

Zn-Doped TiO2 Thin Film Prepared by Spin Coating

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Faculty of Science

School of Materials Science and Engineering

Zn-Doped TiO₂ Thin Films Prepared by Spin Coating

A Thesis in

Materials Engineering

by

Renzhong Zhang

Submitted in Partial Fulfillment

of the Requirements

for the Degree of

Master of Philosophy

March 2012

CERTIFICATE OF ORIGINALITY

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(Signed).....

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Abstract

In the present work, Zn-doped TiO₂ thin films were deposited on soda-lime-silica glass substrates by spin coating. Titanium isopropoxide and zinc chloride were used as sources of Ti and Zn, respectively. The levels of doping were 0.2, 0.4, 0.6, 0.8, 1.0, 1.5 and 2.0 mol% (metals basis). Solutions were dropped on substrates spun at 2000 rpm. Afterwards, the films were annealed in air at 500 °C for 5 h, using a heating rate of 5 °C per min, followed by natural cooling.

Laser Raman microspectroscopy and glancing angle X-ray diffraction (GAXRD) indicated that all of the films consisted of polycrystalline anatase only, without other contaminant phases, such as ZnO. Single-beam focused ion beam milling (FIB) data showed that the thickness, which was consistently ~350 nm, was not affected by Zn. Field emission scanning electron microscopy (FESEM) showed that the films were microstructurally homogenous, pore-free and crack-free. Increasing the Zn doping level did not enhance or suppress grain growth and all of the films showed a consistent grain size of ~40 nm. UV-VIS spectrophotometry transmission data in the visible region indicated that all of the films were of high transparency, with >80% transmission in visible region (400–800 nm). Further, the interference fringes shown in the transmission spectra suggested that the surfaces of the films were smooth and flat, thereby confirming the FESEM results.

The optical indirect band gap of the films, which was calculated using the transmission data, showed three phenomena:

- Undoped TiO₂ gave a band gap of ~3.40 eV,
- TiO₂ doped at what is assumed to be the solubility limit of Zn (0–0.8 mol% Zn) in TiO₂ gave a band gap of ~3.10 eV, and
- TiO₂ doped beyond the solubility limit (1.0–2.0 mol%) gave a band gap of ~3.20 eV.

This can be explained by the potential effects of precipitation and/or segregation, both of which would serve to deposit a monolayer or extremely thin surface coating on the TiO₂.

Testing of the photoactivity by the decomposition of methylene blue supported the preceding interpretation in that:

- The band gaps showed three values: (a) undoped, (b) below the solubility limit of Zn in TiO₂ of 0.8 mol% Zn, and (c) above the solubility limit. The constancy of the band gaps were consistent with the presence of homogeneous solutions (where any graduated differences were beyond the sensitivity of the method) and surface precipitation and/or segregation.
- The methylene blue testing showed two trends: (a) below the solubility limit of Zn in TiO₂, the photoactivity increased owing to the generation of oxygen vacancies (here, the differences could be detected) and (b) above the solubility limit, the degree of coverage and/or thickness of the ZnO surface coating increased with increasing Zn level, consequently inhibiting the photoactivity.

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Chapter 1: Introduction

TiO₂ has been dragging a lot attention recently with its photocatalyticity. It is interesting that such property brings extremely useful applications to the substance. For different applications, various forms of the TiO₂ are applied. There are also many different synthesis methods which strongly influence the properties of the final products. Comparing with nanoparticle powder, a transparent thin film is able to be applied in some particular circumstances. Scientists have developed some fascinating applications such as anti-fogging coating, water treatment and air purification. Thus, it is interesting to study on the properties of transparent thin films made from TiO₂. Spin coating is one of the newly developed techniques with relatively high product rate and low cost. These advantages are interested for the commercial use of thin films fabrication.

Two major polymorphs of TiO₂ namely anatase and rutile have considerably different properties. Anatase is usually considered to have better photocatalytic performance compared with the other common polymorphous phase rutile. Pure anastase material has relatively high band gap energy (~3.20 eV direct) which means that the photocatalysis occurs rapidly under UV-light irradiation rather than visible light. Scientists investigated that doping with some impurities would enhance the photocatalytic activity in certain degrees. Zn, as a transition metal, has a relatively stable valence state. It is interesting to investigate the effect on TiO₂.

It is noticeable that there is not any study on the Zn²⁺-doped TiO₂ thin film prepared by spin coating can be found. Therefore, in this work, TiO₂ thin films are prepared by using spin coating method followed by heat treatment. Different levels of Zn²⁺ ion doping are applied and compared with pure TiO₂ thin films. Specimens are analyzed by using Laser Raman microscope, X-ray diffraction system, and scanning electron microscope and focused ion beam milling to determine their chemical, physical properties such as mineralogy, surface morphology and thickness. Methylene blue tests are operated giving the photocatalytic performance for each specimen. Optical properties of the thin films are also analysed by using UV-VIS spectrophotometer which help to explain the photocatalytic performance.

The aim of this research work is to investigate the effect of Zn-doping on the photocatalytic performance of TiO₂ thin films prepared by spin coating. The scope of this research work was limited to the determination of the optimal Zn-dopant concentration using the analytical tools and methodology adopted previously [111, 149, 151, 152]. At the end of the project, fully dense polycrystalline thin films are expected with no pores or cracks. Anatase phases are expected with different levels of doping. All specimens shall be transparent and have a thickness in the range of 300 to 500 nm. It shall be observed that different Zn^{2+} ion doping levels have different degrees of enhancement on the photocatalytic activities of thin film. The observations of optical properties of different specimens are expected to provide an explanation to the enhancement of photocatalytic activities.

Chapter 2: Literature review

2.1: Titanium dioxide

Titanium dioxide (TiO₂) is the naturally occurring oxide of titanium. It is white in color and is commonly used as the white pigment 'titanium white'. There are two important polymorphs of TiO₂-anatase and rutile. A third polymorph – brookite exists, but is not as commonly seen as the other two. Rutile is the only thermodynamically-stable phase [1, 2] while anatase and brookite are considered to be meta-stable. The metastable anatase and brookite phases tend to convert to rutile after annealing at certain temperature [3]. Other high-pressure phases of titanium dioxide which are of minor significance in terms of research potential are listed below as [3]:

- TiO₂ II or srilankite, an orthorhombic polymorph of the lead oxide structure
- Cubic fluorite-type polymorph
- Pyrite-type polymorph
- Monoclinic baddeleyite-type polymorph
- Cotunnite-type polymorph

Titanium dioxide is non-flammable and non-toxic and this allows it to be used in o several primary applications such as food coloring, toothpastes, pigments, and cosmetics [4]. Other applications such as air purification [5, 6] and water treatment [7–11] are based on the photocatalytic property of TiO₂.

2.2: Crystal structure

2.2.1: Bulk structure

Both anatase and rutile have tetragonal crystal structure containing twelve and six atoms per unit cell, respectively. In bulk TiO₂, each titanium atom is bonded with six oxygen atoms while each oxygen atom is coordinated with three titanium atoms in both polymorphs structure [12] as shown in **Figure 1**. In fact, these two microstructures are slightly different in terms of bonding angles, as anatase has a greater distortion with the O-Ti-O bond angle deviating from 90° compared with that of rutile [13]. In brookite, each cell has an orthorhombic structure with eight formula units. However the inter-atomic distances and bonding angles are similar to those of rutile and anatase [13]. The structures of rutile, anatase and brookite have been described as TiO₆ octahedral with 2, 4 and 3 shared edges respectively [13]. One of the important features of titanium dioxide structure is the oxygen vacancies which influences the surface morphology and photocatalytic properties [14]. The structures and associated crystallographic data are shown in **Table 1**.



Figure 1. Crystal structure of TiO₂: (a) Rutile, (b) Anatase, (c) Brookite [13].

Table 1.	Crystal	structure	data	of TiO2.
----------	---------	-----------	------	----------

	Rutile [15]	Anatase [15]	Brookite [16]
Crystal structure	Tetragonal	Tetragonal	Orthorhombic
Lattice constants(nm)	a=0.45936	a=0.3784	a=0.9184
	c=0.29587	c=0.9515	b=0.5447
			c=0.5145
Space group	P4 ₂ /mnm	I41/amd	Pbca
Molecule/cell	2	4	8
Volume/molecule(nm ³)	0.031216	0.034061	0.032172
Density (kg/m³)	0.00413	0.00379	0.00399
Ti-O bond length (nm)	0.1949(4)	0.1937(4)	0.187~0.204
	0.1980(2)	0.1965(2)	
O-Ti-O bond angle	81.2°	77.7°	77.0°~105°
	90.0°	92.6°	

2.2.2: Surface structure

Anatase and rutile are the major phases under consideration due to their distinctive features such as low surface energy for anatase and high stability for rutile. In bulk materials, different planes in a crystal lattice can constitute surface of a particle. Differences in surface lattice structures can result in varying degrees of reactions occurring on them. Therefore, due to direct contact with the environment, it is important to analyse the surface characteristics.



Figure 2. Schematic representations of faces of rutile: (a) (110), (b) (100), (c) (001) [18]. The red atoms are O and the blue atoms are Ti.

In rutile crystal unit cell surface structure, there are three main crystal planes namely the (110), (100) and (001) planes. (110) and (100) planes are considered to have relatively low energies, while (110) plane possess high thermal stability [17]. In the (110) plane, along which cleavage is mostly like to happen reported by Diebold [14], there are rows of 6-coordinate Ti atoms and also rows of 5-coodinate Ti atoms running parallel to the rows of bridging oxygen atoms [18] which are only bonded to two titanium atoms. On (100) planes, 5-coordinate Ti atoms in rows still can be found but in a different relationship with bridging oxygen row [18]. As shown in the **Figure**

2, the 5-coodinated Ti atoms are directly bonded with bridging oxygen atoms. This relationship leads to differences in bonding energy and distances between the atoms and this consequently influences the properties of the surface. The (001) face possesses lower thermal stability and surface reconstruction/surface relaxation tends to occur at this face on heating at 475°C [17]. This process is considered to lower the surface energy by changing the lattice parameter such that the whole surface plane of atoms moves relative to the bulk position without changes in the lattice order [19]. It is considered to be a two-dimensional change in the position of the surface layer [19].



Figure 3. Schematic representations of faces of anatase: (a) (101), (b) (100), (c) 18

(001) [18]. The red atoms are O and the blue atoms are Ti.

There are also two low-energy faces in the anatase crystal structure, as seen in the review by Fujishima *et al.* [18]. (101) and (001) are the two low energy faces, which are common for the natural anatase [20, 21]. (101) plane is considered as the most stable plane and that is why this plane appears as the highest intensity peak in both Raman and XRD spectra. The (100) surface is less common which will undergo a reconstruction [20]. All three faces contain rows of 5-coordinated titanium atoms and bridging oxygen atoms as shown in **Figure 3**. Comparing the most thermodynamically stable faces for an anatase [*i.e.* (101)] and rutile [*i.e.* (110)], it is seen that the removal of one bridging oxygen atom in each face will produce one 4-coordinated Ti³⁺ atom with another 5-coordinated Ti⁴⁺ for anatase and two 5-coordinated Ti³⁺ atom in the lattice for rutile. This difference in unsaturated state gives Ti cations in anatase (101) less stability than that in rutile (110) [22, 23]. Therefore, anatase is found to display better photocatalytic performance than rutile due to more oxygen vacancies in the structure.

2.3: Anatase to rutile phase transformation

Anatase is the initial crystalline phase formed during titania recrystallisation [24] during the synthesis of titanium dioxide films by various method and has a relatively less-constrained molecular configuration than rutile [25]. Thermodynamically, anatase has a lower surface free energy value [14] while rutile has a lower Gibbs free energy of formation value [3]. This explains why rutile is form from anatase on heating. The anatase to rutile transformation occurs at a considerably wide temperature range of 400°C [3] to 1200°C [3] depending on different methods of preparation [26–32]. This transformation is highly temperature and time dependent due to the structural reconstruction [2, 29, 33]. Several parameters, such as the particle size, shape, surface area, atmosphere, volume of sample, nature of sample container, heating rate, soaking time, impurities and measurement technique, can

dramatically influence the temperature and time conditions for pure anatase transforming to rutile [3, 34–40]. The phase transformation involves lattice reconstruction in which bonds will be broken and reformed [41]. Volume contraction was observed (~8%) [36, 42].

2.4: Surface chemistry

This is an essential factor to consider since the applicability of TiO_2 is based on the surface phenomena including photocatalysis. Adsorptions of molecules and atoms, dissociation and/or reaction to other products are the major phenomena that occur on the surface of TiO_2 .

2.4.1: Hydrogen

UHV (ultra-high-vacuum) studies have shown that hydrogen molecules are not strongly attracted to the surface of TiO₂ [43]. However, titania reduction is found to occur when heating is done in a H₂ atmosphere under high vacuum conditions [44, 45]. On the other hand, atomic H is likely to be adsorbed on TiO₂ (110) surfaces at room temperature [46]. The hydrogen is believed to originate from either the water in residual gas pressure or from the bulk of TiO₂ sample [47]. Irrespective of the source of hydrogen, it eventually causes the hydroxylation of bridging oxygen and the subsequent formation of oxygen vacancies [48].

2.4.2: Water

Water is adsorbed at TiO₂ surfaces for and this is important for photocatalysis which occurs in an aqueous media. The phenomenon is difficult to understand due to the various crystal surfaces involved. Henderson [49] reviewed the water adsorption on

TiO₂ surface in 2002. It was concluded that different planes in the crystal structure have varying abilities of adsorbing and dissociating water molecules due to the difference in the lattice [49]. For example, on rutile (100) surfaces, water can be dissociated while on (110) surface, no water dissociation is seen to occur except at defect sites such as oxygen vacancies [50–52]. This implies that if the rutile (110) surface is perfect in structure with no defects, then water dissociation is very unlikely to occur. Although there is some disagreement on the details of the phenomenon particularly with regard to temperature of dissociation at point defects [50, 53, 54], most the experimental results are consistent with the previous theory. Some studies point out that the production of hydrogen molecules by the dissociation of water at point defects is associated with healing of these defects [55].

It has been seen that different preparation methods will produces samples with varying surface morphologies and crystalinities and this is believed to cause the observed difference in **Figure 4** [49, 56]. Theoretical calculations have been used that the dissociation of water molecules on perfect TiO2 (110) is energetically favored; this is attributed to the intermolecular H-bonding acting as a stabilizing factor [57–59]. Ferris *et al.* [60] investigated water dissociation phenomenon on the (100) and (110) surface planes of rutile, and the results were consistent with other studies; moreover, they suggested a potential barrier could be the cause of the observed differences in experimental results and theoretical calculations.

Henderson [49] developed a structural model as show in **Figure 4**, which explained the differences in the abilities of the (110) and (100) surfaces in TiO_2 to adsorb water. The major factor is the difference in the distance between Ti at which the water molecule adsorbed and the neighboring bridging O^{2-} ion. TiO_2 (110) surfaces have a gap of more than 0.3 nm (3 Å) thereby precluding O-H interactions and this results in enhanced water molecule dissociation at the surface [51].



Figure 4. Schematic model for the interaction of water on the (110) and (100) surfaces of TiO_2 . Water binds at the acidic sites (the fivefold coordinated Ti^{4+} ions) on TiO_2 with the O-H bonds pointing away from the surface. On TiO_2 (110), the distance between the water molecule and the next bridging oxygen atoms is about 0.32 nm (3.2 Å), precluding a hydrogen-bonding interaction between the adsorbed water molecule and the bridging oxygen atoms. On TiO_2 (100), the O-O distance between an adsorbed water molecule and a two-fold coordinated O atoms is smaller, favoring hydrogen bonding and dissociation [51].

The dissociation of water at the oxygen vacancies produces a macroscopic effect on the wetting ability of water as shown by Wang *et al.* [61] in **Figure 5**. In this study, an anatase polycrystalline thin film was prepared with a hydrophobic surface initially. With UV light illumination, water droplets started to spread out across the surface of TiO₂ due to the lowering in the contact angle to 0° [61, 62]. The hydrophobicity can be restored by storing in the dark. Hydrophilic domains will be created by water molecule dissociation at oxygen vacancies due to UV light illumination [61, 62], and these hydrophilic domains will enhance the hydrophilicity of the TiO_2 thin film surface. Production of anti-fogging and self-cleaning coatings is based on this property.



Figure 5. Macroscopic effect related to the dissociation of water at oxygen vacancies during UV illumination. (a) TiO_2 coated glass surface with general hydrophobicity before UV illumination, (b) The formation of a highly hydrophilic surface after exposure to UV light, (c) Hydrophobic surface exposed to watervapour resulting in the formation of small droplets of water, (d) anti-fogging surface after exposure to UV light because of the high hydrophilicity which causes the spreading of the water droplets [62].

Hadjiivanov and Klissurski [63] reported an investigation on surface chemistry of anatase and devised a schematic of the anatase surface, shown as **Figure 6**, which helped to understand the water adsorption mechanisms at point defects. Four

different kinds of titanium cations were described in the report as listed below:

- Four-fold Ti⁴⁺ on the faces of (110), (111), (113) and the edges of (110)
- Five-fold Ti⁴⁺ on the most characteristic faces (101) and (100)
- Five-fold Ti⁴⁺ expected in acidic-basic rows on (001) and (112) and edges (101)x(011)
- Ti³⁺ ions considered to be on the edges of the (001) plane acting as the places of localization of the residual hydroxyl groups.

Alcohol and water molecules were easily adsorbed by anatase while dissociation of molecules occurred most likely on rutile. This is due to the non-parallel and saturated coordinative vacancies of Ti⁴⁺ and O²⁻ in rutile in contrast to anatase. Theoretical studies on the adsorption of water on anatase surface suggest that molecular adsorption of water on anatase (101) is favorable while dissociative adsorption is likely to occur on the (001) surface [22, 64, 65].



Figure 6. Schematic showing an anatase crystal with different exposed surfaces. • represent unsaturated surface Ti^{4+} ions; \circ represent saturated Ti^{4+} ions from the subsurface layers; • represent unsaturated surface O^{2-} ions; O represent saturated O^{2-} ions from the subsurface layers [63].

2.4.3: Oxygen

 O_2 molecules were believed to be every reactive with the oxygen-deficient surfaces of TiO₂ due to the possibility for filling the oxygen vacancies. However, further studies on photocatalytic behavior and co-adsorption of water and ammonia have shown contradictory results [55, 66–68]. Henderson *et al.* [69] found that oxygen does not adsorb to a stoichiometric TiO₂ (110) surface at cryogenic temperature, since the aturation coverage was three times the vacancy concentration at that temperature.



Model for molecular O₂ adsorption at vacancy sites on TiO₂(110) at T_{ads} < 150 K

Figure 7. Models showing O_2 bonded to the vacuum-annealed rutile (110) surface at low temperatures. Model A is the top view of the rutile (110) surface with an oxygen vacancy. Model B represent the top and side (along the [001] direction) views of O_2 molecules bonding at vacancy and non-vacancy sites [69].

A model was invented to explain this through the understanding of O^{2-} species bonding within the vicinity of a vacancy shown as **Figure 7**. These molecules were found to desorb around 137°C (410 K) [68]. When the temperature was increased from -183°C (90 K) to 327°C (600 K), dosing O₂ will fills the vacancies associating with an oxygen adatom [67] shown as **Figure 8**. When the temperature reaches above 327°C (600 K), the adatoms will disappear. These ad-atoms are considered to promote water dissociation significantly.



Figure 8. Model showing the oxygen adatoms forming from the adsorption of O_2 on rutile (110) with oxygen vacancies at higher temperatures, and the role of these adatoms in dissociating co-adsorbed water [67].

2.5: Photocatalytic properties

The photocatalytic properties of titanium dioxide have attracted a lot of attention recently due to the ability of TiO_2 enhance water electrolysis. When TiO_2 is exposed to sunlight, particularly UV light due to its characteristic band gap (between the conduction and valence bands), electrons will be excited by the photons striking the

surface. This will cause them to move from the valence band to the conduction band, leaving behind a hole (positive charge) in the valence band [70]. This process is schematically shown in **Figure 9**. The photo-generated holes and electrons are likely to recombine with each other because of their opposing polarities. They can also react with molecules adsorbed on the surface of TiO₂. The simplified for of this reaction is shown through the series of equations below [3].

$$\text{TiO}_2 + hv \leftrightarrow \text{h}^+ + \text{e}^- \tag{1}$$

$$h^+ + H_2O_{absorbed} \leftrightarrow H^+ + \bullet OH$$
 (2)

$$h^+ + OH_{absorbed}^- \leftrightarrow \bullet OH$$
 (3)

$$e^- + O_2_{absorbed} \leftrightarrow \bullet O_2^-$$
 (4)

As indicated by equation (1) to (4), electrons and holes generated from photons interacting with TiO₂ will react with the species such as O₂ molecules to create free radicals. These oxygen-free radicals which have unpaired electrons will easily react with each other or other oxidizing agents generating new compounds. This is the basic mechanism of decomposition of organic pollutants by photocatalysis using TiO₂ as shown in **Figure 10** [9, 70–73]. During this process, hydroxyl radicals are considered to be the most important species. The photocatalysis produces OH free radicals which will capture organic radicals forming alkalis [14]. **Figure 10** shows the process for air purification in which with sufficient oxygen and UV-light radiation, gaseous organic substrates are completely decomposed to CO₂, H₂O and mineral acids on the surface of titanium dioxide thin films [18]. Even though OH free radicals tend to raise the pH of the solution to alkaline, the CO₂ contamination in air can inhibit the photocatalytic performance by lowering the pH in the solution [18].

If the photo-generated holes and electrons recombine quickly with each other, there will not be sufficient time for them to react with the adsorbed molecules and

consequently there will be no decomposition on the surface. TiO_2 inherently has a low electron-hole recombination rate [3]. Thus, there will be sufficient time for the decomposition to occur. That explains why surface chemistry often happens on the defects site.



Figure 9. Illustration of photo-generation of charge carriers in a photocatalyst [3].



Figure 10. Basic principle of decomposition of organic pollutants in air on photocatalyst surface [3].

Photocatalytic performance of a compound is affected by several intrinsic

parameters such as particle size, band gap energy and contamination of defects. One of the advantage of anatase is its high surface area which gives a high density of localise state involving the energy status between conduction band and valence band [74]. The presence of oxygen vacancies in TiO₂ helps to trap free electrons. The localize states enhance the trapping site which decreases the electron-hole recombination rate [75]. Anatase is considered to have greater number of oxygen vacancies in the structure than rutile which is relatively more stable. Thus anatase shows a better photocatalytic performance.

2.5.1: Air purification

The decomposition of gaseous organic substances due to air purification is strongly influenced by the O₂ concentration. Lichtin et al. [76] measured the molar ratio of CO₂ produced by the decomposition of methanol (CH₃OH) during 15-min period and showed that high O_2 concentrations facilitated the complete decomposition. Humidity is another factor that will affect the rate of decomposition. Obee et al. [77] and Sano et al. [78], reported that the degradation rate of organic compounds decreases with increase in humidity [78, 79]. However, Einaga et al. [80] and Blount and Falconer [81], observed a decrease in removal rate of benzene, toluene and hexane, with decreasing humidity. It is explained as increasing amounts of carbon deposited on titanium dioxide [80]. Deactivation of photocatalysts is a general problem related to the decomposition of gaseous pollutants. The deactivation is caused by the accumulation of intermediate products or products on the photocatalyst surface [82]. Some deactivations are reversible and recovery can take place in humid air [81–83]; deactivations resulting from the decomposition of gaseous pollutants consisting heteroatoms such as S, N, P and Si are irreversible [84– 87]. The addition of noble metals has been found to improve the phocatalyst performance by preventing deactivation on the surface. Rh0 [88] and Pt [80] can

significantly reduce the amount of intermediates formed on the surface of titanium dioxide.

2.5.2: Water treatment

Organic compounds in water (alkanes, halo-aromatics, polymers, surfactants, herbicides, pesticides and dyes) can be decomposed at the titanium dioxide surface exposed to ultraviolet light [89-94]. Similar studies by Ohko et al. [95] defines the quantum yield as the number of molecules decomposed per photon absorbed in the liquid-solid photocatalytic reaction of TiO₂ [96-99]. The studies showed that the maximum quantum yields were obtained with low light intensities and relatively high reactant concentrations [96]. Liquid-solid photocatalystic reactions were shown to have the same mechanism as gas-solid photocatalytic reactions, apart from the limitation of the light incidence on the surface [96]. Quantum yields of liquid-solid photocatalytic reactions were determined for a considerably wide range of conditions, and these yield were observed to be several times lower than those form gas-solid photocatalytic reactions [89, 91, 100]. Similar gas-solid photocatalytic reactions, liquid-solid photocatlytic reactions were accelerated by the addition of noble metals such as Pt, Au and Pd [101]. This improvement is attributed to the enhanced charge separation and catalysing the oxygen reduction reaction. Additions of electron acceptors have been proven to accelerate these actions [94, 102, 103]. Electron acceptors such as hydrogen peroxide, ozone, peculate, etc. dissociate into highly reactive radicals when accepting an electron and this will reduce molecular oxygen further and consequently participate in the photocatalytic reactions [94, 102, 103]. The reaction can be expressed in terms of the following equations:

$$H_2O_2 + e^- \rightarrow OH^- + \bullet OH \tag{5}$$

$$O_3 + e^- + H^+ \to O_2 + \bullet OH$$
 (6)

$$S_2 O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{\bullet-}$$
 (7)

2.6: Enhancement of photocatalytic performance

Introducing foreign atoms/ions to a crystal structure of a material to modulate its properties is known as doping. The atoms/ions introduce will settle into the crystal structure either substitutionally or interstitially as shown in **Figure 11**. Due to the differences in sizes, charges and masses of these dopant atoms, they tend to modify the bonding within the crystal unit cell considerably and cause changes in the properties. Metallic dopants can cause a decrease in electron-hole recombination rate [104] and thus have been used to enhance the photocatalytic performance of titania films.



Figure 11. Introduction of a dopant atom to the crystal interstitially (right) and substitutionally (left). The green sphere indicates the dopant. Red sphere is Ti atom. Blue sphere is O atom. The square in left model indicates an oxygen vacancy.

Several works have focused on the effect of doping titanium dioxide with different metals or metal oxides. It has been seen that the dopants can introduce mid-gap states [105, 106], improve charge carrier separations [107, 108] and increase the amount of surface-adsorbed species (*e.g.* hydroxyl radicals) [109]. Hanaor and Sorrell [3] showed that unintentional impurities or intentional dopants (both substitutional

and interstitial) can inhibit or promote anatase to rutile transformation. If dopants are introduced into the crystal structure substitutionally, the oxygen vacancy level will be affected; in the case of interstitial introduction, the lattice constraints of may change leading to destabilisation or stabilization [110]. It should be noted that the size, valence and content effects will dramatically influence the degree of inhibition and promotion, as well as the possibility of using interstitial or substitutional dopants [14].



Figure 12. Classification of cations as inhibitors and promoters of transformation based on their ionic sizes and valences [3].

Hanaor and Sorrell [3] reviewed the performance of possible cationic dopants and classified then as inhibitors and promoters, shown as **Figure 12**. Zn is a promoter, but Si is a strong inhibitor. The effect of Si has implications on TiO₂ thin films deposited on glass substrates where the transformation of anatase to rutile is inhibited by the presence of Si. The inhibiting effect of Si is more pronounced than the promotional effect of Zn.

2.6.1: Doping zinc (Zn)

Liu *et al.* [111] investigated Zn^{2+} doped nanoparticles prepared by two different methods (sol-gel and sputtering coating). It is noticeable that this study is based on TiO₂ powder which apparently has significantly different properties from thin film studied in author's project. Thus, results from their study may give author some suggestion. However, the figures are not comparable with author's result due to the different preparation methods.

In the literature, it is stated that the particle size of zinc doped titanium dioxide with sol-gel viewed under TEM has an insignificant change compared with pure titanium dioxide. The specimen prepared by sputtering consist smaller particles, shown as **Figure 13**, which mean the surface area of the specimens is higher. The enhancement caused by decrease in particle size is reported by Sun *et al.* [112] in 1998 which suggested that when the particle size of TiO₂ decreased from 30 to 10 nm, 45% increased in photocatalytic activity would be observed.

Photocatalytic activity was tested by decomposing 0.25 mM of Rhodamine B under UV light illumination. Specimens prepared by sputtering showed comparatively better photocatalytic performance that the ones prepared by sol-gel as seen in **Figure 15**. This is attributed to the differences in particle size. Zn²⁺ ions were noted to diffuse into the lattice of titanium dioxide, after re-calcination at 500°C, resulting in the greatest improvement in the photocatalytic activity of the specimen as seen in **Figure 17**. Higher annealing temperature leads to anatase to rutile phase transformation and this will consequently suppress the photocatalytic activity. Moreover, doping with Zn²⁺ does not change the phases formed significantly seen from the XRD spectra shown in **Figure 14**.



Figure 13. The particle size of Zn doped titanium dioxide: (a) pure TiO₂, (b) Zn/TiO₂ (sol-gel), (c) Zn/TiO₂ (SPR) [111].

TiO₂ nanoparticles doped with 0.5 mol% of Zn²⁺ also showed the largest IPCE (incident photon-to-electron conversion efficiency). This is due to the optimal concentration value which results in the thickness of the space charge layer to become almost equal to that as the depth of penetration of light. Thus the rate constant for this optimal doping level is observed to be the highest one among the eight sets of samples (dopant amount was varied from 0 to 2 mol%) [111], shown in **Figure 16**. When the doping level increased over 0.5 mol%, greater number of Zn²⁺ ions will be trapped on the surface of TiO₂ instead of diffusing into the lattice. These ions deposited on the particle surface will impede the adsorption of reactants leading to the inhibition of photocatalytic activity [111].


Figure 14. X-ray diffraction patterns of TiO_2 naoparticles: (a) Zn/TiO₂ (SPR), (b) Zn/TiO₂ (sol-gel), (c) pure TiO_2 [111].



*Figure 15. Photocatalytic activities of TiO*₂ *nanoparticles* [111].



Figure 16. Dependence of the observed rate constant with the Zn^{2+} doping levels [111].



Figure 17. Dependence of the observed rate constant with the re-calcinations temperatures [111].

2.7: Thin film coating

Various techniques have been used to prepare titanium dioxide thin films such as the method [113, 114], sputtering [115–117], gel oxidation [118], sol-gel plasma-enhanced chemical vapor deposition (PECVD) [119], anodic oxidation [120], electrophoretic deposition [121], pulsed laser deposition [122], electron-beam evaporation [123] and spray pyrolysis [124, 125]. Spray pyrolysis is one of the widely used methods with rapid growth rates (≤100 nm/min [126]), large sample size capacity, and mass production capabilities [127]. However the product yield rate during deposition is relatively low [128]. Spin coating is one of the alternative way which offers high production rate and also low cost [129-131]. Figure18 indicates that the conventional methods for thin film coating can be divided into chemical and physical methods. Spin coating is considered to be a chemical method with liquid source of titanium dioxide. It should be noted that the use of different preparation techniques will affect the crystallographic and microstructural features of the TiO₂ thin films.



Figure 18. The categories of thin film coating techniques [106].

Spin coating is a lately developed technique to prepare thin film on a flat substrate using liquid as the source of specimen. It involves four steps namely deposition, spin-up, spin-off and evaporation [132] shown as **Figure 19**. The liquid source is deposited on the substrate at rest or spinning slowly. The initial volume of the liquid is greater than the final volume of liquid film formed on the substrate. This occurs because of the following:

- Liquid starts to flow outwards in the second stage during which the atmosphere considerably affects the film [132];
- During the spin-off stages, the excess liquid flows outwards and fly off consequently reducing the thickness of the film;
- Evaporation affected the process by reducing the thickness of the film further.

The final thickness of the film can be expressed by the following equation [132]:

$$h = \left(1 - \frac{\rho_A^0}{\rho_A}\right) \left(\frac{3\mu e}{2\rho_A^0 \omega^2}\right)^{1/3}$$
(8)

where is the mass of volatile solvent per unit volume, is its initial value of the density, e is a rate constant dependent on gas-phase mass transfer alone, is the viscosity of the solution, is the angular speed of the rotating substrate. Due to the involvement of several factors, it is difficult to calculate the thickness of the film theoretically.



Figure 19. Stages of the spin coating [132].

Annealing is carried out after the thin film is deposited on the substrate. Before annealing, the film on the substrate is not crystalline titanium dioxide, and contains hydrocarbon species. During the annealing process, recrystallisation occurs along with oxidation of the hydrocarbons. Ideally, all the C and H in the original solution will leave the system, leaving behind only TiO₂ on the surface of the substrate. Anatase initially forms and on further heating, anatase to rutile transformation eventually will take place. It is also noticeable that annealing does not only lead to recrystallisation, but also introduces oxygen vacancies if vacuum conditions are used. Diebold *et al.* [14] reviewed the surface science of TiO₂ and reported that point defects were induced thermally in vacuum condition shown as **Figure 20**. It was shown as distributed bright point in STM (scanning tunneling microscope) image [14]. It is well known that oxygen vacancies can be reduced by introducing high amounts of the oxygen [46, 133, 134]. Introduction of oxygen was seen to lower the number of bright spots in the image [135, 136].



Figure 20. Illustration of oxygen vacancies in titanium dioxide thin film [14]. Bright spot A in the image indicates an oxygen vacancy

2.8: Analysis techniques

2.8.1: Laser Raman microspectroscopy

Laser Raman microspectroscopy, based on Raman scattering technique is used to study vibrational, rotational, and other low frequency modes in a system [137]. Photons of light are scattered inelastically from molecule distinguished by different optical frequency from the incident photons is called Raman Effect [138]. Raman scattering is an extremely useful analytical tool which is able to study composition of sample both qualitatively and quantitatively. However, because most of light is scattered elastically, Raman signal is extremely weak which is hard to be collected and may even be masked by fluorescence signals emitted from some materials [138]. Therefore, some techniques such as resonance Raman Effect and surface-enhanced Raman scattering are developed to amplify the signal to give clearer spectrum. In this project, Raman spectroscopy is only used to analyze sample quickly which shows qualitatively the phase of the sample. The standard Raman spectrums of anatase and rutile phases are shown in the **Figure 21**.



Figure 21. The standard Raman spectrums of anatase and rutile phases [3].

2.8.2: X-ray diffraction

X-ray diffraction technique based on a scattering process of X-ray during which X-rays are scattered by electrons of the atoms without change in wavelength is widely used for composition analysis. This scattering phenomenon without change in wavelength is known as Bragg scattering. The diffract beam only can be produced when Bragg law is satisfied. Substances have their own individual diffraction patterns comprising both positions and intensities [139]. It is also possible to know, from the spectrum, the size, shape and orientation of unit cell.

The Bragg equation is generally expressed as:

$$n\lambda = 2d\sin\theta$$
 (9)

Where n is an integer, is the x-ray wavelength, d is the interplanar spacing of the crystal, and is the angle of incidence of the X-ray beam on the crystal.

It is known that the atomic or molecular units in a crystal packs close to each other on plane which are parallel to any other planes having the identical atomic or molecular packs [139]. Therefore, when an x-ray beam strike a specimen, it will not only reflected by the surface plane, but also the parallel plane underneath, even a few layer down depends on the penetration depth. It is able to be expressed as the figure below. The simplest understanding of Bragg equation is that, if two reflected beam shown in the **Figure 22** is in phase, distance AB+AC= . For the moment, the combination of the reflected beams will give a maximum intensity detected by proportional counter [140]. By measuring and analyzing the quantity of combination, the result spectrums will show series of peaks. Large number of plane which has the effect of combined reflections will be indicated as a relatively narrow peak. At any other, the reason that no reflected beam can be detected is the interference of beams. Therefore, for different kind of materials which have different crystal structure, the angles at which the intensities are maximized are their own unique characteristics. The XRD spectra of anatase and rutile are shown in **Figure 23**.



Figure 22. Diffraction according to Bragg's law [141].



Figure 23. The standard XRD spectra of anatase and rutile phases [3].

2.8.3: Scanning electron microscopy

The scanning electron microscope (SEM) is the most powerful and common instrument being developed and widely used for observing and characterizing samples in micro meter or sub micrometer scale. Electron beam is injected into a chamber in which specimen is placed. It swipes across the surface of specimen producing electron signals which are collected and converted into images.

Electron beam is injected by an electron gun which usually is placed at the top of the instrument in various techniques since the SEM instrument has been invented. A few of different types of electron guns have been developed in the history of scanning electron microscope. The emission theories have also been developed with electron guns.

The original electron beam emitted by electron gun usually has a relatively large diameter. It will not be able to generate sharp images at high magnification with such large thick electron beam. Therefore, electron beam has to be condensed by a series of electron lenses after being emitted. Thus, after being condensed, most SEM can produce an electron beam with a diameter less than 10 nm while the current of the beam remains the same.

Two pairs of electromagnetic deflection coils, which is also known as scan coils, are applied underneath the electron lenses. Theses coils control the magnification of images by deflecting electron beam with different swiping distance on surface of specimen.



Figure 24. SEM image of anatase crystals [156].

When electron beam interacts with specimen, signals will be generated and collected by the electron detectors. Secondary electrons and back scattered electrons are the most important two signals which are used to produces images. Everhar-Thornley (E-T) electron detector which consist a scintillator, a light pipe, and photomultiplier tube is used to collect signals [140]. When energetic signal strikes the scintillator material, light will be produced travelling down through the light pipe. The light will be converted to an amplified electrical signal by the photomultiplier tube. Those signals vary and provide different intensities build up the image [140]. **Figure 24** and **Figure 25** show the SEM image of anatase and rutile crystal respectively.



Figure 25. SEM image showing gross morphology of a rutile grain [142].

2.8.4: Focused ion beam milling

Focused ion beam (FIB) system is operated similarly as the scanning electron microscopy. Instead of electron beam scanning the surface for specimen, a beam of focused ions is used to generate image at low current beam as well as sputtering or milling with high current beam. As the thin film milled down in depth, it is able to find the thickness of the film, shown as **Figure 26**. Thus, the thickness is able to be

calculated manually or computationally.



Figure 26. FIB image of TiO_2 thin film coating with tilt angle of 44.6°. (a) One layer of coating; (b) Fourteen layers of coating [143].

2.8.5: Photo-bleaching of methylene blue

Methylene blue is a chemical compound with the molecular formula C₁₆H₁₈N₃SCI. It appears as a dark green solid at room temperature and forms a blue solution when dissolved in water. It is usually used as a redox indicator as it will turn colorless when exposed to a reducing agent. With analysis by UV-VIS spectrophotometry, it is possible to determine the decomposition speed against time, shown as **Figure 27**.



Figure 27. First order linear transforms of disappearance of MB by photocatalysis under UV-irradiation at wavelength of 290 and 340 nm [144].



Figure 28. Representative UV-VIS spectrophotometry data of TiO₂ films as a function of annealing temperature [145].

UV-VIS spectroscopy analyses the absorption or reflectance spectroscopy in the

UV-VIS spectral region. The energy in form of ultraviolet light or visible light can be absorbed by the electrons in molecules. These electrons stroke by photon are excited to higher anti-bonding molecular orbital.

2.9: Summary

Literature review provides tips for the project such as the annealing temperature and doping level. It also introduces the basic knowledge of the mechanism of the photocatalysis and factors affecting the performance.

Since there is no study on the Zn^{2+} -doped thin films and it is also known that different preparation method lead to different phenomenon, the Zn^{2+} -doped TiO₂ thin film prepared by spin coating is worth to be studied.

CHAPTER 3: Experimental procedure



Figure 29. The experimental procedure.

The entire experiment is based on analyzing the characterization and photocatalytic activity of Zn^{2+} -doped TiO₂ thin film. It can be divided into five major steps which are:

- Solution preparation
- Spin coating
- Annealing
- Characterisation including analysis with Raman spectroscopy, X-ray diffraction, scanning electron microscopy, focused Ion beam milling
- Photocatalytic activity analyzed by methylene blue tests and UV-VIS spectrophotometry.

These five steps will be operated in order giving enough information which will lead author to identification of the specimens' features.

3.1: Solution preparation

Titanium isopropoxide (TIP, Reagent Grade, 97 wt%, Sigma-Aldrich) was used as the source of titanium with a valence of +4. A solution of 0.1 M concentration was selected to produce the appropriate thickness of the thin film on the substrate by spin coating. The molar mass of titanium isopropoxide is ~284 g/mol. Therefore, in order to make a 100 mL solution, 2.84 g of titanium isopropoxide was mixed with isopropanol to produce a solution of 100mL. Owing to the presence of group of O-CH(CH₃)₂ in both compound, titanium isopropoxide has good solubility in isopropanol. Also, being an alcohol, isopropanol vaporizes extremely fast, and is thus an ideal candidate to use for production of the thin film.



Figure 30. The molecular structure of (a) titanium isopropoxide and (b) isopropanol [146, 147].

The dopant precursor used here was ZnCl₂. This was used since it is the most commonly used dopant source due to its high solubility in propanol [149, 151, 152]. Investigation of the effect of the alternative dopant precursors is beyond the scope of this work. The following equation was used to calculate the amount of zinc chloride required to produce the specific dopant concentration:

$$x_i = \frac{n_i}{n_{total}}$$
(10)

Where x_i is the mole percentage, n_i is amount of dopant, and n_{total} is total amount of

all molecules. In this case, due to the small amounts of dopant used (0.2, 0.4, 0.6, 0.8, 1.0, 1.5 and 2.0 mol%), the respective amounts of ZnCl₂ used are 0.002, 0.004, 0.006, 0.008, 0.01, 0.015 and 0.02 g (metals basis) for 100 mL. These doping concentrations were chosen according to the work by Liu *et al.* [111]. Undoped titanium dioxide film was fabricated for comparison. Each solution was stirred continuously for 15 min till it became colorless.

3.2: Spin coating

After the preparation of the solutions, syringes were used to transfer and deposit the solution for spin coating (Laurel WS-65052). This is done to control the amount of solution deposited on substrates. Ten drops are used to produce one layer on the substrate with a spin rate of 2000 rpm. It is noticeable that, the whole duration of spin coating for each layer was about 30 s. Substrates were accelerated to 1000 rpm and kept at this speed during the first 10 s. Then it quickly achieved 2000 rpm and kept running for 20 s. It took 3 s to stop spinning. 10 drops of solution were deposited onto the substrate with a constant speed during the first 10 s before it reached the maximum speed. Because it is a manually controlled process, there may be considerable differences between thin films made by different people at the beginning. After a lot of practices, the differences such as the thickness may be minimized. Seven layers are applied on with a few seconds time in between deposition of each layer. It is proved by practice that the solution dries out quickly after the deposition. The time in between of deposition of each layer does not influence the thin film significantly.

3.3: Annealing

Specimens had been taken to muffle furnace to be annealed in air at 500 °C for 5 h

with a heating rate of 5 °C per min followed by natural cooling. This temperature is chosen according to the previous literature review. It gives sufficient heat to generate anastase phase without any transformation to rutile. The temperature-time regime used in the current research work was based on the optimal values derived from similar work undertaken by others[149,151,152].



Figure 31. Spin coater used for this project.



Figure 32. The mechanism of spin coating [148].

3.4: Analysis

When the annealing has been completed, specimens were analyzed by Raman spectroscopy (Renishaw inVia laser Raman microspectrometer with 514 nm argon ion laser) initially to show the contaminant of the thin film. It is able to identify whether specimens are significantly obtained. Therefore, other analytical techniques can be preceded. If the specimens are not appropriate, they must be replaced by new one.

All specimens had been tested by Philips X'pert Materials Research diffractometer. The incident beam was set to raise the angle from 20° to 80° with a potential of 45 kV and operational current of 40 mA. Spectra for each specimen as plotted and compared with data base giving the most perfect match of substance suggested.

Scanning electron microscopy (FEI Nova NanoSEM 230 FESEM) was used to obtain the surface morphology and particle size of the thin film made appropriately. Samples must be coated by chromium making them to be highly conductive before analyzing by the instrument. By using high magnification, the surface structure with small particles stacking together can be viewed clearly. During the operation of scanning electron microscopy, image which detected and converted from the electronic signal may shift in some direction which is very difficult to be captured clearly. It is because of the non-continuous chromium coating. It is able to be fixed by another coating cycle.

Focused ion beam miller (FEI XP200) was operated for the purpose of measuring the thickness of thin film. Specimens were coated by gold to make them more conductive. The reason of using gold coating instead of chromium is that the ion beam will erase particles when it hits the surface of specimen. Chromium coating is

too thin that will be gone quickly and the thin film will be damaged. Gold coating is much thicker so that we will have enough time to measure the thickness of the film. Another layer of platinum was coated right above the area at which the thickness was measured to give a further protection while the measuring process is carried on. Because the spin coating technique was well controlled and almost identical to each specimen, only one sample was measured to show the thickness of the film. The thickness was measured directly on the display screen by the computer program.

3.5: Photocatalytic activity

Methylene blue test was carried out with each composition and also with one container which only have methylene blue solution referencing the results. Specimens were placed in small beakers separately containing the same amount of methylene blue solution which is enough to submerge the specimen. These beakers are sealed preventing impurities and evaporation and exposed under ultra violet light with 365 nm in wavelength using a *3UV Lamp* produced by *UVP, LLC (CA, USA)* for 4 hours. Before the methylene blue test, specimens are soaked in methylene blue solution for a certain long period of time to make them saturated. Thus no further surface-wetting step exists consuming the time and influencing the results. When it is complete, samples were taken out and placed back into the solution in which they are soaked. Small beakers with the decomposed methylene blue solution were transferred to UV-VIS instrument in a box which can prevent further decomposition by the light during on the way.

UV-VIS spectra were obtained for each composite by using PerkinElmer Lambda 35 UV-VIS spectrophotometer. The wavelength range set to be in between of 800 nm to 200 nm according to the wavelength of visible light which is interested in. Solutions are transferred into a small cuvette and tested by a light beam with certain range of wavelength preset initially. The percentage of absorption of the light beam through the cuvette was collected for each specimen. Graphs with absorption percentage against wavelength of light were plotted.

In order to explain the phenomenon of photocatalytic activity, the optical property of thin film were also examined by using UV-VIS spectrophotometer in which light travel through the thin film and give a plot of transmittance against the wave length of the light. It is able to calculate the photo energy according to the collected data.

Chapter 4: Results and discussion

4.1: Structural results

All samples were tested using the Renishaw inVia laser Raman microscope with 514 nm Argon ion laser. All spectra appeared to be identical as seen in **Figure 33**. From the Raman spectroscopy analysis, it is clear that all samples contain anatase. It is shown that there is no other contamination phase such as ZnO. Also, there is no effect on the degree of crystallinity since the intensities of peaks in the spectra are considered to be almost the same. It should be noted that the Raman microscope is only used for qualitative analysis and not for quantitative measurements of the amounts of these phases in the samples.



Figure 33. Laser Raman microspectra for all specimens.

4.2: Mineralogical results

All samples show very similar patterns which are consistent with the presence of

anatase phase only. No evidence of rutile or brookite is seen. XRD patterns confirm the Raman spectroscopy results by showing that there is only TiO₂ anatase phase presented in the films as well as the unchanged crystallinity. The peak with highest value in intensity indicates the most energetically favorable plane (101). Therefore the composition of that plane in the structure is the highest. The other peaks which are shown clearly in the **Figure 34** indicate the planes (004), (200), (211), (105) and (204). It is noticeable that, in these XRD patterns, planes (211) and (105) appear to be represented by the same peak; this is due to the faster scanning speeds used in the analysis.



Figure 34. XRD spectra for all specimens, from bottom to top: undoped, 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0 mol%.

However, it has to be noted that laser Raman microscope only use a point scan. The laser diameter is only 5 μ m. Therefore, the results cannot be representative the whole film. Also, the GAXRD has the limitation that it cannot detect any phase with a volume less than 3% of the whole film. Thus, doping with Zn might possible to create

contamination phases and/or promote the lattice distortion in the film structure without being detected to due to the small amount.

4.3: Thickness

Focused ion beam milling was used to measure the thickness of the thin films prepared by spin coating. The thin films were coated with a layer of gold to increase the conductivity, and another layer of platinum was provided on the top for protection. Samples were milled down to the silica substrate shown as a dark area in the **Figure 35**. At higher magnifications, three layers of different materials can be observed above the dark area. It is believed that the layer with small spherical particles is the TiO₂ film shown as **Figure 36**. The thickness of the thin film can be measured automatically by the instrument and it gave an average value of 350 nm for all specimens.

It is shown that doping with Zn does not affect the thickness of the films significantly since with increasing the doping concentration the thickness of the films did not change considerably. Comparing with studies on other metal doped TiO₂ prepared with spin coating [145, 149–152], the method show the consistent of that the thickness of the film is not affected by different doping agents (Fe, Mn, Zn) and concentrations (0.2-7.0 mol%).



Figure 35. FIB milling image with low magnification.



Figure 36. FIB milling image with high magnification indicating the thin film coating.

4.4: Surface morphology

SEM images of the doped sample microstructures reveal fully dense structure without any cracks and pores shown as **Figure 37** to **Figure 52**. It is seen that bright spots indicating greater conductivity observed in these images, have an increase in quantity with the increase in the dopant level.

There are two possible reasons for this phenomenon:

- This maybe occurring due to exceeded Zn atom spread out over the surface or
- This may be occurring due to the increased number of oxygen vacancies (due to the addition of Zn), which tends to increase the conductivity of the titania thin film.

Zhao *et al.* [153] reported an evidence of increase in oxygen vacancies due to Zn doping proved by their XPS study. This phenomenon also explains the enhancement of photocatalysis.

The SEM analysis revealed that the sample was not flat, and this was evident by the changing in focus quality at different points on the sample. This could have a significant impact on the repeatability of the measurements of the photocatalytic performance (reported in later Sections).

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Figure 37. SEM image of undoped TiO_2 thin film sample.



Figure 38. SEM image of undoped TiO_2 thin film sample with particle sizes measured.



Figure 39. SEM image of 0.2 mol% Zn^{2+} -doped TiO₂ thin film.



Figure 40. SEM image of 0.2 mol% Zn^{2+} -TiO₂ thin film with particle sizes measured.



Figure 41. SEM image of 0.4 mol% Zn^{2+} -doped TiO₂ thin film.



Figure 42. SEM image of 0.4 mol% Zn^{2+} -doped TiO₂ thin film with particle sizes measured.



Figure 43. SEM image of 0.6 mol% Zn^{2+} -doped TiO₂ thin film.



Figure 44. SEM image of 0.6 mol% Zn^{2+} -doped TiO₂ thin film with particle sizes measured.



Figure 45. SEM image of 0.8 mol% Zn^{2+} -doped TiO₂ thin film.



Figure 46. SEM image of 0.8 mol% Zn^{2+} -doped TiO₂ thin film with particle sizes measured.



Figure 47. SEM image of 1.0 mol% Zn^{2+} -dopedTiO₂ thin film.



Figure 48. SEM image of 1.0 mol% Zn^{2+} -doped TiO₂ thin film with particle sizes measured.



Figure 49. SEM image of 1.5 mol% Zn^{2+} -doped TiO₂ thin film.



Figure 50. SEM image of 1.5 mol% Zn^{2+} -doped TiO₂ thin film with particle sizes measured.



Figure 51. SEM image of 2.0 mol% Zn^{2+} -doped TiO₂ thin film.



Figure 52. SEM image of 2.0 mol% Zn^{2+} -doped TiO₂ thin film with particle sizes measured.

No./doping	0	0.2	0.4	0.6	0.8	1.0	1.5	2.0
1	41.7	39.8	39.1	44.9	35.4	50.5	34.0	47.8
2	43.7	34.3	32.7	35.4	41.0	38.4	41.2	39.8
3	48.6	37.0	46.1	29.6	25.6	42.6	40.4	35.5
4	34.0	32.0	43.6	39.6	37.0	51.1	42.7	38.1
5	45.5	38.0	52.2	47.2	35.0	37.0	40.6	49.5
6	-	31.0	-	22.9	39.1	-	-	-
Average	42.7	35.4	42.7	36.6	35.5	43.9	39.8	42.1
STDEV	5.4	3.4	7.3	9.2	5.3	6.6	3.4	6.1

Table 2. The particle sizes (nm) of the all specimens with different doping level(mol%)

Table 2 shows the particle sizes of the all specimens. It is seen that the particles sizes are not influenced by the Zn doping significantly. The average particle size of thin films is \sim 40.0 nm (± 6.6 nm).

The author agrees that the Rietveld analysis would be an useful tool to determine the crystallite sizes. However, the accuracy of the technique is low when used for thin films, particularly the ones analysed here. Based on previous works [111], it has been seen that the grain sizes have an influence on the photocatalytic performance, and thus these values have been determined in this research work.



Figure 53. Representative Transmittance data of TiO₂ films with different doping level.

Optical properties based on the band gap are another important feature of the specimens which directly influences the application. **Figure 53** shows the analysis results for all samples tested using the UV-VIS spectrophotometry. The spectra spectra show that the films are transparency with ~80% in visible region indicating a high similarity of all films. Also, the interference fringes are present in the spectra indicating that the films were smooth and microstructurally homogeneous.

All samples including undoped TiO_2 thin film are divided into two groups according to the transmittance in percentage of light through the thin films. Low level doping samples have a right shift in peaks which are caused by interference of film and glass substrate. Starting with 0.8 mol% of Zn^{2+} , the peaks shift to the left. Based on these
values of transmittance, the band gap energy of each specimen can be calculated by using equation 15.

$$\alpha = -\frac{1}{t}\ln(T) \cong A^*(hv - E_g)^2$$
⁽¹⁵⁾

where: is absorption coefficient (unitless), t is film thickness (cm), T is transmittance (%), A*is a constant that does not depend on hv (unitless) [154]. As shown in **Figure 54**, (α) 1/2 has been plotted by using the value calculated against photo energy. Band gap energy of each specimen can be determined by draw a tangent along and get the intersection point of x-axis.



Figure 54. Optical indirect band gap data of TiO₂ films as a function of annealing temperature

The plot of optical indirect band gap shows that with increase in the doping concentration, the band gap decreases significantly. However, when the doping level is ≥ 1.0 mol%, the band gap trended to increase. The possible explanation is that at

low level of doping (≤0.8 mol%) Zn atom creates the shallow trapping sites of doping agent in the energy band structure. These trapping sites will lead to decrease in the effective band gap. However, at high level of doping, the band gap of Zn itself dominates the trend of the optical indirect band gap. Therefore, the band gap of entire thin film will rise. The phenomenon of difference in band gap energy explains the results to photocatalytic performance.

Photoluminescence can determine if the presence of the zinc dopant also introduces mid gap defect states in the titania matrix. However, the use of PL and determination of mid-gap defects is beyond the scope of the current work, which aimed to determine only the optimal dopant concentration.

4.6: Photocatalytic activities

The photocatalytic performance was analysed using the methylene blue test and the corresponding UV-VIS spectroscopy results are shown in **appendix** which display the variation in the absorption spectra with the wave length of incident light. Since the dopant has the function of reducing bad gap energy to visible light region, the wavelength range of incident light was chosen to be within 200—800 nm [155]. The peaks at ~650 nm are of most interest to assess the effect of doping on the phtocatalyticity of TiO₂.

Consistent results were obtained after repeated tests on the same set of samples. During the repeated tests, beakers which contained different levels of doped TiO₂ and the same amount of methylene blue solution were placed in certain alignment. At the meanwhile the orientations of thin film was controlled to prevent any influence caused by this factor. It is shown that 0.8 mol% Zn²⁺-doped TiO₂ showed the best photocatalytic performance, followed by 0.6 mol% Zn²⁺-doped specimens. The other specimens showed lower photocatalytic performance then pure TiO₂ sample. The minor differences in absorbance for the different sample sets are due to human error and due to minor differences in the distribution of the coating on the substrate. Repeated test measurements were used to minimize this effect on the results statistically by calculating the average value. After all the data have been collected, average value of each peak was calculated and a bar chart of absorbance against different doping levels was drawn as shown as **Table 3** and **Figure 55** respectively.

Table 3. The absorbance for each UV-VIS spectrophotometry (top row indicates the doping level and left column indicates the test number).

No./doping	0	0.2	0.4	0.6	0.8	1	1.5	2	MB
1	0.45	0.47	0.43	0.39	0.36	0.46	0.42	0.49	0.67
2	0.41	0.42	0.44	0.39	0.38	0.47	0.56	0.55	0.67
3	0.45	0.51	0.43	0.43	0.41	0.47	0.53	0.58	0.66
4	0.46	0.49	0.45	0.40	0.37	0.48	0.54	0.53	0.66
5	0.36	0.47	0.38	0.34	0.37	0.39	0.44	0.47	0.53

The UV-VIS spectroscopy test results show that 0.8 mol% Zn doping is the optimal amount which produces the best photocatalytic performance. 0.6 and 0.4 mol% of Zn^{2+} doping also enhanced the photocatalytic activity of TiO_2 while the performance of the remaining samples were comparatively poor.



Figure 55. The average value of appropriate UV-VIS test results.

After getting the optimal concentration of the dopant, the optimal sample was exposed to UV light for different periods of time along with the pure TiO₂ thin film and methylene blue solution samples. 0.8 mol% of Zn²⁺-doped TiO₂ which has been exposed to UV light for different time period gives a clear decrease in absorbance of light through decomposed methylene blue solution. These spectra indicate the time dependence of photocatalytic activity. The longer the time, the more methylene blue molecule will be decomposed. The same test has been repeated for pure TiO_2 thin film. A similar trend of absorbance value was observed. The trend lines which are shown in Figure 56 giving a fact that the rate of decomposition decreases with increasing time. Eventually the decomposition rate will become zero at which point no methylene blue molecules remain in the solution. This phenomenon can be explained that photocatalytic activity is also dependent on the concentration of reactants. Lower concentrations leads to less adsorption of reactants on the surface of TiO₂ thin film. Therefore the degradation of reactants has less possibility to happen even when there are enough free electrons and holes exist. The trends also show the enhancement caused by Zn²⁺ doping giving a considerable increase in

decomposition rate. It is noticeable that methylene blue molecules are not easy to decompose to just with striking by photons.



Figure 56. Absorbance of light by decomposed methylene blue solution with 0.8 mol% Zn^{2+} -doped TiO₂ thin film, pure TiO₂ thin film, and itself against time exposed to UV light.

There is no phase diagram showing the solubility limit of Zn in TiO₂. However, the results can be interpreted in terms of the effect of the assumed value on the results. That is, below the assumed solubility limit of ~0.8 mol% Zn, the homogeneous solid solutions exhibit a consistent band gap of ~3.10 eV. The decrease in band gap from the undoped level of ~3.40 eV is attributed to the presence of oxygen vacancies resulting from the substitution of Ti⁴⁺ by Zn²⁺ [153]. It must be noted that a gradual decrease in the band gap would be expected but it is likely that the sensitivity of the graphical method of determination is insufficient to allow this differentiation. At Zn doping levels greater than the assumed solubility limit of ~0.8 mol%, excess Zn (ZnO) can accumulate on the grain boundaries and thin film surface by two pathways:

• Excess Zn (ZnO) must precipitate on the grain boundaries since the solubility limit is exceeded. Subsequent grain boundary diffusion [156] would assist in distributing the ZnO as a monolayer or similar film across the surface, thereby

yielding a constant band gap.

 Zn in the lattice is forced by stress to the surface of the thin film by the process of segregation [157–159] during heating, probably resulting in a monolayer or bilayer, again yielding a constant band gap. Figure 57 shows the kinetic of surface segration.



Figure 57. Kinetics of surface segregation [160]. Red spheres indicate dopant atom while blue spheres indicate bulk material.

While this explains the decreasing band gap with increasing Zn levels up to 0.8 mol%, it does not explain the decreasing decomposition of methylene blue solution with increasing Zn levels >0.8 mol%. This is explained by the increasing coverage and/or thickness of the ZnO surface layers. This would serve to reduce the adsorption of pollutants and reduce the contact area between TiO_2 and methylene blue solution. In this case, the sensitivity of the detection was sufficient to differentiate the results.

It may be noted that another possibility is that the effect of the ZnO coverage on the photocatalyst may be greater than that of the oxygen vacancies at the higher dopant levels. This also would explain the results in the previous section.

The author agrees that XPS would be a useful tool to investigate the dopant segregation. However, the dopant levels used were quite low and differences in concentrations between samples was even lower (~0.1 %). The accuracy of XPS for these concentrations is low, and thus it was not used in this study. Similarly, the use of TEM for analysing dopant segregation was not attempted since it was beyond the scope of the current work.

The photocatalytic properties of TiO_2 can vary with the method of preparation and the dopant levels used. Therefore direct comparison with work by others would not be accurate. Similar methodology was used by Lin *et al* to prepare Fe- and Mn-doped TiO_2 thin films by spin coating. Nevertheless, they did not investigate the photocatalytic properties.

Chapter 5: Conclusions

- Zn-doped TiO₂ thin films have been deposited on soda-lime glass substrates by spin coating. Different doping levels have been obtained. All samples have been annealed in air at 500 °C for 5 h with a heating rate of 5 °C per min followed by natural cooling. All films have been analysed by using laser Raman micro-spectroscope, X-ray diffractometer, and scanning electron microscope, focused ion beam miller for their structural and mineralogical properties. The optical and photocatalytic properties of all films were tested and analysed by methylene blue degradation and UV-VIS spectrophotometer.
- Raman spectra show that there is no other contamination phase such as ZnO. Also, there is no effect on the degree of crystallinity. XRD patterns confirm the Raman results by showing that there is only TiO₂ anatase phase presented in the films. Furthermore, degree of crystallinity of the films is the same as shown by the similar intensities of the spectra. However, it is suggested that doping with Zn may possibly create contamination phases and/or promote the lattice disorder in the film structure; however there is no evidence of this phenomena due to the small among of dopant.
- FIB milling images show that doping with Zn did not affect the films thickness since increasing the doping concentration does not change the thickness of the films. Comparing spin coating technique with other coating procedures, the former method produces consistent of the thickness with different doping agents (Fe, Mn, Zn) [145, 149–152]; also dopant concentrations (0.2–7.0 mol%) do not affect the thickness of the films
- FESEM images show the ultrafine grain size of the films (~40 nm of grain size). With increasing the dopant concentration the grain size still remains the

same. However, it can be seen that the amount of bright spots increased with increasing the doping concentration. The possible explanation is that with the increasing amount of Zn, oxygen vacancies will be created. This phenomenon will make the film more conductive. Since, the conductive area will provide the bright spot in FESEM, so it can be implied that doping with Zn created oxygen vacancies in the film.

- The UV-VIS spectra show that the films are transparent with ~80 % transparency in visible region. Also, the interference fringes are present in the spectra; this means the films were smooth and microstructurally homogeneous. The plot of optical indirect band gap shows that with increasing the doping concentration, the band gap decrease significantly. However, when the doping level is ≥1.0 mol% the band gap tended to increase.
- The degradation of methylene blue under UV radiation shows the photocatalytic activity of the film. It can be seen that with increasing the doping concentration the efficiency did not increase significantly. These results are similar to Liu *et al.* [111]. The possible explanation is that at low levels of doping (<0.8 mol%), the photocatalytic activity is enhanced progressively with increase in oxygen vacancies introduced by Zn doping. When the amount of dopant is beyond its solubility (>0.8 mol%) in TiO₂, segregation and grain boundary diffusion is likely to occur. As a consequence, the excess Zn atoms spread out all over the surfaces of grains forming monolayer which will prevent pollutants from adsorption. Thus, the photocatalytic activity is progressively suppressed with increase in amount of dopant.

Chapter 6: Problems and solutions

6.1: Humidity

During the experiment section, the major factor which influences the resultant specimens in this project and projects of our students is humidity of the environment. Titanium isopropoxide which has a molecular formula of $Ti\{OCH(CH_3)_2\}_4$ reacts with water extremely fast producing TiO_2 precipitates. The reaction can be expressed as the following formula giving white titanium dioxide precipitate:

Ti
$$\{OCH(CH_3)_2\}_4 + 2 H_2O \rightarrow TiO_2 + 4 (CH_3)_2CHOH$$
 (16)

Although this reaction consequently introduces titanium dioxide, the nature of the product is strongly dependent on the presence of additives, the amount of water and rate of mixing. These parameters are not considered in the project. In the project, as a consequence of high humidity of atmosphere (averagely above 60%), films appear opaque rather than a transparent as being expected. By testing with Raman spectroscopy, it is know that the film still consists pure anatase phase after annealing. But with the different optical properties, it is insignificant for this project. The opacity will restrict the application of the film. It is also the reason of quick stirring mentioned above, just in case to prevent water molecule attacking.

After discussion and practice, it is suggested that a heating source can be applied to decrease the humidity of the environment. It is found that preheat the substrate with the heat source can dramatically reduce the possibility of occurrence of opaque film. The chamber of spin coater also needs to be dried by using the heat source as well as the container in which the unfinished specimens were placed.

6.2: Thickness

The amount of deposited solution also needs to be controlled. The bonding between each layer which has been deposited separately is a fairly weak chemical bonding. It is practically proved that if too many layers were applied, for example 15 layers (it depends on the thickness of the film), it will be wipe off easily even after being annealed. The chemical bonding is not strong enough to hold the structure. At the mean while, if the film is too thing, it is difficult to be analyzed and tested. It also will influence the performance of the film for any application, although it is not proved whether it is a good or bad influence. The relation between thickness of the film and number of layer is not able to be proved mathematically in this project, due to the non-measurable amount of solution that 'fly-off' during the spin coating process. But it is practically analyzed in previous study by other student. It is believed that 7 layers of applied solution will produce a thin film with a thickness between 300nm to 500 nm which is considered to show relatively significant properties that we expected.

6.3: Annealing temperature

Annealing temperature and duration is also very important to the result. Recrystallisation of the thin film and phase transformation of titanium dioxide are strongly heat and time dependent as mentioned previously. Annealing at 500 °C for 5 h is also proved to be an appropriate parameter to generate significant results. Annealing at 200 °C for 2 h has been tried at the first place. Specimens were quickly analyzed by using Raman spectroscopy which showed no peak or maybe just one peak at 140 nm. It indicates that those specimens do not consist pure anatase phase which are expected. Those specimens had been heat treated again at 500 °C and 5 h then analyzed again. It showed identical spectrum as studied in literature. Therefore, the annealing parameter is decided to be kept for this project. It is also stated in literature review that annealing at 500 °C may give the best photocatalytic performance of anatase, although the substance was nano-particle powder.

6.4: Methlyene blue test

Random patterns of spectra against doping level were observed at the earlier tests. All the results were shown in appendix. The results of Test P1 shows very similar values for 0.4 mol%, 0.6 mol%, 0.8 mol% and undoped specimens, leave 1.0 mol% and 0.2 mol% specimens on top which indicated less decomposition happened. Methylene blue solution with no specimen was also exposed to UV light for every single test giving a reference to the others. Those specimens with very similar values were considered to have no difference in performance. The tiny difference in the peak values can be caused by human error during the test. It is noticeable that the 0.2 mol% Zn²⁺-doped specimen shows an unexpected change in position of spectra which is highest at shorter wavelength but lower in longer wavelength. The phenomenon cannot be explained. Inappropriate sample was it considered to be. These spectra did not provide any strong evidence showing the enhancement by Zn doping. It is noticeable that all samples were placed horizontally in the beakers separately submerged by equal amount of methylene blue solution while the UV lamp was also placed on top of them horizontally. Therefore, the distance between each sample to UV light source shall be the same which leading to identical intensity of UV light per unit area.

For the Test P2, new sample with 0.2 mol% of Zn²⁺ doping was used and tests had been running again. Interestingly, the result showed a clear trend of increase in enhancement with decreasing doping level apart from the 0.4 mol% Zn specimen. It was considered that the trend was correct, although it was consistent with the previous study. The exceptional 0.4 mol% specimen might cause by the inappropriate deposition. Since all doped specimens showed a better photocatalytic performance than undoped sample, it was suggested that higher doping level should be tested to investigate whether the trend stayed the same.

For Test P3, it had been repeated with addition of 1.5 mol% and 2.0 mol% Zn doped specimens, but without 0.4 mol% which was considered to be inappropriate earlier. Expected change in trend happened while heavier doped sample showed best performance. Thus, the previous conclusion cannot be consistent. At this stage, nothing can prove the enhancement of Zn doping following a certain trend. Although the previous literature review showed a clear conclusion on the relationship between photocatalysis and doping level, the current work could not provide strong evidence on that conclusion. But it is clear that, all samples did perform as photocatalyst proved by the considerable decrease in the absorption ration of visible light. Some parameters strongly affected the results giving

For Test P4, results showed different performances of TiO₂ photocatalysis with no strong evidence of any reasonable trend. Compared with the previous test, same sample had been exposed to UV light for the same period of time. And the test procedures were considered to be the same with no significant affect on the result. Almost every single one of the specimens showed the different performances for last three tests. Small change of absorption ration can be explained as the human error such as dilution of the solution, time control, processing speed. But all these facts could not explain why the trend of the spectrum changed randomly. Theoretically, because of the identical sample, exposure time, experiment processing, the trend of the spectrum was expected show a relatively steady observation. Therefore, some other factors might not be controlled in the previous tests. It could also be influenced by some systematic problems which were not concerned before. It was suggested that a couple of more sets of test should be repeated and analyzed to lower the

possibility of any influence caused by human error. Author started to concern about the UV-light source.

The next two sets of results (for Test P5 and Test P6) did not show any improvement on the trend of spectra. Random orders had been observed without any reasonable explanation. It is noticeable that the methylene blue solutions which were tested as references in every test, showed a series of similar value in absorption ratio. Therefore, it is proved that there is no dilution of sample occurred during the UV-VIS test. Thus, the processing skill did not have any problem affecting the results. But there were still some parameters which varied during the series of test such as the position of beakers. Since author concerned about the UV light source, the position of beaker may affect the results. Author was considering that the UV light source was partially broken.

Beakers were placed in the sample position with the orientation of sample for the following five tests. The results start to show steadier trend with no strong evidence of any influence caused by different positions of the beakers. For the Test P7, only 0.2, 1.5, and 2.0 mol% Zn²⁺-doped specimens were test during which they were place at the same position as 0.4, 0.6 and 0.8 mol% previously. Author was expected the dramatic enhancement in the photocatalytic performance due to the idea that intensity of the UV lamp are not uniformly distributed. The results show an insignificant change in absorbance suggesting that the previous thought was not correct. The UV light lamp is from a brand named UVP. As the introduction says, the series of UV lamp named 3UV produce uniform and intense source of UV light radiation with three UV tubes housed in on lamp. The one used in the lab has 365nm UV with 8 watt in power. The dimension of the lamp is 394 x 76 x 114 mm. As it is described, three light tubes are place in one lamp which means UV light is emitted from three different tubes. Therefore, no decrease in intensity of UV light is expected

due to the length of the tube. Unfortunately, the design sketch of the lamp was not found. It is not known that how those three lamps are connected, in series or parallel. No matter how they are connected, from the results of UV-VIS test, it is shown that the energy lost across the lamp is insignificant. And the lamp does produce uniform UV light.

Previous review on the TiO₂ photocatalysis showed the performance was strongly depending on the surface area of specimen. For this project, there was any technique which had been used to analyze the surface area specimen. It is able to tell from the SEM analysis that the surfaces of specimens are surely not flat. Consequently, it is necessary to take count the differences in surface area as one of the parameter influencing the results. And this influence cannot be annihilated. Measurements of the surface area in micro scale were not processed. Thus it is not be able to conclude how many affect the surface area actually can cause. In macro scale, because the substrate was manually cut into small slides for each sample, difference in area is expected. Thus, it might cause some difference in absorption ratio for each composed methylene blue solution.

The other reason might cause the random trend in earlier tests may caused by the various concentrate of oxygen vacancies for different samples. Specimens were prepared on different days with some various conditions which were hard to be controlled such as the humidity of atmosphere. And also with different exposure time to the air, there must be some difference in surface structure of properties between each sample. The amount of oxygen vacancies on the surface of thin film is one of the most important factors which influence photocatatlytic activity dramatically. Author accidently left the samples which are used for methylene blue degradation repeatedly in the soaking solution all the time instead of storing in a dry, de-ionized condition. Thus, oxygen vacancies are expected to be healed by

dissociation of water molecules consequently reach a steady state. It is shown in the following figure that absorbance values of samples widely spread and trends are not the same. After soaking in methylene blue solution for a few days, the results becomes steady both in value and trends. It might because of the various oxygen vacancies concentration on the surface of specimen. These specimens are made on different days with a certain degree of environmental condition which cannot be controlled. Thus, there must be some difference in the surface conditions of different specimens. Water molecule from methylene blue solution will be adsorbed molecularly on anatase surface as mentioned in literature review. These molecules will fill up the oxygen vacancies. Healing effect might also happen. Therefore, the oxygen vacancies level will down to a steady state which could be zero with increasing time of soaking. Consequently, the photocatalytic activities of different specimens will become steady too. That explains the reason for random trends from earlier tests and then became steady in later tests.

Since the trends of spectra become steady and reasonable in values, it was considered that the results were significant, and problems were solved. The proper results were used to be calculated and gave significant trends showing the photocatalyticity of each sample.

Appendix



Figure 58. Test P1 UV-VIS spectra.



Figure 59. Test P2 UV-VIS spectra.



Figure 61. Test P4 UV-VIS spectra.





Figure 63. Test P6 UV-VIS spectra.



Figure 64. First set of UV-VIS spectra of all samples.



Figure 65. Second set of UV-VIS spectra of all samples.



Figure 66. Third set of UV-VIS spectra of all samples.



Figure 67. Fourth set of UV-VIS spectra of all samples.



Figure 68. Fifth set of UV-VIS spectra of all samples.

	0	0.2	0.4	0.6	0.8	1	1.5	2	MB
Test P1	0.5	0.58	0.48	0.49	0.52	0.68	-	-	0.79
Test P2	0.47	0.26	0.41	0.35	0.39	0.38	-	-	0.66
Test P3	0.35	0.41	-	0.36	-	0.43	0.31	0.30	0.63
Test P4	0.31	0.35	0.50	0.35	0.39	0.42	0.33	0.38	0.63
Test P5	0.43	0.35	0.47	0.36	0.43	0.47	0.38	0.35	0.65
Test P6	0.43	0.37	-	0.41	0.40	0.43	0.46	0.43	0.65

Table 4.The earlier results for UV-VIS.



Figure 69. Test P7 UV-VIS spectra.



Figure 70. Absorbance of methylene blue solution degraded under UV light illustration with 0.8 mol% Zn^{2+} -doped specimens against time.



Figure 71. All the UV-VIS test results against time of tests in days.

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