IMMOBILISATION OF TiO_2 POWDER ONTO GLASS PLATES VIA DIP-COATING TECHNIQUE USING ENR-50/PVC POLYMER BLEND AS ADHESIVES AND ITS PHOTOCATALYTIC APPLICATION

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by

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NGOH YING SHIN

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LIST OF ABBREVIATIONS

AOPs	Advanced Oxidation Processes
BET	Brunner-Emmet-Teller
COD	Chemical Oxygen Demand
e^-	Negatively charged electron
EDX	Energy dispersive x-ray
ENR-50	Epoxidised Natural Rubber (50% mol)
FTIR	Fourier transform infra red
h	hour
h^+	Positively charged hole
L-H	Langmuir-Hinshelwood
MB	Methylene Blue
min	Minute
PET	Polyethylene Terephtalate
pHpzc	pH at point of zero charge
PVC	Poly (vinyl) chloride
S	Second
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric analysis
UV	Ultra violet
W	Watt

PEMEGUNAN SERBUK TiO_2 PADA PLAT KACA MELALUI KAEDAH PENYADURAN CELUP MENGGUNAKAN ADUNAN POLIMER ENR-50/PVC SEBAGAI PELEKAT DAN APLIKASI PEMFOTOMANGKINANNYA

ABSTRAK

Kajian ini bertujuan untuk menghasilkan serbuk TiO_2 terpegun pada plat kaca yang boleh digunasemula berulang kali dengan menggunakan adunan polimer sebagai pelekat untuk penguraian pemfotomangkinan larutan akueus metilena biru (MB). Serbuk TiO_2 (99 % anatase) dipegunkan secara terus pada plat kaca menggunakan adunan polimer getah asli terepoksi (ENR-50) / poli vinil klorida (PVC) sebagai pelekat melalui kaedah penyaduran celup mudah. Kecekapan pemfotomangkinan serbuk TiO_2 yang dipegunkan pada plat kaca diuji dengan penguraian larutan akueus MB di bawah penyinaran lampu pendafluor 45 W. Nisbah optimum ENR-50 kepada PVC yang didapati adalah 1:3. Kecekapan pemfotomangkinan TiO_2/ENR/PVC yang dipegunkan pada plat kaca dalam penguraian larutan akueus MB adalah lebih baik berbanding dengan kebolehan pemfotomangkinan serbuk TiO_2 dalam mod penyebaran. Muatan mangkin yang optimum adalah sebanyak 1.0 mg cm^{-2} dan kadar penguraian pemfotomangkinan MB adalah paling tinggi pada pH 12. Kehadiran aliran udara sebagai sumber oksigen meningkatkan kadar penguraian MB. Kebocoran UV daripada lampu pendafluor memainkan peranan yang penting dalam keberkesanan TiO_2 yang terpegun pada plat kaca. Kebolehgunaan dan kebolehulangan aktiviti TiO_2/ENR/PVC terpegun meningkat sejajar dengan keamatan kebocoran UV daripada sumber lampu. Pemalar kadar purata pseudo kinetik tertib pertama untuk penguraian MB bagi 10 kali kitaran aplikasi berulangan 90 min menggunakan lampu pendafluor dengan kebocoran UV

sebanyak 1.67, 4.35 dan 6.30 Wm^{-2} adalah masing-masing 0.0174 ± 0.0072, 0.0381 ± 0.0039 dan 0.0577 ± 0.0027 min^{-1}. Analisa menggunakan SEM-EDX, TGA dan FTIR menunjukkan berlakunya penguraian adunan polimer yang digunakan sebagai pelekat selepas digunasemula mengakibatkan penghasilan keperluan oksigen kimia (COD). Penguraian ENR-50 didapati berlaku lebih pantas berbanding penguraian PVC. Sebanyak 50 % daripada MB berkepekatan sebanyak 20 mg L^{-1} dimineralisasikan selepas rawatan pemfotomangkinan selama 4 jam menggunakan plat TiO_2 terpegun yang 'dibersihkan'. Tahap mineralisasi adalah selari dengan peratusan penguraian warna MB. Kehadiran komponen tak organik seperti SO_4^{2-}. NO_3^-, Cl^- dan perubahan pH dalam larutan terawat menunjukkan MB telah dimineralisasikan. TiO_2 yang dipegunkan pada penyokong polimer seperti PVC, akrilik dan PET kesemuanya menunjukkan aktiviti foto dalam penguraian larutan MB walaupun pada kadar yang lebih rendah. Secara keseluruhan, pemegunan serbuk TiO_2 melalui teknik penyaduran celup mudah ini adalah ringkas, berkesan, menjimatkan dan mempunyai kebolehulangan yang baik.

IMMOBILISATION OF TiO_2 POWDER ONTO GLASS PLATES VIA DIP-COATING TECHNIQUE USING ENR-50/PVC POLYMER BLEND AS ADHESIVES AND ITS PHOTOCATALYTIC APPLICATION

ABSTRACT

The objective of this work is to produce a reusable immobilised TiO_2 on glass plate utilizing polymer blend as adhesives for the photocatalytic degradation of methylene blue (MB) in aqueous solution. TiO_2 powder (99% anatase) was directly immobilised onto glass plates using epoxidised natural rubber (ENR-50)/ poly (vinyl) chloride (PVC) polymer blend as adhesives via simple dip-coating technique. The photocatalytic characterization of the immobilised TiO_2 powder was assessed using MB in aqueous solution as the model pollutant under the irradiation of 45W fluorescent lamp. The optimum ratio of ENR-50 to PVC for the immobilisation of TiO_2 was determined as 1:3. The photocatalytic efficiency of the immobilised TiO_2/ENR/PVC was better than the TiO_2 in slurry mode. The optimum catalyst loading was determined as 1.0 mg/cm^2 and the photocatalytic degradation rate of MB was highest at pH 12. The presence of aeration as oxygen source promoted the photocatalytic removal of MB. The photocatalytic degradation of MB was mainly governed by the UV residuals emanated from the 45 W fluorescent lamp. Reusability and reproducibility of the immobilised TiO_2/ENR/PVC improved proportionally with the intensity of UV irradiances from the light sources. The average pseudo first order rate constant of MB degradation for 10 cycles of 90 min repeated applications of the immobilised TiO_2 using light sources with UV irradiances of 1.67, 4.35 and 6.30 Wm^{-2} were 0.0174 ± 0.00072, 0.0381 ± 0.0039 and 0.0577 ± 0.0027 min^{-1}, respectively. Subsequent analysis using SEM-EDX, TGA and FTIR revealed that the reliability of the immobilised TiO_2/ENR/PVC was however plagued by the

degradation of polymer blend used as adhesives upon recycled applications which resulted in the production of chemical oxygen demand (COD). The degradation of ENR-50 was faster than the elimination of PVC in the coating formulation. 50 % mineralization of 20 mg L^{-1} MB was achieved after 4 hours of photocatalytic treatment using the 'cleaned' immobilised TiO_2. The degree of mineralization corresponded positively with the percentage of MB colour removal. The presence of inorganic compounds such as SO_4^{2-}, NO_3^-, Cl^- and the changes of pH in the treated solution represented the mineralized products of the model pollutants. The immobilised TiO_2/ENR/PVC on polymer supports such as PVC, acrylic and PET exhibited photo-activity in the degradation of MB albeit at lower degradation rate. Overall, the immobilization of TiO_2 powder via this technique is simple, effective, economical and reproducible.

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.0 General

Basically, water pollution can be defined as the contamination of water bodies such as lake, sea, groundwater with various pollutants due to humans activities, which does not only endanger the inhabitants in these water bodies but also the consumers of the water. As of today, water pollution is a major global issue that needs to be addressed seriously, notably in fast developing countries. With the rapid growth of population as well as industries, it is inevitable that the demand for clean water also increases. Nevertheless, due to the escalating numbers of industrial and agricultural activities in most countries, effluents containing intolerable level of both organic and inorganic substances are being discharged into water bodies on a daily basis. Statistically, based on a report done by Malaysia's Department of Environment (DOE) in 2004, out of a record of 17,991 water pollution sources in Malaysia, 54% (8,414) of the sources originated from sewage treatment plant, 38 % (8,203) of the sources initiated from manufacturing industries and 3 % (504) came from agro-based industries [1]. Law enforcements and policy prescriptions on the management of industrial wastewater have long been executed extensively to combat water contamination but concurrently, efficient and cost effective water treatment technologies have to be adopted and developed in order to sustain cleaner water resources for the well-being of all.

Water treatment can be well described as the process of eliminating the presence of contaminants or decreasing the concentration of existing pollutants in water to an acceptable level for the purpose of desired end-use such as for industrial

processes and even as drinking water. Accordingly, an ideal water treatment system should be able to totally mineralize contaminants in polluted water without leaving behind any harmful intermediates or by products. Apart from that, the process should be economically sustainable and possibly, time-saving. Due to the recalcitrant nature of most pollutants, many existing water treatment methods have yet to attain this ideal condition.

Physical-chemical treatments such as coagulation, adsorption, membrane processes and reverse osmosis methods have been employed to a varying extent of effectiveness in removing pollutants from water. Nonetheless, these methods are non-destructive since they merely operate by transferring the pollutant from one phase to another phase or initiate secondary pollution by concentrating the contaminants [2]. This can lead to possible problems since many environmental enforcement agencies may classify the used sludge or adsorbents as harmful materials which require post-treatment. Further treatment of these solid wastes is often considered expensive and sophisticated. On the other hand, destructive wastewater treatment methods such as biological treatment, in both anaerobic and aerobic conditions, have proven to be effective but the presence of toxic organic contaminants can stifle the development of the active microorganisms the consequence of which inevitably reduces their degradation efficiency [3]. The maintenance of these bacteria can also be very costly and complicated. In appropriate situations, the destruction of organic pollutants and solid wastes can also be carried out via incineration but this may lead to the production of hazardous organics such as dioxins and furans [4]. Subsequently, these drawbacks have prompted intensive works on novel water treatment technologies which possess better efficiency and

consume fewer resources. This leads to the study of advanced oxidation processes (AOPs), a water cleaning technology which typically involved the formation of very powerful oxidizing radicals that leads to highly effective oxidation processes.

1.1 Advanced Oxidation Processes (AOPs)

AOPs can be generally defined as one type of water treatment technology that mainly involves the generation of very powerful oxidizing radicals (normally hydroxyl radicals with standard reduction potential, E^o = 2.80V vs. SHE) which can unselectively initiate oxidative dissociation of organics or under certain circumstances, inorganic contaminants in aqueous effluents. Hydroxyl radicals are the most powerful oxidizing species after fluorine which possesses E^o = 3.03 vs. SHE. Contrary to other conventional water treatment method such as adsorption processes, AOPs are capable of converting hazardous materials in wastewater effluents into water and carbon dioxide, or otherwise, into other innocuous by-products. Furthermore, these 'destructive' chemical oxidative processes are able to mineralize wide range of contaminants and this has, in particular prevented the accretion of end-products. Major types of AOPs include the employment of ultra-violet (UV) light, hydrogen peroxide (H_2O_2), ozone (O_3), vacuum (V) and semiconductors such as titanium dioxide (TiO_2) [5]. Major AOPs can be summarized as shown in Figure 1.1.

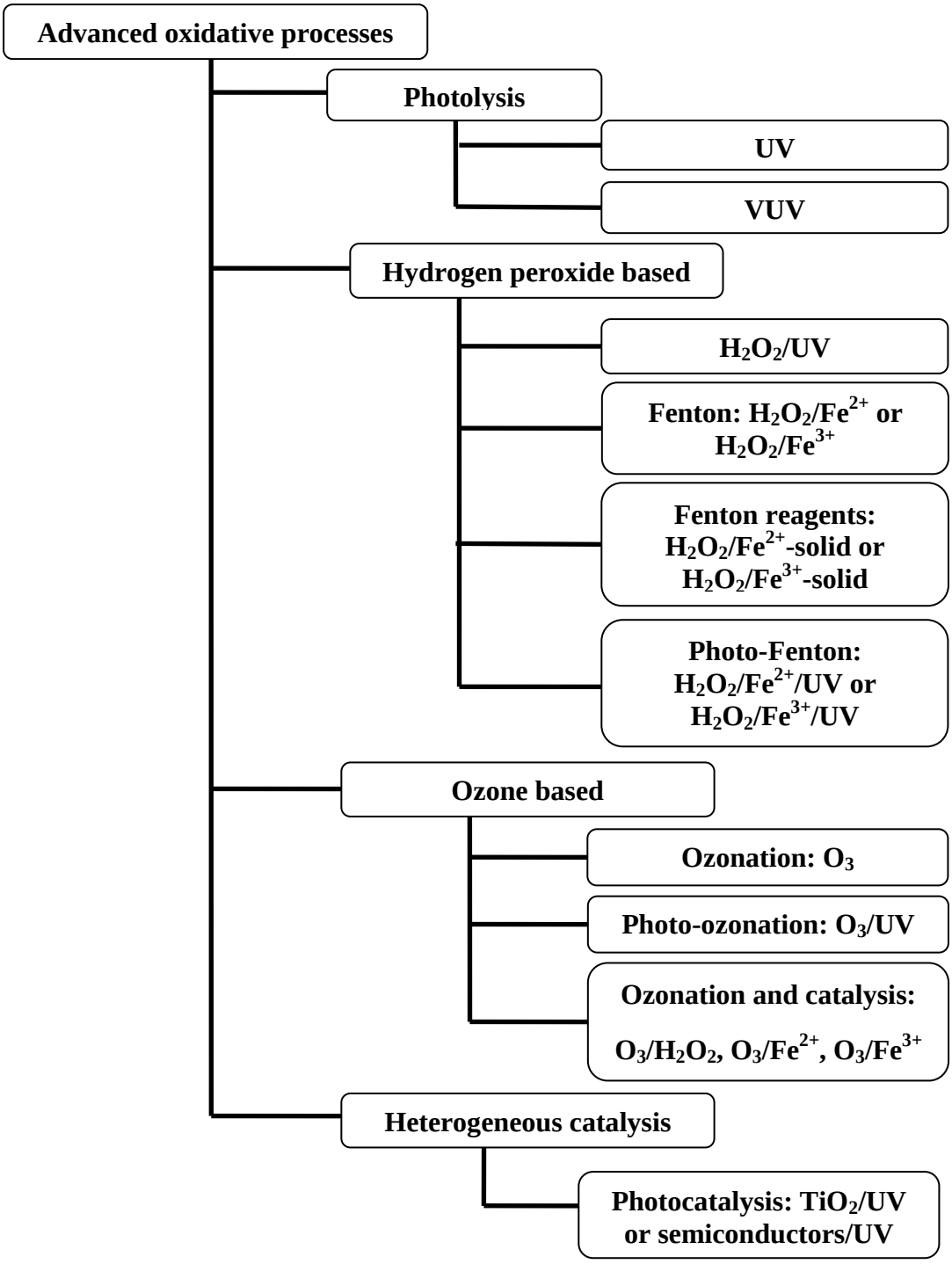

Figure 1.1: Major advanced oxidative processes (AOPs) processes and their various systems [5]

1.1.1 Processes of AOPs

Direct photolysis involves the interaction of UV light with pollutants in water to bring about their dissociation into intermediates which are eventually transformed to harmless by-products in the presence of light. In this process, the organic pollutants undergo absorption of UV light whereby its high energy radiation can result in the breakdown of chemical bonds and consequently, destruction of the organic compounds. Direct photolysis is deemed insufficient and inefficient for the degradation of persistent pollutants such as chlorinated and nitrated aromatics in water [6, 7]. The energy of UV light solely is inadequate to breakdown the chemical bonds of some organic species thus some contaminants are not degraded rapidly or effectively. This was confirmed by comparative studies which had also shown that the practice of direct UV photolysis in degradation of contaminants, namely chlorophenols, azo dyes, diuron and monocrotophos appeared to be less effective compared to other AOPs where irradiation was combined with hydrogen peroxide or ozone, and when homogeneous or heterogeneous catalysis was utilized [8 – 11]. The combination of notably short wavelength UV light with highly reactive chemical species such as hydrogen peroxide and ozone increases the degradation rate by multiple times due to the synergistic effect of efficient generation of hydroxyl radicals and the photon energy from the light.

During the UV based AOPs, organic contaminants are decomposed in two ways. The first way involves the direct photolysis of organic pollutants as mentioned earlier. The addition of H_2O_2 to the process initiates the AOPs conditions by generating $OH^{\cdot}$ radicals. This often increases the destruction rate of pollutants considerably. In another route, H_2O_2 undergoes UV photolysis and a series of

propagation as well as termination reactions to produce $OH^{\cdot}$ radicals. Subsequently, the generated $OH^{\cdot}$ radicals will destroy the contaminants via $OH^{\cdot}$ radical oxidation. Formation of $OH^{\cdot}$ radicals in this process, therefore, determines the degree of pollutants removal. Hence, large dosages of H_2O_2 and long exposure of UV light are required in order to sustain the efficiency of this decontamination method. Another H_2O_2 induced AOPs involves the utilization of Fenton reagents to produce $OH^{\cdot}$ radicals by means of addition of H_2O_2 to Fe^{2+} ions as catalyst. Simultaneously, this also generate Fe^{3+} ions due to the oxidation of Fe^{2+} ions. This process works on the fact that the iron catalyst is very easily acquired and it is a non toxic material. However, this process does not operate on the basis of the sole oxidation reaction only since the adoption of suitable pH value (2.7-2.8) can further catalyzed this reaction by initiating the reduction of Fe^{3+} in order to regenerate Fe^{2+}. The overall reaction is known as the Fenton process. Given that this reversible mechanism occurs at appropriate rate, the decomposition of pollutant via this method can be a sustainable process [12]. Photo assisted Fenton process is an extension of the Fenton process which manipulates the presence of UV light to cause photolysis of Fe^{3+} complexes to allow the reformation of Fe^{2+}. Decontamination of pollutants via H_2O_2 based AOPs however suffers from several drawbacks, namely the usages of expensive reactants such as H_2O_2, the requirement of rigid controlled pH values and the generation of sludge which creates disposal problem.

Another type of AOPs which generates $OH^{\cdot}$ radicals is known as ozonation. This is an oxidation process which the applications have also been tested with the combination of UV light and/or H_2O_2. During ozonation, the dissolved organic contaminants are oxidized directly by O_3 which is a powerful oxidant itself. This is

due to the study that the decomposition of ozone in aqueous solution occurs through the generation of $OH^{\cdot}$, which consecutively oxidize the pollutants. Evidently, when H_2O_2 is added to the ozonation process, the breakdown of O_3 is accelerated with the presence of more $OH^{\cdot}$ radicals. Furthermore, the adoption of UV light into O_3/H_2O_2 system could improve the decontamination rate via photochemical generation of $OH^{\cdot}$ radicals. However, this AOPs process is plagued with the low solubility of O_3 in water and the need of strict pH control since the O_3 decomposition mechanism involves the use of conjugated base [5].

Heterogeneous photocatalysis is another constituent of AOPs which has been studied extensively to decompose refractory compounds in wastewater effluents. This process is a photo-induced reaction that is based on the photocatalytic ability of a semiconductor to produce electron-hole pairs under irradiation which generates free radicals, namely hydroxyl radicals in order to initiate secondary reactions to remove the pollutants. Some of the semiconductors which are normally applied as photocatalyst are TiO_2, ZnO and CdS [2, 6].

1.1.2 Environmental applications of AOPs

In conjunction with insufficient treatment brought by conventional and biological water purification methods, many AOPs induced studies have been carried out in the search of more sustainable water treatment technologies [8 - 10]. AOPs, despite their different pathways of processes, are merged by one similarity which is the presence of the highly reactive species such as the hydroxyl radicals in their overall mechanisms. These reactive radicals would lead to oxidative decompositions

of recalcitrant and non-biodegradable contaminants to harmless by-products or inert end products.

Over the years, apart from the research and development of water and wastewater treatment technologies, AOPs have also initiated other environmental applications such as soil treatment [13], groundwater remediation [14], conditioning of solid sludge [15] as well as treatments of volatile and semi volatile organic compounds [16, 17]. Environmental applications of AOPs on water and wastewater treatment have already been studied on wastewater effluents originated from diverse industries, namely textiles, pharmaceuticals, electronics, cosmetics, plastics, pesticides and so on which contain perilous and less biodegradable compounds such as cyanides, phenols, antibiotics, xenobiotics, ketones, chlorinated compounds, alcohols, aromatic compounds and acetates [18 - 22].

By considering the degree of pollution in effluents and the targeted treatments, AOPs can be applied solely or as feasible supports to the traditional biological and physicochemical treatments methods via combined processes. The combined processes practically offers better treatment results as compared to individual processes due to the synergistic or coupling effect permits by respective methods. Subsequently, AOPs can be engaged either at the pre-treatment stage, in which initial contaminants are converted into biodegradable intermediates ready for biological or physical treatments or at post-treatment level, whereby the ecological content of the pollutants are first removed and/or degraded before being treated by AOPs. As such, investigations on the application of Fenton oxidation process followed by aerobic biological treatment for the remediation of wastewater

containing recalcitrant and persistent compounds such as azo dyes have been documented [23 - 25]. Alternatively, pre-treatment of wastewater from paper industry by customary coagulation-flocculation methods as a preparatory step for subsequent treatment via heterogeneous photocatalysis has been reported [26].

However, amidst various AOPs processes, heterogeneous photocatalysis appears to be more effective and popular due to several advantages. The main advantages of heterogeneous photocatalysis are as the following:

i. Semiconductors for the applications of photocatalysis are easily acquired and relatively inexpensive.
ii. Most of the photocatalysts, especially TiO_2 (anatase) required for this technique are chemically and biologically stable.
iii. Photocatalysts are reusable and many on-going studies are conducted to improve the reproducibility of the catalyst for long term use.
iv. Oxidation processes under heterogeneous photocatalysis are capable of mineralizing wide ranges of persistent pollutants unselectively.
v. Supplementary of expensive oxidants are redundant in this method because atmospheric oxygen from air pump is sufficient to be utilized as oxidant.
vi. This process produces environmental friendly final products or by-products such as CO_2 and H_2O or other mineralized acids.
vii. Water treatment via this method can be operated under the illumination of solar light as the photocatalyst can be stimulated under low energy light sources.

viii. Under heterogeneous photocatalysis, oxidation and reduction can occur simultaneously, and therefore this process does not only have the ability to initiate reactions for the initial pollutants but also has large capabilities in purifying intermediates or by-products which are generated by the process.

1.2 Heterogeneous photocatalysis

1.2.1 Overview

While the subject of heterogeneous photocatalysis for both fundamental and applied perspectives has been immensely investigated, the definition of heterogeneous photocatalysis is still relatively ambiguous due to its rather complicated mechanism and diverse processes. As stated in an article by Herrmann [27], heterogeneous photocatalysis covers a large variety of reactions, namely oxidation, dehydrogenation, hydrogen transfer, isotopic exchange, metal deposition, water remediation, gaseous pollutant control and so on. Heterogeneous photocatalysis has found itself as an emerging AOP for environmental cleanups applications, especially when this fascinating process can be accomplished in various phases such as aqueous solution, pure organic liquid and even in gaseous state.

Similar to the established heterogeneous catalysis, this process mainly engages the migration of reactants in a liquid or a gaseous phase to the surface of the photocatalyst, followed by the adsorption of one or more of the reactants onto the surface and reactions at the adsorbed phase. Subsequently, this process persists on with the desorptions of the reactants and/or products of the reactions and finally, the elimination of products from the interface. The only dissimilarity that separates

heterogeneous photocatalysis from the other conventional catalytic processes is the photocatalytic reaction at the adsorbed stage. The catalyst or rather the photocatalyst in heterogeneous photocatalysis is stimulated via light energy instead of hydro or thermal energy at this stage. The photo activation process only takes place at the adsorbed phase although photoadsorption and photodesorption of reactants may possibly occur [27].

1.2.2 Background

The birth of heterogeneous photocatalysis three decades ago was provoked by Fujishima and Honda's 1972 discovery of photo-induced water splitting on TiO_2 electrodes. Back in late 1960s, the water splitting study was executed with a small electrochemical system in which an n-type TiO_2 semiconductor (rutile) was connected to a platinum black counter electrode through an electrical load. Upon the illumination of the TiO_2 electrode to near UV light ($\lambda < 415$ nm), electrons flowed from TiO_2 electrode to the platinum counter electrode through the external circuit, revealing that an oxidation reaction (oxygen gas evolution) has occurred at the TiO_2 electrode and a reduction reaction (hydrogen gas evolution) has taken place at the platinum electrode. This finding simply proved that water decomposition into oxygen and hydrogen may be possible under the presence of UV-visible light without the application of external electrical supply [28].

Since then, extensive studies had been initiated on the utilization of solar irradiation for the production of hydrogen as fuel source from water. Later, the water splitting study was further investigated without the use of external circuit and this marked the beginning of the phenomenal process by the name of heterogeneous

photocatalysis. Some years later in 1977, researchers Frank and Bard began to examine the possibilities of governing the redox reactions initiated by the illuminated semiconductor TiO_2 for the decomposition of cyanide in water and this has prompted many intensive works on the environmental purposes of heterogeneous photocatalysis until today [29].

1.2.3. Semiconductor mediated heterogeneous photocatalysis

As suggested by its term, 'photocatalysis', this process refers to the chemical transformation reactions initiated by the presence of light energy and catalyst. The catalysts required in this process correspond to semiconductors which are responsive to illuminations of light. Such reactions are due to the particular changes in the monomeric numbers N in the electronic structure of a semiconductor from atomic orbital to clusters. The band electronic structure of a semiconductor consists of the highest filled band (the valence band) and the lowest unfilled band (the conduction band) which are separated by a band gap, E_{bg}, a region depicting energy level in a perfect crystallite form and is normally valued in unit of electronvolts, eV. For the purpose of photo-induced reactions, the activation of a semiconductor photocatalyst can be achieved via the absorption of a photon of ultra-band gap energy, resulting in the transition of an electron, e^- from the valence band to the conduction band with the simultaneous generation of hole, h^+ in the valence band. The photo-generated electron-hole pairs are mainly involved in two processes, namely the reactions with electron donor or acceptors via different interfacial processes and major inhibition process concerning the recombination of electrons and holes. For a semiconductor to be efficient, these two mentioned processes must compete with one another

effectively [30]. These processes can be represented in Equations 1.1, 1.2, 1.3 and 1.4 [31]:

$$\text{Absorption of light} \quad \text{Semiconductor} \xrightarrow{h\nu > E_{bg}} e^-_{cb} + h^+_{vb} \qquad (1.1)$$

$$\text{Recombination} \quad e^-_{cb} + h^+_{vb} \longrightarrow \text{Heat} \qquad (1.2)$$

$$\text{Oxidation} \quad D + h^+ \longrightarrow D^{\cdot +} \qquad (1.3)$$

$$\text{Reduction} \quad A + e^- \longrightarrow A^{\cdot -} \qquad (1.4)$$

As illustrated in Figure 1.2, the valence and conduction band positions of various semiconductors are different. The reactivity of a photo-induced process is very much dependant on the valence and conduction band positions. Therefore, in an oxidation photocatalytic reaction, the redox potential of the photo-generated valence band hole must be adequately positive to generate the highly oxidizing radicals, hydroxyl radicals for the oxidation of pollutants to occur. On the other hand, for a semiconductor to perform as a photocatalyst in a reduction reaction, the redox potential of the photo-generated conduction band must be negative enough to initiate the reduction of molecular oxygen into superoxide. The production of electron-hole pairs are governed by the intensity and the photon energy of the light source used for the activation of a semiconductor.

According to Taghizadeh *et al.* [32], photochemical induced process concerning semiconductors can be divided into two significant categories: (i) the formation of highly reactive radicals resulted from the oxidation of hydroxide ions and reduction of oxygen which would initiate reactions with the pre-adsorbed

substrates at the solution interface and (ii) direct oxidation or reduction of the compounds that diffuse from the batch solution to the semiconductor particle surface.

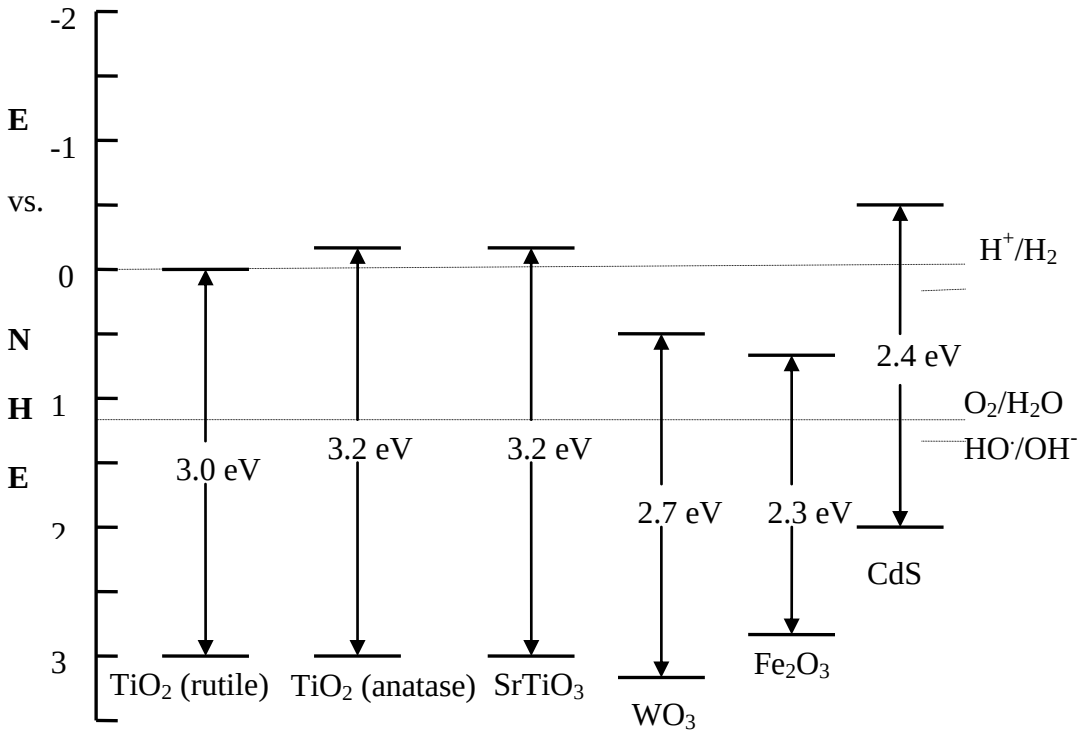

Figure 1.2: Valence and conduction band positions of some the most commonly used semiconductor photocatalysts at pH = 0 [30].

Similarly, in environmental applications, semiconductor photocatalysis essentially involves the irradiation of semiconductors with photon of energies greater than the band-gap energy in order to excite electrons from the valence band to the conduction band, leaving behind the positive holes. The positive valence band gradually generates hydroxyl radicals whereas the negative conduction band initiates the reduction of molecular oxygen or metal ions, which often serves as the oxidizing agent. Hence, the formation of highly oxidizing agents such as hydroxyl and superoxide radicals would attack the contaminants at or near the surface of the

semiconductor photocatalysts, resulting in the detoxification of pollutants via concurrent redox reactions [33]. In photocatalytic water remediation, oxidation reactions are applied to mineralize dissolved organic substances whereas reduction reactions are utilized for the removal of inorganic compounds such as heavy metal ions.

Some of the commercially acquired semiconductors that have been actively researched in photoctalytic studies for environmental cleanup are TiO_2 [29, 34], ZnO [35, 36], ZnS [37], Fe_2O_3 [38], WO_3 [39], CdS [40] and ZrO_2 [41]. In some works, two or more semiconductors are combined and modified with the aim of enhancing the photo-induced reactions [42-44] for better removal of pollutants. Despite of the many other semiconductors, most of the photocatalytic studies are dominated by the application of TiO_2 as the photocatalyst.

1.3 Titanium dioxide (TiO_2)

1.3.1 General

A member of the first transition series metals, titanium has the electronic structure of $3d^2 4s^2$. Discovered in 1791 in England by Reverend William Gregor who recognised the new element in ilmenite, titanium is the world's fourth most abundant metal after aluminium, iron and magnesium and the ninth most abundant element comprising about 0.63 % of the earth's crust. Ilmenite is one of the main ores for titanium and is widely used as a source of titanium metal. Several years later, titanium was rediscovered by a German chemist by the name of Martin Heinrich Klaporth who named the element after the Titans of the Greek mythology. Titanium metal is usually found bounded to other elements in nature. The element occurs

primarily in minerals, especially rutile, ilmenite and leucoxene, and can also be found in rocks, coal, ash, soils and even in human bodies. Titanium commonly appears as impure compounds found in minerals in the form of TiO_2, in which rutile constitutes 93 % to 96 % of TiO_2, ilmenite contains 44 % to 70% of TiO_2 and leucoxene may comprise up to 90 % of TiO_2. Titanium can also appear in the form of titanium tetrachloride ($TiCl_4$) [45].

A metallic element, titanium is usually recognised for its high strength to weight ratio and its excellent resistance to corrosions. Titanium is also a strong metal which has low density and is relatively flexible. The melting point of titanium is 1668 ºC and chemically, titanium is one of the few elements exist that burns in pure nitrogen gas at 800 ºC to form titanium nitride. It is also able to withstand the attack of diluted acids and bases. Titanium dissolves in hot HCI giving Ti (III) chloro complexes and in HF or HNO_3 and HF to form fluoro complexes. Heated in HNO_3 will result in the formation of hydrous oxide [46].

It is estimated that approximately 98 % of the world's titanium production is meant for the refinement into TiO_2, the white permanent pigments, while only the remaining 2 % is used for making titanium metals, rods, fluxes and other products. Due to its two most beneficial features, its resistance to corrosion and strength to weight ratio, titanium is widely applied in chemical industries, aircraft and marine equipments and turbine engines [45].

Titanium dioxide, also known as titanium (IV) oxide or titania, belongs to the family of transition metal oxides. The mass production of TiO_2 began in early 20^{th}

century when TiO_2 started substituting hazardous lead oxides as white pigments in paint. Since then, TiO_2 is utilized actively as white pigments in paint, paper and plastics industries, which make up the major sectors of TiO_2 usages [45]. The applications of TiO_2 as pigments have expanded over the years in some sectors such as textile, food, pharmaceuticals, cosmetics, leather and mixed oxides. Due to its high refractive index, TiO_2 has also found itself as anti-reflection coating in solar cells and in optical devices. Furthermore, TiO_2 is also applied as gas sensors, biomaterials, catalysts, additives, carrier for metal and metal oxides and dielectric materials [45].

On an industrial scale, TiO_2 may be synthesised by either using the sulphate or the chlorine process. Briefly, the sulphate process involves the transformation of ilmenite to metal sulphates after reactions with sulphate acids followed by appropriate steps of hydrolysis, filtration and calcinations according to the desired crystallite forms of TiO_2. On the other hand, the chlorine process employs rutile, which is obtained from ilmenite via Becher process. In Becher process, iron oxide found in ilmenite is reduced to metallic iron and later is reoxidised to iron oxide, unravelling out the TiO_2 as synthetic rutile of 91-93 % purity. Later on, the produced rutile is reacted with chlorine to produce $TiCl_4$, which is purified and reoxidized to yield highly pure TiO_2. Even though both methods are applicable to produce TiO_2, factors such as the accessibility of raw materials, waste management costs, transportation and environment are fairly put into consideration in deciding to use one method instead of the other [45].

1.3.2 Crystal structures of TiO_2

Titanium dioxide has three main polymorphs in nature, namely rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). These three crystallite structures comprise of distorted octahedral (TiO^{6-}_2) that are linked differently by vertices and edges. Anatase can be seen as a zigzag structure in which each octahedron shares four edges with the other four octahedral. As for rutile, two octahedral edges are shared to build linear chains along the direction of 001 plane and the octahedral chains that are connected to one another via vertices shared bonding electrons. In brookite, each octahedron shares three edges and the octahedrals assembly leads to a crystalline structure with tunnels along the *c*-axis [47]. The three crystal structures of TiO_2 are illustrated in Figure 1.3 and their physical properties are summarized in Table 1.1.

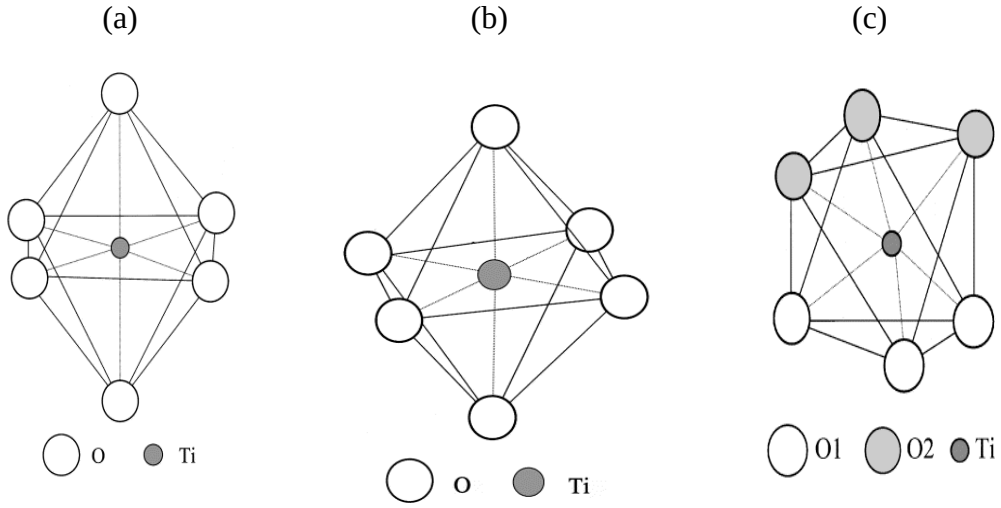

Figure 1.3: The representative crystals structures of (a) anatase, (b) rutile and (c) brookite [48].

Based on thermodynamic calculations, rutile is the most stable of all three crystalline forms of TiO_2 at all temperature and pressure up to 60 Kbar. Anatase and brookite are metastable and are prone to transformation when heated. However, the

slight discrepancy in Gibbs free energy (4-20 KJ/mole) among these three phases shows that anatase and brookite are just as stable as rutile at ambient temperature and pressure [45].

The conversion of anatase to rutile has been studied for mechanical as well as application purposes, especially in photocatalytic driven field, whereby the phase of TiO_2 play a major role in determining the reactivity of the process. At room temperature, anatase is kinetically stable and the phase transition of anatase to rutile occurs during calcinations from 600 ºC to 1100 ºC. The transformation of anatase to rutile is basically due to the increase in pressures and temperatures, in which these two factors are governed by primary particle size as well as the methods, used during preparation [49].

Anatase and rutile phases have been studied most extensively in photocatalytic induced activity whereas another phase of TiO_2, brookite is difficult to prepare and amorphous TiO_2 is not reactive towards light energy [49]. In most photocatalytic studies, however, anatase phase is preferred over the rutile phase because anatase exhibits better electron mobility, lower dielectric constant, less dense and lower deposition temperature which allows the applications of low thermally resistance materials as supports in its immobilisation process.

Table 1.1: Physical properties of anatase, rutile and brookite [45]

Form	Crystal	Space group	Lattice constants (nm)			
			a	*b*	*c*	*c/a*
Anatase	Tetragonal	D^{19}_{4h}- $I4_1/amd$	0.3733	-	0.937	2.51
Rutile	Tetragonal	D^{14}_{4h}-$P4_2/mmm$	0.4584	-	0.2953	0.644
Brookite	Orthorohombic	D^{15}_{2h}-Pbca	0.5436	0.9166	-	0.944

Density (kg m^{-3})		Band gap (eV)	Refractive index	*n*g	*n*p
Anatase	3830	3.26		2.5688	2.6584
Rutile	4240	3.05		2.9467	2.6506
Brookite	4170			2.8090	2.677

Dielectric properties	Frequency (Hz)	Temperature (K)	Dielectric constant
Rutile, perpendicular to optical *c*-axis	10^8	290-295	86
Rutile, parallel to optical *c*-axis	-	290-295	170
Rutile, along *c*-axis	10^7	303	100
Anatase, average	10^4	298	55

1.4 TiO_2 as semiconductor photocatalyst

The application of semiconductor in photocatalysis for water and wastewater treatment technology has attracted attention globally. One of the most crucial factor in determining the effectiveness and efficiency of the pollutants treatment process is the choice of the semiconductor used as the photocatalyst in the treatment system.

The photo-activation of a semiconductor to generate electron-hole pairs for redox reactions is determined by the band gap energy between its valence band and its conduction band. Therefore, the band gap energy is basically used as a benchmark when choosing compatible semiconductors for photocatalytic studies. Table 1.2 depicts the band gap energies of some of the most used photocatalysts and their threshold wavelengths. Although semiconductors with lower band gap energy are

preferred for photocatalysis, especially when solar irradiation is applied, the utilization of semiconductor such as CdS is unfavourable as it is susceptible to photodecomposition. Subsequently, this leads to the leaching of cadmium, a specifically toxic metal itself, into the treated water [31].

Table 1.2: The band positions of some common semiconductors in aqueous solution at pH 1 [31].

Semiconductor	Band gap (eV)	Wavelength (nm)
TiO_2	3.2	380
SnO_2	3.9	318
ZnO	3.2	390
ZnS	3.7	336
WO_2	2.8	443
$CdSi_2$	2.5	491
CdSe	1.7	730
GaAS	1.4	887
GaP	2.3	540

Ideally, a semiconductor photocatalyst must be photoactive, biologically and chemically inert, applicable in visible and/or UV light region, stable towards light, able to unselectively degrade wide ranges of pollutants, easily acquired, easy to handle, inexpensive and does not pose risks or hazards to both environment and humans. Among the available semiconductors, TiO_2 satisfies most of the ideal criteria.

Solar irradiation which contains about 3-5 % UV of wavelength, $\lambda < 380$ nm can be used as a light source to activate TiO_2. The application of sunlight as a light source is encouraged as it is a renewable source of energy. Therefore, this has prompted many works on the modification of TiO_2 to respond to visible light (about 45 % of the solar spectrum) in order to achieve better photocatalytic efficiency under

sunlight [50]. Some of the modification approaches that have been taken are non-metals doping [51-52] and metal oxide mixing [43-44, 50]. Yang *et al.,* [51] synthesised carbon and nitrogen co-doped TiO_2 and found out that due to the increased surface area and optical shift governed by the dopants, the photocatalytic efficiency of the doped catalyst was enhanced as compared with pure TiO_2 under both visible light and UV exposure. In a study conducted by Pavasupree *et al.,* [50], TiO_2-CeO_2 nanopowders with limiting amount of 5 % mol of CeO_2 was produced using modified sol-gel processes and it was observed that the mixed metal oxides demonstrated 2-3 times better photocatalytic activity as compared with pure TiO_2 under visible light.

1.5 General mechanism pathway of TiO_2 photocatalysis

The common process of TiO_2 photocatalysis involves the excitation of an electron from the valence band to the conduction band when it is exposed with UV light ($\lambda < 380$ nm), leaving a hole in the valence band. Detailed mechanism of TiO_2 photocatalysis have been discussed in literatures [27, 34, 53] and summarized here [54]. As TiO_2 is irradiated with light energy of equal or more than its band gap energy (3.2 eV for anatase phase), electrons in conduction band (e^-_{CB}) and holes in valence band (h^+_{VB}) are produced according to Equation 1.5:

$$TiO_2 + h\nu \longrightarrow h^+_{VB} + e^-_{CB} \qquad (1.5)$$

These photo generated species undergo charge transfers with adsorbate such as oxygen, hydroxyl ions or organic substrates on the surface of TiO_2. The charge transfer process is continuous and direct decomposition of the organic substrate is

possible. The trapping of the electrons at the conduction band by charge carriers is faster (100 ps) than the trapping of the hole (10 ns) [53]. The trapped holes react with the surrounding water molecules or hydroxyl ions, leading to the formation of highly reactive radicals, namely hydroxyl radical ·OH. The holes may also initiate direct oxidization of the contaminating species (R). These processes are shown in Equations 1.6, 1.7 and 1.8:

$$h^+_{VB} + H_2O \longrightarrow {}^{\bullet}OH + H^+ \quad (1.6)$$

$$h^+_{VB} + OH^- \longrightarrow {}^{\cdot}OH_{ad} \quad (1.7)$$

$$h^+_{VB} + R_{ads} \longrightarrow R^+ \quad (1.8)$$

The excited electrons react with electron acceptors such as the oxygen adsorbed or dissolved in the water as represented in Equation 1.9:

$$e^-_{CB} + O_2 \longrightarrow O^{\cdot}{}_2^- \quad (1.9)$$

It is believed that the hydroxyl radicals (·OH) and superoxide radical anions ($O^{\cdot}{}_2^-$) are the major oxidizing agents in the photocatalytic reactions [54-55]. Some other oxidizing species that may be produced are reported as H_2O_2 and $HOO^{\cdot}$ [56]. Without the presence of electron acceptors and donors, there is also a possibility that the electrons and holes may recombine either on surface or in the bulk of TiO_2, as shown in Equation 1.10:

$$e^-_{CB} + h^+_{VB} \longrightarrow TiO_2 \quad (1.10)$$

These processes can be illustrated as in Figure 1.4.

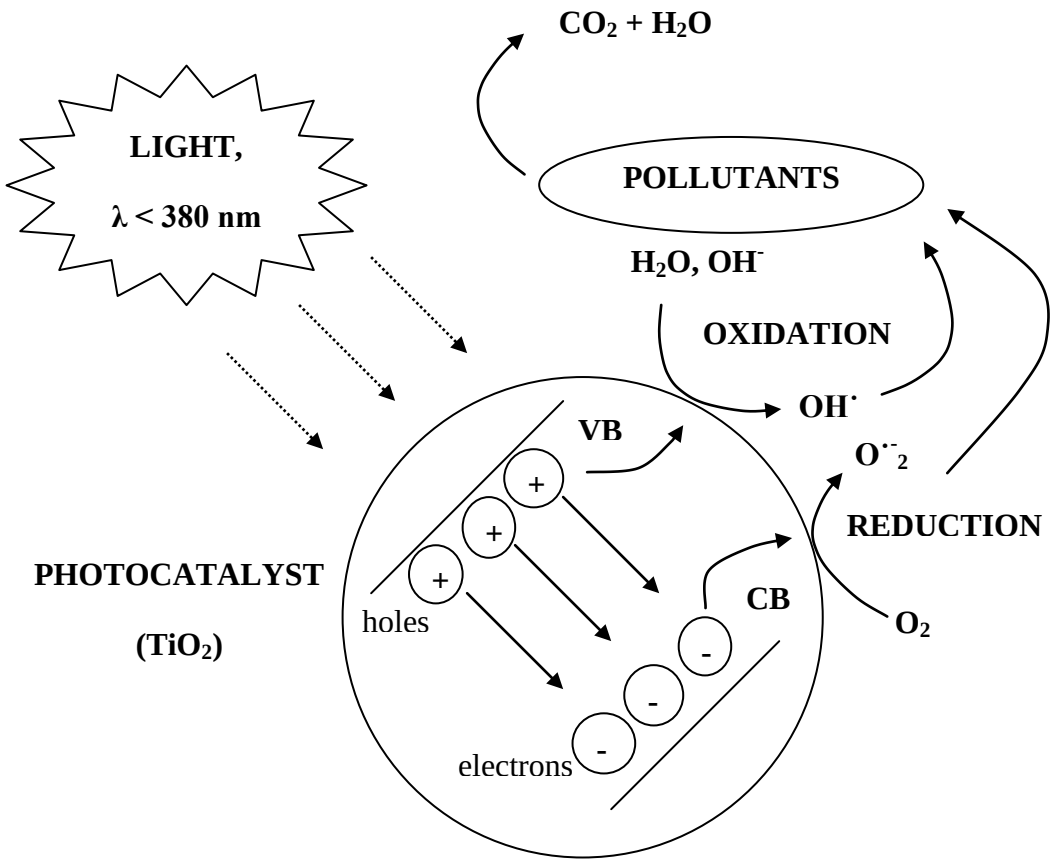

Figure 1.4: General mechanism pathway of TiO_2 photocatalysis [54].

1.6 Langmuir-Hinshelwood process

Direct photocatalytic reactions pathway discussed earlier in Section 1.5 can be well described as the Langmuir-Hinshelwood process. This process follows the formation of electrons and holes upon the photo excitation of a catalyst. As explained previously, the hole is trapped by the adsorbed substrates and subsequently generates highly reactive radicals. This reactive species then decays via two ways, namely recombination with the photo generated electrons or undergo chemical reactions,

yielding the product of the reactions. This process can be accessed and evaluated quantitatively using the Langmuir-Hinshelwood kinetic model [5].

Initially studied for the quantification of gaseous-solid reactions, the Langmuir-Hinshelwood kinetic model is presently used to describe the reactions between liquid and solids. Based on this kinetic model, the rate of the reaction corresponds linearly with the portion of surface (r) covered by the substrate (Θ) as shown in the following Equation 1.11 (adapted from Valente *et al.*, [57]):

$$r = \mathrm{d}C/\mathrm{d}t = \mathrm{k}\Theta \tag{1.11}$$

Langmuir's model that ascertains adsorption on solid substrate can be described as in Equation 1.12. Therefore the previous Equation 1.11 becomes proportional to the Equation 1.13:

$$\Theta = KC / (1+KC) \tag{1.12}$$

$$r = \mathrm{d}C/\mathrm{d}t = \mathrm{k}\Theta = \mathrm{k}KC / (1+KC) \tag{1.13}$$

In Equation 1.13, k is the true rate constant which covers a number of operational parameters such as mass transfer, aeration rate and so on, whereas K is the constant of adsorption equilibrium in Langmuir-Hinshelwood. For photocatalytic studies, the value K is attained empirically through kinetic study in the presence of light and is better than that obtained during adsorption studies. C is the concentration of the substrate at time t.