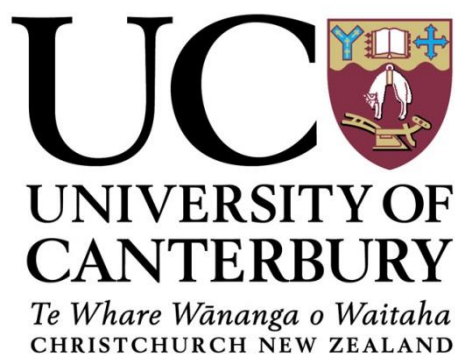


Towards new generation of sustainable catalysts: Study of shape and size controlled TiO₂ nanoparticles in photocatalytic degradation of industrial dye

*Thesis submitted in partial fulfillment of the requirements for the Degree of
Doctor of Philosophy*

By

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Chapter 1

Introduction

1.1 Background

Due to industrialization and population growth, environmental contamination caused by organic pollutants is becoming an increasing problem worldwide. Environmental pollution on a global scale, particularly water pollution, has drawn scientists' attention to the vital need for environmentally clean and friendly chemical processes. The demand for higher quality water has increased due to population growth, more stringent health regulations and economic development.¹⁻³ Untreated wastewater contains a variety of organic compounds with variable toxicities as well as carcinogenic and mutagenic properties. Most contaminants in wastewater contain aromatic rings, which are generally resistant to chemicals, photochemicals and biological degradation. These compounds are very persistent in the environment and have a high potential to negatively affect human health and the ecosystem. Therefore, the removal or degradation of hazardous material and contaminants from wastewater is a significant global challenge.

Among various industries, the textile industry ranks first in the usage of dyes for fibre colouration. In addition, textile activities are constantly expanding, thus leading to the high potential for pollutants.⁴ Pollution created by the textile industry attracts significant attention due to the consumption of large volumes of water and chemicals during wet textile processing.⁵⁻⁷ The chemical reagents used are very diverse in chemical composition, ranging from inorganic compounds to polymer and organic products.⁸ These reagents include different colouring agents such as dyes, inorganic pigments, tannins and lignins, which impart colours.⁹ In all, 10,000 different textile dyes are commercially available worldwide, with an approximate annual production of 7×10^5 metric tonnes.^{10, 11} Of these dyes, 30% are used in excess of 1000 tonnes per annum, and 90% of the textile products are used at the level of 100 tonnes per annum or less.¹²⁻¹⁴ The presence of even a very low concentration of dye in the effluent is highly visible and undesirable¹⁵ because the dyes and their breakdown products are toxic, carcinogenic or mutagenic to lifeforms, mainly due to carcinogens such as benzidine, naphthalene and other aromatic compounds.

Although the textile industry is required to minimize the release of chemicals resulting from the dying process, the presence of coloured discharge in wastewater cannot be eliminated. In general, wastewater treatments applied to overcome this problem include chemical oxidation, sorption, photo-oxidation and a combination of these treatments, as well as an activated sludge-type biological oxidation process.¹² Unfortunately, these methods are plagued with secondary problems. The most conventional treatment method for textile wastewater is biological activated sludge treatment, which sometimes accompanies the coagulation-flocculation process.¹² Even

though this biological treatment is very beneficial because of its low cost and simplicity, it is generally not an effective method, especially when dealing with synthetic dyes, due to its resistance to aerobic bio-degradation.^{16, 17} The toxicity of target pollutants and their intermediates, as well as extreme experimental conditions, can also be lethal to the microorganisms intended to degrade the pollutants.¹⁸

Physical treatments, such as coagulation and flocculation, suffer from the high operational costs related to the post-treatment of solid and coagulated waste.^{17, 19-21} In addition, chemical treatments also have some drawbacks, including the production of toxic and carcinogenic by-products, the high dosage of chemicals required throughout the process, low efficiency and incomplete mineralization.^{16, 22} Selected wastewater treatment methods for removing dye and colourant from industrial wastewater are summarized in **Table 1.1**^{9, 12, 13} Since all the current systems have limitations, the development of a significantly improved wastewater treatment method is of paramount importance to the textile industry's long-term environmental viability. The most successful methods for removing colour generally involve the oxidative degradation of dyes. These methods are collectively known as advance oxidation processes (AOPs).

The rationales of the AOPs are based on the in-situ generated of highly reactive transitory species (i.e H_2O_2 , $\text{OH}\cdot$, $\text{O}_2\cdot^-$, O_3) for mineralization of organic compounds, water pathogens and disinfection by-products.^{23, 24} The motivation behind this study originates from the vast number of research and development in the AOP in general and TiO_2 -based photocatalyst in particular in the past three decades. This chapter briefly describe the photocatalysis and the mechanism of photocatalytic process. Since many applications of TiO_2 nanomaterials are closely related to their optical properties, this

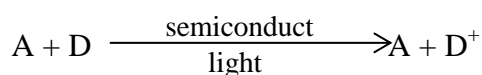
chapter also present a section on the challenges and issues with possible solutions related with modification of TiO_2 . Lastly, this chapter also discussed on the targeted pollution that is being used throughout the study.

Table 1.1: The advantages and disadvantages of wastewater treatment methods.²⁵⁻³²

Wastewater treatment method	Advantages	Limitations
Precipitation, coagulation-flocculation	Short detention time and low cost; relatively good removal efficiency	Agglomerates separation and post-treatment
Electrokinetic coagulation	Cost-efficient	High sludge production
Fenton process	Effective for soluble and insoluble coloured contaminants	High sludge production
Ozonation	Effective for azo dye removal	Not suitable for dispersed dye and short half-life of ozone
Photochemical process	No sludge production	By-product formation
Electrochemical oxidation	No additional chemicals needed	Not cost-effective; very high costs for electricity
Ion exchange	Regeneration with low loss of adsorbents	Not effective for all types of dye
Aerobic process	Partial or complete decolourization of all types of dye	Expensive treatment
Fungal, algae or bacterial	Good removal efficiency for low volume and low concentration of dye	Not cost-effective for culture maintenance
Membrane filtration	Removal of all types of dye	High running cost; concentrated sludge production; dissolved solids are not separated in this process
Enzymatic treatment	Effective for specific compounds	Not cost effective; time-consuming in enzyme isolation and purification

1.1.1 Definition

The initial interest in photocatalysis was generated by the discovery of the “Honda-Fujishima Effect” in the early 1970s.³³ In general, the term ‘photocatalysis’ can be defined as the acceleration of a photoreaction in the presence of catalyst activated by light.³⁴ The overall process of semiconductor photoreactions can be summarized as follows:



Equation 1.1

As an AOP, heterogeneous photocatalysis is more favourable in wastewater treatment compared to the homogeneous system due to the ease of catalyst removal after the reaction.³⁴

1.1.2 Principle of semiconductor photocatalyst

A semiconductor is a material with electric resistivity between an insulator and a conductor. It is usually characterized by an electronic band structure in which the highest occupied energy band, the valence band (VB), and the lowest empty band, the conduction band (CB), are separated by a band gap.³ The activation of the semiconductor photocatalyst is achieved through the adsorption of a photon light corresponding to the band gap energy, which results in the excitation of electrons in the valence band towards the conduction band thus leaving behind holes in the valence band.³⁴ The activation of

the semiconductor photocatalyst is achieved through the adsorption of a photon light corresponding to the band gap energy, which results in the excitation of electrons in the valence band towards the conduction band thus leaving behind holes in the valence band.³⁴ Basically, when an energy photon higher or equal to the band gap is absorbed by the semiconductor particles, an electron (e^-) from the VB is promoted to the CB with simultaneous generation of positive holes (h^+) in the VB (see **Figure 1.1**).

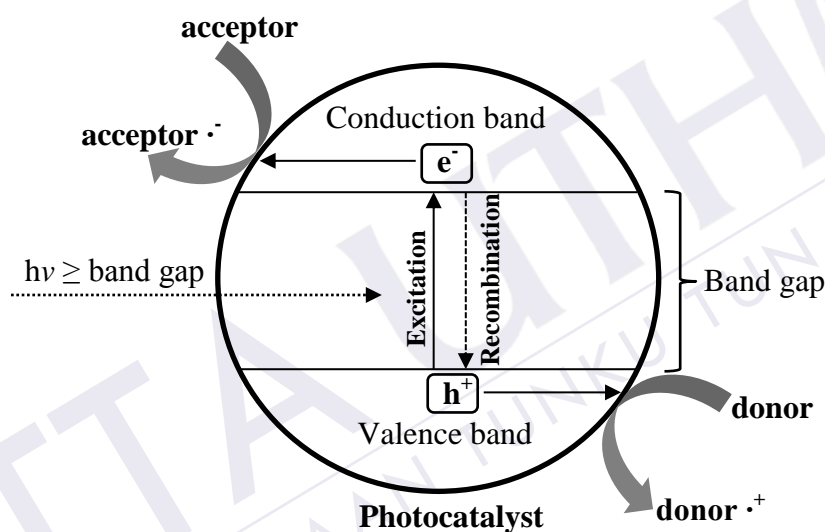


Figure 1.1: Schematic illustration of the photoinduced holes and electrons over photon activated semiconductor photocatalyst.

The e^- and the h^+ can recombine on the surface, or bulk, of the particles or can be trapped in surface states where they can react with an electron donor (such as an organic molecule or OH^- groups) or an electron acceptor (such as oxygen molecules or H^+) adsorbed or close to the surface of the particles. The primary criteria for photocatalyst to be efficient is that the different interfacial electron processes involving electrons and holes must compete effectively with the major deactivation process involving electron-hole recombination. Moreover, the use of a semiconductor as a photocatalyst depends

upon its ease of production and use, cost-effectiveness, photo stability, non-toxicity for human beings and the environment, effective activation through solar light and ability to catalyse the reaction effectively.³⁵

A photocatalyst is characterized by its capability to adsorbed simultaneously two reactants, which can be reduced and oxidized by a photonic activation through an efficient absorption ($h\nu \geq E_g$). Various semiconductors with different band gaps energies such as TiO_2 , ZnO , GaP , CdS and etc has been used in literature (**Figure 1.2**)³⁶. They are used in photocatalysis because of the favourable combination of electronic structure, light absorption properties, charge transport characteristic and excited state lifetime.³⁷ The surface area and the number of active sites offers by the photocatalyst for the adsorption of pollutant, plays an important role in deciding the overall rates of degradation.^{30, 38}

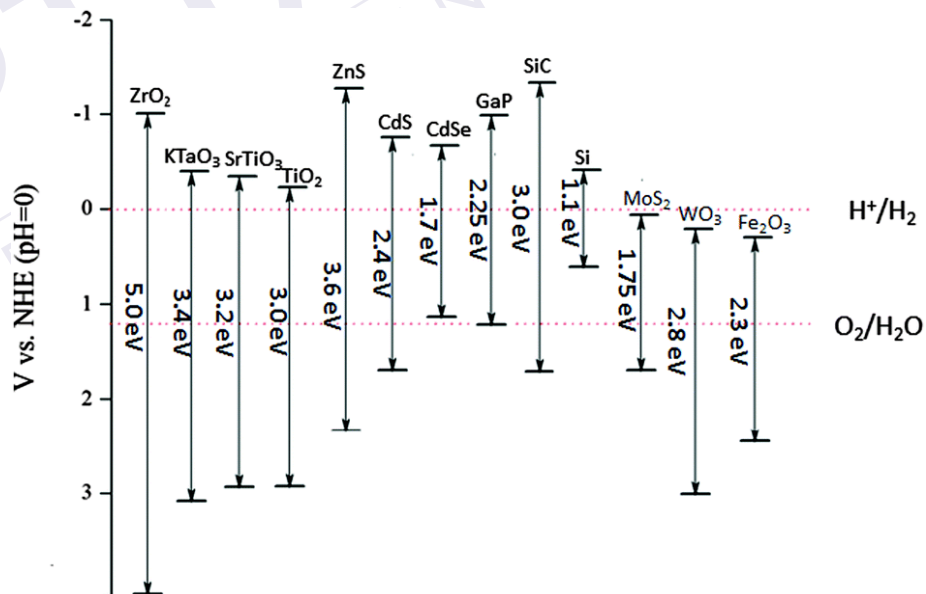


Figure 1.2: Diagram of band gap and band edges (CB bottom and VB top) of some wide bandgap semiconductors.

1.2 Titanium dioxide (TiO₂)

1.2.1 Background

Titanium dioxide (TiO₂) belongs to the family of transition metal oxides and is used widely in technology.³⁹⁻⁴¹ It is chemically and biologically inert, photocatalytically and thermally stable, has high photoconductivity, and is relatively easy to produce and use.³⁴ TiO₂-based nanomaterial had been broadly studied as the most promising photocatalyst for environmental remediation such as air purification, water purification, heavy metal degradation and hazardous remediation.⁴²⁻⁴⁷

Table 1.2: The development of TiO₂ in photoactivated processes.

Year	Reference	Remarks
1972	Fujishima and Honda ³³	The first photochemical cell for water splitting ($2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$) using a rutile TiO ₂ photoanode and Pt counter electrode
1977	Frank and Bard ^{48, 49}	The first implication of TiO ₂ in environmental purification in the reduction of CN ⁻ in water
1977	Schrauzer and Guth ⁵⁰	The photocatalytic reduction of molecular nitrogen to ammonia over iron-doped TiO ₂
1983	Pruden and Ollis ⁵¹	Implementation of semiconductor –sensitized reactions for organic pollutant oxidative mineralization
1985	Matsunaga <i>et. al.</i> ⁵²	The application of TiO ₂ as a microbiocide which is effective in photo killing of <i>Lactobacillus acidophilus</i> , <i>saccharomyces cerevisiae</i> and <i>Escherichia coli</i>
1991	O'Regan and Gratzel ⁵³	Reported the efficiency of a solar cell using nanosize TiO ₂ particles

TiO₂ is of special interest science it can be use natural (solar) UV light because it has an appropriate energetic separation between its valance and conduction band (**Figure**

1.2) which can be surpassed by the energy content of a solar photon ($390 \text{ nm} > \lambda > 300 \text{ nm}$).⁵⁴ Some major cornerstones in the development of TiO_2 in photoactivated processes are presented in **Table 1.2**.

1.2.2 *Properties of TiO_2 semiconductor*

The crystalline structure and size of TiO_2 has been reported as two factors affecting its performance.⁵⁵⁻⁵⁷ It is interesting to note that TiO_2 exists in three commonly known polymorphs: anatase, rutile and brookite. In general, rutile is the most thermodynamically stable and common form of TiO_2 at most temperatures and pressures.⁵⁸ It is formed by edge sharing in octahedra to form long chains, while anatase is predominantly composed by point sharing in octahedra. Brookite, on the other hand, is formed by a combination of edge sharing and point sharing. Upon heating concomitant to coarsening, the anatase and brookite forms of TiO_2 tend to convert to the rutile form.^{3, 40, 41} Of these three TiO_2 phases, anatase and rutile (see **Figure 1.3**⁵⁹) are the most studied phases for photocatalytic applications.⁶⁰

Brookite has a major drawback in photocatalytic applications because it is often difficult to synthesize reliably⁵⁷ and is generally photocatalytically inactive.^{61, 62} Although rutile has a lower band gap (3.0 eV) compared to anatase and brookite, the performance of rutile as a photocatalyst is generally poor.^{58, 63} The low photocatalytic activity in the rutile phase of TiO_2 is believed to be due to the poor light absorption of this type of TiO_2 near the UV region.⁶⁰

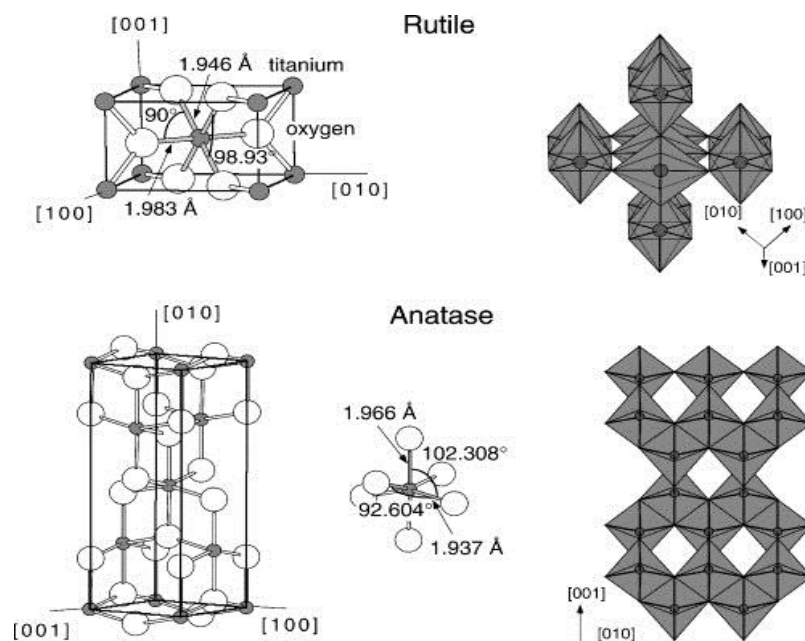


Figure 1.3: Basic crystalline structure of anatase and rutile TiO_2 .

Furthermore, the conduction and VB edges in rutile are not as advantageously positioned as in anatase.⁶⁰ Anatase, on the other hand, is preferred over the other phases for photocatalytic applications^{62, 64, 65} because of its higher electron mobility, low dielectric constant, lower density, lower capacity to adsorbed oxygen and higher degree of hydroxylation compared to rutile and brookite^{58, 66}

1.2.2.1 *Mixed-phase TiO_2*

The photocatalytic activity performance of anatase and rutile TiO_2 has widely been discussed in literature. Observation of comparable reactivity on anatase and rutile TiO_2 nanoparticles point to greater need for understanding how issues such as morphology,⁶⁷ surface structure and surface chemistry,^{68, 69} the properties of the targeted

molecules⁷⁰ and the overall mechanistic details of a photocatalytic reactions^{71, 72} play their roles when comparing inherent photoactivities of anatase and rutile TiO₂. It is becoming apparent that mixed-phase TiO₂ shows interesting properties as compared to single phase TiO₂.⁷³⁻⁷⁹ The widely acknowledge exceptional photoactivity of Degussa P25^{62, 80-88} is frequently attributed to a cooperative effect between its composite mixture of ~ 75% anatase and ~ 25% rutile. The enhancement in photocatalytic activity of P25 and other anatase and rutile mixture is generally reported to be due to the interfacial properties between anatase and rutile TiO₂.^{80, 81, 89-93} Chemical contact between particles of these phases has been shown to be necessary to obtain an enhancement from mixed-phase TiO₂.^{88, 93, 94} A widely held explanation of the need for anatase-rutile contact relates to their relative band edge position. Due to the different band gap values for anatase rutile (3.2 eV and 3.0 eV respectively), there exist the possibilities for the formation of a heterojunction between the two in which electron transfer can occur.^{75, 80, 89, 91, 92, 95-97} Hence, anatase-rutile interface can potentially facilitate charge separation. Further, literature also reported that after Fermi level alignment, the conduction band (CB) edge of rutile should be lower than that of anatase, resulting a favourable condition for electron transfer from anatase to rutile.^{78, 89, 91, 95, 96, 98}

Manipulation of the anatase-rutile ratio has been shown to vary the degree of enhancement in the mixed-phase TiO₂. The “optimal” rutile TiO₂ content for mixed-phase TiO₂ reported in literature varied over a wide range, from < 10% up to > 70% depending on the preparation method and the photocatalytic reaction of interest.^{73, 79, 92, 93, 99-101} Method for differing the ratio of rutile-anatase mixture differs, including the use of

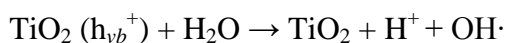
controlled sol-gel growth,¹⁰¹ etching of one phase relative to the other,^{96, 102} or thermal processing through the anatase to rutile phase transformation.^{73, 79, 92, 103-105} The anatase to rutile phase transition starts at the surface of anatase particles^{106, 107} or at anatase-anatase interface^{108, 109} at temperature above ~850 K.^{108, 110-112}

1.2.3 *TiO₂ in photocatalysis*

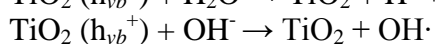
TiO₂ is considered a benchmark semiconductor for photocatalysis because it is the most efficient and photocatalytically active photocatalyst compared to other semiconductors. Its hydroxyl radicals, a strong oxidizing agent are capable of degrading organic pollutants (such as dyes, polymers, pesticides, etc.) present at or near the surface of TiO₂, which usually results in their complete mineralization into H₂O and CO₂ through irradiation with UV light.^{34, 58, 113, 114}

TiO₂ possesses a quantum mechanical forbidden energy region called band gap (E_{BG}) extending from the top of the valance band (VB) to the bottom of the conduction band (CB). TiO₂ photocatalytic activity is due to the production of an excited electron-hole pair when the material is exposed to UV light. The UV radiation leads to a charge separation due to the excitation of electron (e⁻) from the VB towards the TiO₂ CB, thus simultaneously forming holes (h⁺) in the VB. The photoinduced holes in the VB will eventually diffuse to the TiO₂ surface and react with adsorbed water molecules or hydroxide ions (OH⁻) in the aqueous solution to produce hydroxyl radicals (OH[•]). Meanwhile, electrons in the CB typically participate in the reduction process; they react

with dissolved oxygen molecules to produce various species such as superoxide radicals ($O_2^{\cdot-}$), hydroperoxyl radicals ($HOO^{\cdot-}$), hydrogen peroxide (H_2O_2) and OH^{\cdot} radicals. Such oxygen-containing species can be photocatalytically active during the mineralization of organic contaminants. Akapan *et al.* reported that these radicals will readily oxidize most azo dyes.¹¹⁵ Reactions relevant to the photodegradation of organic dyes on the surface of TiO_2 are shown in **Equation 1.2** through **Equation 1.8**.²¹



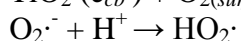
Equation 1.2



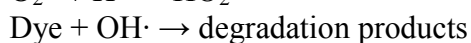
Equation 1.3



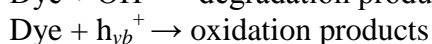
Equation 1.4



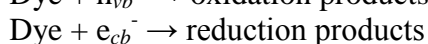
Equation 1.5



Equation 1.6



Equation 1.7



Equation 1.8

Among many other semiconductors, there is a general consensus among researchers that TiO_2 is more superior. Okaomoto *et al.* observed the greater photocatalytic activity for TiO_2 compared to CdS catalyst for the decomposition of phenol as target organic species.^{116, 117} Sakthivel *et al.* reported that under similar study conditions, TiO_2 had greater photocatalytic efficiency than $\alpha\text{-Fe}_2\text{O}_3$, ZrO_2 , CdS , WO_3 , and SnO_2 .¹¹⁸ However, Augugliaro *et al.* Indicates that although ZnO had a lower surface area compared to TiO_2 , it gives a higher activity. It was also reported in the same study that the TiO_2 was photochemically more stable in aqueous media compared to ZnO .¹¹⁹ Further, Wu also observe higher photocatalytic activity for TiO_2 compared to ZnO and SnO_2 .¹²⁰

1.2.4 Drawbacks of TiO_2 as a photocatalyst

Although TiO_2 has some advantages that make it an excellent photocatalyst, it has some unattractive properties that impede its efficiency as a photocatalyst. First, TiO_2 has a large band gap (~ 3.2 eV) and thus absorbs only a small portion (5–7%) of the solar spectrum in the UV region, thus leading to a low degradation rate and quantum efficiency.^{34, 121, 122} In addition, the use of a high-energy UV light or a strong oxidant can cause serious hazards to human beings and is expensive. Therefore, by sufficiently decreasing the band gap so the catalyst can absorb visible light, it may be possible to utilize up to 40% of the solar spectrum.¹²³ Second, photoexcitation causes the formation of a region of positive charge density (hole) created by the removal of an electron from a site can cause a drop in photocatalytic activity of TiO_2 . The recombination process (the drop of electron into its original molecular orbital) to fill this hole is not desired in photocatalysis. The charge recombination in bulk and in surface defects can severely limit the photocatalytic activity of the material.^{121, 124-126} These drawbacks restrict the large-scale applications of TiO_2 .

Therefore, it is necessary to modify TiO_2 to improve its photocatalytic performance. In recent years, extensive research has focused on addressing the above-mentioned problems. There has been great interest in modifying TiO_2 to shift the band gap into the visible light region and/or to prevent the recombination of photogenerated electron-hole pairs using various methods, which will be discussed later in this chapter.¹²⁶⁻¹²⁸

1.3 *Modification of TiO₂ photocatalytic activity*

The improvement of the photocatalytic activity of TiO₂ is one of the most important aspect of heterogeneous photocatalysis. TiO₂ generally possesses numerous surface and bulk defect. These defect can behave as a recombination centre for the photoinduced electron-hole pairs and result in a decrease of photocatalytic activity.¹²⁹ Therefore, a highly crystalline samples with low number of defects suppresses electron-hole recombination and consequently increases their availability to react with species adsorbed on its surface. Further, the anatase phase is photocatalytically more active than rutile as explained earlier in this chapter. Hence, proper control of thermal treatment conditions leading to high crystallinity of anatase phase is crucial to obtain high photocatalytic activity.

Photocatalytic activity of TiO₂ can be enhanced by controlling the size of TiO₂ particles.⁴⁴ Small particle size may provide a relatively small migration distance for charge carrier to reach the surface where they can react with adsorbed species. The decrease in particle size also plays an important role in modifying the band gap as well as other physical and chemical properties of TiO₂.⁴⁴

A wide range of approaches has been conducted to enhance the photocatalytic efficiency of TiO₂. This can be achieved by morphological modification, such as increasing the surface area and porosity, or by chemical modification, such as incorporating additional components in the TiO₂ structure to shift the response and

increase the sensitivity of TiO₂ towards the visible light region and/or increase the lifetime of the photoinduced electron-hole pairs.¹²¹

1.3.1 Doping

Attempts to improve the performance of TiO₂ as a photocatalyst under UV illumination and extend its light absorption and conversion capacity into the visible portion of the solar spectrum have primarily concentrated on promoting it with foreign species. Doping is a commonly used method to narrow the band gap and change the electronic properties of TiO₂. TiO₂ is doped by loading other organic or inorganic components into the bulk material, thus modifying its optical activity. The literature has reported that TiO₂ doping can be achieved using metal³ or non-metal substances.^{3, 130-133} Doping with non-metal substances tends to raise the VB maximum energy level because most non-metallic dopants are less electronegative than oxygen. On the other hand, dopants with metallic elements tend to lower the CB minimum energy level because most metals used in doping are more electronegative than titanium. Noble metal dopants may also act as sinks for the photogenerated charge carriers and may support interfacial charge-transfer processes, thus inhibiting electron-hole recombination.⁶²

The electronic characteristic found in TiO₂ is modified by creating a small band (mid-gap state) within the band gap (see **Figure 1.4**). This state allows the material to absorb energy $E_{\gamma} < E_{BG}$ by exciting electrons from the VB to the mid-gap state (if it lies above the Fermi level) or from the mid-gap state to the CB (if it lies below the Fermi level).

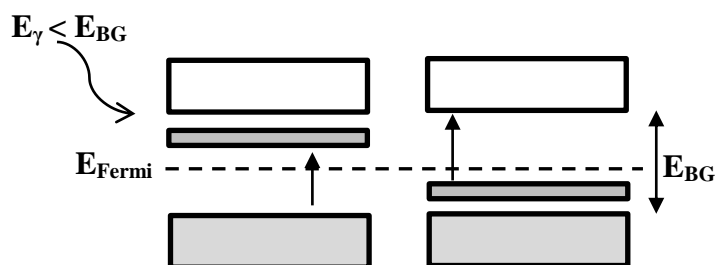


Figure 1.4: The addition of dopants can improve the photoresponse of the semiconductor by introducing the mid-gap state.

When this method is employed, the chemical composition of TiO_2 can be altered by replacing the cations (Ti^{4+}) with other transition metals or the anions (O^{2-}) with other anions. These changes affect not only the material's electronic properties but also its thermal stability.¹³⁴ The literature has reported attempts to improve the photoresponse of TiO_2 by cationic doping with alkaline metal,^{58, 135, 136} transition metal,^{58, 137-141} post-transition metal¹⁴² and noble metal.^{58, 143} Unfortunately, these types of doping have some drawbacks, including thermal instability and a high recombination rate.¹⁴⁴⁻¹⁴⁶ In contrast, Karakitsou and Verykios reported that TiO_2 photoreactivity can be enhanced by doping with cations of valency higher than that of Ti^{4+} .¹⁴⁷

A considerable amount of literature has reported on anionic TiO_2 doping. Although the visible light response of anion-doped TiO_2 was reported as early as 1986 by Sato,¹⁴⁸ recent work by Asahi *et al.*¹⁴⁴ reignited interest in this system. Few innovative preparation methods have been discussed in the recent literature for nitrogen-,^{144, 145, 149-152} phosphorus-,¹⁵³⁻¹⁵⁵ sulphur-,^{149, 156-158} iodine-,^{159, 160} fluorine-^{156, 161, 162} and chlorine-doped¹³⁵ TiO_2 catalysts. Among other anionic dopants, nitrogen doping is the most popular dopant, especially for enhancing the photocatalytic activity of TiO_2 . A summary of photocatalytic activity studies on N-doped TiO_2 is presented in **Table 1.3**.

Table 1.3: Previous studies on photodegradation activity of N-doped TiO₂.

Reference	Application
Gole <i>et al.</i> ¹⁶³ Sathish <i>et al.</i> ¹⁶⁴ Chen <i>et al.</i> ¹⁶⁵ Sathish <i>et al.</i> ¹⁶⁶	Photocatalytic degradation of methylene blue using different types of N-doped TiO ₂
Naik <i>et al.</i> ¹⁶⁷	
Yang <i>et al.</i> ¹⁶⁸	
Peng <i>et al.</i> ¹⁶⁹	
Kitano <i>et al.</i> ¹⁷⁰	
Huang <i>et al.</i> ¹⁷¹ Shang <i>et al.</i> ¹⁷² Buzby <i>et al.</i> ¹⁷³	Photocatalytic degradation of 2-chlorophenol
Wang <i>et al.</i> ¹⁷⁴	
Asahi <i>et al.</i> ¹⁴⁴	Photocatalytic degradation of phenol Photocatalytic decomposition of acetaldehyde

While the introduction of dopants may increase the photoresponse of the material, it also introduces a bulk defect, which encourages electron-hole recombination.¹⁷⁵ It is generally observed that photoactivities increases with dopant concentration to a given point, after which activity decreases due to excessive recombination.^{58, 126, 176}

1.3.2 Dye sensitization and noble metal deposition

The photoassisted catalytic decomposition of organic pollutants in water and wastewater employing semiconductors as photocatalyst is a promising method.^{34, 63}

Although TiO₂ has positive attributes, a few drawbacks^{177, 178} are associated with it, as discussed earlier in this chapter. Therefore, in order to circumvent these limitations, a number of strategies have been proposed. The literature has reported that surface derivatization of TiO₂ with a number of organic dyes extends the sensitivity of TiO₂ in the visible region¹⁷⁹ through the injection of electrons from an excited level of the dye

into the semiconductor band. Photocatalytic TiO_2 activity can also be enhanced by loading noble metals on the surface of the semiconductor. Many investigators have demonstrated that enhanced photocatalytic activity is made possible by impregnating depositing a noble metal on the TiO_2 surface.

1.3.2.1 Dye sensitization

Modifying TiO_2 with dye is an interesting research area because dye is capable of absorbing visible light as a photosensitizer for transferring energy to TiO_2 or O_2 . Thus, this makes the reaction mixture more sensitive to light and therefore promotes the degradation efficiency of pollutants.¹⁸⁰ This process of transferring electrons or holes from a dye to a catalyst, such as TiO_2 , can be incredibly efficient when a monolayer of dye is absorbed on the TiO_2 surface by covalent bonding, ion pair association, physisorption, entrapment in cavities or hydrophobic interaction.^{58, 181, 182} This has been used extensively, especially in the production of TiO_2 solar cells.¹⁸³ The literature has reported that the incorporation of dye in TiO_2 photocatalytic systems is the most efficient way to extend the photoresponse of TiO_2 into the visible region.^{58, 184-186} This is due to the prominent photophysical properties of dyes.¹⁸⁷

The initiation process of solar photocatalytic degradation with the aid of TiO_2 as a photocatalyst is described in **Equation 1.9** through **Equation 1.11**, where the generated hydroxyl radicals will eventually oxidize the pollutant. For a dye-synthesized solar photocatalytic system, the initiation of this process could proceed through the mechanisms shown in **Equation 1.12** and **Equation 1.13** in addition to the previously

mentioned process. In this additional process, the adsorbed dye on the TiO_2 surface is excited by solar irradiation. The excited dye then transfers the adsorbed energy to TiO_2 or O_2 , thus leading to the production of more electron-hole pairs to promote higher degradation efficiency.^{180, 185} This mechanism is further explained in **Figure 1.5**.¹²¹

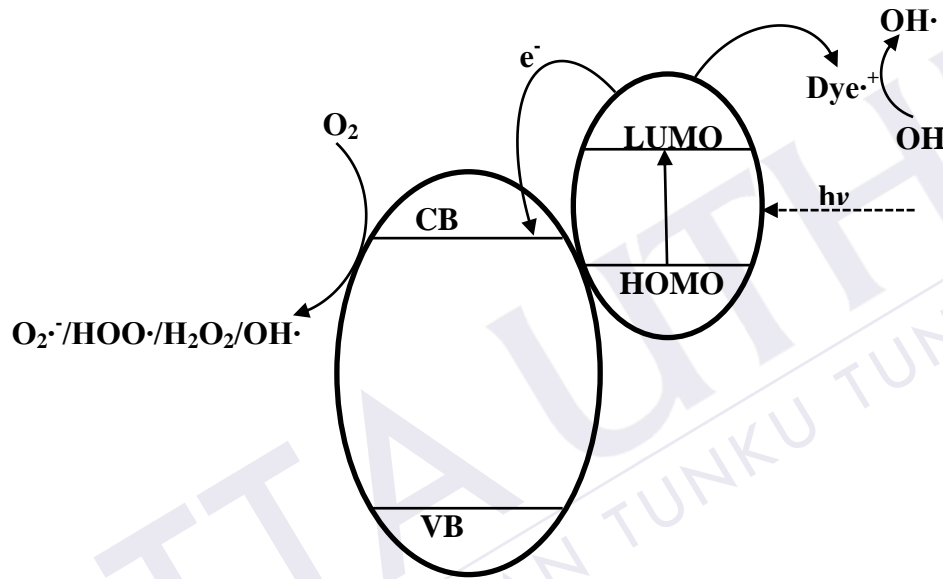
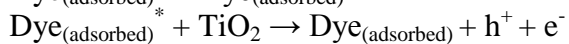
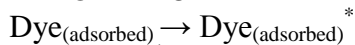
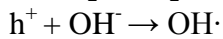
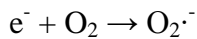
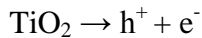


Figure 1.5: Mechanism of the dye-sensitized TiO_2 photocatalyst. An electron is excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of a dye with the absorption of visible light. The excited dye transfers an electron into the TiO_2 conduction band, while the dye itself is converted to its cationic radicals. The injected electrons hop over to the surface of TiO_2 where they are scavenged by molecular oxygen to form superoxide radicals ($\text{O}_2^{\cdot-}$), hydroperoxyl radicals (HOO^{\cdot}), hydrogen peroxide (H_2O_2) and hydroxyl radicals (OH^{\cdot}).



Equation 1.9

Equation 1.10

Equation 1.11

Equation 1.12

Equation 1.13

1.3.2.2 Noble metal deposition on metal oxide

TiO₂ is known to exhibit photocatalytic activity due to photogenerated charge carriers (negative electrons (e⁻) and positive holes (h⁺)).¹⁸⁸ Although TiO₂ photocatalytic activity is among the highest of all semiconductors, one of the critical drawbacks of TiO₂ is its high photogenerated electron-hole pair recombination rate, which hinders its photocatalytic efficiency.^{60, 189} Many attempts have been made to improve the photocatalytic activity of TiO₂ by doping with noble metals, which act as electron acceptors. Capturing photogenerated electrons from noble metals is thought to repress the recombination of electron-hole pairs and facilitate the transfer of holes on the TiO₂ surface, thus enhancing the TiO₂ photocatalytic activity.^{144, 182, 190} Because the deposition of noble metals on TiO₂ is of great interest, many reviews have been published illustrating the behaviour of noble metals in photocatalysis (see **Table 1.4**).

Basically, noble metals such as Pt, Pd, Au, Ag and Ir deposited on the TiO₂ surface act as electron sinks because their Fermi levels are lower than that of TiO₂. Therefore, photoexcited TiO₂ can act as an electron source for these clusters, which in turn provides charge separations for TiO₂.^{58, 175} Bulk Au in particular has long been regarded as a highly inert metal with little or no chemical and catalytic activity.^{191, 192} However, Haruta *et al.* found that Au can exhibit surprisingly high catalytic reactivity when it is highly dispersed on selective metal oxide (Au/ metal oxides).^{193, 194} Up till now, Au/metal oxide catalyst have become one of the hottest system in catalysis, being widely applied to many important processes such as CO oxidation, selective oxidation of

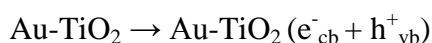
propene, nitrogen oxide reduction and most importantly photocatalytic oxidation used for environmental clean-ups.¹⁹⁴⁻¹⁹⁷

Table 1.4: Brief summary of research directions discussed in the recent reviews focused on the use of noble metal nanoparticles in photocatalysis.

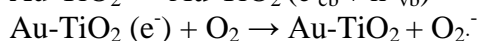
Reference	Remarks
Pelaez <i>et al.</i> ¹²¹	<ul style="list-style-type: none"> • Focused on the development of different strategies to modify TiO₂ for the utilization of visible light. • This includes metal doping, non-metal doping, dye sensitization and coupling semiconductors.
Hou <i>et al.</i> ¹⁹⁸	<ul style="list-style-type: none"> • Focused on the studies performed on plasmon-enhanced photocatalytic water splitting and the reduction of CO₂ with H₂O to form hydrocarbon fuels. • Also touches on the degradation of organic molecules.
Zhou <i>et al.</i> ¹⁹⁹	<ul style="list-style-type: none"> • Focused on the different methods employed in the synthesis and photocatalytic properties of noble metal-based plasmonic composites under visible light.
Linic <i>et al.</i> ²⁰⁰	<ul style="list-style-type: none"> • Focus on water-splitting reaction on plasmonic-metal semiconductors. • Also discussed the mechanism of the effect of surface plasmon resonance (SPR) on the photocatalytic activity of the semiconductor.
Kumar <i>et al.</i> ¹⁸⁵	<ul style="list-style-type: none"> • Focused on modified TiO₂ photocatalysis. • Also touches on the advancements made in enhancing the surface-electronic structure of TiO₂ with high efficiency.
Xuming <i>et al.</i> ²⁰¹	<ul style="list-style-type: none"> • Focused on the major mechanism in plasmonic photocatalysis. • Also discussed various material systems that have superior photocatalytic performance.
Kowalska <i>et al.</i> ²⁰²	<ul style="list-style-type: none"> • Focused on explaining the mechanism of photocatalytic reaction on Au/TiO₂ under visible light. • Also discussed in detail the properties of photocatalysts required for a high level of activity.
Wang <i>et al.</i> ²⁰³	<ul style="list-style-type: none"> • Focused on recent synthetic methods and photocatalytic reactions with the aid of different types of plasmonic photocatalysts.

Gold nanoparticles have been reported to display distinctive visible-light absorption due to surface plasmon resonance effects,²⁰⁴⁻²⁰⁶ which can be used to inject

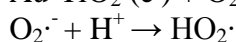
electrons into the TiO₂ CB.²⁰⁷⁻²⁰⁹ These injected electrons can further be transferred to the adsorbed molecular oxygen to form superoxide radical anions O₂^{•-} (**Equation 1.15**), followed by protonation, thus producing hydroperoxyl radicals HOO[•] (**Equation 1.16**).²¹⁰⁻²¹² The production of superoxide radical anions and hydroperoxyl radicals plays an important role in enhancing the photocatalytic activity of this type of catalyst.



Equation 1.14



Equation 1.15



Equation 1.16

1.3.2.3 Photocatalysis by gold supported on metal oxide

In plain TiO₂, absorption of a photon whose energy is larger than the band gap produces the creation of electrons and holes to migrate from the place in which initial event of charge separation has occurred to the surface of the particles. The surface of TiO₂²¹³ plays a key role in the photocatalytic activity. Several strategies have been developed to further enhance the photocatalytic efficiency of pure TiO₂ and modification of TiO₂ with gold nanoparticles has attracted many researchers.²¹⁴⁻²¹⁹ Further, a larger number of studies has reported the enhancement in photocatalysis over TiO₂ from the addition of Au as a co-catalyst.²²⁰⁻²²⁸ It has also been confirmed by various studies that the catalytic properties of Au/metal oxide catalyst depends significantly on the size of Au particles, the interaction between Au and the supporting oxide, as well as the nanostructure of the active site.^{194, 229, 230} For the purpose of obtaining structure which can facilitate high performance catalyst, many chemical and physical methods such as co-precipitation,²²⁹ chemical vapour deposition,²³¹ co-sputtering,²³² deposition-precipitation^{194, 221} and photodeposition²³³⁻²³⁹ Deposition-precipitation has been

demonstrate to be one of the most successful method for depositing highly dispersed Au nanoparticles because it allows the size of the gold particles to be adjusted by controlling the pH of the preparation and calcination temperature.²³⁷

Modifying nanoscale wide-band gap semiconductor such as TiO_2 with plasmonic nanoparticles introduce visible-light activity, expanding the applicability of these aqueous stable oxide for solar-driven technologies.^{202, 240-245} Since the pioneering work of Haruta shows the unique catalytic activity of Au/TiO_2 for the selective low temperature CO oxidation,¹⁹⁴ the number of reports describing the use of Au/TiO_2 as heterogeneous catalyst for thermal reactions has grown considerably.^{246, 247} Although low temperature CO oxidation obey different laws compared to photocatalysis, having a stable noble metal nanoparticles strongly anchored onto the surface of TiO_2 as an independent phase typically used in heterogeneous catalysis could in principle enhance the photocatalytic activity of TiO_2 .

Deposition of nanosized noble particles on the surface of the TiO_2 lead to an efficient charge separation of light generated electron-hole pairs in a semiconductor and to an increase of the lifetime resulting in an improved diffusion to the surface.^{236, 248, 249}

Noble metal nanoparticles such as Au nanoparticles are very effective traps for the electron due to the formation of Schottky barrier at the metal-semiconductor contact hence preventing electron-hole recombination in photocatalyst. Further, it could be assumed that upon depositing noble metal nanoparticles on the surface of TiO_2 the increase of quantum yield of the photodegradation of dye is mainly due to the increased separation of electrons and holes, the higher rate of $\text{OH}\cdot$ radicals formation and

- **Poster presentation**, “Effect of reaction parameters on photodegradation efficiency of reactive dye RB19 by TiO_2 ”, MacDiarmid Institute Student and Post-Doc Symposium. (Christchurch, New Zealand: November 2012).
- **Poster presentation**, “Effect of reaction parameters on photodegradation efficiency of reactive dye RB19 by TiO_2 ”, Advance Material and Nanotechnology 6 (AMN6). (Auckland, New Zealand: February 2013).
- **Oral presentation**, “Enhanced photocatalytic activity in F- TiO_2 : Effect of solvent and fluorine modifiers towards the morphology of TiO_2 ”, 38th Condensed Matter and Material Meeting. (Waiheke Island, Auckland, New Zealand: February 2014).

In addition, the author has contributed to the paper on work related to but not directly relevant to this thesis

- M.Z. Ahmad, V.B. Golovko, R.H. Adnan, **F.A. Bakar**, J.-Y. Ruzicka, D.P. Anderson, G.G. Andersson and W. Wlodarski “Hydrogen sensing using gold nanocluster supported on tungsten trioxide thin films.”³⁸⁰

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