Faculty of Manufacturing Engineering

CHARACTERIZATION STUDY OF SILVER TITANIUM DIOXIDE
(AgTiO$_2$) THIN FILM DEPOSITED ON VARIOUS SUBSTRATES VIA
SOL-GEL TECHNIQUE

Fatimah Md Radzai

Master in Manufacturing Engineering (Industrial Engineering)

2012
CHARACTERIZATION STUDY OF SILVER TITANIUM DIOXIDE
(\text{AgTiO}_2) \text{ THIN FILM DEPOSITED ON VARIOUS SUBSTRATES VIA}
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FATIMAH MD RADZAI

A thesis submitted
in fulfillment of the requirement for the degree of Master of
Manufacturing Engineering (Industrial Engineering)

Faculty of Manufacturing Engineering

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

2012
Anatase Titanium Dioxide (TiO$_2$) sol was synthesized in room temperature 27°C and ambient pressure by hydrolysis of Titanium Tetraisopropoxide (TTiP) in acidic aqueous solution (Hydrochloric acid, HCl), ethanol and deionized water. Degussa P25 powder was used as a precursor to enhance the anatase presence in the crystalline phase, as Degussa P25 powder is comprised of anatase and rutile phase with the ratio of 70:30. At room temperature and in ambient atmosphere, crystalline TiO$_2$ thin films were deposited on Acrylic Perxpex (AP), glass, stainless steel and ceramic from the as-prepared TiO$_2$ sol by a dip-coating process. TiO$_2$ layers on the substrate were thickened by consecutive coatings. Then the TiO$_2$ coated substrates were finally dipped into pure nanosilver to ensure protection against microbial. Sintering was applied at different temperatures from 120 to 600 °C in order to enhance crystallization. AgTiO$_2$ thin film is found to be in good adhesion to the substrates through means of ultrasonically immersed in water and sticky tape adhesion. Anatase crystallite size was calculated through full-width at half-maximum (FWHM) in the X-ray Diffraction (XRD) intensities of anatase (101) peak at $2\theta = 25.3^\circ$ using Scherrer equation. The increase in calcinations temperature is parallel with the increase of the crystallite size. The anatase/rutile percentage was calculated through anatase and rutile intensities, to show the coherent ratio relevant to the Degussa P25 powder presence. Field-emission type scanning electron microscope (FE-SEM) investigations revealed that the AgTiO$_2$ thin films on each substrates were porous and uniform, while the average particle sizes of the nanoparticles composing the AgTiO$_2$ thin films on different substrates are in range of 37~87 nm corresponding with the calculated particles achieved by the Scherrer equation. The AgTiO$_2$ thin films exhibited smooth porous surface, anatase phase and increasing crystallite size with increasing calcinations temperature. These are the characteristics that are proned to achieve high photocatalytic conditions.
ABSTRAK

Cecair anatase Titanium Dioxide (TiO$_2$) telah di sintesis pada suhu dan tekanan bilik melalui proses percampuran Titanium Tetraisopropoxide (TTiP) ke dalam Hidroklorik asid (HCl), etanol dan air suling. Serbuk Degussa P25 yang komersial telah digunakan sebagai pemangkin untuk membantu pembentukan anatase kristal dalam fasa penkristalan. Pada suhu dan tekanan bilik, substrat yang berlainan seperti Acrylic Perspex (AP), potongan gelas, keluli tahan karat dan seramik di celup ke dalam cecair TiO$_2$ melalui proses celupan yang terkawal. Sebanyak 5 celupan telah dilakukan untuk menghasilkan ketebalan saput nipis yang optima pada permukaan substrat. Pemanasan dan pengkalsinan pada suhu 120 sehingga 600 °C telah dilakukan terhadap substrat yang telah dicelup dengan AgTiO$_2$. Ini adalah untuk memastikan proses pembentukan anatase kristal berlaku. Saput nipis AgTiO$_2$ didapati dalam keadaan yang baik iaitu ia melekat dengan sempurna terhadap semua permukaan substrat. Saiz kristal anatase telah diikir menggunakan data yang didapati melalui data belauan sinar x (XRD) iaitu nilai FWHM pada anatase (101) yang sepadan dengan nilai pada darjah 2$\theta$ = 25.3°. Nilai yang didapati diikir menggunakan persamaan Scherrer. Apabila suhu pengkalsinan meningkat, saiz anatase kristal juga akan meningkat. Pengiraan terhadap nisbah anatase/rutile juga dilakukan untuk menunjukkan keseragaman terhadap penggunaan serbuk Degussa P25. Penggunaan pancaran medan kemikroskopan electron imbasan (FE-SEM) telah menunjukkan bahawa saput AgTiO$_2$ adalah berliang dan seragam. Manakala, saiz nilai purata zarah pada saput tersebut di dapat dalam lingkungan 37~87 nm, iaitu sama dengan kiraan partikal kristal menggunakan persamaan Scherrer. Saput nipis AgTiO$_2$ merangkumi permukaan yang berliang dan seragam dan juga mempunyai kewujudan fasa anatase kristal Ciri-ciri tersebut diperlukan untuk mendapatkan keadaan fotopemangkin yang terbaik.
ACKNOWLEDGEMENT

I would like to thank Dr Zulkifli Mohd Rosli and Associate Professor Dr Jariah Mohamad Juoi for being such enthusiastic and involved supervisors throughout the course of my short master research. Thank you both for the continual guidance, encouragement and advice. I also thank Universiti Teknikal Malaysia Melaka (UTeM) and Kementerian Pengajian Tinggi (KPT) for awarding me the fellow scholarship throughout my journey in furthering master studies.

Many people have helped me out along the road in completing this work. My first thanks must go to my partner in research, Norhamizah Mohd Rusli - thank you for the never-ending discussion and for sharing the research experience. There are abundant of people who had assisted me here and I extend my gratitude to them. Everyone at UTeM, Faculty of Manufacturing Engineering, Manufacturing Material Lab, in particular: En Hairul, En Azhar and En Jaafar for the usage and assistance in XRD, SEM and CMM, AMREC SIRIM Hi-Tech, Dr Kadir, Puan Suhaina and Cik Farina for the assistance in the sol-gel dipping method, University of Technology Malaysia (UTM), UTM Department of Mechanical Engineering, Dr Muhammad Azizi Mat Yazid for the assistance in gold coating of the specimen, En Jefri (FESEM UTM) and of course my fellow UTeM fellowship scholars, Nurul Izuwa and Nor Fadzilah for the advice and support. My final thanks must go to Mum and Dad for their continued support and interest in what I’ve been doing for the past year. Thank you so much for being there and putting up with me and never stopped in giving relentless advice and encouragement.
APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment of the requirements for the Master of Manufacturing Engineering (Industrial Engineering). The member of the supervisory committee is as follow

………………………………………….

DR ZULKIFLI MOHD ROSLI

(Main Supervisor)
DECLARATION

I declare that this thesis entitle “Characterization study of AgTiO$_2$ thin film coating deposited on various substrate via sol-gel technique” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ..............................
Name     : ..............................
Date     : ..............................
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CHAPTER 1

INTRODUCTION

1 Overview

1.1 Background

In the advanced technology world, an increasing level of nanocoating has been achieved. There had been an introduction of antimicrobial coating in throughout the industry, for instance in hospital working area. However, the application of the actual antimicrobial coating, specifically with Silver Titanium Oxide (AgTiO$_2$) is still under research and development. The addition of silver (Ag) to the titanium oxide (TiO$_2$) formula has been known for its antibacterial properties, and silver nanoparticles offer superior antibacterial activity while being non-toxic.

The importance of surface contamination is quite serious in the healthcare industry, thus providing greater care for us to inhibit in such cleaner environment. These substrates, non-metallic or metallic material, has a capability to be contaminated with a handful of bacteria. In most researches, these coatings demonstrated efficient antibacterial activity toward Escherichia coli (E. coli) and Staphylococcus aureus (S. aureus). The antibacterial property is important for hospitals and other public buildings that are prone to bacterial growth, a main cause of infection and disease.
1.2 Role of Surfaces of Substrate

For years, researchers and scientists had believed the importance of surface in the pool of microbes implicated in the wide variety of hospital applied infections. The role of surfaces of substrates used in healthcare industry and household applicants are widely known for its cleanliness. There are also other applications for metallic and non metallic substrates of 316L stainless steel, glass, ceramics and acrylic.

Many researchers have developed various methods to apply Titanium Oxides (TiO$_2$) coating on various substrates. Thus, TiO$_2$ was deposited on ceramic, fiber glass, glass and sand, quartz and stainless steel, pebbles, activated carbon, polyester fabric using polyvinyl alcohol as binder and Ti–TiO$_2$ prepared by thermal as well as flame oxidation of Ti sheet, silica, polystyrene beads and cellulose-based non-woven supports, photocatalytic\(^1\) paper, pulp, and TiO$_2$ coated cotton/cellulose fibers (Neti & Joshi, 2010). These substrates were chosen based on their properties and significance of applications.

1.3 Thin films of AgTiO$_2$ on substrate

Solid thin films has been in various investigations and titanium oxide (TiO$_2$) has been studied with regards to their amazing optical, electrical and photo-electrochemical properties. The addition of silver (Ag) to the composition was due to its conductive layer because of its low absorption in the visible region (Sun, et al., 2008).

TiO$_2$ thin films have been a source of interest in environmental cleaning such as a photo-catalytic purifier in solar energy converters and photochemical solar cell, and in other applications such as gas sensors, ceramic membrane, and waveguide (Barati, et al., 2009).

\(^1\) Photocatalytic – comes from principle of photocatalytic reaction was to accelerate the nature’s cleaning and purifying process using light as energy.
A number of TiO$_2$ deposition techniques have been used for the fabrication of thin films such as sputtering process, chemical vapor deposition, electron beam evaporation, and sol gel process. However some of these techniques have limitations pertaining to the geometry and size of the support material and the process is very expensive (Barati, et al., 2009). Therefore, sol–gel process based dip-coating can be considered more practical, economical and have the advantage of low processing temperature. The preparation of TiO$_2$ thin film on different substrates using several sol–gel deposition techniques has also been studied.

The addition of Ag to the solution is due to the fact that silver ion (Ag$^+$) makes DNA molecules to lose their replication abilities. Silver-doped materials are chemically durable and release ion Ag for a long time (Sun, et al., 2008). If the silver nanoparticles are immobilized in the TiO$_2$ film on glazed surface of ceramic tiles, the release time of silver ions can be delayed for a long time so that the ceramic tile with this film will be of great potential for antibacterial application (Sun, et al., 2008).

1.4 Problem statement

Household applications, hospitals and facilities in industries are always in danger of being cohabited by microbes. The bactericidal activity could be enhanced by modification of TiO$_2$ with the addition of Ag to the formulation, it had been recognized that AgTiO$_2$ have excellent antibacterial activity against bacteria i.e. E.Coli (Sondi & Salopek-Sondi, 2004). Using the commercially available TiO$_2$ powder, Degussa P25, it has been known that this titania powder sample is composed of anatase and rutile crystallites (Ohno, et al., 2001) and its anatase and rutile particles exist separately. The TiO$_2$ thin film is investigated at different calcinations temperatures in order to obtain different sizes of crystallites which may leads to the higher porosity surface of the thin film. There were other coatings that
inhibit the same characterization of antimicrobial such as Silver Silicon Dioxide (AgSiO$_2$) and zinc oxide (ZnO). However, these two coatings were not as compatible to photocatalytic test but have the capability in enhancing of the bactericidal activity. Therefore, TiO$_2$ has been chosen as the coated thin film as it has both capabilities for the best photocatalytic activities and antimicrobial test.

It had come to a realization that the sol gel dipping method of AgTiO$_2$ can be one of the economical and practical methods for an antimicrobial coating onto different type of substrate due to its advantage of low processing temperature, low cost, homogeneity$^2$ and better micro-structural control. In comparison to liquid phase deposition (LDP) or pressure vapour deposition (PVD), both of the coating method uses expensive equipment compared to sol gel dipping method. Even in sol gel there are also other methods can be found such as brush coating, spin coating and flow coating. However, sol gel dipping method conveys a better technique of controlling the homogeneity of the thin film and the possibility to coat on bigger sized-specimens. Not to mention out of all coating techniques, sol gel dipping method can be considered one of the low-cost techniques.

The substrates concentrated in this research are stainless steel, glass, acrylic perspex and ceramic. The thin film may have variety of porous surface when deposited on different substrates. While, on the other hand, all of these materials have different applications and thus will enable the wide application of the AgTiO$_2$ coating.

Therefore, in this current project, the antimicrobial coating is AgTiO$_2$ thin film which is deposited onto the substrates; glass, acrylic Perspex, stainless steel and ceramic, via sol gel dip coating method.

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$^2$ Uniform in composition or character
1.5 Objectives

The objectives of this research are:

i. To determine the characteristics of Degussa P25 powder as a precursor in sol gel for dip-coating

ii. To investigate the effect of the deposited AgTiO$_2$ thin film calcined at different temperatures on different substrates

iii. To evaluate the characteristics of deposited AgTiO$_2$ antimicrobial coating by using X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM)

1.6 Scope and Significance of Study

The scope of this research should be focused on the coating ability to be bonded onto the substrate surface and the substrates are stainless steel, glass, acrylic perspex and ceramic. The coating method chosen in this research is by using sol gel dipping method, due to its economical cost, high purity and low processing temperatures. The characteristics study is to find the anatase peak and the porosity of the crystallization structure of the coating.

The significance of this study is to ensure that the AgTiO$_2$ antimicrobial coating will be able to be deposited onto different types of substrate by using the TiO$_2$ formulation with a method of sol gel dip coating deposition. Thus an antimicrobial coating will be applied to all related industry for better enhancement of future prevented microbes contaminated surface.
CHAPTER 2

LITERATURE REVIEW

2 Introduction

Antimicrobial coating has been introduced in various applications and it has helped
the environment to be free of microbes and prevents microbes’ breeding place.

2.1 Antimicrobial coating

Antimicrobial surfaces have been utilized in lots of application, not only in the health
industry, but also home and industrial uses. Antimicrobial coatings are functionalized in
diverse processes. A coating may be applied to a surface that has a chemical compound
which is toxic to microorganism.

Microorganisms can appear anywhere, spreading rapidly and endangering our health.
Objects that people come into contact with every day are particularly prone to microbial
colonization. An antimicrobial coating a tad differs from a microbial coating, whereby the
latter only focus on providing protection against bacteria, while the first one provides
protections against bacteria, fungi, virus and algae.
2.2 Types of antimicrobial application

In a study achieved by a Tiger DryLac®, (2011), they had managed to come up with a powder-surface-coating that give surfaces lasting protection against bacteria, viruses, fungi and algae, without impairing the color, gloss or structure of the powder coating. Their design exhibits a highly dynamic and sustainable effect, with no change needed in the processing conditions for applying the coating.

Their coating application has a variety usage onto the glossy surfaces such as:

1. Refrigerators
2. Door handles
3. Hospital beds
4. Public facilities
5. Medical laboratory equipment
6. Shower cabins
7. Surfaces in schools and kindergartens
8. Ventilation and air-conditioning systems

2.3 Substrate Surface Application

2.3.1 Metal - Stainless Steel

Stainless steel has become one of worldwide metallic substance features for most of applications. In the study investigated by (Barati, et al., 2009), the TiO$_2$ thin films has been coated onto 316L stainless steel. They had achieved to find the anatase formation at the temperature 300 °C to 500 °C, and the most optimum temperature to create a uniform distribution of nanoparticles of anatase, is at 400 °C. However, the cracks on the steel were hindered through a drying process by using alcohol as a drying atmosphere. This had resulted in achieving a uniform coating.

Metal has its own surface preparations before coating, differing from other substrates such as glass and polymer. Metal especially stainless steel with different finish
surface may result to different adhering of the thin films. The surface finishing was performed in order to remove the oxide layer before the substrate could be coated with the thin film. This is to ensure no contamination would affect the thin film outcome and surface morphology. The surface finishes have different surface roughness (spread of height distribution) as they gave visual appearance of a mirror finish, diffuse reflection and regular appearance. As shown in Madina, et al., (2010), the steel was mechanically and electrochemically polished, thus deposited with TiO$_2$ and SiO$_2$ via sol gel dip coating, spraying and RF magnetron sputtering. The substrates were then tested upon its durability in terms of characteristics, morphology, antimicrobial efficacy and evaluation of active hygienic properties.

2.3.2 Glass

Glass has been one of the common substrate applied in the thin film coating. Numerous studies had conducted transparent and opaque layers deposited onto the glass surface. In one study performed by Page, et al., (2009), they had applied TiO$_2$ and AgTiO$_2$ thin film using sol gel dip coating. They had differentiated the difference in each sol gel in regards to the silver weight percentage content. All films calcined at 500 °C showed similar crystallite sizes and anatase peaks, and it turns out that AgTiO$_2$ thin films demonstrated the best photoactivity and antimicrobial coating.

2.3.3 Ceramic

Ceramic glass is one the material that acquires excellent decorative and chemical durability. It is also widely used in various areas such as in the hospital environment and in every household. Unfortunately, ceramic tile by itself does not have antibacterial activity and microorganisms easily breed on its surface, especially in moist environment.
By applying AgTiO$_2$ thin films onto the surface, will eventually protect ceramic tiles/glass from microbes’ breeding. In the study by Sun, et al., (2008), a method of coating via Liquid Phase Deposition (LPD) was used. They had done a comparison of antimicrobial activity between TiO$_2$ film and AgTiO$_2$ film. The results shows that the AgTiO$_2$ thin films obtained adhered well were homogenous and coloured by interference of reflected light. Their XRD and SEM experiments showed that silver nanoparticles were completely trapped in TiO$_2$ matrix and reduction could be achieved at 600°C annealing temperature. AgTiO$_2$ thin films show high antibacterial activity eliminating the E. coli which showed to be useful as an antimicrobial material.

Since the previous study used the LPD method, this project is to move forward with using the sol gel dip coating method for the AgTiO$_2$ antimicrobial coating.

### 2.3.4 Polymer - Acrylic Perspex

Acrylic Perspex is one of the polymers widely used for the application of glass windows replacement, sale displays, newspaper stands and other useable products. Some polymers has a lower melting temperature as stated in Table 2.1, therefore the annealed temperature should be reduced accordingly.

Table 2.1: Acrylic properties (courtesy from Wikipedia and CV Plastic website)

<table>
<thead>
<tr>
<th>Acrylic / Perspex Physical Properties</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>(C$_5$O$_2$H$_8$)$_n$</td>
</tr>
<tr>
<td>Melting point</td>
<td>160 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>200 °C</td>
</tr>
</tbody>
</table>

According to Neti & Joshi, 2010, it is a challenge to obtain an adherent TiO$_2$ film on acrylic plastic sheet, a fabrication material for falling film reactor (FFR). The method
used was by brush painted on the surface of acrylic plastic sheet and the result came out as the films detached as flakes on drying. It was due to the smooth and hydrophobic surface of acrylic plastic that caused the flaking. Following that, they had tried on gritting the surface first before brush coating it again to ensure proper bonding of the cellulose-TiO$_2$ slurry film to the substrate surface. The microstructure was found through XRD, SEM and AFM.

While in another study conducted by Sisti, et al., (2012), they have prepared TiO$_2$ thin film on commercial fluorinated polymer (FEP) with a treated surface, by using the sol gel dipping method. The focus on the subject was to cure at two different curing temperature; 120 and 200 °C. As it turned out, the annealed temperature does not affect the photocatalytic activity of the samples. Furthermore, the best dipping layer gives out the best result for oxide film adhesion and the characteristics of the thin film was characterised through XRD, SEM and AFM.

These two studies concluded that polymer as a substrate can be used to be coated for TiO$_2$ film. In some studies, the sol gel was hydrolysed at a temperature of 60 °C to 70 °C in order to enhance the formation of anatase crystals in the TiO$_2$ sol gel solution. However, in the present project, the calcinations temperature was to be chosen between 120°C and 160 °C, below its melting point. However, since they did not focus on the addition of silver, this present research will mostly focuses on the affects of AgTiO$_2$ film bonding onto the substrate surface.

2.4  Formulation of Ag-TiO$_2$ solution

2.4.1  Sol gel dipping method

In the study investigated by Page, et al., (2009) the solution of TiO$_2$ was formulated through a combination of chemicals. There are two ways of producing the crystalline products, either by having the TiO$_2$ in terms of powder or thin film. In referring to Figure
2.1, the sol was transformed in different process in order for the sol to become powder. The sol that was configured from the addition of precursor, catalyst and solvent, was aged to transform it to gel. It was followed by drying the gel in room temperature or at most 70 °C for 24 hours (Eshaghi, et al., 2010), removing most of the alcohol and water trapped in the matrix. Then, to obtain the crystalline material, the xerogel is calcined at high temperature, typically 450 °C to 500 °C, resulting in crystalline TiO$_2$.

Figure 2.1: Schematic representation of the sol gel process (Page, et al., 2009)

There is also a comparison being made towards the ability of AgTiO$_2$ powder and the thin film as being investigated by Page (2009). He had similarly compared the sol gel characteristics, being found out that the powders resulted greater intensity of anatase matching peaks of 101. Therefore, the procedure for turning into the sol gel into powder was proceeded as heating the 25ml sol gel at 60 °C in oven for 48 hours. The heating was to dehydroxylise the sol gel to transform it into xerogel powders.

The sol gel in Figure 2.1 resulted in solid powder, rather than a thin film. There is also the thin film strategy, deposited via dip coating method. The steps and process are shown in Figure 2.2, revealing that the process from Figure 2.1 is modified so that the sol gel is casted onto a substrate in the form of thin film. Casting as a thin film has the
advantages of quickening the drying of precursor. A precursor thin film is formed on the substrate almost immediately with minimal drying required. The coated substrates are then calcined at 500 °C to produce dense, crystalline thin films.

![Schematic representation of the sol gel preparation of a thin film by dip coating](Page, et al., 2009)

**Figure 2.2**

### 2.4.2 Degussa P25 Powder

It has been known that the titania powder sample is composed of anatase and rutile crystallites (Ohno, et al., 2001). The Degussa P25 powder (surface area of 55m$^2$/g, mean average particle size of 25nm and ratio of 30 rutile: 70 anatase crystallinity) was usually used for TiO$_2$ solution as a precursor due to its composition containing anatase and rutile ratio. According to a study by Ohtani, et al., (2010), they had studied and compared the original P25 and a modified P25 with isolated anatase and rutile phases. Comparison of activities of original P25 and reconstructed P25 from amorphous titania sample suggested a less probable synergetic effect of the co-presence of anatase and rutile.
In addition, the results showed that P25 contains more than 70% anatase with a minor amount of rutile and a small amount of amorphous phase. The composition anatase/rutile/amorphous could be determined by analysis of P25 mixed with an internal standard, nickel (II) oxide. However, it was also found that the composition of P25 used was inhomogeneous and changed depending on the position of sampling from the same package. Therefore, it was determined that original Degussa powder with the combination of rutile/anatase phases would enhance the photocatalytic activity. On the other hand, the calcination temperature was chosen as 450 °C as the temperature showed the most optimum calcinations of sol gel and powder (Ibrahim, et al., 2012).

2.4.3 TiO$_2$ sol preparation

Titanium dioxide (TiO$_2$) has been widely studied as an effective photocatalyst for water, environment purification and also for self-cleaning surfaces. It is also can be used as bactericidal material, due to its superhydrofilic property and strong oxidation activity (Viana & Mohallem, 2009) (Zaleska, 2008). Crystalline TiO$_2$ exists in three phases; anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic) (Yuna, et al., 2004). The formation of each crystalline phase depends on deposition method, calcinations temperature, and sol composition. TiO$_2$ film can transform from amorphous phase into crystalline anatase and then into rutile phase during calcination. For the purpose of photocatalytic property of TiO$_2$ film, it depends on the type and grain size of crystallite phases. In case of photocatalytic efficiency, anatase is superior to the rutile as anatase is usually considered to be the most photoactive of the three polymorphs for the degradation of organic pollutants.

There are other methods using the combination of different precursors for TiO$_2$ sol gel solution. The usage of Titanium (IV) Tetraisopropoxide (TTiP), tetrapropoxy-ortho-
titanate (TPOT) and titanium n-butoxide had played a role in obtaining a similar yet different photocatalytic and antimicrobial performance. According to Page, et al., (2009), TiO$_2$ sol preparation was prepared with a combination of chemicals; Acetyacetone and butan-1-ol, titanium n-butoxide, distilled water dissolved in isopropanol, acetonitrile and the formula is aged overnight. The thin film resulted in transparent layer on the glass substrate. While in another investigation done by Yao, et al., (2009), they had focused on the effects of pure and ion doped metallic elements into TiO$_2$ thin films, by sol gel dip coating deposited onto metallic and non-metallic substrates. The resulting films were dried in air, followed by annealed in a furnace at different calcinations temperatures ranging from 400°C to 600 °C and characterized by optical spectroscopy and X-ray diffraction. In general, both doped and undoped TiO$_2$ crystals appeared in anatase phase and the photocatalytic activities of the TiO$_2$ thin films varied with substrates, calcination temperature, doping ions and ions concentrations.

Another study resulted that the TiO$_2$ thin films deposited using electron beam evaporation, onto fused silica and found out that the anatase phase was observed regardless of the temperature used. It can be concluded that as the temperature increases the grain size would also increase.

### 2.4.4 AgTiO$_2$ sol preparation

Even though TiO$_2$ formulation has its own capabilities, but with adding the silver ion ($\text{Ag}^+$) onto the formulation either by doping or forged, will increase the solution enhancement. Chen, et al., (2008) studied the antibacterial mechanism of silver ion ($\text{Ag}^+$) on bacteria. $\text{Ag}^+$ makes DNA molecules to lose their replication abilities. Silver-doped materials are chemically durable and release $\text{Ag}^+$ for a long time. If silver nanoparticles are immobilized in the TiO$_2$ film on glazed surface of ceramic tiles, the release time of silver
ions can be delayed for a long time so that the coated TiO\textsubscript{2} film on ceramic tile will be of great potential for antibacterial application. This excellent antibacterial activity is not restricted by UV illumination (Sun, et al., 2008).

There are many techniques of immersing doped Ag into the TiO\textsubscript{2} solution, by choosing to variant the weight percentage, or photodeposited onto the TiO\textsubscript{2} thin film substrate.

### 2.4.5 AgTiO\textsubscript{2} thin film layers on different substrates

According to (Barati, et al., 2009) and (Falaras, et al., 1999) various withdrawal speeds have an effect onto the thickness of the thin film. The thickness of the thin films increases as the withdrawal speed increases. However, the deposited thin film has a variant effect on different substrate due to its hydrophobic and hydrophilic state. For instance, AP has a hydrophobic surface, therefore, when applying the thin film may be thicker compared to the glass surface. Therefore, the range of layers deposited onto different substrates may differ in terms of its capabilities to absorb the thin films onto the substrates. In this present project, 5 layers of AgTiO\textsubscript{2} thin film are deposited to gain the optimum layers for the experiment.

In order to find out the AgTiO\textsubscript{2} thin film thickness, a mathematics procedure which is called the gravimetrically analysis can be applied (Murali, 2007). By measuring the change of the weight before coating and after coating, calculating the area of the coatings deposited onto the substrate, and lastly, by using the bulk density of the AgTiO\textsubscript{2} thin film, the thickness of the AgTiO\textsubscript{2} thin film can be calculated. Also, a method of using Coordinate measuring machine (CMM) can be implemented by calculating the difference between 4 different datum of the coated substrate and the as-supplied substrate. The value was then compared with the SEM cross section morphology study.
Not only that, the thin film condition can also be affected by the method of drying. There were also studies shown that these coated substrates skipped the drying in room temperature for 24 hours. An investigation studied by Yao (2009), he had conducted experimental process on the metallic and non-metallic substrates, confounding that once the substrates were covered with the thin films, it was then straight away dried in the furnace at 100 °C. While in another study showed that there existed cracks formation when substrates were pre-dried in room temperature, followed by drying in oven. Therefore, Barati (2009) opted to go through the pre-drying process in a controlled condition using a solvent bath and followed by drying in the oven at 150 °C for 30mins.

2.5 Material characterization for AgTiO$_2$ antimicrobial coating

2.5.1 Appearance and mechanical properties

According to the previous methods and investigations, there are currently four different test has been taken into account (Page, et al., 2009). By using these four variables of substrate, the bonding test would be according to below descriptions:

i. Wipe test using finger: searching for loose material at coating surface. It is the most simple common test for physical endurance quality checking

ii. Scotch-tape test: this test is about finding the adherence and capability of the coating material to substrate

iii. Water Drip-test, used to see any loose materials or coating that can be washed off easily.

   a. For example, Circulating water onto the surface coating to find the stability of the cellulose-reinforced TiO$_2$ coatings for several cycles at a flow rate of 100 mL min$^{-1}$. This test was conducted because it is important to know the
stability of the coating under the experimental flow rate regime (Neti & Joshi, 2010).

iv. **Scratch test**, a simple test by using sophisticated equipment. A stylus with diamond tipped glass marker will be used to scratch the coating surface, thus examining the hardness and durability of the coating material.

### 2.5.2 X-ray Diffraction (XRD)

Glancing angle x-ray diffraction can be used to analyse the composition of thin films such as the antimicrobial coating because crystalline material diffracts x-rays in a material specific manner. However, the XRD that needed to be investigated onto the substrate is using the method of glancing angle due to the nature of the thin films. An angle of incidence of 1.5° over an angular range of 10-90° was used to investigate the thin film by using glancing angle. The XRD has the X-ray wavelength $\lambda$ is typically 0.7-2 Å, which corresponds to X-ray energies ($E = 12.4 \text{ keV/Å}$) of 6 - 17 keV (Brundle, et al., 1992). An example of the anatase peaks of TiO$_2$ thin film on stainless steel XRD in Figure 2.3:
The peaks as stated in the Figure 2.3 showed that once the diffracted X-ray intensity recorded at diffraction angles meet the Bragg condition. The anatase peaks exists at the degree 25.3°, 37°, 48°, 54°, 55.6°. The XRD results will be analysed to achieve the calculations for the percentage of anatase/rutile in the crystalline phases and the crystallite nanoparticle size. The anatase/rutile phase was determined through the intensity XRD peaks and the Spurr and Myers equation (Spurr & Myers, 1957) in Equation 2.1.

\[
F_R = \frac{1}{1 + 1.26[I_A(101)/I_R(110)]} \tag{2.1}
\]

Equation 2.1: Anatase/rutile ratio where \(F_R\) is the percentage content of rutile at each temperature, \(I_A\) (101) and \(I_R\) (110) are the integral intensities of (101) anatase and (110) rutile, respectively.
While the average crystallite size was estimated by Scherrer equation (Cullit, 1987) is as shown in the Equation (2.2).

\[
L = \frac{K\lambda}{\beta \times \cos \theta}
\]  

Equation 2.2: Scherrer equation, where \( L \) is the crystallite size, \( K \) is Scherrer constant given value at 0.89, \( \lambda \) is the wavelength of the X-ray radiation (CuK\(\alpha\) = 0.15418), \( \beta \) is the width at half maximum height and \( \cos \theta \) is the Bragg angle.

Another study conducted by Atabaki, et al., (2010), they had investigated the degree of crystallinity influences dissolution of hydroxyapatite (HA) coating. The results showed that the presence of higher extent of crystalline structure induced lesser dissolution of the coating. The strongest peaks for HA coating sintered at 900 °C appears in the range 29.234–31.038 of 2\(\theta\) angles. They concluded that as the sintering temperature increases, intensity also increases due to high crystallization rates at high temperature.

2.5.3 Scanning Electron Microscopy (SEM)

The AgTiO\(_2\) antimicrobial coatings that deposited onto different substrates are examined through a Scanning Electron Microscopy (SEM). SEM is conducted in order to find the surface morphologies of the coatings, i.e. porosity. In Figure 2.4, is an example of the 316L stainless steel with TiO\(_2\) thin films from the study conducted by Barati, et al., 2009 showing that as the calcined temperature increases, the grain size increases.
2.6 Antimicrobial activity testing

In Sun et al. (2008)’s investigation, the antibacterial activity against E. coli has been studied by applying the so called antibacterial-drop test. The drop test was completed by attaching a film of both TiO\textsubscript{2} and AgTiO\textsubscript{2} thin films against E. coli. The result was taken after leaving the specimen in 24hours, revealing that AgTiO\textsubscript{2} thin films are more effective antibacterial materials than TiO\textsubscript{2} thin films under conditions without UV light illumination.
The AgTiO\textsubscript{2} thin films exhibited high antibacterial activity. The comparison for both films is shown in Figure 2.5. The calculation for the antibacterial efficiency of coating was calculated as:

\[
\text{Antibacterial efficiency} = \frac{A_0 - A_1}{A_0}
\]  

Equation 2.3: Antibacterial efficiency equation where \(A_1\) and \(A_0\) are the antibacterial number of the control sample and antibacterial sheet sample, respectively.

![Graph](image)

Figure 2.5: In case of E. coli, relative number of bacteria survived for TiO\textsubscript{2} films and Ag/TiO\textsubscript{2} film, (Sun, et al., 2008)
Figure 2.6: Antibacterial activity of Ag-TiO$_2$ films, test results on E.Coli after 24hr: (a) incubated with a ceramic tile, (b) incubated with TiO$_2$ film and (c) incubated with AgTiO$_2$ film (Sun, et al., 2008)

As shown in Figure 2.6, the method used to coat the ceramic tiles is via liquid Phase Deposition (LDP) technique, while in this present project will show the effect of using sol gel technique onto metal, ceramic, glass and acrylic perspex. The antimicrobial activity was compared between both films and the result analysed is shown in terms of percentages of how many bacteria survived within 24 hours of time measurement.
CHAPTER 3

METHODOLOGY

3 Methods and procedures

3.1 Schematic flow chart of the project

The schematic flow chart of the project is categorized as:

Figure 3.1: Schematic Project Flow-chart
Referring to Figure 3.1, the substrate must be defined first then all the other process will follow in precedence. It is ensured that the process has no flaws as to the time restriction for this project. Each of the projected tasks was done in exquisitely extreme care.

### 3.2 Substrates preparation

In this project, there are five substrates that were focused on; acrylic perspex, 316L stainless steel, glass, glazed ceramic and ceramic glass. All of the substrates, except acrylic perspex, underwent a method of surface cleaning in order to remove the organic components as shown in the Figure 3.2. Acetone is used in order to remove the organic impurities from substrates and is well suited for greasy/oily contaminations. Then ethanol is used to remove and rinse away the contaminated acetone as well as removing particles from surfaces.

![Substrate surface cleaning process](image)

**Figure 3.2: Substrate surface cleaning process**
3.2.1 Acrylic Perspex

This material, in the scientific name of Poly-methyl Methacrylate, has the application for various usages. The application covers the usage of sale displays, newspaper stands, confectionary stands, lenses, panel covers, kitchen utensils, kitchen splash guards, window replacement. The melting and boiling point is a factor that should be concentrated on as acrylic perspex will have a different annealing temperature. The acrylic (3mm thickness) was cut out into dimension of 20 mm x 60 mm by using laser cutter and jig saw.

![Figure 3.3: Acrylic Perspex before coated](image)

3.2.2 Glass

The glass substrates were bought from Soon Lee Ltd., Melaka Baru. The 2 mm thick glass was cut into dimension of 20 mm x 50 mm by using glass cutter. For the surface preparation, glass substrates were cleaned with acetone and ethanol in an ultrasonic machine. This process is to ensure the surface is free from organic contaminants.
3.2.3 **Metal (316L Stainless Steel)**

The stainless steel sheet (4 mm) was cut by using shearing machine and cut into smaller dimension of 15 mm x 30 mm by using band saw. The surface preparation was to eliminate the pitting and oxides contaminants in the surface layer. Referring to Figure 3.5, when grinding and polishing the substrates, the resulted substrates has a reflective mirror surface.

The stainless steel substrates undergone the surface polishing, followed by ultrasonically cleaning process of the specimens by immersing in acetone, ethanol and distilled water in an ultrasonic bath, before starting the procedure for sol gel dipping.
3.2.4 Ceramics

In this study, there are two different types of ceramics; glazed and non-glazed ceramics. Glazed and non-ceramic was bought from industrialized company and the glass ceramic was produced under development research in UTeM.

Figure 3.6: Different types of ceramic substrates before coated with AgTiO$_2$ thin film (a) Glazed ceramic (b) Non-glazed ceramic
3.3 Sol gel AgTiO$_2$ formulation

There are multiple ways of formulating the TiO$_2$ thin film. For this present research will use the industrial-based TiO$_2$ formulation which consists of a series of chemicals such as precursor, solvent, catalyst and doped ion as stated in Table 3.1. The calculation for Degussa P25 powder weight in sol gel solution is determined through the ratio of the solution is based on precursor (Degussa powder and TTiP): solvent (ethanol and distilled water): catalyst (hydrochloric acid) with 1:16:4:1. Thus, giving a total volume for the solution = 88ml, with molar is the same for all solution. Degussa powder is calculated to be 1.0g

<table>
<thead>
<tr>
<th>Types</th>
<th>Chemical</th>
<th>Volume (ml)</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td>TTiP (Titanium (IV) Tetraisopropoxide)</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Titanium powder (Degussa P25)</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Solvent</td>
<td>Ethanol</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Distilled water</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>Catalyst</td>
<td>Hydrochloric acid</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Doped</td>
<td>Silver nitrate</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

In producing the formula, this project used the infamous TiO$_2$ powder of Degussa P25, a standard material in the field of photocatalytic reactions. The Degussa P25 powder was calcined to 450 °C before added into the sol gel preparation. TiO$_2$ nanoparticles undergo a single-phase transition: from amorphous to anatase when calcined at 450 °C. There had been a difference between the intensity of anatase peaks of the Degussa powder (as received from the supplier) and the calcined Degussa powder. This exchange is discussed in Section 4.1.
The process of the sol gel preparation was done in the fuming box as oxidizing chemicals were in used. Therefore, a range of protective equipments were used. The process for the formulation is as shown in Figure 3.7. The process of stirring involved using a magnetic stirrer stirred at 350 rpm to 700 rpm within 30 minutes to 24 hours.

Solution X comprised of distilled water, ethanol and hydrochloric acid was prepared separately from solution Y which is consisted of ethanol and TTiP. Then both solution were mixed and degussa P25 powder were dropwise into the solution. Thus sol gel TiO$_2$ were formed and aged overnight while stirring at 400 rpm.

### 3.4 Sol gel dip coating to produce thin films of AgTiO$_2$

The sol immersion is 5 seconds and the speed of dipping is in the range of 0.5 mm/s, while the equipment used is called the dip-coater machine. Moreover, the procedure is tedious since it can only coat one specimen per dip per layer per day. There are also studies
concluded that the optimum layers for substrates are 5 layers. The layers were optimum in terms of the film thickness that is coated smoothly on the surface. Thus, to ensure five layers to be coated, the procedure included a five day planning, since once a layer has been coated, it must undergo a stage of drying overnight for 24 hours in an electronic drying cabinet with a controlled temperature of 25°C and 30% humidity. This is due to the natural ambient temperature needed so that the layers do not evaporated and heated before heating through an oven at the temperature of 110°C to ensure the water content was seized to exist and dried. The steps were repeated into five cycles (five layers). These substrates were then doped with one layer of pure nanosilver (Nanosilver – NS, NAG-WG1000, Silver sol, 25ml) solution via sol gel dip coating method. Prior to sintering, the dip coated specimens were completely air dried.

Figure 3.8: Sol gel dip-coating procedure

![Sol gel dip-coating procedure diagram](image-url)
The dipping method was achieved using a mechanical machine that can control the thickness of each layer coated by having the same withdrawal speeds. The dip coater machine was configured in AMREC, SIRIM. The precision dip coater was set to have a moving vertical rate of 0.5mm/s and an immersing time of 5 seconds. The details of the set-up were shown in Figure 3.9. While the procedure for sol gel dip-coating process is shown in Figure 3.10, which is similar for all substrates.

Figure 3.9: Sol gel Dip-coater machine
Figure 3.10: Steps of immersion dip coating procedure.: (a) substrate moving vertically downwards towards solution (b) substrate immersed in solution (c) substrate moving out from solution

In the present research, two variants of pre-drying methods were conducted onto the stainless steel substrates. The first method was to be pre-dried in room temperature for 24 hours, while the other method is to dry the coated samples straight away in the oven at 110 °C for 30 minutes. The coating surface distinction was observed through Optical Microscopy (OM, Inverted Research Microscope with Processing and Analysis, LEICA).
3.5 Sintering

In this work, furnace (Box Furnace Fabricated, $T_1 = \text{annealed T}, R_1 = 5 \degree C/min$) was used to sinter the coating layer on the stainless steel, ceramic, glass and acrylic substrates. This process reduces dehydroxylation\(^3\) and increases the crystallization structure of the coating material, which is to focus on the anatase structure. For this purpose coated specimens were sintered in furnace with an annealing temperature below the melting point of each substrate.

In this research, various sintering temperatures were applied to obtain good mechanical properties for thin film coating. The substrates covered with AgTiO\(_2\) thin films were calcined through annealing treatment in a furnace at 120, 160, 200, 400, 600 \degree C soaked for 1 hour, within an increasing rate of 5 \degree C/min. Only acrylic substrates needs to undergone a heat treatment at a lower temperature (120 and 160 \degree C) compared to other substrates due to its low melting temperature. Following this, the substrates were directly cooled down to the room temperature.

The range of temperatures was chosen because 200-600 \degree C was the value where all crystal anatase were gradually transformed and can be compared to each of their own variances. At the starting temperature of 200 \degree C was to predict the beginning of crystal anatase transformation while at 600 \degree C was the starting of anatase transformation rutile phase. However, for ceramic, the calcined temperature was only at 600 \degree C because of its optimum calcinations temperature had been performed onto ceramics. The same reason was applied for the substrates involved for the deposited AgTiO\(_2\) thin film without the Degussa P25 powder as precursor. The dipping steps for each substrate are defined in the Table 3.2.

---

\(^3\) Loss of structural hydroxyl (-OH) ions as water molecules on heating
Table 3.2: Total samples and characterized by annealing temperatures

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Layers</th>
<th>Calcined Temperature for AgTiO$_2$ thin film, ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>120</td>
</tr>
<tr>
<td>316L SS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cleaned surface</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Without degussa</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Glass</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cleaned surface</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Without Degussa</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Acrylic Perspex</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cleaned surface</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Without Degussa</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Ceramic Glass</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Glazed ceramic</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

3.6 Thin film characterization

The X-ray diffraction is used to characterize the anatase peaks in the crystalline phase. The AgTiO$_2$ coating as informed is thin in nature, therefore it has to be examined with glancing angle; an angle of incidence 1.5° over an angular range of 10-90° for a 30 minute period. The surface morphologies of the AgTiO$_2$ thin films treated at different temperatures were observed using scanning electron microscopy (SEM) and Field-emission scanning electron microscope (FE-SEM) while the thin film surface composition is determined through Energy-dispersive X-ray spectroscopy (EDS). The substrates were gold-coated beforehand.
CHAPTER 4

RESULTS

4 Analysis of result on thin film coatings

This chapter discussed the AgTiO$_2$ thin film characteristics and how does they relate to the objective. For example, as the temperature of calcinations increases, the crystallite size of AgTiO$_2$ powders and thin films increases. Meanwhile, the characterization was achieved through XRD and the surface morphology was investigated through SEM to show the porosity of each coating on different substrate surface. Each thin film on different substrate was calcined at different temperatures 120 °C to 600 °C, and the result of the anatase/rutile percentage and the crystallite size was calculated through Scherrer equation as stated in Equation 2.2 in the literature. In achieving the highest photocatalytic activities, it involves the dependence on the surface area, porosity and crystal structure/composition and variation of crystal size and crystallinity (You, et al., 2005) and (Porter, et al., 1999), while the doped silver ion also plays a role in the antimicrobial activity against E.Coli. However, these two activities (photocatalytic and antimicrobial test) were not studied in the present project. It would be the continuation of this project.

4.1 Degussa P25 powder characterization

It is commonly accepted that high temperature calcination, at least at 400 °C is required to obtain anatase TiO$_2$ powder. It is also had been acknowledged that Degussa P25 powder had been known to have the existence of the crystalline phases of anatase and rutile. Thus, by
studying the characteristics of the powder through XRD, the Degussa powder possessed evident diffraction peaks characteristics of anatase. It showed the major anatase peaks at 25.3°, 37.8°, 48° and 53.9°. As shown in Figure 4.1, the anatase peaks indicates that even without calcining, the powders evidently existed in anatase and rutile crystal phase.

Therefore, it can be affirmed that the anatase phases exist at a lower calcined temperature but with lesser intensity range. This has been proven by Yuan & Hu (2006), they had prepared the anatase nanocrystalline particles at 75 °C without further treatments in which titanium-n-butoxide, Ti(OBu)₄ was used as the precursor. The results showed that the TiO₂ particles acquired a perfect crystallinity of anatase, which indicates that in comparison with the heat treatment at 500 °C, the heat treated film remarkably enhanced the degree of crystallization of the TiO₂ particles, accompanied by the growth of the crystallites (Yuan & Hu, 2006).

In this present project, the Degussa powder was calcined to 450 °C, in order to gain higher intensity of the crystalline anatase peaks. Referring to Figure 4.1, it showed that at the anatase peak 25.3° the intensity of calcined Degussa powder was proven to have higher intensity compared to the as supplied Degussa powder. The comparison proved that the intensities of anatase diffraction peaks increased when calcined at 450 °C. This is due to the fact that the higher the temperature, the higher the intensity of the crystalline anatase phase. In addition, the calcination temperature obviously influences the crystallization and phase composition of the P25 powders. This had been proven by (Wang, et al., 2012), as the calcination temperature is raised, XRD reflections corresponding to both the anatase and rutile phase become narrower, which indicates the increase of crystallite size. However, when increased to higher temperature (600°C to 800 °C), anatase to rutile transformation could be seen clearly.
Figure 4.1: Powder XRD of Degussa P25 powder – peak assignments confirm anatase and rutile phases of TiO$_2$
Figure 4.2: Powder XRD of Degussa P25 powder calcined at 450°C for 1 hour – peak assignments confirm anatase and rutile phases of TiO₂
4.2 AgTiO$_2$ thin film mechanical and physical observation

4.2.1 AgTiO$_2$ sol gel observation

Following the calcination of Degussa P25 powder at 450 °C, the powder was then added up to the sol gel of with TTiP as precursor in order to produce sol gel thin film deposited on substrates Ethanol (Ethyl Alcohol, R & M Chemicals, C$_2$H$_5$OH, ~99.7% V/V min, 64ml) and the distilled water was dissolved in hydrochloric acid (Sigma-Aldrich Co. Ltd, ACS Reagent, 4ml), forming a clear and colourless solution. The resulted solution called solution X was stirred for 30 minutes, after which no changes could be observed. At the same time, ethanol, 16ml was stirred together with Titanium (IV) Tetraisopropoxide (TTiP, C$_{12}$H$_{28}$O$_4$Ti, Aldrich, M = 284.22g/mol) at 350 rpm for 30 minutes. The solution became white coloured and appeared without agglomerating. The solution called solution Y was observed to be fully adhered after 30 minutes. Then slowly, solution Y was added to solution X dropwise while stirring. The resulted sol, solution A, was at first changed to white colour but then remained clear after stirring for an hour. Lastly, the calcined degussa powder, 1.04g was added to solution A, which changed the colourless solution to white. The sol was allowed to age overnight before being used for dip coating.

There is also a comparison being made towards the ability of AgTiO$_2$ powder and the thin film as being investigated by Page, et al., (2009). He had similarly compared the sol gel characteristics, being found out that the powders resulted greater intensity of anatase matching peaks of 101. Therefore, the procedure for turning into the sol gel into powder was proceeded as heating the 25ml sol gel at 60 °C in oven for 48hours. The heating was to dehydroxylise the sol gel to transform it into xerogel powders. The powders were then calcined in furnace at 600°C for 1 hour. The characterization of the powders were carried out through XRD and SEM and compared with the thin film characteristics.
4.2.2 Observations on coating

When coated with AgTiO$_2$, the thin film adhered consistently well on the substrate as observed in the Figure 4.3. Commercially available nanoscaled particles like P25 (Degussa) are synthesized by the aerosil-process. However the small primary particles tend to agglomerate during the synthesis process so that it is not possible to get transparent coatings. Therefore, all thin films showed white opaque layer on the substrates.

As observed under naked eye in Figure 4.3(a), the stainless steel substrate heated in oven treatment resulted in less corrosion compared to the sample treated in the room temperature. Stainless steel with coated AgTiO$_2$ thin film when calcined at 600°C turned colour from brownish to blue hue on the surface layer. The reason for the changed colour was unknown.

The thin film on glass substrate showed a smooth white opaque layer in Figure 4.3(b). Limited visible light can still penetrate the thin film, however due to the white-coloured appearance due to Degussa existence; the coated substrate is no longer transparent.

While focusing on the acrylic perspex (AP) in Figure 4.3(c), there are patches of AgTiO$_2$ that seemed not adhered well to AP’s surface. The white patches resembled the Degussa powder that had not agglomerated well to the solution. The thin film was observed to be transparent yet white splotches appeared to be visible on the coating. The coating would be consistent if the surface preparation was performed using other methods as investigated by Su, et al., (2010), the surface preparation of the AP was performed by using a low pressure DC glow plasma pre-treatment to achieve effective coating of the homogenous TiO$_2$ thin film. Once the plasma treatment has been accomplished, the samples were then dipped coated
into TiO$_2$ sol gel. A transparent layer of TiO$_2$ films were obtained with no white spots of the powders due to non-existence of the degussa powder in the sol gel cossoidal solution.

The white precipitates was also inevitable on the ceramics substrates in Figure 4.3(d) and (e). The glazed ceramic was the most obvious that showed the lumped white layer of the AgTiO$_2$ thin film covering the clear yellow brown glazed coating.

While for the mechanical observation of the surface adherence, the substrate was put under running water and further insured that the coating did not washed away with the water. To mechanically prove the concept, the specimens were immersed in water and were ultrasonically cleaned for 10 minutes. The result still remains the same as there were no thin films peeled away, under the naked eye observation. In addition a simple bonding test of sticking the coated substrate with adhesive tape, indicating that there are no remains stuck to the adhesive tape, thus showing the adherence of the thin film on the substrates. Both resulted that the adhered thin film was still intact.
Physical observation on coating on different substrates

Figure 4.3: Physical observations of the AgTiO$_2$ coated substrates (a) Stainless Steel (b) Glass (c) Acrylic Perspex (AP) (d) Non-glazed ceramic (e) glazed ceramic
The thickness of the 5 layer coating was estimated using Coordinate Measuring Machine (CMM). The 5 layers thin film was coated as it was difficult to find the thickness of the one layer using the SEM cross section due to the size of the substrate. The thickness was calculated by measuring 4 different points which referred as datum between the coated layer and the as supplied surface substrate. The result was defined in Table 4.1, concluding that the coating on AP was thicker compared to the coating on glass substrate. However, since this is estimation only at a certain point on the surface, therefore, it cannot be hold as a significant value, as the thin film surface may possess a not-uniformed layer of coating.

Table 4.1: Thickness of AgTiO$_2$ thin film

<table>
<thead>
<tr>
<th>Substrate</th>
<th>AgTiO$_2$ Thin Film, $\mu$m</th>
<th>Average Thickness, $\mu$m</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Data 1</td>
<td>Data 2</td>
</tr>
<tr>
<td>Glass</td>
<td>12.80</td>
<td>2.80</td>
</tr>
<tr>
<td>Acrylic Perspex</td>
<td>195.40</td>
<td>176.10</td>
</tr>
</tbody>
</table>

4.2.3 Stainless Steel

As stated in the literature, stainless steel surface was to be cleaned and grinded in order to remove the oxide layer before it can be coated with AgTiO$_2$ thin film. The resultant substrate is as shown in Figure 4.4.
It was experimented that stainless steel should have a different range of drying methods due to the different thermal expansion of both substrate and thin film. According to the first observation through Optical Microscope (OM, Inverted Research Microscope with Processing and Analysis), the coating layer is not clearly visible in the image. The result is as shown in Figure 4.5 with the magnification of x10. Assumption of corrosion occurs in both situation due to the existence of water in the sol gel formulation and air in the room temperature dry-condition. Both of the cooling conditions were controlled at the respective temperature. The big black spots in sample b are assumed to show the corrosion pitting. Also, there exist white lines in sample b, which shows the evidence of cracks on the thin films due to fast evaporation of the solvent.

As it turned out, the solution nature is acidic, 0.89 pH, when tested with the pH tester equipment. Therefore, it was realized that the solution is not compatible with coating thin films onto the stainless steel substrate, thus there exists corrosion in both samples. After five cycles of coatings, the OM results are as shown in Figure 4.6. The OM images had detected
the difference between thin films that had been dried in the oven and pre-dried in the room temperature. The layers had completely coated the surface of the sample. However, it shows that the layers are not smoothly layered on top of the substrates.

Figure 4.5: Optical Microscopy images (10x magnification) of Stainless Steel coated with TiO$_2$ Degussa P25, after coating in first layer (a) Heated in oven for 30 minutes at 110°C and (b) dried in electronic dry cabinet at 45% humidity, 30°C for 24 hours
Figure 4.6: Optical Microscopy images (10 x magnifications) of 5 layer coated stainless steel substrate, calcined at 600°C (a) dried in oven (b) dried in room
4.2.4 Glass

Figure 4.7: Optical Microscopy images of glass substrate, calcined at 600°C

While under the OM, the surface layer was found out to be not smooth and films cracks exist. Further SEM image is investigated in order to confirm the crystal size that had been calculated through Scherrer equation.

4.2.5 Ceramic

Figure 4.8: Optical Microscopy images of Ceramic substrate, calcined at 600°C (a) Non-glazed ceramic (b) Glazed ceramic
Under OM images in Figure 4.8, showed that the films are indeed porous and not uniformed. This is due to the fact that the ceramic was only coated with one layer. It is assumed that with consecutive layers and controlled dipping method, the surface will be smooth.

4.2.6 Acrylic Perspex

![Figure 4.9: The effects of acrylic perspex prepared substrates before coated; (a) immersed in acetone (b) heated in oven for 1 hour at 200 °C](image)

The effects of cleaning and heated in high temperature are shown in Figure 4.9. Acrylic reacted to acetone into making liquid acrylic glue. Since the cleaning of the substrates were combined in one beaker, thus resulting samples into sticking and adhered to each other as shown in Figure 4.9(a). Therefore, it was justified that acrylic did not undergone the process of cleaning and it was dip coated just as it is. While the temperature for sintering was lowered down for acrylic substrate, to 120 °C and 160 °C due to the restriction of low boiling temperature which is at 200 °C, resulted to flaking and melted layers as shown in Figure 4.9(b).
4.3 XRD characterization of AgTiO$_2$ powders and thin films

The effect of calcinations temperature was shown in terms of the crystallization phase and size. The percentage of rutile and anatase was inevitably higher in anatase side, due to the calcinations temperature increment. The Degussa (P25) powder as supplied had an average crystallite size of 25nm.

Table 4.2: AgTiO$_2$ powder and thin films phases and crystallite size, at different calcined temperatures

<table>
<thead>
<tr>
<th>Samples</th>
<th>Calcination Temperature, °C</th>
<th>Percentages of phase</th>
<th>Crystallite size$^c$, nm</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>X%$^a$</td>
<td>Y%$^b$</td>
</tr>
<tr>
<td>TiO$_2$ Powder</td>
<td>60</td>
<td>60.47</td>
<td>39.25</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>66.18</td>
<td>33.56</td>
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<tr>
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<td>200</td>
<td>70.67</td>
<td>29.08</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>77.17</td>
<td>22.62</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>79.30</td>
<td>20.50</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>200</td>
<td>61.19</td>
<td>38.53</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>69.22</td>
<td>30.53</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>49.14</td>
<td>50.57</td>
</tr>
<tr>
<td>Acrylic perspex</td>
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<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>100.00</td>
<td>0.00</td>
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<tr>
<td>Ceramic Glass</td>
<td>600</td>
<td>55.48</td>
<td>44.23</td>
</tr>
<tr>
<td>Glazed Ceramic</td>
<td>600</td>
<td>61.14</td>
<td>38.58</td>
</tr>
<tr>
<td>Non-glazed ceramic</td>
<td>600</td>
<td>79.92</td>
<td>19.88</td>
</tr>
</tbody>
</table>

$^a$ X% - anatase percentage  
$^b$ Y% - Rutile percentage  
$^c$ Crystallite size was calculated using Scherrer equation - Equation 2.2

As showed in Table 4.2, the average crystalline of anatase was estimated from the value of full-width at half-maximum (FWHM) in the XRD intensities of anatase (101) peak at 20 = 25.4° using Scherrer equation. In AgTiO$_2$ films on all substrates, the presence of rutile is of course inevitable, since it exists also in the starting precursor material (P25). While, the rutile and anatase content was determined by comparing the X-ray diffraction intensities of anatase (101) and rutile (110) faces. Overall, the anatase crystal size in TiO$_2$ thin film
increases as the calcination temperature increases from 200 to 600 °C. Similar findings were also observed by other studies (Wang, et al., 2012) and (You, et al., 2005).

4.3.1 Characterization of TiO$_2$ sol particles

In order to produce TiO$_2$ powder from the sol gel, the TiO$_2$ solution was dried at 60 °C for 48 hours in oven. Then, it was calcined to 600 °C to compare with the dried powder in terms of the phase structure and crystallite size from the XRD results. In Figure 4.10, even when as dried at 60 °C, there exist anatase peaks with higher intensities similar to TiO$_2$ powder calcined at 600 °C, thus showing that even at lower temperature, the anatase peaks presence was inevitable due to the existence of Degussa powder. However, the crystallite size decreased as the TiO$_2$ dried powder was calcined at 600 °C. The rutile crystallite size also had been calculated, showing that the values 161.18nm and 17.27nm respectively at powders heated at 60 °C and calcined at 600 °C. This may due to the starting transformation of rutile at higher temperature, thus resulting in smaller crystallite size at higher calcinations temperature.
For the TiO$_2$ powders, both heated at 60 °C and calcined at 600 °C showed the crystals agglomerated and chunked together and there is a limitation on the SEM image in Figure 4.11 and 4.12 to show the estimation of the crystal size of the powder as it has a low magnification value. However the calculated value from Scherrer equation from Table 4.2 still stands at the value of 68 and 160 nm for the dried powder at 60 °C and calcined at 600 °C. Also shown in the figures, the particles tended to aggregate, which results from the competition between electrostatic repulsion and natural attractive Van der Waals forces (Yuan & Hu, 2006).
Figure 4.11: SEM images of TiO$_2$ powder dried at 60 °C

Figure 4.12: SEM images of TiO$_2$ powder dried at 600 °C
4.3.2 XRD Characterization of AgTiO$_2$ thin films

The further investigation was moved towards the thin film deposited onto different substrates. The deposition was completed through the sol gel dipping method and the thin films were then calcined at different temperature.

Specifically for thin film deposited on glass substrate, after the heat treatment at 200, 400 and 600 °C the rutile/anatase ratio did not particularly change, with the 79% of anatase and 20% of rutile (in Table 4.2). Also the average crystallite size of thin film on glass substrate produced a slight increase from 27.29 to 32.75 nm as the calcined temperature from 200, 400 and 600 °C respectively. Thus this goes to show that the crystallite size increases as the calcined temperature increases. Referring to the Figure 4.13 in the diffraction pattern of the AgTiO$_2$ sol films deposited onto glass substrates, peaks at 25.3, 37.8, 48.1 and 55.2° could be identified. They correspond to (101), (112), (200) and (211) reactions of the anatase phase of TiO$_2$ respectively (Falaras, et al., 1999). Then, at the temperature 600 °C, a significant rutile peak was starts to show at $2\theta$ angle of 27.4° at the reflection (110).
Figure 4.13: Glancing angle XRD pattern of AgTiO$_2$ thin film coated onto Glass calcined at 200, 400 and 600 °C
The same thin-film XRD is used to investigate the phase constitutions of the AgTiO$_2$ films coated on Acrylic Perspex (AP). The thin films were calcined each at 120 and 160 °C for 1 hour. The results in Figure 4.14 revealed that the as prepared AgTiO$_2$ coated AP and local AP exhibit the presence of two large humps (amorphous halos) centered around 10 and 30°, due to the diffuse scattering of amorphous AP (Su, et al., 2010). For AgTiO$_2$ coated AP calcined at 160°C, the amorphous humps included a small matching peak at 20 values of 25.3°, corresponding to TiO$_2$ anatase (101) crystal planes. While for the AgTiO$_2$ thin film calcined at 120 °C showed the relatively low matching peaks of anatase in the amorphous range 50-80°. The thin film also did not show the matching peaks of rutile, as TiO$_2$ sol gel materials synthesized using titania alkoxides which is without chemical additives typically transform from anatase to rutile at ~600 °C (Seery, et al., 2009).

The XRD pattern achieved in Figure 4.14 was merely significant for the substrate surface. The layers were not enough for for XRD to detect any other peaks that had been achieved during the calcinations at both temperatures of 120 and 160 °C.
Figure 4.14: Glancing angle XRD pattern of AgTiO$_2$ thin film on Acrylic Perspex calcined at 120 and 160 °C
As shown in Figure 4.15, the XRD of AgTiO$_2$ thin film deposited onto stainless steel, calcined at different temperature illustrated significant anatase peaks of 25.3, 37 and 48° respectively.

![Figure 4.15: Glancing angle XRD pattern of AgTiO$_2$ thin film coated onto stainless steel - calcined at 200, 400 and 600 °C](image)

According to the stainless steel surface composition resulted from XRD at 600°C, the highest peak at the 44.3° is the Cobalt Iron Gallium. However, in the calcined thin film at 200 and 400 °C, both have copper existence at the peak 43.7°. There are two reasons as to why both of these elements exist:
a) The control sample was not cleaned with acetone, ethanol and distilled water. Therefore the debris from the grit paper was still intact. There are significant differences in XRD pattern for both cleaned and not cleaned substrates.

b) For the thin films, the other elements exist due to the contaminated sol gel solution as the solution was used numerously and repetitively for other substrate as well. Therefore, the debris or contaminants from other substrates may lead to the formation of cobalt iron gallium, ferum and copper.

Thus, the result of the anatase composition for both annealed temperature cannot be used for further analysis, as the thin films have turned into a layer of corrosion on the stainless steel surface. The element composition of AgTiO₂ on the substrate was further confirmed through the means of Energy Disperse X-ray Analysis (EDX).

There are also samples of the different types of ceramic coated with the AgTiO₂ thin film. As referred to Table 4.2, the crystallite size and anatase phases were different due to the different porosities involved in the ceramic surface. For instance, the non-glazed ceramic has the lowest crystallite size which is 53.5nm compared to the higher sizes of ceramic glass and the glazed ceramic which is 96.36 nm and 98.72 nm respectively. The calcination was not varied for ceramics. The anatase peaks was confirmed to show at the matching 2θ angle of 25.3°.

In Figure 4.16, even when coated with AgTiO₂, the glazed ceramic showed a high content of relative intensity on the rubidium and zircon which is the ceramic glazed layer composition, both respectively at the angle of 25.1°, 26.8° and 32°. With these peaks in mind, it showed that the XRD data for the AgTiO₂ thin film coated layer is affected by the substrate composition values.
In Figure 4.17, for non-glazed ceramic the rutile formation also has been acknowledged to exist in the matching peaks at 27.3°, 37°, 48°, 54°, 56° and 63°. While the highest peak for non-glazed ceramic is armophous silicon dioxide. Both ceramic compounds exist at the XRD angle of 26.6 and 27.0° which showed the composition of the non glazed ceramic.
Figure 4.17: Glancing angle XRD pattern of Ag\(\text{TiO}_2\) thin film on non-glazed ceramic calcined at 600 °C

In general, the XRD characterization of the Ag\(\text{TiO}_2\) thin films and TiO\(_2\) powders had remarkably showed that with the increased calcinations temperature, the crystallite size had also increased. On the other hand, the anatase and rutile percentage did not change drastically from the calcined temperature of 200 °C to 600 °C. The percentage of anatase is also widely influenced by the calcinations temperature, the substrate surface porosity and roughness.

A further clarification was done using SEM, in order to show the surface morphology of the thin films, which is differed from each substrates.
4.4 SEM surface morphologies of AgTiO$_2$ thin film and TiO$_2$ powders

The thin films were coated with 5 layers of coating and had undergone a different calcinations temperature. The surface morphology had shown the different crystallite size in thin films on different substrates. Figures 4.18 to 4.20 showed the surface FE-SEM images of the 5-coat dip-coated AgTiO$_2$ thin films on AP treated at 120 °C to 160 °C for 1 h, glass treated at 200 °C to 600 °C for 1 h and stainless steel treated at 600°C for 1 h, respectively. As shown in the figures, the films were porous and the particles were approximately spherical. The average particle sizes were estimated to be about 87, 57, 37 and 55nm in diameter by the intercept measurement method from Figs 4.18, 4.19 and 4.20 respectively. The particles were assumed to aggregate during the calcination and heat treatment.

For instance in Figure 4.18, there is also possibility of the particles to be aggregated during the deposition dipping process on the substrates i.e AP as, the particles calcined at 120°C was bigger than the calcined AP at 160°C. There were no matching anatase peaks in the XRD of AP calcined at 120°C, therefore the particles are assumed to be the armophous TiO$_2$ particles, thus it cannot be compared to the anatase formed in AP calcined at 160°C.

No cracks were observed on the surfaces of the TiO$_2$ films as shown in all Figures 4.18-4.20. As investigated through Yuan & Hu (2006), they had deposited the TiO$_2$ coating onto AP approximately at 12 layers with 15 minutes interval at the withdrawal rate of 1cm/min. As the surface of AP is hydrophobic, therefore, cracking occurs on the surface while glass is hydrophilic, thus no cracking occurs. Since in the present project, there were no significant cracks occurs on AP, this goes to show that the the 5-coated layer of AgTiO$_2$ was able to adhered well on the AP surface.
Figure 4.18: Surface FE-SEM images of a 5-coat dip-coated AgTiO$_2$ thin film on AP (a) calcined at 120 °C (b) calcined at 160 °C
While for glass substrate, in Figure 4.19, it showed that the AgTiO$_2$ coating was not uniformed for all calcination temperature. The 5-layer film is not smooth and many aggregates were found on its surface. This may due to the occurrence of lack of enough coatings to ensure the roughness uniformness of the coating. In relevance to the study conducted by Paez & Matoušek (2004), they had found out that enough coatings on glass was estimated to be 3 layers, in order to gain smooth surface. However, their content of TiO$_2$ hydrolisis deferred from this current project as they have used different precursor which is Tetra-n-butyl-orthotitanate, alcooxide and the other compounds, which might be together with relatively low heating temperature the reason for good adhesion to the glass surface. While in another study, a smooth surface from 10 layers was investigated by (Ibrahim, et al., 2012) being the most optimum layers. They had used tetrapropoxy (ortho) titanate, (TPOT) as precursor with the addition of polymer additives, with different viscosity investigated. This goes to show that different precursor and different layers of coating may result to different surface condition in terms of smooth and porosity of the coated surface.

The porous surface was seen when the magnification was increased to 50000 times. The significant increase of the crystal size can be seen when compared the image in Figure 4.19(a), (b) and (c) which the temperature calcined is at 200, 400 and 600 °C respectively.
Figure 4.19: Surface FE-SEM images of a 5-coat dip-coated AgTiO$_2$ thin film on Glass (a) calcined at 200 °C (b) calcined at 400 °C (c) calcined at 600 °C
For the surface morphology of AgTiO$_2$ on stainless steel in Figure 4.20, it showed spherical particles and somewhat flat surface. Looking at the surface morphology, the particle size, 55nm, was bigger than the estimated crystallite size, 32.75 nm, calculated using Scherrer equation in Table 4.2. This may due to the particles may have been contaminated by the oxides layers from the dried stainless steel. The consecutive layers were approximately coated onto the substrate as there are 5 layers were deposited. Once each layer was dried in oven at 110°C, there exist an oxide surface layer that will dilute in the used TiO$_2$ sol gel.
Figure 4.20: Surface FE-SEM images of a 5-coat dip-coated AgTiO$_2$ thin film on Stainless Steel (calcined at 600 °C)
4.5 EDS composition in AgTiO$_2$ thin film on different substrate

While for the EDS composition, which had been done simultaneously through the SEM procedure, all substrate have high percentage of Ti and O, with the addition of small value of C and Ag. Figure 4.21 to 4.23 showed the EDS comparison between the substrates.

For AP, the thin film has the weight (wt%) composition of C 6.51%, O 45.17%, Ti 48.02% and Ag 0.3%. While for glass, the composition is comprised of C 3.76%, O 43.9%, Ti 51.40%, Ag 0.94%. For SS, the thin film has the weight composition of elements C 3.83%, O 7.58%, Ti 1.27%, Cr 21.67%, Fe 58.16%, Ni 7.4%, Ag 0.08%. There are authors pointed out that the diffusion of Fe ions from stainless steel during high temperature treatment would form an underlayer of the rhombohedral phase Fe$_2$O$_3$ at the film substrate interface. Cr and Ni still existed in the metallic state and only Fe was oxidized during TiO$_2$ film annealing owing to the highest sensitivity of iron toward oxygen (Duminica, et al., 2009). Therefore, it is assumed that the high percentage of Fe in AgTiO$_2$ thin film on SS was due to the oxidized Fe that transformed in to Fe$_2$O$_3$. 
<table>
<thead>
<tr>
<th>Element</th>
<th>App Conc.</th>
<th>Intensity</th>
<th>Weight%</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
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<tbody>
<tr>
<td>C K</td>
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<td>1.4507</td>
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<td>1.54</td>
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<tr>
<td>O K</td>
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<td>Ti K</td>
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Figure 4.21: EDS of AgTiO$_2$ thin film on Acrylic Perspex calcined at 160 °C
Figure 4.22: EDS of AgTiO$_2$ thin film on Glass calcined at 600 °C
<table>
<thead>
<tr>
<th>Element</th>
<th>App Conc.</th>
<th>Intensity</th>
<th>Weight%</th>
<th>Weight%</th>
<th>Atomic%</th>
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Figure 4.23: EDS of AgTiO$_2$ thin film on stainless steel calcined at 600 °C
CHAPTER 5

DISCUSSION

5 Discussion on relations of different surface morphology to crystallite size

5.1 Surface morphologies of TiO$_2$ thin films on different substrates

SEM micrographs of the surface morphology of the AgTiO$_2$ thin films onto different substrates calcined at different temperature indicated that the coating was smooth and uniformed and it seemed to agglomerate at certain areas. It was shown that the glass coated surface was not smooth and uniformed, leads to the assumption that the layers were not sufficient enough to accommodate to the uniformed layer on the surface. There is also another possibility that the lack of layers that have been coated onto the substrates may have shown the inconsistent coating layers. For the dip-coated glass substrates, large agglomerate size can also be observed due to the coagulation formed in the dip-coating process, which can affect the effective surface area of the coating and may further reduce the photocatalytic activity. The surface may also have been affected by the way the dipping method and the drying of each substrate were applied. The dipping method has to be ensured that the substrate is placed vertically at 90° degree and dipped in different sol gel solution that should not be shared with other substrates. While the drying method which is to ensure the water was dehydrated and the way the substrate was to be put in such a way that the sol gel would not puddle on the surface.
As stated before, the films were porous and the particles were seen approximately spherical. It was assumed that the particles aggregated during the deposition and calcinations processes. The average particle sizes of glass and AP were estimated to be about 37 and 57 nm in diameter, respectively correspond to the calculated particles from Scherrer equation.

EDS test was carried out simultaneously with SEM analysis. The high weight composition analyses corresponded with the concentrations of all the elements in the coating i.e Ti and O. As Ag was found remarkably low at each substrate, it is due to the fact that Ag was doped only one layer, thus giving the value of low intensity height. There was also the existence of carbon content, C, as it came from the hydrolysis of ethanol (C₂H₅OH) and TTiP (Ti[OCH(CH₃)₂]₄) with the formulation.

5.2 XRD Characterization of the AgTiO₂ thin films

In general, the full width at half-maximum of XRD peak corresponds to the crystal size of porous materials. When the width was narrower, the crystallites exhibited larger size. As the calcinations temperature increases, the crystallite size increases. This is shown remarkably in the AgTiO₂ thin film deposited on the glass and stainless steel. While for AP, the lower calcinations temperature did not produce a matching peak of anatase, thus the value of crystallite size could not be compared. Since layers of coating had an effect to the penetration XRD reading, it is to be reminded that in the next study, the AgTiO₂ coating on the substrate should be thicker than 5 layers.

The readings on XRD consistently showed that AP had the most armophous peaks that resemble its substrates. Only when calcined at 160°C the AP showed small intensity matching peaks at 25.3° in regards to the crystallite phase (101). This showed that the anatase crystals did not grow through the hydrolysis of the AgTiO₂ deposition, but grew through the calcinations temperature as presented though glass, SS, non-glazed and glazed ceramics.
which showed the presence of anatase at matching peaks of (101), (004), (200) and (105) at 25.3°, 37°, 48° and 54° when calcined at 200-600 °C.
CHAPTER 6

CONCLUSION AND RECOMMENDATION

6.1 Conclusion

At room temperature, the thin film of AgTiO$_2$ was successfully deposited onto different types of substrates i.e AP, SS, glass and ceramic through the method of dip-coating process from the anatase AgTiO$_2$ sol, which was synthesized by hydrolysis of TTiP, Degussa P25 powder, ethanol, acidic aqueous solution and distilled water. The current project had achieved the objectives stated in Chapter 1, which are:

i. The usage of Degussa P25 powder did indeed remarkably enhance the presence of anatase and rutile phases, especially when calcined at the temperature of 450°C. Also, the dried sol gel that was turned into powder (heated at temperature of 60°C for 48 hours) also had indicated the presence of anatase and rutile with the ratio of 70:30 through XRD pattern.

ii. The experiment demonstrated that for glass substrate, as the calcined temperature from (200-600 °C) increased the crystallite size increases (27-32 nm). The AgTiO$_2$ sol particles aggregated remarkably during the calcinations on the glass, AP, SS and ceramic substrates. Since Degussa powder was used as precursor, it was already predicted that the anatase phase existed at lower temperature. There is an inevitable presence of rutile, since Degussa P25 powder itself has already composed of
anatase and rutile phases approximately at ratio of 70:30. The surface porosity and crystallite size plays a role in achieving the anatase phase.

iii. Through XRD (calculation of Scherrer equation) and comparison with the SEM images, the crystallite size for glass and stainless steel remained similarly the same, which is the range of 27 – 32 nm. While for AP, the anatase crystal was only shown in the thin film that was calcined at 160 °C. It is safe to say that the anatase crystal did not aggregated during the sol gel process but rather than during the calcinations of the thin film.

The acidic solution may have an effect to the metallic substrate as it may lead to corrosion; therefore, it is recommended that this sol gel is modified to have a neutral pH in order to be able to be deposited onto different types of metallic substrates.

6.2 Recommendation

This project can be improved through these three steps:

i. The sol gel dipping method can be improved by increasing the thickness of the thin film on the substrates through consecutive coatings up until 10-12 layers. In most studies, especially for glass and AP substrates, the coatings were performed in the range of 10-12 coatings in order to increase the film thickness.

ii. In addition, a further study should focus on the crystallite transformation during the sol gel formulation. The anatase phase in AgTiO$_2$ sol gel can be enhanced with the hydrolysis increased at magnetically stirring at thermal temperature of 60-70°C in order to inhibit the crystallization transformation under the heating condition. Then the sol gel can be deposited onto polymers as the substrates need not go through higher temperature of calcinations.
iii. The future works of this project may lead to the study of the photocatalytic and antimicrobial test of the AgTiO$_2$ thin film as the photocatalytic depended on the crystallite phases and sizes, surface porosity and surface areas. Furthermore, the existence of AgTiO$_2$ will help to reduce the microbial activity by measuring the performance in the antimicrobial test.
7 References


Figure 8.1: Glancing angle XRD pattern of AgTiO$_2$ thin film on glass – calcined at 200 °C

Figure 8.2: Glancing angle XRD pattern of AgTiO$_2$ thin film on glass – calcined at 400 °C
Figure 8.3: Glancing angle XRD pattern of AgTiO$_2$ thin film on glass – calcined at 600 °C
Figure 8.4: Glancing angle XRD pattern of AgTiO$_2$ thin film coated onto Acrylic Perspex calcined at 160 °C.
Figure 8.5: Glancing angle XRD pattern of AgTiO$_2$ thin film coated onto Acrylic Perspex calcined at 120 °C

Figure 8.6: Glancing angle XRD pattern of AgTiO$_2$ thin film on stainless steel – calcined at 200 °C
Figure 8.7: Glancing angle XRD pattern of AgTiO$_2$ thin film on stainless steel – calcined at 400 °C
Figure 8.8: Glancing angle XRD pattern of AgTiO$_2$ thin film on stainless steel – calcined at 600 °C
Table 3: XRD phase transition calculation

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