Synthesis and characterization of nanostructured Cr doped TiO₂ materials for photocatalytic applications

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**SYNTHESIS AND CHARACTERIZATION OF
NANOSTRUCTURED Cr DOPED TiO₂ MATERIALS FOR
PHOTOCATALYTIC APPLICATIONS**

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in fulfillment of the requirement for the degree of
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~·~ *Dedicated to my family* ~·~

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SUMMARY

Titanium Dioxide for applications as a photocatalyst has received much attention since its water splitting capability was discovered in 1972. However, the efficiency was a big drawback due to its large bandgap of 3.2 eV. Since 1990s, minded researchers have been focusing on shifting its bandgap into the visible light range so as to increase its efficiency. The various techniques utilized are not complex and cost effective. Visible light activity was not observed and efficiency remains low. Hence, its novelty through cheaper alternatives of synthesis suitable for commercialization proved to be very appealing.

In this project, Chromium and Chromium Oxide doped titanium dioxide synthesized by high energy ball milling technique are studied. The high energy ball milling technique is cheap and is a solid state top-down method where breaking and making of new bonds can lead to the synthesis of novel materials suitable for photocatalysis applications. Their physical and optical characteristics were studied. A test of its photocatalytic reactivity was also investigated.

The powders were then fabricated into composite films, using the modified sol-gel technique, for ease of application testing. In this method, the synthesized powders are distributed and incorporated into a film, whose conditions is symbolic to a coating on a wall. Similarly, their optical and physical properties were discussed.

CHAPTER 1 INTRODUCTION

Photocatalytic reactions is based on the principle of using catalysis/s in combination with photochemistry to bring about or accelerate a chemical transformation. This implies that two important ingredients, light(or photons) and a catalyst or catalysts, are nessesary. The catalyst may accelerate the photoreaction by interacting with the substrate in its ground or excited state and/or with a primary photoproduct, depending on the mechanism of the photoreaction. A type of photocatalytic reaction termed photosensitization is a process which a photochemical alteration occurs in one molecular entity as a result of initial absorption of radiation by another molecular entity called the photosensitizer [1]. (One of the major advantage of this chemical process is its use of photons to induce chemical changes. This is because photons (both artificially induced and natural radiation) are readily available. In fact, photon radiation from the sun is a huge resource for photocatalysis. This resource is widely utilized today to disintegrate pollutants and organic compounds. There the study of using the sun as a photon source for photocatalytic reactions are important. Attributes of a good photocatalyst using solar radiation should include the following features:

- Stability and sustained photocatalytic activity
- Good overlap of absorption cross-section with solar spectrum
- High conversion efficiency and quantum yield

- Compatibility with a variety of substrates and reaction environments
- Low cost of synthesis

One of the most studied materials with many of the above features is TiO_2 . During the early 1970s, scientists began to understand the propensity of TiO_2 to absorb energy from the ultra-violet (UV) end of the light spectrum and in the presence of water vapour to generate oxidation reactants [2]. It further received more attention in the 21st century when it was found to have photocatalytic reactivity in the visible light spectrum [3, 4] as well.

Investigations into the degradation of organic compounds in air are a keen object of study for many environmental researchers. In recent years, outstanding research has been carried out on sterilization, self-cleaning agents and disinfectants using TiO_2 [4-7]. However, little has been done on breaking down harmful bacteria. The wide spread of epidemics and diseases in recent years had indirectly led to the exploration and modification of more promising materials suitable for self-cleaning and anti-bacterial applications.

1.1 Applications of TiO_2

Many white wash of buildings have been using TiO_2 formulated paints due to its self cleaning ability. As TiO_2 is non-toxic it is also used in cosmetic products (sunscreens, lipsticks, body powder, soap, pearl essence pigments, and toothpastes) and special

pharmaceutics. It is also used in food products such as the wrapping of salami, in solar cells for the production of hydrogen and electric energy, as gas sensor, as corrosive protective coating and as optical coating [8]. By far, it is the most actively pursued applied research material for photo-assisted degradation of organic molecules.

Another useful property of TiO_2 is that it is super hydrophilic. As such, together with its decomposition capabilities, contaminants collected on the surface are easily washed away by water. These tiles are significantly easier to maintain in exterior applications because they don't require the use of bleaches and detergents, and they allow for the creation of exterior ceramic facades and roofs that are self-cleaning with rainwater.

1.2 Present Status

Degussa P25 is the current market leader for TiO_2 based active component for photocatalytic reactions. It is manufactured by the Aerosil process which subjects TiCl_4 to hydrolysis in the vapour phase at an elevated temperature [9-11]. It is a mixed phase material, containing anatase and rutile crystallite in the ratio of 8:2 [12-14]. It is in the form of highly dispersed white nano-sized powders whose primary particle size is 85 and 25 nm for anatase and rutile phase [11] respectively. It has a BET surface area of $50 \text{ m}^2/\text{g}$ [15], similar to the pure anatase phase TiO_2 from Aldrich. This ratio has presumably allowed for rapid hole transfer from anatase to rutile for extending the photoactivity into the visible light range.

The strong photocatalytic activity of P25 has been attributed to its mixed phase and has been widely studied.[11, 16-18] However, P25 at the current stage is photo-active only in the UV light range. Besides, the problem with P25 powder is that it disperses in water, forming a white colloidal solution that is difficult to separate from the reaction mixture for reuse. Using filtration to separate the mixture is possible but it is energy intensive. It will be a much more desirable solution to have the powder settling easily by itself for the purpose of easy removal [19].

1.3 Motivation

In the past five years, there is a surge of scientific literature [4, 7, 20-22] as well as many new promising TiO₂-based self cleaning products from TOTO Inc. and Taiyo Kogyo Co. in Japan for outdoor applications. More of such environmental friendly products emerge as people become more conscious of the damages to the mother earth.

The main challenges are related to wide bandgap of the photocatalyst material, because it limits the usage of the photocatalyst to activation by UV light. UV photon is less than 360 nm in wavelength and is less than 4 % of the light spectrum that reaches the earth's surface. By extending the activation energy to that of the visible light spectrum it could mean a 40% increase in the efficiency of the photocatalyst. This had led to exploration of new ways to shift the bandgap towards the visible light spectrum. The route to commercialization is imminent and due to a large market for this product, researchers strive to come up with

cheaper and effective products. Even so, fabrication and synthesis techniques remain complex.

As a result, there is a strong drive to synthesize high performance TiO_2 based photocatalyst that could be used efficiently in the UV and visible light spectrum, and at the same time maintain high hydrophilicity [23, 24] to fulfill the requirement of automated clean-up. Unexplored synthesis techniques that are cheap, convenient to end users can potentially open up the doors to more important breakthroughs.

1.4 Objectives

The objective of this Master of Engineering project is to examine the photocatalytic properties of transition metal doping in TiO_2 , and probe the performance of Degussa P25 as compared to the doped and un-doped mixed phase TiO_2 that are synthesized cheaply in the laboratory. For this purpose, TiO_2 was doped with chromium metal and chromium (III) oxide (Cr_2O_3). The High Energy Ball Milling technique [25] which is possible for cheap large scale production was used throughout the experiment for the synthesis of nano-structured TiO_2 – Cr based materials.

The physical properties of the powders were analyzed and different mixed phase ratios of anatase and rutile phases of TiO_2 were obtained. The reason for the phase transition to take place was explained. The relationship between surface area, particle size and photoactivity

was understood. The optical properties of the powders were also studied to examine how much the mixed phase ratio can affect the bandgap leading to enhancement in photocatalytic activity. Last but not least, a known contaminant, methylene blue, was used to observe the photocatalytic activity of the TiO_2 powders under visible light irradiation.

The eventual goal of commercialization of the powders means the ease of applications or integration with existing products realistically. In order to make the project more holistic, composite films using the TiO_2 powders were also synthesized. This section of the project aimed at verifying the integrity of the powders when synthesized into films. Material characterization was done and it showed that the properties of the powders were maintained even after it was synthesized into composite films.

1.5 Major Contribution of the Thesis

Under the research topic mentioned above, the major contributions achieved in this thesis are summarized as follows:

- I. Synthesis of mixed phase TiO_2 .
- II. Mixed phase TiO_2 was successfully synthesized using the high energy ball milling technique. Different mixed phase ratios were obtained by changing the milling duration and the desired 8:2 ratio with excellent repeatability was obtained. The mixed phase ratio was essential to form an interface between

the anatase and rutile phases of TiO_2 , so as to increase the charge separation between the electron and hole pairs.

- III. Introduced Cr and Cr_2O_3 into the mixed phase TiO_2 by the high energy ball milling technique to change its electronic structure,
- IV. Low concentrations of Cr and Cr_2O_3 powders was doped into TiO_2 . The ball milling duration to obtain the desired mixed phase ratio could be maintained. The crystallinity of the anatase and rutile phases of TiO_2 could also be maintained.
- V. Examined the physical and optical properties of synthesized powders to better understand how it affects the photocatalytic activity
- VI. Important physical properties of TiO_2 like its surface area, particle size, stoichiometry and phase composition were measured. The absorption spectra of the powders were also tabulated using diffuse reflectance. The photocatalytic activity of the TiO_2 powders were measured by the rate it degraded the organic contaminant in the presence of light irradiation. The relationship between photocatalytic activity and material properties were drawn and important characteristics that led to photo-activity enhancement were deduced.
- VII. Discovered and understood the presence of the high pressure phase TiO_2 II synthesized from high energy ball milling technique, and its effects on the photocatalytic reactivity of the material.

- VIII. The TiO_2 II phase was studied and the effectiveness of the photocatalyst in its presence was analyzed. Results showed that TiO_2 II is a persistent phase that has no improvements to photocatalytic activity of the powder.
- IX. Studied the photocatalytic efficiency of the TiO_2 powders
- X. The photocatalytic efficiency of the synthesized powders were normalized and compared. The sample with the best photo-efficiency was identified.
- XI. Verification of properties of TiO_2 powders upon fabrication into composite films
- XII. It was verified that the desired characteristics of the TiO_2 powders will not change after it was fabricated into composite films. Hence, mass production for applications on coatings using this technique is realistic.

1.6 Organization of Report

Special attention were place on the Ball Milling duration, different phases of TiO_2 as well as the doping concentration since these parameters provide for the most interesting evaluation of the materials. After obtaining the raw data, knowledge extraction and data mining begin in earnest. The evaluations and findings are then presented clearly and systematically in this report.

In Chapter 2, a literature overview of the physical and chemical properties of TiO_2 is presented. The photocatalysis fundamentals are put forward and the types of modified TiO_2

are outlined. The descriptions of the Ball Milling technique and modified sol-gel technique are also given. The procedures for calculating the bandgap of the new materials as well as the photocatalytic activity test are elaborated.

In Chapter 3, the experimental procedures for the project are presented. This includes the preparation of various types of doped and un-doped TiO₂ based nano-powders by the high energy ball milling technique followed by the microstructure, diffuse reflectance and photocatalytic characterization. The next segment of the work includes fabrication of the composite film using the powder synthesized.

Chapter 4 & 5 then consolidates all the various results obtained throughout the project for the powders and composite films respectively. The microstructure, crystallographic structure and elemental composition of the synthesized materials were first evaluated. After which, its optical properties and photocatalytic characterization results were acquired. The same procedure was carried out for the composite film samples. Analysis of these results and subsequently, a discussion on the results acquired will be presented.

Chapter 6 concludes the work done and findings of this project. Finally in Chapter 7, future work and recommendations are discussed.

CHAPTER 2 LITERATURE REVIEW

Metal oxide semiconductors like TiO_2 , ZnO , WO_3 , Ag_2O , CdS etc... are well studied as they can be easily prepared with high degree of crystallinity. [26, 27] Because of their nano scale particles, intriguing quantum size effects in their absorption and luminescence properties could be achieved. The absorption of light of suitable wavelength by a semiconductor promotes electrons from the valence band (V_b) to the conduction band (C_b). Consequently, electron hole pairs formed have potential energy corresponding to the thermodynamic levels E_{C_b} and E_{V_b} for electrons and holes respectively. The bandgap energy, $E_{C_b} - E_{V_b} = \Delta E_{\text{gap}}$, is the minimum threshold energy for light absorption. If the radiation energy is higher than the threshold value, excess energy would be absorbed as vibrational energy and other forms which would eventually be lost to the environment as heat. In the absence of reactive species on the surface, the photogenerated electron hole pair would be recombined. However in the presence of such reactive species like traps, it would undergo some chemical reaction with suitable particles or solutes on its surface before undergoing recombination.

2.1 Titanium Dioxide (TiO_2)

TiO_2 exists mainly in 3 crystalline polymorphs of anatase, brookite and rutile though only widely studied in the 2 mineral phases of anatase and rutile. Its crystal structure is

illustrated in Figure 2-1. Both anatase and rutile phases have a tetragonal crystal structure and the same electronic configuration, having 1 Ti atom surrounded by 6 O atoms. However, its crystal structure differs by the distortion of each octahedron and the assembly patterns of the octahedral chains [28]. The octahedron in rutile is not regular, showing a slight orthorhombic distortion. The octahedron in anatase is significantly distorted hence its symmetry is lower than orthorhombic. The Ti-Ti distance in anatase is greater whereas the Ti-O distance is shorter shorter than in rutile. In the rutile structure each octahedron is in contact with 10 neighbour octahedrons (two sharing edge oxygen pairs and eight sharing corner oxygen atoms) while in the anatase structure each octahedron is in contact with eight neighbours (four sharing an edge and four sharing a corner). These differences in lattice structures cause different mass densities and electronic band structures between the two forms of TiO_2 [29].

Figure 2-1: Crystal structures of anatase and rutile phases of TiO_2 .

TiO₂ is white in colour, biologically inert, chemically and physically stable, inexpensive, has high photosensitivity under UV irradiation, and has small influence of variations in humidity. The anatase phase is regarded as the photoactive phase of TiO₂ with a bandgap of 3.2 eV corresponding to an optical wavelength of 385 nm. Rutile on the other hand exhibits low catalytic activity but has a bandgap of 3.0 eV (410 nm). This is mainly due to the higher reduction potential of photogenerated electrons in anatase phase TiO₂ since the bottom of its conduction band is located 0.1 eV more negative than that of rutile phase.[22] Having a wide bandgap also mean that TiO₂ can only make use of the 3-4 % UV light source reaching the earth's surface. As a result, applications of TiO₂ as a photocatalyst for daylight induced chemical reactions are hampered. Sensitization of TiO₂ to react to a much larger visible region is therefore ideal for practical and widespread uses [20, 30].

Thermodynamic calculations have shown that large bandgap materials like TiO₂ are thermodynamically stable. The thermodynamic potentials for oxidation and reduction are, in this case, energetically situated below or above the forbidden energy region respectively and therefore out of reach for photogenerated holes or electrons [1]. This is probably the reason why TiO₂ is widely used for the purpose of photocatalysis as it would not be depleted of electron and holes during the catalytic reaction.

Mixed phases can co-exist, depending on the grain size of the TiO₂ particles, and phase transition can take place due to various factors. This includes impurity, defect concentration, grain size, synthesis conditions, particle packing, valency etc.[26, 31-34] At high temperatures, anatase phase can be converted to rutile phase [35]. Hence, rutile is the more

stable phase and abundant in TiO_2 in its bulk material. Mixed phase TiO_2 would be further discussed in Section 2.4.

Last but not least, TiO_2 self-cleaning capabilities owe it to its super-hydrophilic properties as illustrated in Figure 2-2. In the presence of light and moisture, contaminants that were decomposed by the photocatalytic effect could be washed off easily. This kind of hydrophilicity also mean that having a TiO_2 coated glass would diminish fogging. Self-cleaning thus saves time and cost.

Figure 2-2: schematic diagram for the decontamination process on a superhydrophilic self-cleaning surface [7].

2.2 Photocatalysis [12, 27]

Semiconductor photocatalysis with a primary focus on TiO_2 as a durable photocatalyst has been applied to a variety of problems of environmental interest in addition to water and air purification. It can act as photosensitizers for light-induced redox process due to its electronic structure, which is characterized by a filled valence band and an empty

conduction band. When a photon with energy $h\nu$ matches or exceeds the threshold energy ΔE_{gap} of TiO_2 , e_{cb}^- is promoted to the conductance band leaving h_{vb}^+ in the valence band. This is schematically shown in Figure 2-3 and can be represented by equation (2.1).

Figure 2-3: Photocatalysis mechanism

The excited-state e_{cb}^- and h_{vb}^+ can recombine and dissipate the input energy as heat, get trapped in metastable surface states, or react with electron donors and electron acceptors adsorbed on the semiconductor surface or within the surrounding electrical double layer of the charged particles.

Charge-carrier trapping

Charge carrier recombination

In the absence of suitable electron and hole scavengers, the stored energy is dissipated within a few nanoseconds by recombination. If a suitable scavenger or surface defect state

is available to trap the electron or hole, recombination is prevented and subsequent redox reactions may occur.

Interfacial charge transfer

Where $>Ti^{IV}OH$ is a hydrated surface functionality group of TiO_2 , Red is an electron donor and O_x is an electron acceptor, $(>Ti^{IV}OH\bullet)^+$ is the surface bound hydroxyl radical and $(Ti^{III}OH)$ is the surface trapped conduction band electron. The valence band holes are powerful oxidants, while the conduction band electrons are good reducing agents. Most organic photodegradation reactions utilize the oxidizing power of the holes either directly or indirectly. However, to prevent a buildup of charge, reducible species to react with the electrons are required.

2.3 Doping TiO_2

Doping is an action of introducing impurities into a material. It can be done on the surface or integrated into the material. Also, by doping the equilibrium concentration of electrons and holes can be changed. Doping is often used in semiconductors to modify its optoelectronic properties. The impurity can occupy a lattice site or a vacancy. This changes the energy level of the original semiconductor at its impurity site and as a result changes its electrical and optical properties. The current area of interest is to modify TiO_2 to be visible

light sensitive. The 2 possibilities are anion and transition metal doping summarized in Figure 2-4.

Figure 2-4: Electronic structure of TiO_2 photocatalysts by substitution of metal ions or anions in the design of visible light responsive TiO_2 photocatalyst [20].

2.3.2 Anion doping

Choice of dopant for substitution is also a contributing factor to the effective reduction in bandgap. Nitrogen [3, 14, 33, 36-40] and sulphur [41, 42] doped TiO_2 has attracted considerable attention. For the N-doped samples, N atoms are substituted as N^{3+} ions at O^{2-} sites, forming an impurity level above the valence band [37]. As a result, visible light photoactivity could be achieved at the expense of its photocatalytic reactivity when compared to UV irradiated TiO_2 . Although S-doping shows bandgap narrowing, it is difficult to incorporate it into TiO_2 as compared to N doping as larger formation energy is required because its ionic radius is much larger than TiO_2 [3].

N is also claimed to be most effective in bandgap narrowing because of its p states contribution by mixing with O 2p states [3]. However, an important factor to note as reported by Hashimoto et al [36] was that the increased doping of N, that led to increase in O vacancies, promoted the recombination of electrons and holes. These additional doping sites could also have acted as recombination centres resulting in reduced quantum efficiencies.

2.3.3 Transition metal doping

The outstanding role of transition metals cannot be overlooked. Many classical studies have been performed with transition metal catalyst which showed optimum absorption energy [43, 44]. M. Kitano and M. Anpo et al has also shown that doping of transition metals like V, Cr, Fe, Co by the ion implantation method has enabled TiO₂ photocatalyst to work in the visible light region [4, 20]. Many reported doping TiO₂ lattice with transition metals can improve photocatalytic activity and extend its absorption edge into the visible light range [5, 7, 12, 13, 30, 45-48] while others beg to differ, as summarized by Choi et al [49] and S. Tanemura et al [50]. In addition, oxides of transition metals have been thoroughly investigated and found to have many applications in catalysis [51]. The valence and conduction bands of transition metals compose of hybridized d-orbitals from the metal atoms. The d-band mixes with the s and p electronic states to provide a larger concentration of low-energy electronic states and electron vacancies states that are ideal for catalysis. In addition, the sites are most active in breaking and forming chemical bonds where the

degenerated electronic states have the highest concentrations. Charge fluctuations involving electrons and electron vacancies can thus occur within these electron states [1, 47]. Moreover, a density function theory study by H. Yamashita et al [52] shows that mixing Ti(d) orbital of TiO₂ and metal(d) orbital of implanted metal ions at low electric charge essentially decreased the energy bandgap between Ti(d) and O(p) orbitals of TiO₂.

The proposed idea of transition metal doping was to create an appropriate heterojunction to improve the separation of photogenerated electrons and holes through ‘organized’ electron transfer. Doping such metal ions into the bulk material induces change to its electronic structure to enable it to absorb visible light without changing its surface properties. Hence, this will not limit the reactivity and sensitivity of TiO₂ but allow it to absorb and operate more efficiently under UV and decrease the photocatalyst threshold energy towards the visible light range [1, 30]. However, the current disadvantages of using transition metal doping are thermal instability which can increase recombination centres and need of expensive ion-implantation equipment [30, 37]. Chemical methods like impregnation were also reported but it forms small impurity energy levels within the bandgap which could act as recombination centres for the excited electrons and holes, thus decreasing photocatalytic activity [5, 49].

2.3.4 Doping with Chromium

The doped Cr ions go into the lattice as substitutional dopant could be determined by chemical analysis. Its ionic radii at 0.69 Å give it great substitutability for Ti

since both radii are very close in value [45, 53]. Doping elements with larger or smaller atomic radius could lead to undesirable crystal dislocations. It is also found that suitable Cr dopant concentration can increase the photo-activity and the mechanism is mainly attributed to the change in anatase grain size [4, 5, 45, 46]. More importantly, the energy level for Cr^{3+} is above the valence band edge of anatase TiO_2 making it suitable as a photogenerated hole trapper. The better separation between the electrons and holes in modified TiO_2 surface allows for more efficient oxidation and reduction reactions. The enhanced photocatalytic activity is mainly attributed to the increased amounts of O_2^- reactive species and surface Ti^{3+} reactive centre on Cr loaded TiO_2 photocatalyst. Although the electronic structure of the doped material changes, the crystalline integrity of TiO_2 should be maintained. Such a particle is shown in Figure 2-5.

Figure 2-5: Illustration of an enhanced photo catalytic reaction upon Cr doping

When a photon is incident on TiO_2 , it transfers energy to the core level electron leading to photo ejection of an electron.

At the valence band

The electrons are excited from the valence band to the conduction band. In the presence of Cr ions on TiO_2 surfaces, the holes created in the valence band are injected into the Cr ions.

Since the electrons and holes are not 'free', the charge separation increases and the tendency of recombination to form electron hole pairs is reduced. As a result, the electrons formed will more likely form 2 highly reactive substance of interest, $\text{OH}^\bullet$ and O_2^- .

Cr^{4+} reacts with surface hydroxyl groups like water to produce superoxide anion radicals to produce hydroxyl radicals:

At the conduction band

The photogenerated electrons at the conduction band react with surface absorbed oxygen to produce anion radicals:

Hence, a photocatalytic reaction is initiated [6, 46, 53].

2.4 Mixed Phase TiO₂

Many studies have been done on P25 and other doped TiO₂ materials as well as post-processes that led to their enhanced photoreactivity. The anatase phase is reported to be the contributing factor to photoactivity with low rate of recombination and high absorptive capacity. On the other hand, the rutile phase is reported as inactive due to its rapid rates of recombination of electrons and holes, otherwise known as electron sink [18]. However, the pure anatase TiO₂ does not exhibit any activity due to a lack of interface for photocatalysis to occur [1]. Mixed phase TiO₂ consists of interwoven anatase and rutile crystallites that would maximize hole transfer from anatase to neighbouring rutile lattice trapping sites. Figure 2-6 shows how interfacial anatase and rutile TiO₂ led to better electron hole separation. Hence, upon light illumination, a more stable charge separation can be achieved which leads to the holes travelling to the surface for oxidation to take place [15, 18].

Figure 2-6: Illustration of electron-hole separation of mixed phase TiO₂ materials [16].

2.5 Synthesis Techniques

TiO₂ is an established material and different techniques of synthesizing the TiO₂ polymorphs of anatase and rutile have already been demonstrated. A variety of physical and chemical approaches have been used to fabrication TiO₂ films. These include radio frequency(rf) magnetron sputtering deposition, wet-chemical methods, mechanochemical reaction, ion implantation and plasma enhanced chemical vapour deposition (PECVD).

Using the physical approach to deposit TiO₂ nanostructures involves good controls of the reactive gases and partial pressures to obtain the right stoichiometry. Specific patterning is required to obtain the desired nanostructures. It could also be time consuming as deposition rates are system dependent, with possible contamination by incident ion beams.

Methods like PECVD, hydrothermal, wet chemical have a common procedure to obtain crystalline TiO₂ via the heating route[46, 54, 55]. These chemical methods usually require post annealing treatment, which consequently leads to agglomeration and sintering of the particles [39] in order to achieve good crystal structure and long term stability of the film. Other problems like residual impurities incorporated from precursors are also a major limiting factor of these techniques. RF magnetron sputtering deposition on the other hand produces well controlled crystalline films but involves complex patterning to achieve porous structures prior to deposition of TiO₂ [56]. In this project, the high energy ball milling technique is used. It is a solid state reaction technique capable of synthesizing

crystalline TiO₂ at room temperature and pressure. In addition, the different TiO₂ phases of anatase and rutile can be properly controlled to co-exist concurrently.

2.5.1 Radio frequency magnetron sputtering deposition

Magnetron sputtering is one of the most widely used methods for preparing films with uniform structures that are well crystallized, or large-area composite films. Desired parameters like the film thickness, composition and structure can be controlled by varying the sputtering power, substrate temperature, partial pressures of the sputtering power and reactive atmosphere, sputtering time and distance between target and substrate. Doping films with other elements like transition metals or non-metals can also be done with composite targets or additional sources. Different transition metals could be doped by using a co-sputtering source, or gases (e.g., N₂ gas) can be introduced into the vacuum chamber as a reactive atmosphere [57-59].

2.5.2 Ion Implantation

Ion implantation is a method where metal ions are accelerated in the electric field at high kinetic energy and injected into the sample target. The metal ions injected can interact with the sample surface, leading to change in physical or chemical characteristics of the bulk material [60, 61]. This method is usually used in transition metal doped TiO₂ materials, where the sample target is a TiO₂ coated wafer or pellet.

2.5.3 *Wet chemical methods*

Popular wet-chemical synthesis techniques include sol-gel, hydrothermal treatment, co-precipitation, chemical vapour deposition were reported to yield TiO₂ films and powders with different structures and morphologies [21, 40, 62]. Chemical methods are a good way of obtaining small crystallites in the range of tens of nanometers to submicron, because they are formed from aqueous solutions like TiCl₃ [63], Ti(OBu)₄, Ti(OPrⁱ)₄ [64]. The sol-gel technique is usually accompanied by post-annealing as it forms amorphous TiO₂. The residual elements (C, H, N, Cl) can be vapourized during the annealing process, forming anatase and rutile TiO₂ depending on the annealing temperature. Alternatively, co-precipitation is also used to separate the product from its residues by centrifugation, washing and drying [40]. However, repeated washing and centrifugation is required to maintain its purity and annealing at high temperature is necessary to obtain crystalline powders.

2.5.3.1 Sol-gel technique

A colloid is a suspension where its dispersed phase interactions are dominated by Van der Waals forces and surface charges. Sol is a colloidal suspension of solids particles in a liquid. The sol could be prepared using starting compounds also known as the precursor which consists of a metal or metalloid element surrounded by various ligands. The precursors go through a hydrolysis or condensation process to form aqueous systems. Acid or bases can be added to influence the hydrolysis and condensation rates and the structure of the condensed product. Subsequently, polymerization takes place and ceramic materials can be

produced in various forms. The ultimate material is dependent on the time required to age, viscosity of the sol adjusted or solvent extraction means. Therefore, it enables production of sophisticated structures such as thin film, fiber, monoliths, porous membranes for wide area of applications [65, 66].

2.5.3.2 Hydrothermal treatment

Hydrothermal treatment is a technique to crystallize aqueous solutions at high vapour pressures in an autoclave. It has been used widely for making highly crystalline ceramic powders at low temperature in the range of 160-300 °C [35]. The crystallinity of TiO₂ particles is changed without a dramatic change in particle size. Hydrothermal treatment complements the sol-gel synthesis technique as crystallization could take place at lower temperatures. Under different hydrothermal conditions, different morphologies and structural forms like rutile and anatase can be obtained under the influence of temperature. However, phase transformation from anatase to rutile can only occur over 240 °C unless acid was added [67-69].

2.5.4 *High Energy Ball Milling Technique [25, 70]*

The Ball Milling is a mechanical alloying process where powder mixture in the ball mill is broken down into small particles when subjected to high energy collision. Mechanical alloying, as its name suggests involves rotational movements controlled by a motor with a rotating shaft and belt. It is a solid state process that could take place in different atmosphere, including ambient air. There are 3 different alloying systems: Attritor,

planetary mill and horizontal mill. As planetary mill could be done at high speed with small amount of materials, most people reported the use of this method [31, 33, 71].

2.5.4.1 Working Principle

Figure 2-7 shows the schematic diagram of how high energy ball milling of a planetary mill takes place. The equipment includes 2 to 4 milling vials and balls with ranging size and density. The vials are placed on a turn disc, where the disc and vials rotate in opposite directions. The balls are placed inside the vials to ‘mix’ the powder. The opposing motion causes the centrifugal force to be alternately synchronized. This causes the balls and powder to be rolling in alternate directions on the inner walls of the vials and impact results when they are lifted and thrown across the bowl to strike at the opposite wall. In addition, higher impact results when the balls strike each other. The impact energy could be modified by changing the rotational speed of the turn disc as well as impact frequency by incorporating temperature control elements as reaction rate could increase with temperature.

Figure 2-7: Schematic diagram of the Ball Milling mechanism [25]

There are 4 stages of the milling process. In the initial stage, collision between the balls and the particles change the shape of the particles. In the intermediate stage, fracturing of the particles occur. In the final stage, a refined and homogeneous alloy is formed and in the completion stage, a deformed metastable structure is formed. Due to high energy collision, the crystal structure of the powder will undergo plastic deformation, producing stress and strain. Such defects cause high distortion energy and surface energy [33, 37]. As a result, it will break bonds and form new bonds and other by-products.

Although the high energy ball milling technique is carried out in ambient, pressure experienced by the powder particles is caused by the compression of 2 colliding balls. To analyze the average pressure developed across the contacting surfaces of the milling media at maximum compression, the Hertz Impact Theory is used [72]:

$$P_{\max} = 0.4646 v^{0.4} \left(\frac{\rho}{E} \right)^{0.2} E \quad (2-11)$$

where E is the elastic modulus of the balls, ρ is the density of the balls, and v is the precollision relative velocity that is computed through

$$v = \frac{1}{3} \omega R_a \quad (2-12)$$

Where ω is the rotational velocity of the impeller arms and R_a is the radius of the canister.

2.5.4.2 Advantages and Disadvantages

Ball Milling has its advantages in terms of compositional requirements; particle size, contamination-free, no-loss grinding due to its sealants and more importantly, although the process results in fracturing and deformation of the particles, there is no change in proportion of the materials throughout the process. Because of the high impact energy,

anatase phase could be transformed into rutile phase over time, forming duo phase TiO_2 materials. This is termed mixed phase TiO_2 . This method provides the flexibility of synthesizing duo phase materials with different mixed phase concentrations. This opens up many different areas of application, because both the anatase and rutile phases have different properties and forming composite materials like the mixed phase TiO_2 can result in novel materials having the advantage of both structure types. Doping of Cr into TiO_2 lattice requiring high acceleration energies in order to change the electronic structure of the modified TiO_2 catalyst, could also be carried out using this synthesis technique [30]. Most importantly, post annealing is not a required process since crystalline TiO_2 materials are directly synthesized. For these reasons, it is widely used in industries as well as research laboratories for work on materials.

The main disadvantage is the introduction of defects due to high energy collision. Introduction of defects could lead to sub-bandgap illumination as a result of impurity energy levels within the bandgap. In addition, fresh surfaces formed by the high energy mills possess high surface energies, hence particle agglomeration is inevitable.

2.5.5 Modified Sol-gel Technique

The modified sol-gel technique is unique as it incorporates both the sol-gel and high energy ball milling technique to fabricate a wide range of composite films. A sol with controlled gelation rate was first prepared and the hydrolysis and ageing processes were eliminated. In this method, the sol acts as a binding material for the nanopowders. The synthesized nanopowders were added into the sol and ball milled to obtain a uniformly dispersed

suspension (slurry). The slurry is spin-coated onto a substrate to form uniformly distributed nanopowders embedded in a matrix. Both thick and thin films could be fabricated using spin coating. Further annealing processes are carried out to form preferred crystallized structure.

Spin coating can be divided into four stages: deposition, spin-up, spin-off, and evaporation as shown in Figure 2-8 [73]. Excess liquid is dispensed on the surface during the deposition stage. In the spin-up stage, the liquid flows radially outward driven by centrifugal force. In the spin-off stage, excess liquid flows to the perimeter and leaves as droplets. As the film thins, the rate of removal of excess liquid by spin-off slows down. This is because the thinner the film, the greater the resistance to flow, and the higher concentration of the nonvolatile components increases and raises the viscosity. In the fourth stage, evaporation takes over as the primary mechanism. Therefore, the thickness of the film is affected by the viscosity of the liquid, the angular velocity and the time of spinning. The advantage of spin coating is that a film of liquid tends to become uniform in thickness during spin-off and, once the uniformity is achieved, it tends to remain so provided that the viscosity is not shear dependent and does not vary over the substrate [65].

Figure 2-8: The four stages in the spin coating process [73].

2.6 Bandgap calculation

The most direct way of calculating the band structure of a semiconductor is to measure its absorption spectrum. In the absorption process, a photon of known energy excites an electron from a lower to higher energy state. Observations in change in the transmitted radiation hence provides information about the possible electron transitions and distribution of states [74]. For simple parabolic bands, the number of energy states $N(E) \propto E^{1/2}$ and hence for direct bandgap transitions,

$$\alpha(h\nu) = A^* (h\nu - E_g)^n, \quad (2-13)$$

Where $n = 1/2$ or $3/2$ for allowed or forbidden transitions respectively.

In the case of indirect bandgap material like anatase phase TiO_2 , a two step process involving change in energy and momentum has to be taken into account as photon cannot provide change in momentum. All occupied states of the valence band can connect to all

the empty states of the conduction band. The absorption coefficient is thus proportional to all combinations of states and the probability of interacting with phonon. Hence, the absorption coefficient for a transition taking into account phonon absorption or emission, for allowed transitions ($n=2$) is,

$$\alpha(h\nu) = A(h\nu - E_g)^2 \quad (2-14)$$

2.7 Photocatalytic Test on Methylene Blue

The photocatalytic activity of the modified TiO_2 were measured using a simple setup comprising of a light source, black box, magnetic stirrer and most importantly, the compound to quantify the activity. It is an heterocyclic aromatic compound known as Methylene blue (MB), $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$ shown in Figure 2-9.

MB is an odourless, solid dark green powder which becomes a blue solution when dissolved in water. Solutions of this substance are blue when in an oxidizing environment, but will turn colorless if exposed to a reducing agent. It is widely used as a redox indicator in analytical chemistry. Many reported the use of MB for research on photocatalytic degradation [11, 38, 75-78]. In the experiments, photocatalytic characterization would be limited to the use of MB as a contaminant.

Figure 2-9: Chemical structure of MB

The initial step of MB degradation is described by the cleavage of bonds of the C-S+=C functional group, forming the sulfoxide group. This requires the conservation of the double bond conjugation, it induces the opening of the centre aromatic ring containing both the heteroatoms N and S. The sulfoxide undergoes a second OH[•] attack leading to the dissociation of the 2 benzene rings. A third attack results in sulfonic acid and finally a last attack would lead to the release of sulphate ions.

As for the N-groups, the centre N=C cleavage is induced by the C-S+=C cleavage to form amino groups. The amino groups can be substituted by OH[•] to release NH₂[•] radicals which generates ammonia and ammonium ions. The ammonium groups are then slowly oxidized into nitrate or directly oxidized into hydroxylamine leading to nitrate [79].

CHAPTER 3 EXPERIMENTAL PROCEDURES

This project is divided into 3 components and follows a systematic study that will eventually lead to the synthesis of a TiO₂ based film for photocatalytic applications. First is synthesis of TiO₂ based materials using the high energy ball milling technique. Detailed experimental procedures for the development of mixed phase TiO₂ and doped TiO₂ are described. Next, the TiO₂ materials were examined using standard materials characterization tools. The photocatalytic activity of the material can be influenced by factors like particle size, phase composition, surface area, optical bandgap and dopant. Understanding the material synthesized is of utmost importance. Finally, verification of the characteristics of the nanopowder samples when it is incorporated into a composite film. This is to ensure that under different conditions, the synthesized powders will still work as efficiently. The process flow in which the investigations are carried out is summarized in Figure 3-1.

Figure 3-1: Flowchart to illustrate the experimental procedures

The high energy ball milling technique was used to synthesize mixed phase TiO₂ and Cr-doped mixed phase TiO₂ nanopowders. The ball milling was carried out over time and the duration to achieve 8:2 ratio of anatase and rutile TiO₂ was determined. Different mixed phase ratios could be obtained at well controlled milling duration and conditions. The Cr nanopowders were successfully doped into TiO₂ to form Cr-doped mixed phase TiO₂ powders. The 8:2 mixed anatase to rutile ratio was not breached under similar milling

conditions. Different concentrations of Cr nanopowders were doped into TiO₂ and the sample which yielded the best photocatalytic activity was identified.

Comparative studies between pure anatase phase TiO₂, mixed phase TiO₂, pure rutile phase TiO₂, Cr-doped TiO₂ and Degussa P25 was done using material characterization tools. Optical property tests were also carried out to observe the red shift in the optical bandgap of the material as a result of change in crystal structure and doping. It was a preliminary test to assess the photocatalytic activity of the TiO₂ based materials using a wide wavelength range of 200-800 nm. A photoreactor was set up to test the photodegradation of methylene blue in the presence of the TiO₂ based photocatalyst material. The organic dye degraded faster in the presence of the mixed phase TiO₂ powder as compared with the pure anatase phase TiO₂ powders. Similarly, the photocatalytic efficiency of the Cr-doped mixed phase TiO₂ materials was examined. The photocatalyst prove to be stable, as repeated test showed that the time duration taken for full degradation of the organic dye remained unchanged.

Composite film samples were fabricated using the modified sol-gel technique. Slurries of Cr-doped mixed phase TiO₂ nanopowders and mixed phase TiO₂ powders were synthesized. As it is more commercially viable to incorporate the photocatalyst into a coating than a powder form, the focus of this set of experiment was to verify that the characteristics of the nanopowders were not compromised when it is fabricated into composite films.

3.2 Powder synthesis

The synthesis of powders involve the high energy ball milling technique using pure anatase phase TiO_2 (99.9 %) from Alfar Aesar. Two 250 ml tungsten carbide (93 % WC and 6 % Co) vials with inner wall diameter of 75 mm were used. This type of vial was used because of its very good resistance to abrasion. 20 balls of 10 mm in diameter and 10 balls of 20 mm in diameter were placed in each vials and the ball to powder weight ratio was maintained at 20:1. The speed of rotation was kept at 200 rpm and each round of rotation was 15 min with 8 min interval.

3.2.1 *Synthesis of mixed phase TiO_2*

The pure anatase phase TiO_2 powder was ball milled for a 20 h duration. A small quantity of powder was retrieved regularly at 2 h intervals until the 20th hour for analysis of the mixed phase ratio and particle size. The distribution of change in anatase to rutile phase TiO_2 could be observed over time. The objective of this experiment was to determine the milling duration required to obtain an 8:2 ratio of anatase and rutile phase TiO_2 respectively. Balls were also removed from the vials as a result to maintain the 20:1 ball to powder ratio in the vials.

3.2.2 *Synthesis of Cr-doped TiO₂ and Cr₂O₃-doped TiO₂*

Cr and Cr₂O₃ nanopowders from Sigma Aldrich were used. 0.1 wt% of Cr and Cr₂O₃ were added to pure anatase TiO₂ and subjected to similar high energy ball milling conditions in section 3.2.1. The objective of this experiment was to observe changes between doped and un-doped TiO₂ as well as differences between the 2 doping materials. The first run was done to determine the milling hours required to achieve the desired mixed-phase and observe changes in milling hours required compared to un-doped TiO₂. The second run was done to obtain ample amount of material for subsequent experiments. In order to replicate the experiments, the number of intervals stopped, milling hours, idle hours and number of balls used to obtain the final material during the second or subsequent runs remained unchanged.

Three other doping concentrations of 1, 1.5 and 5 wt% were explored for Cr in TiO₂. It has been reported that the doping concentration in the range of 0.2-1.5 wt% yields best performance [4, 5, 45, 46]. Similar ball milling experimental runs were carried out.

3.3 Characterization of powder

Photocatalytic activities of TiO₂ materials strongly depend on its surface morphology and crystal structure [11, 12, 19]. The synthesized powders were characterized using X-ray Diffraction (XRD) Spectrometer, Field Emission Scanning Electron Microscope (FESEM), X-ray Photoelectron Spectroscopy (XPS), Diffuse Reflectance Spectroscopy (DRS), Laser

Particle Sizer, Brunauer-Emmett-Teller (BET) Surface Area and Ultraviolet-Visible (UV/Vis) Spectrometer to observe its physical and optical properties.

3.3.1 X-ray Diffraction

Several data could be extracted from the XRD, namely average particle size, phase composition, and element composition. The crystallographic structure of the TiO₂ powders were quantified using the XRD-6000 Shimadzu at a range of 20-60 ° at 2 °/min, using 1 mm scattering and receiving slits. The full wave at half maximum (FWHM) of the 3 most significant peak of both the anatase and rutile phase obtained from the XRD pattern were taken into consideration when calculating the average particle size and phase composition.

3.3.1.1 Average grain size calculation

Based on the Scherer's Equation and the Williamson-Hall Plot, assuming that there is broadening of the XRD peak is solely a result of the particle size; the Scherer's equation is given by

$$\beta = \frac{c\lambda}{d_c \cos \theta} \quad (3-1)$$

Where, β is the FWHM at different 2θ angle, λ is the wavelength of X-Ray, and $c = 0.9$ is the particle shape constant

To take into account peak broadening as a result of finite crystalline size, micro-straining and instrumental broadening, the Williamson-Hall Plot is used.

$$\sqrt{(B_m^2 - B_i^2)} \cos \theta_i = \frac{c\lambda}{d_c} + \varepsilon \sin \theta_i \quad (3-2)$$

Where, B_m is the measured FWHM, B_i is the FWHM due to instrumental broadening, ε is strain constant, and θ_i is the Bragg's angle

3.3.1.2 Phase composition calculation

The phase composition calculation takes into account the integrated area under the 3 most significant peak of the anatase and rutile phases of TiO_2 . In this calculation, it is assumed that there are no other crystal structures like brookite significant to be taken into consideration. The percentage of anatase phase and rutile phase of TiO_2 in the sample can be represented by the equation (3.3) and (3.4)

$$\%A = \frac{I_a A_a}{A_a + A_r} \times 100 \quad (3-3)$$

$$\%R = \frac{I_r A_r}{A_a + A_r} \times 100 \quad (3-4)$$

Where, $I_{a(r)}$ is the intensity of the anatase (rutile) peak and $A_{a(r)}$ is the integrated area under the anatase (rutile) peak

3.3.2 *X-ray photoelectron spectroscopy*

Powdered samples were pressed into pellets of 10 mm diameter and 3-4 mm in thickness, left in the dry box for at least one day before it was analyzed. A wide scan at 1 eV/step was first done to identify the different types of element present in the sample. Narrow scans of each element identified were done at 0.1 eV/step. Narrow scans were repeated 5 to 10 times

for samples with very weak signals so as to reduce the noise. As the samples were semiconducting, the charge neutralizer was always switched on every scan.

The elemental compositional studies of the various TiO₂ based powders were examined using Kratos Axis-Ultra XPS. All curve fitting was done using the 70 % Gaussian 30 % Lorentzian model and Shirley's background for consistency. Carbon C 1s at 285.0 eV was used for calibration. The fitted curves were then mapped against the standard data XPS peak data from Physical Electronics.

3.3.3 Laser particle sizer

The particle size distribution was obtained using a Laser Particle Sizer at a fixed concentration of 0.01g/20 ml solvent. A laser beam is incident onto the suspension containing the particles of concern. When the laser hits the particle, it would lead the vibration motion of surrounding particles. Using the laws of Brownian motion, it is able to calculate the particle size of the sample. The mean is calculated and the distribution of the particle sizes of the samples could be obtained.

3.3.4 Scanning electron microscope

The micrographs were captured by FESEM using the JOEL JSM-6340F to provide a qualitative analysis of the particle size using the JOEL JSM-6340F. The SEM is a very simple and instant method for obtaining graphical analysis of the synthesized samples. In

addition it was used to complement the calculations made using the XRD data and the laser particle sizer.

3.3.5 Brunauer-Emmett-Teller (BET)

For the BET measurements, the powders were degassed for 12 hours to eliminate trapped moisture in the samples. BET was used to obtain a quantitative analysis of the surface area of the samples. A large surface area leads to a greater exposed area for photocatalytic reaction to take place. Therefore, this information is essential for comparison between P25 and other TiO₂ based samples synthesized, to understand how surface area affects photocatalytic reactivity.

3.3.6 UV-Vis spectrometer

Preliminary optical bandgap measurements were done using the UV-VIS Spectrometer (Shimadzu MPC-2200) in the range of 300-800 nm. Diffuse reflectance of the powder materials was measured. Diffuse reflectance relied upon the focused projection of the spectrometer beam into the sample where it was reflected, scattered and transmitted through the sample material. The back reflected, diffusely scattered light (some of which is absorbed by the sample) was then collected at the detector. The part of the beam that was scattered within a sample and returned to the surface was considered to be diffuse reflection. Using the Kubelka-Munk model, the absorption spectra could be tabulated. The Kubelka-Munk equation can be represented as

$$f(R) = \frac{(1-R^2)}{2R} = \frac{k}{s} \quad (3-5)$$

Where, R is the absolute reflectance of the sampled layer, k is the molar absorption coefficient, and s is the scattering coefficient.

From the absorption spectra, the optical bandgap of the powder samples could be estimated. Characteristic “turning point” energies refer to the position where the absorbance decreases more rapidly with wavelength below the turning point than above it. This observed turning point was used to measure the bandgap of the samples.

3.3.7 Photocatalytic activity test

This experiment was carried out to observe the degradation of organic dyes in water under the influence of photocatalyst materials. It gave a good representation of the photoreactivity of the material as the parameters used in the setup were used to simulate real time environment.

The MB solution was first retrieved from a suspension of the photocatalyst powder and NaCl solution by centrifugation. Then, the concentration of MB solution was measured using the UV-Spectrometer (Shimadzu UV-2450) after different periods of irradiation under fluorescent light. The Beer-Lambert law was used to draw a relationship between absorbance and concentration of solution. According to the equation, the absorbance is linear with the concentration (or number density of absorbers)

$$A = \epsilon lc \quad (3-6)$$

The different types of TiO₂ based materials as well as low Cr-doped TiO₂ up to 5 wt % were analyzed. The flowchart in Figure 3-2 summarizes these procedures. The different concentrations of MB solution over a period of time using different photocatalysts were then summarized to compare the efficiency of each photocatalyst.

Figure 3-2: Flowchart of the MB dye degradation test

3.4 Composite film fabrication

Composite films of modified TiO₂ were fabricated to better test its applications. A solution of titanium butoxide and 2-methoxy-ethanol were used as the molecular precursor of TiO₂.

Acetyl-acetone is a chemical additive to moderate the gelation rate. Powders synthesized earlier on were added to the precursor and ball milled to form a well dispersed slurry. The ratio of the powder-sol slurry was 1:10. The mixture was ball milled at 200 rpm over 12 h and spin-coated onto glass slides. The hydrocarbons and other organic molecules were removed during baking, otherwise known as the dehydration process, to form amorphous TiO_2 from the sol. Annealing was subsequently carried out as it is important for the crystallization of TiO_2 [21]. Single layer and multi-layer films were spin coated to observe the requirements for uniform thickness.

Previous work was done on ball milled powder samples to obtain the desired mixed phase ratio suitable for photocatalysis. This experiment aimed at verifying the phase composition of the powder was not compromised after it is being fabricated into a composite film. Low Cr and Cr_2O_3 -doping samples, mixed phase TiO_2 composite films were fabricated. P25, pure TiO_2 composite films and sol-only coatings were fabricated for calibration.

3.5 Composite film characterization and verification

Characterization was repeated to understand the properties of the composite films, how and in what ways it differed from the powder samples. The Siemens D5008 Diffractometer was used to reveal their phase composition. FESEM was used to capture both the surface and cross-sectional micrographs as well as to estimate the thickness of the composite films. UV-VIS spectrometer was used to study the optical properties and to calculate the bandgap

calculation of the films. For films samples, the bandgap calculation differs and the method was discussed in section 3.5.1.

3.5.1 Bandgap calculation for composite films

Since the films were semi-transparent, transmittance of the sample could be measured. The absorption coefficient, α could be calculated from the transmittance data of the sample [74].

The transmission coefficient is defined as the ratio of transmitted power to incident power, I/I_0 .

Referring to Figure 3-3, for a specimen with thickness d , an absorption coefficient α , and a reflectivity R , the radiation

Figure 3-3: Illustration of transmittance through a film

traversing the first interface is

$I(1-R)I_0$, the radiation reaching the second interface is $(1-R)I_0 \exp(-\alpha x)$ and only a fraction of $(1-R)(1-R)I_0 \exp(-\alpha x)$ emerges. The portion internally reflected eventually comes out, but considerably attenuated.

The end result of the overall transmission is given by

$$T = \frac{(1-R)^2 \exp(-\alpha x)}{1 - R^2 \exp(-2\alpha x)} \quad (3-7)$$

When αx is large,

$$T \approx (1-R)^2 \exp(-\alpha x) \quad (3-8)$$

Since R is unknown, α can be obtained from the relative values of T from 2 samples,

$$\frac{T_1}{T_2} = \exp \alpha(d_1 - d_2) \quad (3-9)$$

The sample was done in ambient and the equation can be reduced to

$$\alpha = \frac{1}{d} \ln\left(\frac{100}{\%T}\right) \quad (3-10)$$

Where it was assumed transmittance is 100 % in air.

The samples concerned consist of direct and indirect bandgap, hence 2 types of calculations were taken into consideration [80]. From equation (2-13) where $\alpha(h\nu) = A^*(h\nu - E_g)^n$, for $n = 1/2$ and $n=2$ for direct and indirect bandgap material respectively, the graph of $[\alpha(h\nu)]^{1/n}$ vs $(h\nu)$ was plotted. The tangent at the turning point where $[\alpha(h\nu)]^{1/n} = 0$ is the optical bandgap of the material.

CHAPTER 4 RESULTS & DISCUSSIONS OF TiO₂

POWDERS

Powder samples were synthesized using the High Energy Ball Milling Technique. The TiO₂ powder was initially 99.9 % pure anatase phase. Transformation from anatase to rutile phase can happen by means of heat treatment higher than 600 °C, chemical treatments or by high energy ball milling [31]. The transformation process was investigated and the physical and optical properties of the doped and un-doped mixed phase TiO₂ powders were discussed.

4.1 Physical Properties of TiO₂

The high energy ball milling technique was particularly useful as it can transform anatase to rutile phases in varying degree depending on the milling time. Figure 4-1 shows the XRD pattern of TiO₂ milled over a period up to 20 h. it was observed that gradual anatase to rutile phase transition took place over time and the amount of anatase phase was close to 0 after milling for 8 hours and from 8th to 20th hour, the complete transition to rutile phase was reached. The diffraction lines were also broadened, since the milling process introduced lattice strains and caused a decrease in crystallite sizes [81].

8 different types of powder samples would be discussed in this chapter. Its phase composition and composition and doping concentration are summarized in

Table 4-1. The first 2 samples, P25 and T-A are commercially available powders whereas the rest are synthesized powders.

Figure 4-1: XRD pattern of TiO₂ samples ball milled to 20 h.

Table 4-1: Summary of the different sample types

Sample	Description	% Anatase	% rutile	% Cr (wt)
P25	commercial	80	20	0
T-A	anatase	99.9	0	0
T-M	mixed phase	80	20	0
T-R	rutile	5	95	0
A1	doped with Cr	80	20	0.1
A2	doped with Cr ₂ O ₃	80	20	0.1
B	doped with Cr	80	20	1
C	doped with Cr	80	20	1.5
D	doped with Cr	80	20	5

This anatase to rutile phase transition can take place without the need for post annealing as required by other synthesis techniques because of the high impact energy in the vials during the ball milling process. Two types of collision, 1) between the balls and the vial and 2) amongst the balls, cause the powder to change in shape and deform. It gains energy in the process and overtime, new bonds were formed and the anatase phase TiO_2 transforms into the more stable rutile phase of TiO_2 . However, homogeneity does not take place immediately and since the phase change is an irreversible process, the transformed powders remained as rutile phase TiO_2 . This makes the mixture stable and yet able to retain the duo phase condition. Hence, variations in the mixed phase ratio could be easily obtained and maintained. It was also observed that there is a formation of an additional phase which is identified as the high pressure TiO_2 phase (TiO_2 II) for samples ball milled for a short duration [82]. This phase will be discussed further in Section 4.3.3.

In order to ensure that the XRD pattern comparisons were good representations of the actually properties of the ball milled materials, sample preparations had to be meticulous. As the amount of powder used for each scan could also change its intensity, a standard size powder holder was used throughout the experiment. The systematic errors could be minimized by using the monochromatization techniques [83]. The challenges in monochromatization is not only to reduce angular and wavelength dispersions, but more importantly to minimize loss of intensity of the incident and diffracted x-ray beams. These include the use of divergence slit at the x-ray tube and soller slits at the both the incident and diffracted beam path. This slit is used to minimize in-plane divergence. A second soller

slit is added at the incident and diffracted beam to further minimize angular divergence parallel to the goniometer axis. Choice of slit size is important to ensure that divergence is minimized. The use of β -filter is also essential to absorb $K\beta$ radiation and to transmit $K\alpha_1$ and $K\alpha_2$ parts of the x-ray spectrum. In addition, to standardize the XRD patterns, the background elimination was done before calculations were made.

4.1.2 Mixed phase ratio

The mixed phase ratio was calculated based on the integrated peak intensities of the 3 most preferred orientations of anatase and rutile phases of TiO₂, as line broadening effects could lead to inaccuracy if peak intensities were used [83]. In order to obtain the desired mixed anatase to rutile phase ratio of 8:2 (the same ratio of P25), short milling duration was required. The TiO₂ powder was ball milled for a maximum of 6 hours at smaller intervals. Figure 4-2 shows how the anatase and rutile phase composition changes over time. The final time needed to achieve this ratio of 8:2 is 3.5 hours.

Figure 4-2: Mixed phase ratio of TiO₂ for different milling duration

The same experiment was carried out for samples doped with concentrations of Cr nano powders ranging from 0.1-5 wt%. In the this process, 2 things occurred; first, the phase transition from anatase to rutile to attain 8:2 ratio was completed after 3 hours of ball milling. Second, the Cr was doped into the TiO₂ simultaneously. The Cr³⁺ has a substitutional effect on the Ti⁴⁺. Its XRD patterns are shown in Figure 4-3.

Similarly, the mixed phase 8:2 ratio could be attained after milling for 3 hours for all the samples and the mixed phase ratios of doped samples do not differ much as a result of doping (see Figure 4-4). This shows that Cr nano powders are in no way a barrier to the phase transformation. Hence, the milling duration of mixed phase TiO₂ and doped mixed phase TiO₂ was fixed at 3.5 h and 3 h respectively hereafter. The mixed phase TiO₂

samples ball milled for 3.5 hours are labeled as T-M and doped samples ball milled for 3 hours are labeled A-D according to its doping concentration.

Figure 4-3: XRD pattern of mixed phase ratio of TiO₂ samples doped at different Cr concentration

Figure 4-4: Mixed phase ratio of TiO_2 samples doped at different Cr concentration after milling for 3 hours

However, it was also observed that there is a decrease in the peak intensities of the preferred orientations of TiO_2 as Cr doping concentration increases from 0.1- 5 wt% for sample A-D. (see Figure 4-3) This could be due to the increasing substitutional effect of Cr doping, leading to the formation of imperfect TiO_2 crystals.

In addition, there is a 0.2 to 0.4 ° shift of the [101] anatase phase peak when compared to the pure anatase phase TiO_2 . A summary of the peak shift is shown in Figure 4-5. This peak shift could be attributed to the disordered substitution in solid solution, corresponding to weakening of the peak intensity and line broadening due to introduction of lattice strains during the ball milling process. Similarly for the Cr- doped ball milled TiO_2 samples seen

in Figure 4-4, shift in the [101] anatase phase peak could be observed and summarized in Figure 4-6.

Figure 4-5: Summary of trends of anatase phase peak shift for ball milling TiO₂.

Figure 4-6: Summary of trends of [101] anatase phase TiO₂ peaks with increasing Cr doping.

From the Bragg's equation, $n\lambda = 2d\sin\Theta$, a change in theta corresponds to a change in the lattice constant, since the wavelength of the x-ray remains unchanged for all XRD analysis. Despite the same percentage of phase change occurring in all the TiO₂ samples seen in Figure 4-4, ball milling has led to different degree of change in the lattice constants in different samples. There are several reasons for change in lattice constant. First the high energy ball milling technique can cause the removal of oxygen ions leading to increase in oxygen vacancies. This oxygen deficiency will lead to an increase in bonding energy among the rest of the atoms in the TiO₂ structure. As a result of the increase attractive force between the electrons and protons due to the loss of negative charges, there will be a decrease in lattice constant. The reduction in oxygen ions in the sample due to imperfect crystal structure can also be observed by the darkening of the sample material from white to grayish colour [84].

Sample T-M was at a turning point in Figure 4-5 where, beyond the milling duration of 3.5 h there was an increase in lattice constant. This was likely due to heating or increase in energy [85]. During the high energy ball milling, heat was caused by friction and the high energy transfer caused by impact energy between the walls of the vials and the balls during the alternating rotating planar motion [25]. In the second stage of the milling process, stress on the lattice leads to changes such as like deformation and fracture. Part of this stress could be released after the milling process stops, in the form of agglomeration of particles as could be observed in SEM in Section 4.1.4. The residual stress (not eliminated upon

cooling down) could cause a plastic deformation of the powders that lead to a permanent increase in the lattice constant.

In addition, Cr³⁺ is the most stable electronic configuration of Cr. When Cr successfully substituted the Ti at the lattice site, a hole will be created. As a result, the lattice surrounding the impurity atom becomes distorted and could extend to a few lattice planes surrounding it [86]. Pan. X et al [87] see this increase in oxygen vacancies as the cause of phase transformation from anatase to rutile, which could also explain why the sample ball milled for 20 hours was almost fully transformed to the rutile phase.

Both formation of oxygen vacancies and stress would occur in all the ball milled powders. The extent of which is more would thus lead to an ultimate increase or decrease in lattice constant. In Figure 4-5 and Figure 4-6, we can observe that both the doped and un-doped powders followed a certain trend, and were not random processes. The addition of Cr into TiO₂ probably led to a higher increase in oxygen vacancy that is advantageous to suit the application of an oxidizing agent.

4.1.3 Average grain size

The average grain size calculations were based on the Scherrer's Equation and the Williamson-Hall Plot. To eliminate instrumental broadening, un-milled TiO₂ samples (both doped and un-doped) were annealed to 950 °C. The increase in grain size as a result of annealing to half the melting point of TiO₂ would ideally produce discrete XRD peaks.

Since it is not possible to obtain discrete peaks practically, the FWHM (B_i) of the peaks obtained from the XRD plot is the result of the error in the instrument. A root-mean-square value is taken to further reduce the errors in averaging.

It could be observed from Figure 4-7 that the average grain size of the nano powders decreases with milling duration, stabilizing at less than 20 nm after 3.5 hours. L.B. Kong et al [88] and A. Gajovic et al [81] had also reported this technique was favourable in producing nanosized powders. R.M. Ren et al [82] reported a reduction of crystallite to about 4-20 nm and the crystallites were embedded into sub-micron sized particles.

Figure 4-7: Average grain size of TiO_2 sample at different milling duration

A similar observation was made in Figure 4-8 for the doped samples, where the average grain size hovered at about 20 nm as compared to the un-milled TiO_2 powders which has a

grain size of about 140 nm. As the powders are polycrystalline materials, it indicate that there are many grains in each particle and hence the grain size is not a representation of its average particle size. However, the grain size analysis is still important because the reduction in grain size provides good interface between the anatase and the rutile phase as well as the doped Cr particles. The interface between anatase and rutile phases of TiO_2 is important because the rutile phase is used as an electron sink, thus increasing the charge separation. Similarly for Cr ions, the photogenerated electrons are trapped, which can lead to a reduction on the recombination rate.

Figure 4-8: Comparing the average grain size of TiO_2 samples doped at different Cr concentration ball milled for 3 hours with pure anatase phase TiO_2

4.1.4 Average particle size

The average particle size of the powders was estimated by both laser particle sizer and FESEM. The laser particle sizer gives a quantitative measurement whereas the FESEM can give a more direct and qualitative proof of the case.

The micrographs in Figure 4-9 show that the particles are agglomerated with some particles close to 200 nm. The particle size distribution from laser particle sizer is consistent with the estimations from SEM and is shown in Figure 4-10. In order to get a reliable distribution, the sample has to be well dispersed in either water or ethanol suspension. A vehicle was also added to the powders to reduce agglomeration. The mixed phase TiO_2 powders at the 8:2 ratio is close to 200 nm, similarly for the TiO_2 sample milled for 20 hours. In Figure 4-11, the doped samples saw increase in particle sizes to 222 nm for Cr_2O_3 doped (A2) samples and 283 nm for Cr doped (A1) samples. As mentioned earlier in Section 1.2, the particle size for P25 was 25 nm and 85 nm for rutile and anatase phase respectively.

Figure 4-9: Micrograph of doped powder sample at a) 30 K magnification and b) 70 K magnification.

Figure 4-10: Particle size distribution comparison of P25 and mixed phase TiO_2 materials.

Figure 4-11: Particle size distribution comparison of doped mixed phase TiO_2 materials.

The BET surface area of 2 materials – sample T-M and sample B were measured and a comparison with P25 was made and shown in Figure 4-12. It shows that P25 has a surface area is about twice of sample T-M and more than 2.5 times that of sample B. The relationship between particle size and surface area between the samples shows that an increase in particle size leads to reduction in surface area but not a linear relationship. When P25 is mixed with water, an anatase and rutile interface is formed [16], which explains why the measured particle size of P25 using the laser particle sizer is way beyond that of the indicated 85 nm. How particle size and surface area will affect the efficiency of the photocatalyst material will be discussed in Section 4.3.

Figure 4-12: Relationship between BET surface area and particle size of selected materials

4.1.5 Chemical Structure & Stoichiometry

Structural changes caused by ball milling and doping were further analyzed using the XPS. 5 samples, namely sample T-A, T-M, T-R as well as A1 and A2 are discussed. Figure 4-13 shows the survey scan of pure anatase phase TiO₂ sample and Figure 4-14 shows each of the elements' peaks in greater detail. Clearly C contamination, Ti and O could be observed in the wide scan. In the narrow scan, the spin orbital with highest probability of occurrence was examined. A very distinct Ti 2p doublet was observed for pure anatase phase, the asymmetric O 1s curve was caused by surface adsorbed oxygen. Carbon contamination other than C=C and C=H include C=O and CO₃²⁻. However, the carbon contamination is inevitable, which is less than 20 % as shown in Table 4-2. In Figure 4-14 the O 1sa corresponds to oxide in TiO₂ at binding energy (B.E.) 529.9 eV as suggested in the XPS handbook [89]. O 1sb corresponds to C=O (C 1s) bonds and carbonates (C 1sc). Lastly, O 1sc denotes the surface adsorbed oxygen.

Figure 4-13: XPS survey spectrum of sample T-A

Figure 4-14: XPS narrow scan spectra for O 1s, Ti 2p and C 1s of sample T-A

Table 4-2: Quantitative analysis of sample T-A

element	BE (eV)	FWHM (eV)	RSF	Atomic Conc %	sum
O 1sa	529.84	1.15	0.78	46.19	61.35
O 1sb	531.11	1.61	0.78	12.24	
O 1sc	532.57	1.82	0.78	2.93	
Ti 2p3/2	458.64	1.07	2.00	15.34	23.26
Ti 2p1/2	464.33	2.04	2.00	7.92	
C 1sa	285.00	1.38	0.28	10.37	15.39
C 1sb	286.63	1.45	0.28	3.47	
C 1sc	288.59	1.51	0.28	1.55	

Similarly for the mixed phase TiO₂ samples shown in Figure 4-15, Ti 2p doublets as well as O 1s singlet were analyzed. A similar structure was observed for the ball milled TiO₂ except with increase in carbon content and a slight drop in O/Ti ratio to 1.89 as shown in Table 4-3.

Figure 4-15: XPS narrow scan spectra for O 1s, Ti 2p and C 1s of sample T-M

Table 4-3: Quantitative analysis of sample T-M

element	Position BE (eV)	FWHM (eV)	RSF	Atomic Conc %	sum
O 1s a	529.936	1.199	0.78	34.44	47.51
O 1s b	531.322	2.414	0.78	13.07	
Ti 2p 3/2	458.63	1.131	2.001	12.22	18.25
Ti 2p 1/2	464.298	2.069	2.001	6.03	
C 1s a	284.998	1.293	0.278	27.76	32.31
C 1s b	286.247	1.628	0.278	4.55	
C 1s c	288.991	1.256	0.278	1.92	

Figure 4-16 shows the XPS spectra for sample T-R (see Figure 4-1) that has been ball milled for 20 h. Table 4-4 shows the quantitative analysis for sample T-R. The TiO₂ structure was distinct and the O/Ti ratio is 1.69. An increasing carbon contamination was

also observed with increasing milling time. This C-contamination could also have resulted when the powders were periodically retrieved from the bowl.

Figure 4-16: XPS narrow scan of sample T-R

Table 4-4: Quantitative analysis of sample T-R

element	Position BE (eV)	FWHM (eV)	RSF	Atomic Conc %	sum
O 1s a	529.759	0.993	0.78	33.58	48.25
O 1s b	530.421	0.821	0.78	7.42	
O 1s c	531.507	1.498	0.78	7.25	
Ti 2p 3/2	458.578	1.094	2.001	13.55	19.91
Ti 2p 1/2	464.284	1.935	2.001	6.36	
C 1s a	285.01	1.421	0.278	24.93	31.84
C 1s b	286.561	1.197	0.278	3.25	
C 1s c	288.907	1.645	0.278	3.66	

Figure 4-17 shows the XPS spectra for sample A1 and Figure 4-18 shows the XPS spectra for sample A2. Table 4-5 and Table 4-6 tabulate their respective elemental composition of Ti, O, C and Cr. The Cr 2p doublets observed in Figure 4-17 and Figure 4-18 are very noisy and cannot give a proper analysis. However, I. Grohmann et al and E. Unveren et al did an XPS study on the nature of Cr_2O_3 . They found that the reason for the noisy signals is because Cr 2p has strong satellites on higher binding energy side of the photoelectron peaks [90, 91]. As a result, the Cr $2p_{3/2}$ peak will overlap the Cr $2p_{1/2}$ peak. In that study, it explained the 2 scenarios that will occur. First, 3d orbitals and unfilled (radially extended) 4s-p orbitals of a transition metal are pulled down to higher binding energy upon creation of a core hole. One of these levels could then become populated to locally charge-compensate the core hole. Second, in the case of transition-metal insulators, the electron charge may be drawn from the p-band of the hybridized ligand. Thus, two final states are possible. One state corresponds to a fully relaxed (local screened) condition involving occupancy of a Cr 3d electron level. The other (non-local screening) state corresponds to a partial population of the radially more extended cation 4s-p screening orbitals, excluding the occupancy of the localized 3d electron level. This is possible due to the strong overlap (both in energy and in space) of the spatially extended cation 4s-p and ligand 2p orbitals.

Figure 4-17: XPS narrow scan spectra for O 1s, Ti 2p, Cr 2p and C 1s of sample A1

Table 4-5: Quantitative analysis of sample A1

element	Position BE (eV)	FWHM (eV)	RSF	Atomic Conc %	sum
Cr 2p	577.021	4.055	2.427	0.66	1.26
Cr 2p 3/2a	579.555	3.389	2.427	0.27	
Cr 2p 3/2b	582.314	3.725	2.427	0.15	
Cr 2p 1/2a	589.424	3.389	2.427	0.13	
Cr 2p 1/2b	592.865	2.092	2.427	0.05	
O 1s a	529.856	1.179	0.78	31.84	42.8
O 1s b	531.248	2.399	0.78	10.96	
Ti 2p 3/2	458.546	1.12	2.001	11.25	16.83
Ti 2p 1/2	464.236	2.039	2.001	5.58	
C 1s a	284.998	1.309	0.278	35.06	39.1
C 1s b	286.557	1.205	0.278	2.45	
C 1s c	288.936	1.41	0.278	1.59

Figure 4-18: XPS narrow scan spectra for O 1s, Ti 2p, Cr 2p and C 1s of sample A2

Table 4-6: Quantitative analysis of sample A2

element	Position BE (eV)	FWHM (eV)	RSF	Atomic Conc %	sum
Cr 2p 5/2a	575.556	1.904	2.427	0.17	1.24
Cr 2p 5/2b	577.384	2.46	2.427	0.64	
Cr 2p 5/2c	580.22	3.228	2.427	0.43	
O 1s a	530.026	1.139	0.78	33.1	52.6
O 1s b	530.707	1.047	0.78	9.12	
O 1s c	531.849	1.589	0.78	10.38	
Ti 2p 3/2	458.784	1.211	2.001	11.7	16.97
Ti 2p 1/2	464.484	1.945	2.001	5.27	
C 1s a	285	1.49	0.278	19.94	29.2
C 1s b	286.494	1.715	0.278	6.01	
C 1s c	288.825	1.928	0.278	3.25	

The O/Ti ratio and Cr/Ti ratio can be calculated from the samples' respective table of quantitative analysis and are summarized in Table 4-7. The O/Ti ratio for pure anatase phase TiO_2 was close to 2. After ball milling for both doped and un-doped TiO_2 , the O composition for all samples reduced, especially in the sample ball milled for 20 h. This shows that ball milling can increase the oxygen vacancies. These results were in line with XRD observations where decrease in lattice constant was a result of the removed oxygen.

With Cr and Cr_2O_3 doping, the oxygen content was slightly increased when compared to the un-doped mixed phase TiO_2 . This was especially the case in the Cr_2O_3 doped sample where the O/Ti ratio is 1.95. In the Cr doped sample, the bonding of Cr_2O_3 occurs more easily than substituting Ti in the TiO_2 lattice. As a result, O 1s at 529 eV is loss to O 1s bond with Cr as well as the creation of oxygen vacancies in Ti. As for the Cr_2O_3 doped sample, the possible inter-substitution of O^{2-} between TiO_2 and Cr_2O_3 resulted in a relatively higher O/Ti ratio overall. Hence, the increase in lattice constant of un-doped mixed phase TiO_2 could have been due to an increase in the oxygen content. Comparing the doped and un-doped samples ball milled for the same duration, it could be observed that the lattice constant reduction is a result of Cr doping (see Figure 4-6).

In addition, for the doped samples, Cr/Ti ratio compared with the actual doping concentration was found to be in agreement with the initial doping concentration. Despite a small portion of powder used in the XPS analysis, it has shown that the high energy ball milling could produce homogeneous powder samples.

Table 4-7: Comparison of the elemental composition of each sample

sample type	Milling duration	O/Ti ratio	Cr/Ti ratio
T-A	0 h	1.986	
T-M	3.5 h	1.887	
T-R	20 h	1.687	
A1	3 h	1.892	0.075
A2	3 h	1.951	0.073

4.2 Optical Properties of TiO₂

The optical properties of TiO₂ were measured so that information including bandgap and its absorptive capabilities could be quantified. Since it is a powder material, diffuse reflectance would most appropriately be used to study its optical properties.

4.2.1 Absorption spectra

The absorption spectra of the different modified TiO₂ materials, as well as P25 and pure anatase phase TiO₂ were calculated from its diffuse reflectance spectra and shown in Figure 4-19. It was observed that there was minimum band shift in all the modified TiO₂ samples. Amongst them, Cr-doped mixed phase TiO₂ sample appeared to have the most red shift.

From the diffuse reflectance results, P25 did not show significant red shift but has excellent photocatalytic activity cited by many [11, 17]. Studies by Bo Sun et al [16] showed that P25 has good interparticle contacts formed between anatase and rutile phases, leading to band bending, in the presence of water that led to increasing charge separation. Referring to Figure 2-6, the conduction band energy bending in the space charge layer of anatase stops

electrons going from anatase to rutile, but the holes in the anatase particles can be transferred to rutile particles through the valence band bending. As a result holes are concentrated in rutile and electrons are left in the anatase particles. It was also indicated that the presence of metals will not increase charge separation but will reduce charge recombination because it diverts some photogenerated electrons into the metal leading to the reduction of water that cannot take place on pure TiO₂.

This initial positive result for Cr-doped samples led to the investigation of how higher Cr doping concentration in TiO₂ would affect the bandgap of TiO₂. Figure 4-20 shows the Cr doped samples up to 5 wt% Cr. It was generally observed that for doping concentration above 1.5 wt%, the amount of red shift would be reduced. In addition, increasing the Cr content led to a gradual increase in absorbance towards the infra-red region as could be observed in the 5 and 10 wt% Cr samples. This is believed to be caused by the increasing inter-band states as a result of transition metal doping. This could be observed from Figure 4-20 that there is a gradual upward trend in absorbance towards the infra-red region. Hence, the doping concentration of transition metals should be maintained at a low level.

Figure 4-19: Absorption spectra of TiO_2 and modified TiO_2 samples

Figure 4-20: Absorption spectra of Cr-doped TiO_2 samples

4.2.2 Bandgap calculation

The optical bandgap of the powder samples could be estimated from the absorption spectra of the samples. The spectra in Figure 4-19 and Figure 4-20 show characteristic “turning point” energies. The bandgap were estimated by taking the gradient of the band edge. The results of the band edge of different samples were located and summarized in Table 4-8. It shows that bandgap narrowing will occur for Cr doping concentrations less than 1.5 wt%. The broadening of absorption edge leading to increase in absorbance energies lower than the bandgap could be contributed by various reasons which are also suggested by both Parker and M.Anpo et al [30, 92]:

- absorption of the defect and impurity states in the sample,
- optical scatter due to rough top surface, and
- reflective losses resulted from the sample and substrate

Table 4-8: Bandgap estimation using the band edge of the absorption spectra

Sample	band edge (nm)	calculated bandgap (eV)
A1	365.44	3.399
B	366.51	3.390
C	367.78	3.378
D	365.25	3.401
10 wt% Cr	365.25	3.401

4.3 Photocatalytic Characterization

The photocatalytic test shows the effectiveness of the photocatalyst in degrading an organic contaminant, chosen for this project to be methylene blue (MB). Based on the Beer-Lambert Law where absorbance of a material is directly proportional to the concentration of the solution concerned, the drop in concentration of MB solution could be quantified as its absorbance over different exposure time with and without the influence of the photocatalysts.

4.3.1 UV-VIS Absorption Spectra

The UV-VIS Spectrometer was used to measure the absorption of the MB solution in the low frequency UV range and the visible light range. The UV-VIS absorption

spectra in Figure 4-21 show the degradation of MB solution without a photocatalyst over a maximum period of 60 hour under fluorescent irradiation of 0.42 W/cm^2 . Similarly, in Figure 4-22, a suspension of MB containing photocatalyst powder sample T-A undergoes the same irradiation. During the experiment, it was observed that the presence of the photocatalyst decolourized MB at a faster rate. From the spectrum in both Figure 4-21 and Figure 4-22, the absorbance of the MB solution in the presence of sample T-A decreases at a higher rate and the disappearance of the absorption peak of MB at 664 nm could be observed.

Figure 4-21: Absorption spectra of MB solution under normal fluorescent light irradiation

Figure 4-22: Absorption spectra of MB solution using pure anatase phase TiO₂ photocatalyst under normal fluorescent light irradiation

Based on the most significant absorption peak of MB at about 664 nm, its decomposition rate was tabulated. It was normalized with respect to its initial concentration measured in the dark. Different TiO₂ photocatalyst materials were used in the same experimental set up

and its rate of degradation were compared in Figure 4-23 and Figure 4-24. Its time to full degradation was tabulated in Table 4-9. It could be observed that MB would remain as a stubborn stain even after 60 hours but in the presence of TiO₂, it was able to degrade MB in water in less than 20 hours of light irradiation. Illustrated earlier in Figure 2-9 the benzene ring of MB corresponds to the peak at around 300 nm. It was broken down much later than its pigmentation (664 nm); after 36 hours of irradiation for sample T-A. This shows that the presence of the TiO₂ photocatalyst does speed up reaction of removal of organic compounds from water.

Figure 4-23: Comparing the rate of degradation of MB dye with and without the influence of different TiO₂ materials.

Figure 4-24: Comparing the rate of degradation of MB dye with and without the influence of doped mixed phase TiO₂ materials.

The summary in Table 4-9 shows that the presence of sample B allows the MB solution to be degraded after 48 hours of irradiation. This is the most ideal synthesized photocatalyst although it is not comparable with the commercial P25.

Table 4-9: Time required for degrading MB using different TiO₂ based photocatalyst

Sample	Duration to degrade (hr)
P25	18
T-M	60
A1	60
A2	60
B	48
C	54
D	60

4.3.2 Effectiveness of Photocatalytic Activity

The efficiency mixed phase TiO₂ samples like P25 and the synthesized TiO₂ powders were compared in Table 4-9. P25 fully degraded MB after 18 hours. MB solution could not be degraded by light without a photocatalyst after 60 hours of irradiation. Sample T-M can degrade MB after 60 hours and the best among the modified samples was the sample B which was fully degraded after 48 hours. P25 has shown that it can degrade MB about three times faster than sample B. This is largely because of the surface area and particle size. In Section 4.1.4, it was shown that P25 which degrades MB 2.7 times faster than sample B, is 3.5 times smaller in terms of particle size and 2.7 times greater in terms of surface area. These characteristics made P25 superior over the synthesized powders. When Sample B was compared with sample T-M, it was observed that sample T-M which degraded MB slower than sample B, was 1.5 times smaller in terms of particle size and 1.3 times greater in terms of surface area. This shows that surface area and particle size are important criterion for increasing the efficiency of the photocatalyst. However, the importance of metal doping in TiO₂ [4, 5, 13, 16, 30, 45, 46] cannot be overlooked, shown in the case where T-M was compared with sample B. Although sample B had small surface area and larger particle size, as a result of doping, the diversion of photoelectrons onto the metal has led to a greater separation between the electron hole pairs. Therefore, it led to higher efficiency photocatalytic activity compared to an un-doped T-M sample.

The ineffectiveness of doped TiO₂ compared with P25 could be due to presence of amorphous phases of synthesized TiO₂ powders. Amorphous phases could be formed

during breaking down of the TiO_2 anatase phase and before it transforms to the rutile phase. The amorphous phase could be gradually removed by high energy ball milling but trace amount could still be present. Its ineffectiveness could also be due to the presence of high pressure phase TiO_2 , which would be discussed in the subsequent section.

4.3.3 High Pressure phase TiO_2 II

The much agreed high pressure phase of TiO_2 at around 31.4° of the XRD pattern was experimentally shown by P. Y. Simons in [32] and A. Gajovic in [81], or some refer to it as the srilankite phase [87, 93, 94]. The phase diagram of pure TiO_2 is illustrated in Figure 4-25. With increase in pressure greater than 2 GPa, anatase phase could be transformed to TiO_2 II even at low working temperatures. This is the reason why it can be transformed to the TiO_2 II phase easily. In addition, It was also investigated that TiO_2 II could be prepared by the anatase phase, producing broad peaks and introducing errors in the 2θ measurements. This phase is isostructural to α - PbO_2 . It is persistently metastable in atmospheric condition but reported to be able to convert to rutile phase on heating over 600°C at atmospheric pressure for a few hours.

Figure 4-25: A non-equilibrium temperature-pressure phase diagram of pure TiO_2 [72].

It could be observed that the TiO_2 II phase occurs in all the samples ball milled over a short period of time in Figure 4-26. Powder XRD was repeated for one ball milled sample and the results showed that the peak at 31.36° remained after more than 6 months observed in Figure 4-27. It was initially believed that this peak should cease if it is a metastable state. A 0.2° right shift across board is attributed to release of stress.

Figure 4-26: XRD pattern emphasizing on TiO_2 II phase existing only in shorter milling duration samples

Figure 4-27: Diffraction pattern to compare changes in sample B over a period of six months

S. Indris et al reported the presence of this phase in anatase powder from which he concluded that this phase is formed on the surface of anatase particles resulting in a thin cover layer [71]. It was also reported that the high pressure phase TiO_2 was inferior to anatase TiO_2 in terms of its photocatalytic activity [93].

S. B. Collin et al [31] also studied ball milling parameters that would cause the phase transition from anatase to rutile, consequently leading to the intermediate phase. These include the nature of the grinding media as well as the powder to ball weight ratio. It was found that high powder to ball ratio hasten the TiO_2 II formation process. The transformation is reportedly an irreversible nucleation-growth process [31]. The contact pressure is inevitably caused by trapped volume of powder in between 2 balls when bombarded as shown by Hertz Impact theory in Section 2.5.4.1.

A side tracked experiment was done to reduce the amount of high pressure phase. The XRD data in Figure 4-28 shows that annealing has an effect on phase change and increasing the crystallinity of TiO_2 . The size of the crystallites also increased, which is obvious as annealing could lead to sintering and crystal growth. The anatase to rutile mixed phase ratio also changed, favouring an increase in rutile phase [34] to 33 % as tabulated in Table 4-10. Although the percentage of crystalline TiO_2 had increased, the amount of TiO_2 II phase in the sample remained unchanged as opposed to what was suggested by Simons and Gajovic et al. This experiment also suggested that amorphous phases of TiO_2 were present. Upon annealing, stress was released and the transition from amorphous phases to the more stable phase of rutile TiO_2 occurred.

Figure 4-28: Effect of annealing on the XRD pattern of Sample B showed no change in the quantity of TiO₂ II phase although crystallinity of TiO₂ phases of anatase and rutile increased.

Table 4-10: The before and after annealing phase and grain size calculations from XRD data

sample	%Anatase	%Rutile	d _{CA} (Å)
A2 A600	66.67	33.33	37.84
A2	80.87	19.13	15.89

The diffuse reflectance of the A2 before and after annealing is shown in Figure 4-29. The annealed sample showed a bandgap reduction of 0.08 eV. More interestingly, the photocatalytic activity of the annealed sample at 67 % anatase phase showed more efficient MB degradation (see Figure 4-30). This could be due to several reasons like the mixed phase ratio kinetics and reduction in defects after crystallite growth. Mixed phase ratio can affect the photocatalytic activity because the rutile TiO₂ is used as an electron sink. Therefore, a considerably small amount of rutile TiO₂ is required as interfacial material

with anatase TiO₂. Over emphasis of rutile will diminish the amount of anatase TiO₂ active sites available for photocatalytic reaction to take place. The reflectance percentage also increased for the annealed sample. This is largely because after crystallite growth and defects reduction, the crystallites became more transparent. This could be observed by the whitening of the powder sample, leading to higher reflectivity in the visible light region.

Figure 4-29: Diffuse reflectance of sample A2 before and after annealing

Figure 4-30: Comparing the MB degradation of annealed and non-annealed samples

With the TiO₂ II phase remaining constant, it shows that annealing was unable to reduce this metastable phase but it can be achieved through high energy ball milling for a longer duration. It was observed in Figure 4-1 that the disappearance of the TiO₂ II phase took place gradually from the 6th milling hour onwards. Second it also showed that the increase in photocatalytic activity could not have been due to the high pressure phase. Rather, it is due to the crystallinity of the sample. The photocatalytic activity test has shown that the annealed TiO₂ powder degraded MB within 36 h of exposure to visible light, despite having a greater rutile composition compared with sample A2. This showed that crystallinity, not just mixed phase ratio, plays a very big role in photocatalytic efficiency.

CHAPTER 5 RESULTS & DISCUSSIONS OF TiO₂ COMPOSITE FILMS

The composite film samples were fabricated using the ball milled powders as seen in the previous Chapter. A TiO₂ precursor was prepared by chemical method. The synthesized powders were added to the precursor and mixed to form uniformly dispersed slurry. The slurry was then spin-coated onto glass slides soft-baked at 150/300 °C for 5 minutes before annealing at 450 °C for 1 hour.

The physical properties of the composite film samples were analyzed because of the importance in maintaining the mixed phase ratio as seen in the powder samples. This was to ensure that the properties of the powder would not be compromised when it is being fabricated into films. Its optical properties were also measured to see its capabilities when applied as a coating on glass.

5.1 Physical Properties of TiO₂

5.1.1 Mixed phase ratio

XRD patterns of the TiO₂ samples as well as commercial powder P25 are shown in Figure 5-1, all of which are annealed at 450 °C for 1 hour. In the TiO₂ samples, it could be

observed that the anatase, rutile and TiO₂ II phases are present. To ensure that the crystallization is not a result of the already crystallized powder, sol-only films were annealed at different temperature to obtain the minimum annealing temperature required for crystallization. Figure 5-2 shows the XRD pattern of the sol-only film annealed at 450 °C and could be observed that crystallization has occurred.

Figure 5-1: XRD pattern for composite film samples after annealing

Figure 5-2: Diffraction pattern of TiO₂ precursor annealed to 450 °C.

Next, to ensure that the crystallization was not a result of only the powder samples or only the sol in the composite film, the ratios of the peaks at ~25.2 ° anatase (101) and 31.4 ° (TiO₂ II) of both types of films were compared. The ratios were taken because the intensity of each XRD scan might differ and the anatase phase peak to peak comparison will not be accurate. Anatase was chosen because it is the preferred orientation of anatase phase and the 31.4 ° was chosen since this peak is not seen in the sol-only sample. i.e., the TiO₂ II phase peak originated from the powder only. The ratio of the peaks after baselining shows

that the ratio of $\left[\frac{\text{anatase}(101)}{\text{TiO}_2 \text{ II}} \right]_{\text{anneal}} / \left[\frac{\text{anatase}(101)}{\text{TiO}_2 \text{ II}} \right]_{\text{spincoated}}$ is 1.4. This meant that the

amount of crystalline anatase phase has increased, which is substantial for us to conclude that the sol has been crystallized even though the amorphous content is indeterminate.

Next, P25 and sample T-M were annealed to 450 °C and its XRD pattern is shown in Figure 5-3 and Figure 5-4 respectively. A comparison was also made with its respective powder-XRD pattern. The areas under the 2 most significant peaks of the anatase and rutile phase were taken into consideration. The results were tabulated in Table 5-1. Both P25 and sample T-M were still in agreement with the initial mixed phase ratio of 8:2.

Figure 5-3: Comparing the diffraction pattern of P25 for both powder and film

Figure 5-4: Comparing the diffraction pattern of mixed phase TiO₂ for both powder and film

Table 5-1: comparing phase composition of composite films and powder samples

Sample	Phase	Powder	film
P25	Anatase	85.7	84.2
	Rutile	14.3	15.8
T-M	Anatase	85.4	82.7
	Rutile	14.6	17.3

5.1.2 Porosity, Uniformity

The quality analysis of porosity and uniformity of the composite film samples were carried out using FESEM. Figure 5-5 to Figure 5-9 show the micrograph of the composite films at 5 000 and 30 000 magnifications. The first micrograph of each sample shows that the modified TiO₂ powders were well dispersed in the TiO₂ sol and the film does not show micro-cracks formation. The second micrograph at 30 K magnification shows that surface

of the film is porous. These types of films are suitable for photocatalytic reactivity firstly because of a larger surface area. More importantly, the photocatalytic reaction of TiO_2 that takes place at the surface and can be enhanced. It allows the photogenerated electrons to move to the surface to react with surface moisture required for the redox reaction to take place.

Figure 5-5: SEM micrograph of P25- TiO_2 composite film at a) 5 K and b) 30 K magnification

Figure 5-6: SEM micrograph of T-M powder- TiO_2 composite film at a) 5 K and b) 30 K magnification

Figure 5-7: SEM micrograph of sample A1- TiO_2 composite film at a) 5 K and b) 30 K magnification

Figure 5-8: SEM micrograph of sample B- TiO_2 composite film at a) 5 K and b) 30 K magnification

Figure 5-9: SEM micrograph of sample A2-powder- TiO_2 composite film at a) 5 K and b) 30 K magnification

5.2 Optical Properties of TiO₂

5.2.1 Bandgap calculation

Figure 5-10 to Figure 5-13 shows the $(\alpha h\nu)^n$ vs $h\nu$ curves for the various composite film samples. The transmission data were obtained from UV-VIS spectrometer in the range of 200-900 nm, where α was tabulated. Due to the presence of both crystalline and amorphous phases, both models were calculated. $N=2$ was used for amorphous materials while $n=1/2$ was applied to materials with direct allowed transitions. The optical bandgaps of the amorphous phase and its crystalline phase were assumed to have a common optical bandgap E_g . Using Tauc extrapolation [95], its optical bandgap can be determined by the intercept of the extrapolations to zero with the photon energy axis $(\alpha h\nu)^n \rightarrow 0$ [96] and labeled in each graph respectively.

The 4 samples, T-M, A1, A2 and B would be compared and discussed. A bandgap range is shown because all the samples contain both amorphous and crystalline phases. The bandgap of the original pure anatase phase TiO₂ powder was 3.2 eV. Cr doped samples (A1 and B) showed most red shift in the optical bandgap, especially sample A1 at 2.61 eV for crystalline part and 3.13 eV for the amorphous part. The optical bandgap using the crystalline model cannot be taken as an absolute value because there are no means to determine the amount of both amorphous and crystalline content in each sample at this point. Nevertheless, this calculation gives a more accurate representation of the bandgap of the material compared to the bandgap estimation done for powder samples. Unfortunately,

it could not be carried out for the powder samples because there was no means of obtaining the absorption coefficient, α without carrying out transmission measurements which, to the best of my understanding is not possible for powder samples. This is also why, bandgap estimation using the absorption edge is widely used for bandgap estimation for powder samples [14, 19, 20, 39].

Figure 5-10: Optical bandgap calculation for sample T-M.

Figure 5-11: Optical bandgap calculation for sample A1.

Figure 5-12: Optical bandgap calculation for sample B.

Figure 5-13: Optical bandgap calculation for sample A2.

CHAPTER 6 CONCLUSION

Two main types of modified TiO₂ films were discussed in this thesis, namely mixed phase and doped mixed phase TiO₂ powders. Besides detailed analysis of the synthesis, and materials characterization, photocatalytic behaviour of the modified TiO₂ powders were also demonstrated. In addition, fabrication of the powders into composite films were also carried out. Finally, the integrity of the powders when fabricated into films, was also investigated.

Both the mixed phase TiO₂ and doped mixed phase TiO₂ materials were synthesized using high energy ball milling technique. TiO₂ powders with different mixed phase ratios were successfully synthesized using time controlled milling. Its physical characteristics like crystallinity and grain size were thoroughly examined. From there the desired mixed phase ratio suitable for applications as photocatalyst materials was achieved. Mixed phase TiO₂ powder was obtained after ball milling at 200 rpm for 3.5 h and Cr-doped mixed phase TiO₂ after 3 h. The grain size calculated from XRD data indicated that there is good interface between the anatase and rutile phase, which is necessary for the electron movement to increase the charge separation distance. Further studies with XPS on the shift in the XRD peaks in relations to the anatase phase lattice constant showed that changes in lattice constant was a result of increase in oxygen vacancies and the increase in energy as a result of the milling process.

The role of Cr in TiO₂ has become clearer from this study. First from the XPS study, Cr facilitated in the relaxation of the lattice as more oxygen vacancies were seen in the doped samples than that of the un-doped mixed phase samples. This was further substantiated from the O/Ti ratio over different milling duration and different doping concentration. Cr-doped TiO₂ appeared to show the best red shift in the absorption edge. The doping concentration of TiO₂ was limited to less than 1.5 wt% because excessive doping leads to the formation of imperfect crystals and thus the formation of inter-band states. These reasons delimit the amount of TiO₂ active sites available for the photocatalytic reaction to take place.

Sample B (1 wt % Cr-doped TiO₂) photocatalyst had successfully degraded methylene blue stain after 48 hour of fluorescent light irradiation. It was the most effective among all the synthesized TiO₂ samples. However, it was less effective compared to the commercial material P25.

The additional TiO₂ II phase that was observed in samples ball milled for less than 6 hours led to the investigation of its role in the photocatalytic activity of the sample. Annealing the samples did not reduce composition of TiO₂ II phase but increased the crystallinity of the anatase and rutile phases of TiO₂ in the samples. These annealed samples also showed better photocatalytic activity despite having an increased rutile composition which led to an important observation that crystallinity has an equally important role to play in the photocatalytic activity enhancement of the photocatalyst material.

The film fabrication was done on an application point of view since solutions to visible light photocatalytic activity needs to be film based. XRD patterns showed that the mixed phase ratio was maintained when fabricated into film. The films were uniform but porous, thus allowing the electrons to move to the surface for redox reactions to take place. Fabricating samples into composite film also facilitated bandgap calculations. 2 models were used separately to calculate the bandgap based on a fully amorphous or crystalline film. This was done as the composite film consists of both amorphous and crystalline phases. It showed that all Cr-doped TiO_2 samples could reduce the bandgap of TiO_2 and the sample A1 showed the smallest bandgap. However, this cannot be taken as an absolute value because TiO_2 consist of both direct and indirect bandgaps. Hence, photoluminescence is essential for a more conclusive account.

All in all, the photocatalytic capabilities of transition metal doped TiO_2 has shown good potential. The quantum efficiency is decided by the competition between charge carrier recombination, trapping and interfacial charge transfer. Doping concentration hence should be kept to a minimal (just enough for the metal to trap electrons so as to minimize recombination). The photocatalytic activity of the sample is also dependent on many physical parameters like particle size, mixed phase ratios, surface area and importantly, doping elements. It was shown that the dopant and its quantity relative to the total amount of TiO_2 had a bigger impact on the reactivity of the material when exposed to light as compared to the mixed phase ratio. This implies using Cr doped TiO_2 to narrow its bandgap (leading to the red shift in the bandgap) plays a big role in attaining enhanced photocatalyst materials.

CHAPTER 7 FUTURE WORK & RECOMMENDATIONS

The High Energy Ball Milling technique is an excellent tool to synthesize doped mixed phase TiO₂ powders. However, one drawback is that, rutile being the most stable phase of TiO₂ makes it difficult to further decrease the particle size of the modified TiO₂ materials using this technique while maintaining the anatase phase concentration.

Some other materials characterization that could be carried out to further complement the data include photoluminescence and the calculation the amorphous content of the material. Amorphous content could be calculated by incorporating a fixed amount of known crystalline material into the sample. This is important as amorphous TiO₂ does not contribute to its photocatalytic activity [97].

The MB degradation test to compare the different modified TiO₂ samples has been effective in evaluating the relative efficiency of each material. However, this well established test was put to an assessment due to its incompetence when compared to others' techniques [19, 79, 98, 99]. In a modified experiment, a piece of quartz was placed as a top cover to the MB suspension to better the irradiation light transmission. This is on the assumption that the highest light intensity is perpendicular to the surface of the suspension concerned. Evaporation in the suspension leading to undesirable increase in the MB concentration over time was taken into consideration by weighing the suspension before and after each irradiation time period using a micro-scale. This was opposed to filling up

small bottles of suspension disregarding evaporation and the transmission mechanism. Figure 7-1 below shows the 3 different considerations using the same sample. First, MB solution was degraded using the original technique in the presence of sample A2 photocatalyst. The other 2 were degraded using the new technique, difference being one (A2i) takes into account the evaporation over time, one (A2ii) does not. The preliminary results show that slow degradation of the powder could be due to the technique used as the time needed for MB to be fully degraded by the same photocatalyst was about half the original time required.

MB is just one dye that can be used to correlate the reduction power in the presence of a photocatalyst. To have a more in depth understanding of how the process takes place, a study of the breakdown of MB (as described in Section 0), using High Performance Liquid Chromatography (HPLC) would be valuable. In addition, other test techniques like measuring the amount of H_2 and CO_2 , released during the process or detecting intermediate products during the photocatalytic oxidation process through the use of other contaminants like salicylic acid, trichloroethylene or phenol [7, 16, 21, 100] could lead to a fuller understanding of the capabilities and limitations of TiO_2 as a photocatalyst.

Figure 7-1: Comparing the degradation of the same material using different tests

Last but not least, to move a step further, the composite films could be tested in real life tests, to understand the life cycle or durability of the photocatalyst. This would be an important step towards the commercialization of the final product.

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