous to the 'Highest Occupied Molecular Orbital' (HOMO) in a molecule, is called the valence band (VB). The next higher band, which is analogous to the 'Lowest Unoccupied Molecular Orbital' (LUMO) in the molecule, is called the conduction band (CB). The VB and CB are separated by the band gap (E_{bg}). The size of E_{bg} for each material can be determined for the conductor, semiconductor or insulator as can be seen in Figure 1.3. In general, for electron to flow in a solid under the application of an electric field, they must be in a partially filled band or have access to a nearby empty band [19,20]. In Figure 1.3, there is no possibility of electron flow for insulator because the valence band is completely filled with electrons and the conduction band is too far away in energy to be accessed by these electrons. For a conductors like metals, valence band overlaps with conduction band. Thus, the electrons can access empty areas within the valence band and move freely across all atoms in metal. For a semiconductor, there is a special case in which the band gap is small enough (generally less than 4 eV) that can be bridged either by heat or light to promote electron from the VB to the CB. The mechanism of a semiconductor activated by light is illustrated in Figure 1.4.

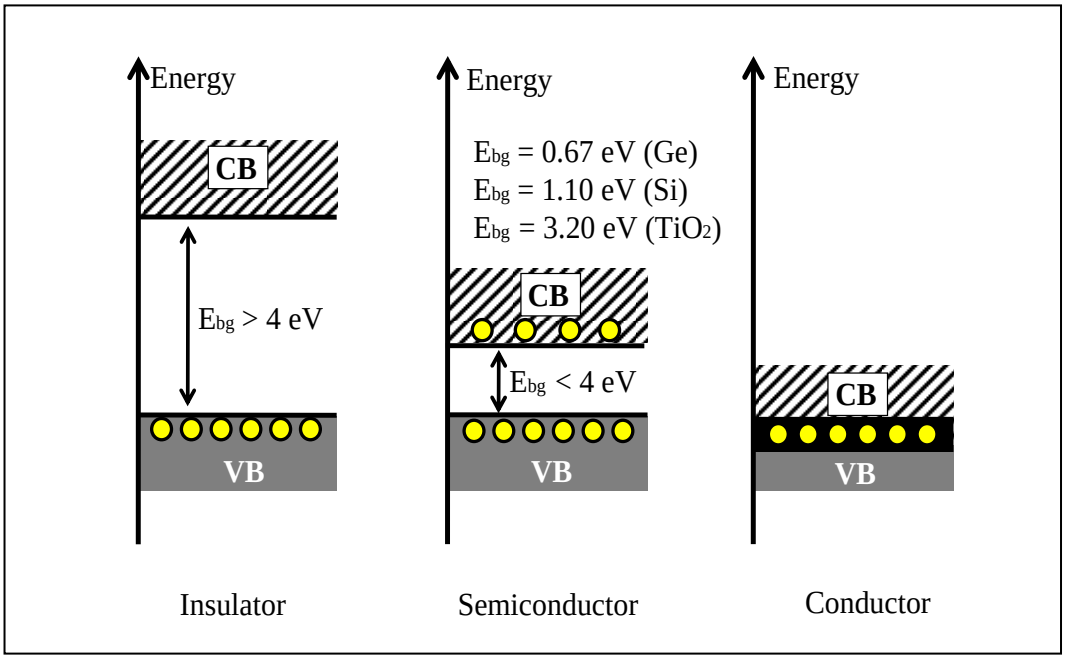

Figure 1.3:Band gap energy (E_g) of the insulator, semiconductor and conductor. CB; conduction band, VB; valance band [19].

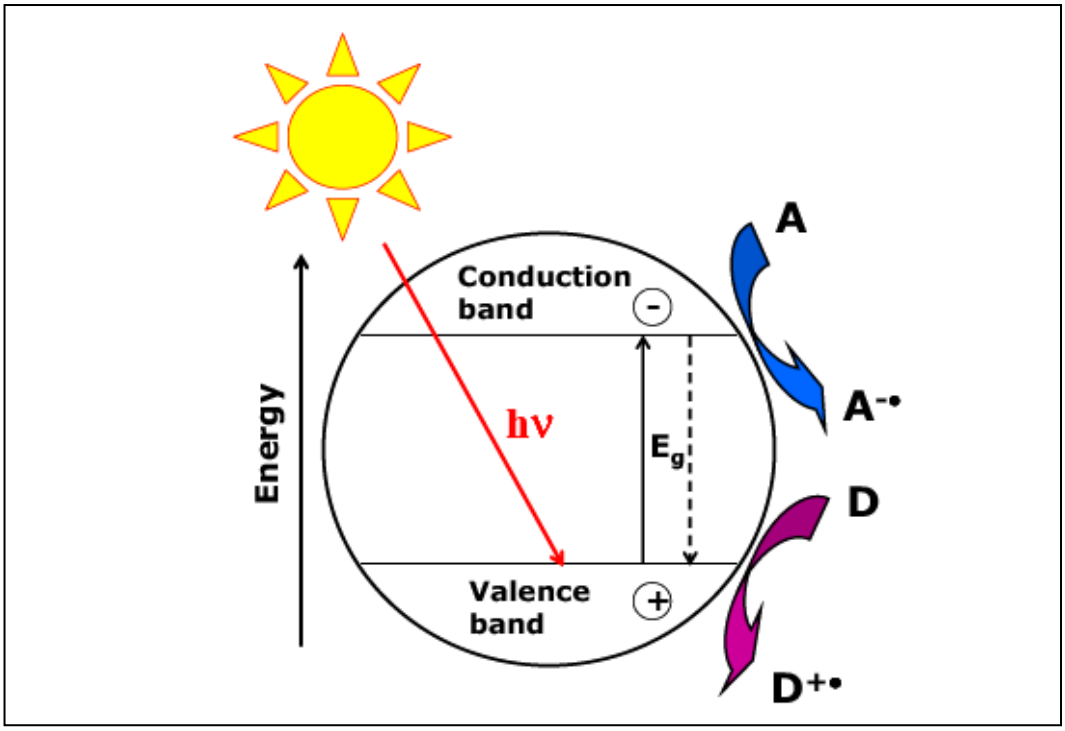

Figure 1.4: Simplified scheme of semiconductor activation [19].

Activation of a semiconductor photocatalyst is achieved through the absorption of a photon into its bandgap energy which results in the promotion of an electron from the VB into the CB, with the concomitant generation of a hole in the valence band. For an example, when a semiconductor is used as a photocatalyst in the environmental remediation, it should be capable to generate a valence band hole with a redox potential that is positive enough to oxidize the organic pollutant. At the same time the photogenerated electron in the conduction band should be negative enough to reduce adsorbed O_2 to superoxide radical anion [21]. The probability and the rate of charge transfer processes depend on the position of the conduction and valence band edges and on the redox potentials of the adsorbed species [19].

Figure 1.5 shows the band gap values of different semiconductors and their position on the electrochemical scale. A substrate can successfully interact only with some semiconductors, it is necessary that the electrochemical potential value of the electron acceptor is more positive (down in the graph) than the semiconductor conduction band potential, and that the electron donor potential is more negative (up in the graph) than that of the semiconductor valence band. A photocatalytic reaction can take place only under such conditions. Recombination of electron-hole pairs can occur in competition with a charge transfer to adsorbed species [21] as shown in Figure 1.6. This phenomenon represents the major deactivation path which could significantly decrease the photocatalytic efficiency. The detrimental process of back-donation to the semiconductor after charge transfer to the adsorbed species can also occur.

The main reaction scheme of a photocatalytic process can be summarized in the following equations (1.3-1.12).

a) Charge separation

$$TiO_2 + hv \rightarrow e^-_{CB} + h^+_{VB} \quad (1.3)$$

b) Bulk/surface recombination

$$e^-_{CB} + h^+_{VB} \rightarrow \text{heat} \quad (1.4)$$

C) Surface trapping

$$h^+_{VB} + \equiv Ti - OH \rightarrow \equiv Ti - O^\bullet + H^+ \quad (1.5)$$

$$e^-_{CB} + \equiv Ti - OH \rightarrow \equiv Ti - O^\bullet + OH^- \quad (1.6)$$

d) Surface recombination

$$e^-_{CB} + \equiv Ti - O^\bullet + H^+ \rightarrow \equiv Ti - OH \quad (1.7)$$

$$h^+_{VB} + \equiv Ti^\bullet + OH^- \rightarrow \equiv Ti - OH \quad (1.8)$$

e) Interfacial charge transfer

$$Red_1 + \equiv Ti - O^\bullet \rightarrow Ox_1 + \equiv Ti - OH \quad (1.9)$$

$$Ox_2 + H_2O + \equiv Ti^\bullet \rightarrow Red_2 + \equiv Ti\text{-}OH \quad (1.10)$$

f) Back reaction

$$Red_2 + \equiv Ti - O^\bullet \rightarrow Ox_2 + \equiv Ti - OH \quad (1.11)$$

$$Ox_1 + \equiv Ti \rightarrow Red_1 + \equiv Ti - OH \quad (1.12)$$

The process of photocatalytic reaction by TiO_2 takes place by the absorption of ultraviolet (UV) or near-ultraviolet photons (hv) that is equal or exceed the band gap energy (E_g) value for anatase 3.2 eV, or 3.0 eV for rutile onto its surface. An electron would be photoexcited from the valence band (VB) to the empty conduction band (CB) of the TiO_2 and a positive hole would be left in the valence band in femtoseconds (equations 1.3). Surface trapping of the induced charges could also occur via equations 1.5-1.6. Subsequently, various possible reactions could occur

such as charge recombination (equation 1.4 and 1.7-1.8) and a series of reductive and oxidative reactions will be induced on the TiO_2 surface (equations 1.9 -1.12).

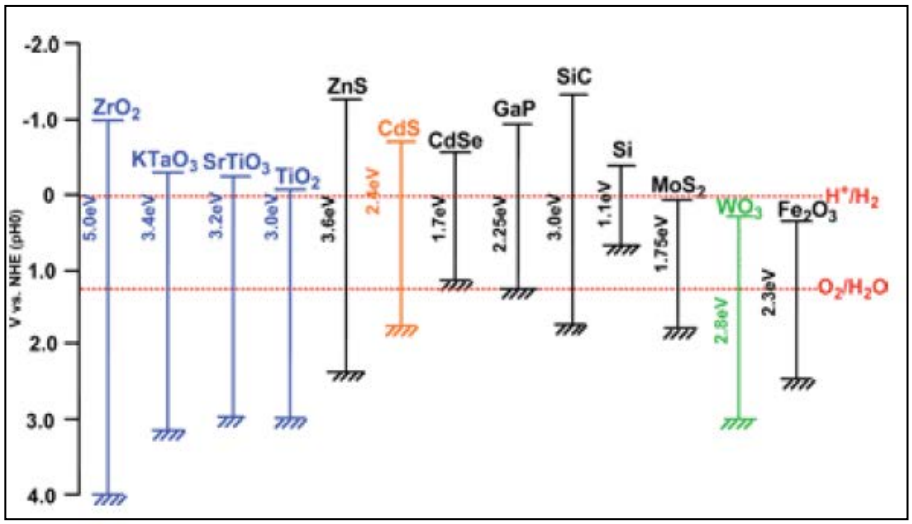

Figure 1.5: Relationship between the band structures of some selected metal oxide and non oxide semiconductors and the redox potentials of water splitting [22].

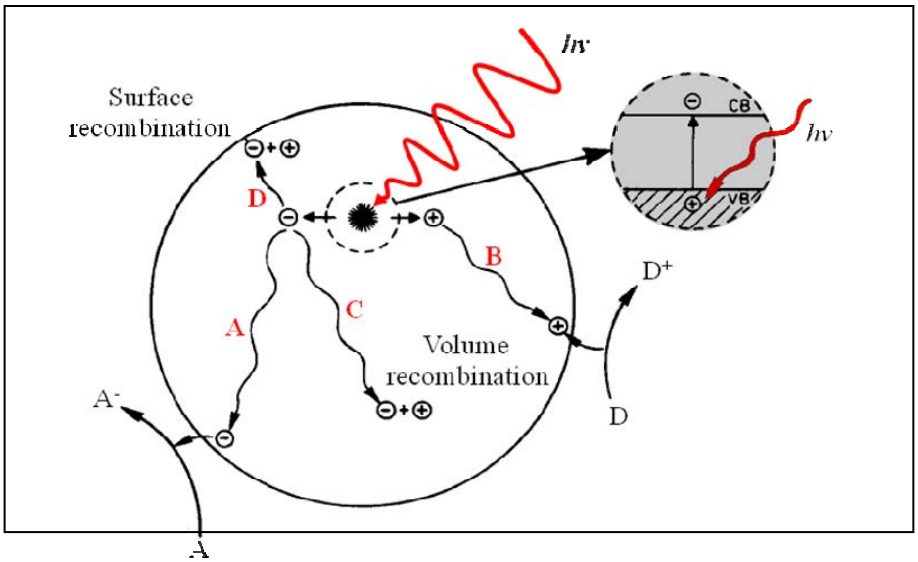

Figure 1.6: Schematic representation of a nanosized photocatalyst particle where the deexcitation process (following the initial irradiation) can occur in four general ways : (A) surface recombination,(B)volume recombination, (C) reduction with electron acceptors, and (D)oxidation with electron donors [19].

1.5 TiO_2 as photocatalyst

Any common catalytic material is not consumed during the course of a chemical reaction. Similarly, a photocatalyst must be stable and not tend to decompose due to long exposure to light. In addition, a good photocatalyst must be:

- photoactive
- able to absorb visible and/or near UV light
- biologically and chemically inert
- photostable (*i.e*. not liable to photoanodic corrosion)
- inexpensive
- non-toxic

In many cases, the semiconductor itself risks to incur oxidative decomposition by the photogenerated holes. Generally, only *n-type* semiconductor oxides are stable towards photoanodic corrosion, although such oxides usually have large band gap energy which means that the semiconductor is active only under UV light. CdS is an example of a highly active semiconductor which can be activated using visible light due to the low bandgap energy of 2.4 eV [23]. However, CdS is subject to photoanodic corrosion and this feature makes it unacceptable as a photocatalyst for water purification [24]. Among different semiconductor photocatalysts, TiO_2 appears as the most active and most suitable one for a wide variety of energy and environmental applications. In fact, TiO_2 has a high oxidation ability since its photogenerated holes is at E^0 = 2.9 V vs. NHE at pH 0. Moreover, TiO_2 is biologically and chemically inert, photostable and relatively cheap [19, 25]. TiO_2 was used intensively in industrial products in order to replace the older toxic

lead oxides as a pigment for white paint. Recently, the world production of TiO_2 passed 4 million tons every year with China as the world's largest production country [26]. TiO_2 has been used as a pigment in various applications involving paints, plastic, rubber, ink, papers and textile, in addition to the considerable amount of the global production used in food and pharmaceuticals product [25]. There are two commercial ways of manufacturing TiO_2 namely pyrogenic and precipitation processes [25].

The pyrogenic process was improved in 1920. However, this process was not commercially applicable until the late 1950s. In this process, TiO_2 was reacted wih gaseous chloride in the presence of coke to produce liquid titanium tetrachloride. The product was distilled and oxidized in the vapor phase to obtain TiO_2. The precipitation process involves direct reaction between TiO_2 ore and sulfuric acid, the product was then hydrolyzed to produce a hydrate oxide, which was followed by calcinations process at 900°C to produce TiO_2 [25]. Figures 1.7(a) and 1.7 (b) show the production of TiO_2 using pyrogenic and precipitate processes respectively. The type of crystalline form of TiO_2 is the most important part in the determination of good photocatalyst.

There are three types crystalline forms of TiO_2 namely anatase, rutile and brookite [27, 28]. Brookite is a natural phase, which is quite difficult to synthesize in a laboratory. It is also rare in nature and structurally more complex than the other two polymorphs (anatase and rutile). The rutile and anatase phases are the most used in photocatalytic studies (Figure 1.8).

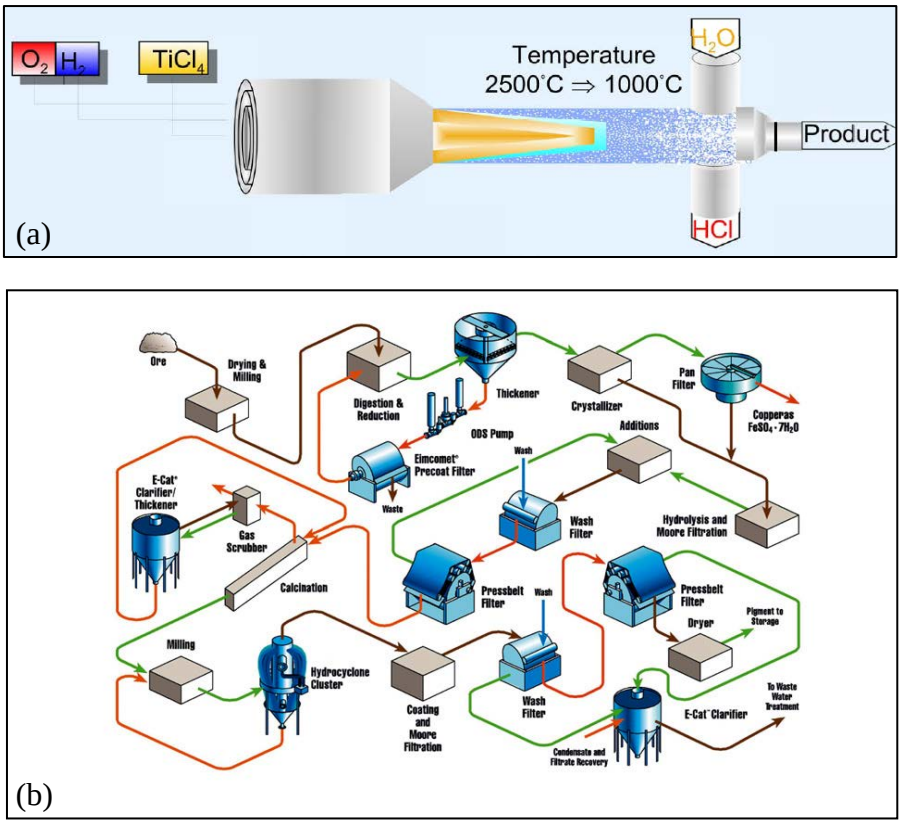

Figure 1.7: The manufacturing of TiO_2 using: a) pyrogenic process, b) precipitation process [25].

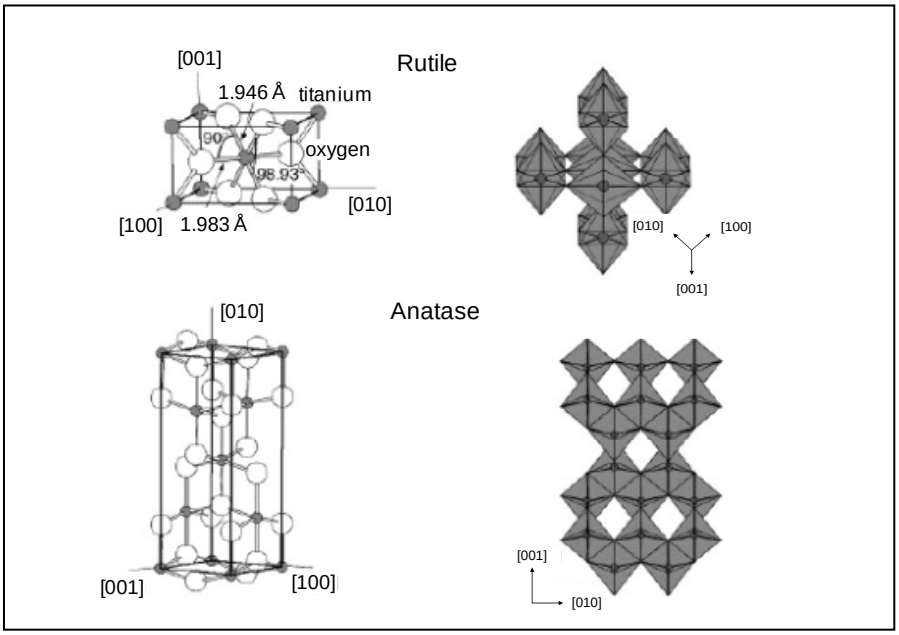

Figure 1.8: Bulk crystal structure of rutile and anatase in TiO_2 [28].

Both anatase and rutile are semiconductors with the bandgap located at about 3.2 eV and 3.0 eV, respectively. Rutile does adsorb some visible light while anatase only absorb in the UV region of spectra. Unfortunately, rutile is not a good photocatalyst [28]. Many researchers have concluded that rutile is catalytically inactive or a much less active form of TiO_2 [29, 30]. Rutile form of TiO_2 however suffers from strong recombination of electrons and holes due to the lack of defects within its crystal lattice. Anatase form of titanium dioxide therefore appears to be the most efficient semiconductor for environment application. Its phocatalytic activity is higher than most available crystalline forms of TiO_2.

Rutile is the most common crystalline form of TiO_2 in nature. The rutile structure is not compact. Its unit cell is tetragonal where one axis is 30% shorter than the other two axes (a = 4.593 Å, c = 2.959 Å) [27,28,29]. The structure is constituted by distorted octahedral TiO_6, with oxygen atoms shared with other adjacent Ti atoms. Every Ti atom is an octahedral surrounded by six O atoms, and every O atom is surrounded by 3 Ti atoms at the edges of an equilateral triangle. It can be envisaged as a central body cubic lattice of Ti atom that is considerably distorted. The crystallites can be present in nature as black or reddish mineral and also transparent when it comes completely without impurities. The color can also be orange if the mineral is in a very thin needle form [28].

Anatase from has tetragonal bipyramidal symmetry, with a structure similar to an elongated octahedron (a = 3.785 Å, c = 9.514 Å). The structure is based on a polyhedral chain of TiO_6. The difference with rutile is that anatase presents a more distorted structure, where every polyhedron shares 4 edges with the adjacent one. In particular, the tetragonal elementary cell contains 4 units, instead of 2, and the cell sides are a = 3.785 Å and c = 9.514 Å. The anatase crystals are really small and the

color ranges from blue sapphire to yellow-brown [29]. These differences in lattice structures cause different mass densities and electronic band structures for the two main TiO_2 polymorphs. The band gap energy for anatase and rutile is equal to 3.2 and 3.1 eV, respectively. The valence band are mostly O 2p atomic orbitals-derived, while the conduction band is mostly Ti 3d-derived (Figure 1.9) [25,28]. Moreover, TiO_2 like other oxides is thermodynamically stable as a non-stoichiometric compound, with anion deficiencies. Therefore, a more correct denotation would be TiO_{2-x}. Generally the material defects, such as vacancies, can introduce localized ionized states. In the case of TiO_2, oxygen vacancies are formally compensated by the adoption of the +3 oxidation state by an equivalent number of titanium atoms. These Ti^{3+} ions operate as electron donors, introducing localized levels next to the conduction band. This is due to the *n-type* semiconductor character of TiO_2 [25, 30].

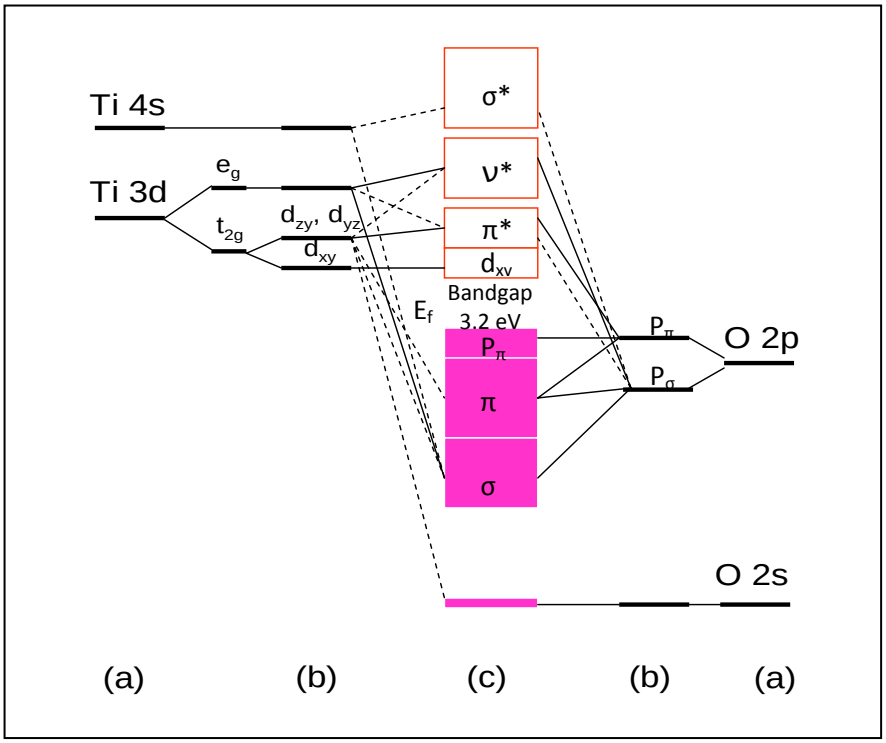

Figure 1.9: Molecular orbital structure of anatase: a) atomic levels, b) crystal – field split levels, c) final interaction states [30].

1.6 Mechanism of TiO_2 in photocatalytic reaction

Although the overall reactions of the photocatalytic semiconductor are oxidation and reduction, the main steps that cause both oxidation and reduction are still not well understood. The photocatalytic processes are divided into four phase systems namely electronic, solid, liquid and gas phases [31]. Electronic phase is the UV light source which relates to the excitation of the electron in the valence band into the conduction band. The liquid phase is the wastewater, solid phase is the catalyst and gas phase is the oxygen that contained in water. Some of the explanation about photocatalytic process of the semiconductor has been discussed in the previous section (Section 1.4). This section will provide a more detailed discussion about the mechanism involved in TiO_2 semiconductor photocatalyst. Figure 1.10 shows the overall mechanism of the production process of radicals from TiO_2. The process of photocatalytic reaction by TiO_2 takes place by the absorption of ultraviolet (UV) or near-ultraviolet photons ($h\nu$) that equal or exceed the band gap energy (E_{bg}) values for anatase and rutile (3.2 eV and 3.1 eV) respectively onto its surface [25,32].

An electron would separate out by photoexitation from the valance band to the empty conduction band of the TiO_2 and positive hole would be left in the valence band. The mechanism of electron-hole charge separation is provided in equation 1.13. Since the catalyst is always in contact with the liquid solution, transferring of the charge would occur until it has achieved an electrostatic equilibrium [33]. In metal, excessive charge is confined on the surface. However, in a semiconductor, the excessive charge would be distributed in a region, which is called space-charge region. The existence of this region is due to the expanding region from the surface to bulk of the semiconductor. This region plays a very important role in the photocatalytic process. Due to the presence of the surface charge region, the photo-

excited electron can be separated from the hole and migrates to the particle surface. This would produce the potential gradient of electron and hole between the bulk solid and its external surface [25,31-34]. Equations 1.14 and 1.15 represent the electron-hole pairs migration.

Basically, two possibilities could occur after electron hole charge separation. The first one is the recombination of the photo-exited electron with holes and the input energy is released in the form of PL photon ($h\nu_{PL}$) and heat as can be seen in Figure 1.10 and equation 1.16. Another one is that the separated electron and hole will react separately with either an electron acceptor or an electron donor (from O_2 and H_2O respectively), which accumulate on the particle surface. Consequently, they initiate the reduction and oxidation processes. The O_2 molecules scavenge the electron from the surface of TiO_2 forming superoxide radical ($O^{\bullet -}_2$). This superoxide radical then reacts with proton, eventually forming hydroperoxide radical ($HO^{\bullet}_2$, see equations 1.17 and 1.18). While, the reaction of trapped holes in aqueous solution (H_2O) eventually produced hydroxyl radical ($^{\bullet}OH$) as can be seen in equation 1.19 [19, 25].

Eventually, the degradation process of the pollutant occurred by the reduction-oxidation (redox) process with $^{\bullet}O_2^-$, $HO^{\bullet}_2$ and $OH^{\bullet +}$ radicals into the polluted species (P) and hydroxyl radicals as illustrated in Figure 1.10. However, these entire occurrences in photocatalysis reaction depended totally on the presence of both dissolved oxygen and water molecule. In fact, without the presence of water molecule, the highly reactive hydroxyl radicals ($OH^{\bullet +}$) could not be generated and impeded the photocatalytic reaction of the aqueous organic pollutants [21].

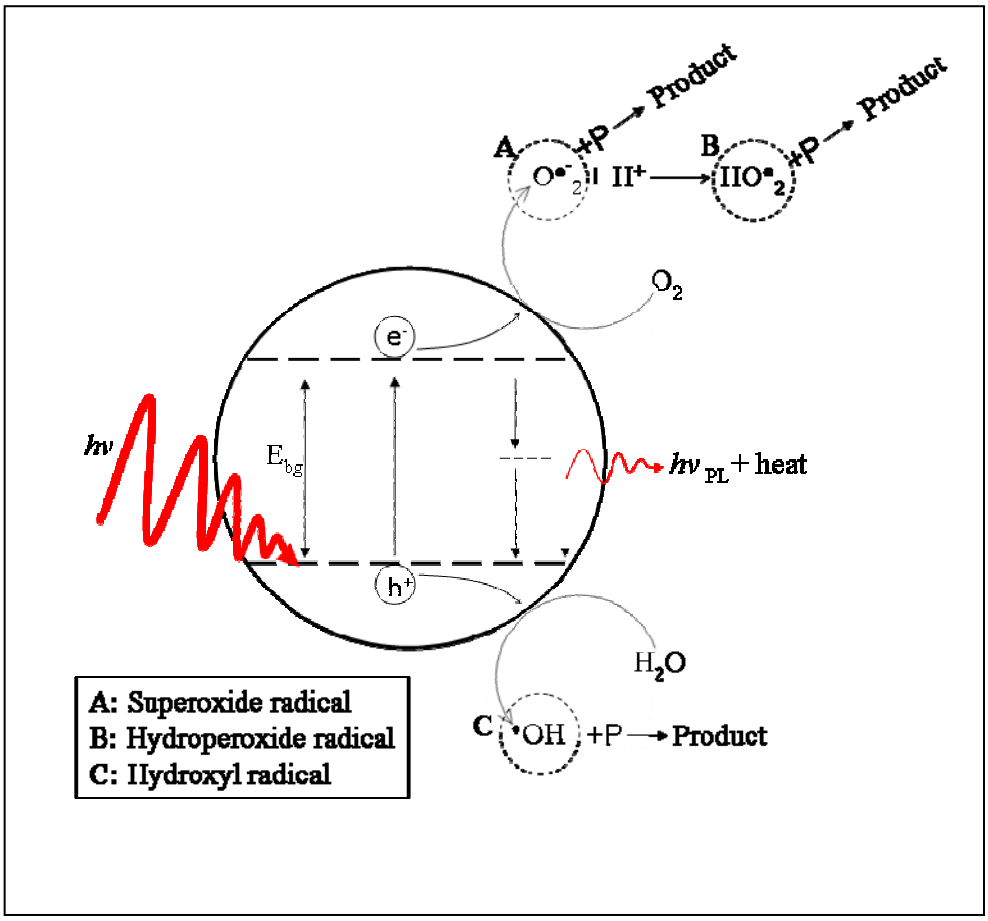

Figure 1.10: The overall mechanism involved in TiO_2 photocatalyst [25].

$$TiO_2 \xrightarrow{hv} e^-_{CB} + h^+_{VB} \quad \text{CB: Conduction band, VB: Valance band} \qquad (1.13)$$

$$e^-_{CB} \xrightarrow{K^{e-}_{diff}} e^-_{TR} \qquad (1.14)$$

$$h^+_{VB} \xrightarrow{K^{h-}_{diff}} h^+_{TR} \quad \text{diff: diffraction, TR: tapped} \qquad (1.15)$$

In other words, the fundamentals task of the heterogeneous photocatalyst is to generate the free radicals of the solution, mainly the high reactive hydroxyl radical, which traditionally, responsible for oxidizing almost all organic pollutions to CO_2 and H_2O. Thus, during the heterogeneous photocatalytic reactions, the dissolved organic pollutants are degraded to its corresponding intermediates and subsequently mineralized to CO_2 and H_2O [31-33]. The overall photocatalysis reaction can be depicted by equation 1.20.

Generally, in TiO_2 semiconductor, the incidence of recombination between electrons and holes is high which unfortunately reduce the efficiency of the photocatalytic process. The next point of view is to see the modification of TiO_2 to enhance its photocatalytic activity.

$$e^-_{CB} + h^+_{VB} \longrightarrow h\nu_{PL} + \text{heat} \qquad h\nu_{PL}\text{: PL photon} \qquad (1.16)$$

$$O_2 + e^-_{TR} \longrightarrow O^{\bullet -}_2 \qquad O^{\bullet -}_2\text{: superoxide radical} \qquad (1.17)$$

$$O^{\bullet -}_2 + H^+ \longrightarrow HO^{\bullet}_2 \qquad HO^{\bullet}_2\text{: Hydroperoxide radical} \qquad (1.18)$$

$$H_2O + h^+_{TR} \longrightarrow OH^{\bullet +} \qquad OH^{\bullet +}\text{: hydroxyl radical} \qquad (1.19)$$

$$\text{Organic contaminants} \xrightarrow{TiO_2/h\nu} \text{Intermediates} \longrightarrow CO_2 + H_2O \qquad (1.20)$$

1.7 Improving TiO_2 photocatalytic activity

As stated earlier, one of the most active fields of research in heterogeneous photocatalysis using semiconductor particles is the development of a system capable of using natural sunlight to degrade a large number of organic and inorganic

contaminants in wastewater. The overall photocatalytic activity of a particular semiconductor system for the stated purpose is measured by several factors including the stability of the semiconductor under illumination, the efficiency of the photocatalytic process, the selectivity of the products, and the wavelength range response. TiO_2 is a quite stable photocatalyst, however the band gap is large (E_{bg} = 3.2 eV) [31-34] making it only active in the ultraviolet region which is only 5% of the overall solar intensity [13, 14]. The limitations of TiO_2 as a photocatalyst for a particular use can be overcome by modifying the surface of the semiconductor to become active under visible light irradiation.

Nowadays, three benefits of modifications of photocatalytic semiconductor systems have been identified: (1) inhibiting recombination by increasing the charge separation and therefore the efficiency of the photocatalytic process; (2) increasing the wavelength response range (i.e. excitation of wide band gap semiconductors by visible light) and (3) changing the selectivity or yield of a particular product [19, 25]. A few examples will be given in the following sections illustrating the large body of work conducted in the area of photocatalyst surface modification.

1.7.1 Modification with metal

The modification of TiO_2 by noble metal enhanced the photocatalytic process by changing the semiconductor surface properties. The metal can enhance the yield of a particular product or the rate of the photocatalytic reaction. The enhancement in reactivity was first observed using the Pt/TiO_2 system. The addition of Pt to the TiO_2 surface is beneficial for photocatalytic reactions evolving gas, especially hydrogen [35-37]. The metal actually modifies the photocatalytic properties of the semiconductor by changing the distribution of electrons. The electronic modification

of TiO_2 via metal deposition can also be observed with other noble metals such as Au and Ag [38-40]. Beside photocatalytic enhancement, the modification through noble metals enables TiO_2 particles to be active in the energy range of visible light. However, the extensive utilization of noble metals for TiO_2 modification as a practical remediation technology is limited because the noble metals are expensive.

For an alternative way, the modification of TiO_2 with transition metals provides a successful and cost effective method as compared to the costly modification with noble metals. The modification of TiO_2 with transition metal enhances the photocatalytic activity of the photocatalyst by UV irradiation and exceeds its application in the visible light region. It was reported that the doping of a series of transition metals in TiO_2 such as V, Cr, Mn, Ni and Fe brings about a red shift in the absorption pattern of the TiO_2 semiconducting catalyst [41,42]. The order of the effectiveness in the red shift was found to be V > Cr > Mn > Fe > Ni [43]. The transition metal modified photocatalysts exhibited absorption in the range of 400-600 nm and thus could be effectively utilized under solar and visible light irradiation. Moreover, doping of TiO_2 with Fe^{3+} was affirmed to introduce much more oxygen vacancies in surface of TiO_2 [44]. High concentration of the Fe^{3+} dopant however increased the recombination rate and accordingly reduced the efficiency of the photocatalytic activity [45].

1.7.2 Modification with nonmetals

Modification of TiO_2 with nonmetals is an advance modification process in the development of visible light responsive TiO_2 photocatalyst. Nitrogen (N), carbon (C) and sulphur (S) are the most popular elements being studied by researchers and may have a bright potential for commercialization.

1.7.2.1 Nitrogen doped TiO_2

The modification of TiO_2 using nitrogen was first discovered by Asahi et al. [46,47]. They proposed that N atoms became incorporated into the lattice of TiO_2 by substituting the site of oxygen atoms. The corresponding N (2p) states results in a reduction of the band gap of the N-doped TiO_2 thus increasing the possibility for the modified photocatalysts to be utilized under visible light irradiation [48].

In general, the N-doped TiO_2 has been successfully prepared either by a reduction process using gaseous NH_3 [49,50], oxidation of TiN [50,51], treating of TiO_2 and urea mixtures [50,52-54], sputtering of the TiO_2 target in N_2 atmosphere [50,55], or hydrolysis or hydrothermal treatment of a titanium containing precursor with NH_3 solution [56]. The improvement of visible light photocatalytic activity of nitrogen doped TiO_2 was usually attributed to the decrease of the band gap through hybridization of the N 2p states with O 2p states on the top of the valence band or the creation of a N-induced mid-gap level just above the O 2p valence band maximum (VBM) [49-56]. However, recent electronic structure calculation indicated that there was virtually no shift of the upper edge of the O 2p valence band for the nitrogen doped TiO_2. Instead, occupied N 2p localized states appeared slightly above the valence band edge [57].

The current interesting focus in the field of N-doped TiO_2 is to clarify the N states in TiO_2 which are usually investigated by X-ray photoelectron spectroscopy (XPS). However, the assignment of N 1s peaks is still in controversy in the literatures [58]. In general, the peak of N 1s in the XPS spectra mostly lies in the range of 396–404 eV [51,56,58,59]. Most reports agreed that N 1s peak at 396–398 eV was the characteristic peak of Ti–N linkages, indicating that nitrogen atom is doped into the TiO_2 lattice and is responsible for the enhanced activity [51,56,59].