UNIVERSITI MALAYSIA KELANTAN

Preliminary Study on Different Calcination Temperature of TiO_2-Eggshell Composite Using Sol-Gel Method

Nik NorHidayah Binti Nik Jid

J20A0538

A reported submitted in fulfilment of the requirements for the degree of Bachelor of Applied Science (Materials Technology) with Honours

FACULTY OF BIOENGINEERING AND TECHNOLOGY

UMK

2024

DECLARATION

I declare that this thesis entitled Preliminary Study on Different Calcination Temperature of TiO_2-Eggshell Composite Using Sol-Gel Method is the results of my own research except as cited in the references.

Signature : ____________________________

Student's Name : ____________________________

Date : ____________________________

Verified by:

Signature : ____________________________

Supervisor's Name : ____________________________

Stamp : ____________________________

Date : ____________________________

ACKNOWLEDGEMENT

Bismillahirrahmanirrahim,

In the name of Allah, the Most Gracious and the Most Merciful

Alhamdulillah, all praises to Allah for the strengths and His blessing in completing this Final Year Project, a Preliminary Study on Different Calcination Temperature of TiO_2-Eggshell Composite Using Sol-Gel Method.

First and foremost, I would like to express my deepest appreciation to my FYP's supervisor Dr. Hidayani Binti Jaafar, who has been a continual source of encouragement, support, and guidance from the start until the completion of my thesis writing. I'm really grateful for the time spent supporting me and rectifying each mistake I made along the way to completing my undergraduate studies.

Besides that, I would also like to thank all the staff of the Faculty of Bioengineering and Technology (FBKT), UMK for their cooperation and, in particular for aiding with the analytical evaluation of the tested samples.

Additionally, I would like to express my deep gratitude and appreciation to all of my family members, as they have always encouraged and supported me during my years of university study. Finally, I would like to thank all my friends and colleagues who helped and given me encouragement to complete this project. Their contributions are highly respected. Thank you very much.

Preliminary Study on Different Calcination Temperature of TiO_2-Eggshell Composite Using Sol-Gel Method

ABSTRACT

The incorporation of titanium dioxide and eggshell composite at different calcination temperatures was studied. This study is focusing the effect of different calcination temperature on band gap of TiO_2-Eggshell composite. In this research, TiO_2-Eggshell composites were synthesized using sol-gel method and being calcined at different temperature (400 °C, 450°C and 500 °C). Thermogravimetric analysis (TGA) , UV Visible spectroscopy (UV- Vis) and X-Ray Diffraction (XRD) analysis were used to characterize the samples. the crystallize size of the TiO_2, Eggshell, TE 400 °C, TE 450 °C, and TE 500 °C was estimated using Scherer's method and found to be 16.86nm, 18.29nm, 27.80nm, 23.10nm, and 27.10nm respectively. Among three different calcination temperatures, TE 450°C composite demonstrated optimal absorbance at 3.14 a.u, suggesting a potential enhancement in photocatalytic performance. The band gap measurement of TE with different calcination temperatures range from 3.25 eV to 3.48 eV, it is can help retain the inherent stability of TiO_2 while achieving sufficient light absorption.

Keywords: TiO_2-Eggshell, Calcination Temperature, Composite

Kajian Awal Suhu Pengkalsinan Yang Berbeza Terhadap TiO_2-Kulit Telur Komposit Menggunakan Kaedah Sol-Gel

ABSTRAK

Campuran antara titanium dioksida dan kulit telur komposit pada suhu pengkalsinan yang berbeza telah dikaji. Kajian ini memfokuskan kesan suhu pengkalsinan yang berbeza ke atas jurang jalur komposit TiO -Kulit Telur. Dalam penyelidikan ini, komposit TiO_2-Kulit Telur telah disintesis dengan menggunakan kaedah sol-gel dan dikalsinkan pada suhu yang berbeza iaitu 400 °C, 450 °C dan 500 °C. Analisis Termogravimetrik (TGA), spektroskopi UV Visible (UV-Vis) dan analisis X-Ray Difraction (XRD) digunakan untuk mencirikan sampel. Saiz kristal TiO_2, Kulit Telur, TE 400 °C, TE 450 °C, dan TE 500 °C dianggarkan menggunakan kaedah Scherer dan didapati masing-masing 16.86nm, 18.29nm, 27.80nm, 23.10nm, dan 27.10nm Di antara tiga suhu pengkalsinan yang berbeza, komposit TE 450°C menunjukkan penyerapan optimum pada 3.14 a.u, ianya menunjukkan kepad kemampuan peningkatan dalam aktiviti fotokatalitik. Pengukuran jurang jalur TE dengan suhu pengkalsinan berbeza berjulat dari 3.25 eV hingga 3.48 eV, boleh membantu mengekalkan kestabilan sedia ada TiO_2 untuk mencapai penyerapan cahaya yang mencukupi.

Kata kunci: TiO_2-Kulit telur, Suhu Pengkalsinan, Komposit

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

TiO_2	Titanium Dioxide
CaO	Calcium Oxide
$CaCO_3$	Calcium Carbonate
C_2H_50H	Ethanol
HNO_3	Acid Nitric
$MgCO_3$	Magnesium Carbonate
SnO_2	Tin Oxide
WO_3	Tungsten(VI) oxide
ZnO	Zinc Oxide
UV-VIS	Ultra violet Visible
TGA	Thermogravimetric Analysis
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Background of Study

TiO_2 is a well-known semiconductor substance with various uses, including photocatalysis, sensors, solar cells, and water purification. According to Mali et al. (2012), TiO_2 has proven to be an ideal material for extensive solar energy conversion and environmental applications due to its biological and chemical inertness, excellent oxidizing ability, cost efficiency, and long-term resistance to photo corrosion and chemical corrosion. TiO_2 is a popular metal oxide used in photoelectrochemical water splitting and dye-sensitized solar cells due to its high photocatalytic efficiency under visible light Hung et al. (2021). Titanium Dioxide (TiO_2) is a metal oxide that has a wide band gap of around 3.2 eV, which means that it can absorb photons with energies greater than 3.2 eV, which are in the ultraviolet (UV) range of the electromagnetic spectrum (Skočaj et al., 2011). TiO_2 may go through a process known as photocatalysis when it absorbs UV photons, which allows it to degrade organic contaminants into harmless byproducts.

Eggshell is a waste material that is rich in calcium carbonate ($CaCO_3$) which has similar properties to TiO_2 such as a significant refractive index and a high level of light scattering. In addition, eggshells are very cheap, and using the eggshell can create cost-effective of DSSCs. Eggshell-derived calcium carbonate ($CaCO_3$) can be added to TiO_2

to act as a co-catalyst to enhance charge transfer, efficiency and improves photocatalytic performance Hung et al. (2021). Eggshells can also increase the surface area of the TiO_2 photoanode, which further enhances its performance in photoelectrochemical water splitting and dye-sensitized solar cells.

To synthesize the eggshell mixed Titanium dioxide, TiO_2 can be achieved through the sol–gel method. According to Bokov et al. (2021), The sol-gel technique is a more chemical (wet chemical) approach to the manufacture of different nanostructures, specifically metal oxide nanoparticles. The sol-gel method is very popular due to its simplicity, low cost, and ability to produce high-quality materials with controlled properties. The sol-gel synthesis is preferred over solid-state synthesis for preparing metal oxide nanoparticles, including TiO_2, due to its ability to produce more homogenous and pure materials with better control over particle size and shape Elbushra et al. (2018). Using the eggshell as a co-catalyst can improve the photocatalytic efficiency of TiO_2 under visible light Eddy et al. (2023). In addition, sol-gel synthesis can reduce the annealing temperature required for the synthesis of TiO_2, which is beneficial in terms of energy consumption and cost-effectiveness Elbushra et al. (2018).

1.2 Problem Statement

The incorporation of eggshell into TiO_2 composites has shown promising outcomes in terms of improving the material's mechanical and photocatalytic capabilities. Furthermore, research on the impact of calcination temperature on the characteristics of TiO_2-Eggshell composites, particularly when synthesized via the sol-gel process, is restricted. As a result, (overcome) the purpose of this research is to look into how different calcination temperatures affect the structural, mechanical, and photocatalytic characteristics of TiO_2-Eggshell composites synthesized using the sol-gel technique. As know, TiO_2 is widely used as photocatalytic due to its high reactivity and non-toxicity. However, the use of TiO_2 has a limitations. TiO_2 is low visible light absorption due to the wide band gap of TiO_2 which means that it can only absorb photons with energies greater than 3.2 eV. It also low charge absorption capacity. According to the Dong et al. (2015), TiO_2 has a poor capacity for adsorbing hydrophobic pollutants, which restricts its ability to remove certain pollutants in photocatalytic activity. In DSSC, TiO_2 is imperfect alignment of the energy levels(Raguram & Rajni, 2022) and recombination which means the efficiency of N-doped TiO_2-based DSSCs is constrained by the propensity of photogenerated electrons to recombine at mono-doping type of dopant sites (Lim et al., 2016).

By mixing eggshell with TiO_2, the limitations of TiO_2 may be overcome due to some unique properties of chicken eggshell. The major component of chicken eggshells is calcium carbonate ($CaCO_3$), with a trace amount of organic material. Eggshell is a possible source of calcium ions that may be employed as a support material for a variety of applications, including catalysis and water treatment, due to its high $CaCO_3$ concentration (Shiferaw et al., 2019). According to the Awogbemi et al.(2020), chicken eggshells is very effective dispersion and has high specific surface area. It is means that, the eggshell can effectively disperse TiO_2 nanoparticles, helping to get over the material's constraints of aggregation and uniform distribution and Due to the high specific surface area of eggshell, there are many active sites that can be used for the deposition of TiO_2 nanoparticles. This might help to enhance TiO_2's ability to adsorb pollutants that are hydrophobic.

1.3 Objectives

The objective of this study are:

1.To fabricate eggshells mixed TiO_2 composite using sol-gel method.

2.To investigate different calcination temperatures on band gap of TiO_2-Eggshell composite.

1.4 Scope of Study

In this study, eggshells were employed as precursors in the study for the sol-gel technique used to create TiO_2-Eggshell composites. TiO2-Eggshell powder were calcined at different temperature which were 400 °C, 450 °C and 500 °C. In addition, the samples of TiO_2, Eggshell, and TiO_2-Eggshell with different temperature during calcination Thermogravimetric (TGA), X-ray diffraction (XRD), and UV-vis spectroscopy were used to investigate the crystal structure, shape, and optical characteristics of the synthesized composites.

1.5 Significances of Study

The initial study of various TiO_2-Eggshell calcination temperatures by means of the sol-gel process is important because it advances our knowledge of the ideal circumstances for producing TiO_2-Eggshell with improved characteristics. This work will contribute to the identification of an appropriate calcination temperature range that can produce TiO_2-Eggshell nanoparticles with desirable qualities, including greater stability, increased surface area, improved photocatalytic activity, and effective light absorption properties. Additionally, this research may have effects on a number of different disciplines, including water treatment, solar energy conversion, environmental cleanup, and the creation of new materials for use in sensors, electronics, and optics. The outcomes of this research may lay the foundation for cost-efficient and environmentally sustainable methods in crafting TiO_2-Eggshell composites. Furthermore, the study offers valuable perspectives into the correlation between calcination temperature and the resultant characteristics of TiO_2-Eggshell. Additionally, it has the potential to augment the existing knowledge base concerning the sol-gel synthesis technique, particularly its role in fabricating advanced materials. In essence, the importance of this investigation is underscored by its capacity to propel scientific comprehension and unveil fresh avenues for both the synthesis and utilization of TiO_2-Eggshell composites.

CHAPTER 2

LITERATURE REVIEW

2.1 Metal Oxide

Recently, metal oxide semiconductor has various applications including photocatalyst and photoanode due to their configurable band gap, cheap cost, huge specific area, and simplicity of manufacture (Yoon et al., 2021). Metal oxides are oxygen-metal binary compounds. The direct heating of elements with oxygen, high-temperature reactions of oxygen with compounds, or nitric acid oxidation of metals and nonmetals can all be used to produce inorganic oxides. The oxides of elements in a period in the periodic table get increasingly more acidic from left to right; basic oxides are found on the left side of the periodic table, while acidic oxides are found on the right side. The size and dimension of oxides may regulate and adapt the band gap and electrical structure, leading to a wide range of possible uses (Grilli, 2020). For example, TiO_2, ZnO, SnO_2, WO_3, CuO, and ZrO_3 are the metal oxide.

Another important field of investigation is the synthesis and manufacturing of metal oxide materials. Researchers investigate various approaches and procedures for producing desirable metal oxide nanoparticles, thin films, and bulk materials. To manage the size, form, and composition of metal oxide materials, multiple synthesis techniques such as sol-gel, hydrothermal, chemical vapor deposition, and physical vapor deposition are used. Researchers want to improve the performance of metal oxide materials in applications ranging from electronics and catalysis to energy storage and conversion by improving synthesis techniques (Alhalili,2023).

2.1.1 Titanium Dioxide (TiO_2)

Titanium Dioxide (TiO_2) is an opaque white natural mineral that occurs in a variety of crystalline forms, the most noteworthy of which are rutile and anatase. This natural oxide may be mined and utilised as a commercial titanium source. TiO_2 has no odour and is quite absorbent. It is available in powder form and is mostly used as a pigment to add whiteness and opacity (Patra, 2023). Titanium dioxide (TiO_2) has a variety of properties, including chemical stability, a high refraction index of visible light, semi-conductivity, and photosensitivity, making it an excellent material for photocatalytic applications and as the anode of photovoltaic cells in energy generation systems (Camaratta et al. 2013). TiO_2 is composed of three crystalline polymorphs: anatase, brookite, and rutile as shown in Figure 2.1(Khataee & Kasiri, 2010). The basic structural unit of all these crystalline forms of TiO_2 is an octahedron made up of one titanium atom and six oxygen atoms. The four sides of the octahedron are zigzagged linked to produce a crystalline structure in anatase. By linking the corners of the oxygen atoms, the sides of the octahedron form a chain that forms a three-dimensional structure in rutile. Brookite has an orthorhombic structure because its edges and vertices are octahedral (Khataee & Kasiri, 2010). Both anatase and rutile have a tetragonal structure, while brookite has an orthorhombic structure.

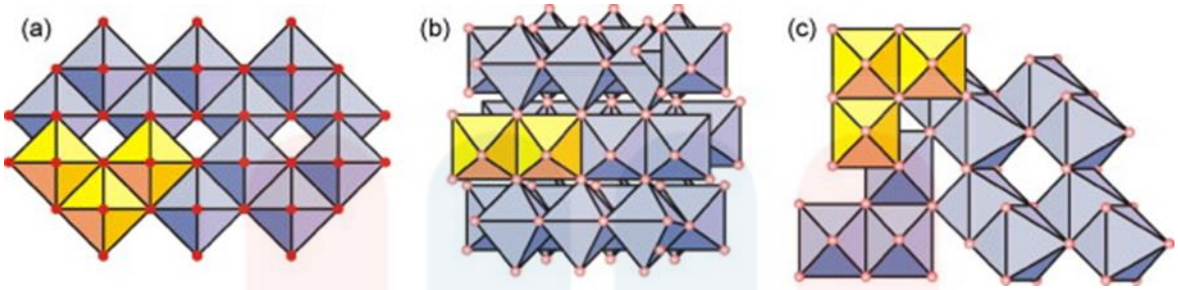

Figure 2.1 Crystalline Structure of TiO_2 a) Anatase b) Brookite c) Rutile (Khataee & Kasiri, 2010)

According to Allen et al. (2018), among these three crystalline forms, anatase TiO_2 is the best option for application in photocatalytic processes. Anatase has a higher energy bandgap than rutile, reducing light absorption but increasing electron oxidation power and electron transport from TiO_2(Zangeneh et al., 2015).

2.1.2 Type of Metal Oxide

ZnO is a metal oxide that has photocatalytic properties. ZnO has a band gap energy of 3.3 eV and can exhibit greater decomposition efficiency across a wide range of solar wavelengths (Khaki et al., 2017). Furthermore, ZnO has great electron availability, outstanding stability, and mechanical strength (Ong et al., 2018). ZnO with a high specific surface area is very useful for organic pollutant adsorption. Liang et al. (2018) They claim that nanometric ZnO is less expensive than TiO_2. ZnO can therefore be employed for heterogeneous photocatalysis. ZnO, on the other hand, exhibits quick electron-hole pair recombination because to its high energy band gap. (Ong et al., 2018).

Next, Tin Oxide (SnO_2) has a wide band gap energy of 3.6 eV, which may be activated by the UV irradiation spectrum to form free radicals, it degrades organic substances into less hazardous chemicals like carbon dioxide and water molecules. (Al-Hamdi et al., 2017). Furthermore, SnO2's huge specific surface area and porous structure led to its outstanding photocatalytic degradation (Zhao & Wu, 2018). In addition, some researchers also claimed that Tin Oxide (SnO_2) has high stability and lower toxicity properties.

According to Szilágyi et al. (2012), Tungsten(VI) oxide (WO_3) was the second-most explored metal oxide semiconductor after TiO_2 because of its relatively modest band gap range of 2.5 eV to 3.0 eV, which may absorb visible light for electron excitation. WO_3 was a key player in the photocatalysis process (Szilágyi et al., 2012). This indicates that the photocatalytic degradation of organic dyes performs better in oxidized monoclinic WO_3 than in oxidized hexagonal WO_3(Szilágyi et al., 2012). Moreover, WO_3 has high availability, is non-toxic, has chemical and physical resistance, and is a powerful oxidation powder (Alghoul et al., 2014).

TiO_2 is more suitable than other metal oxides due to its unique properties. According to Wu (2021), (TiO_2) has a high melting point, which makes it ideal for high-temperature applications. Additionally, TiO_2 has a complex crystal structure, which allows for various modifications and applications, including photocatalysis, electronic materials, energy, environment, health, medicine, catalysts, and more (A. Wu & Ren, 2020). TiO_2 is also highly reflective, making it ideal for use in pigments. It is insoluble in water, which makes it suitable for various industrial uses (Wu, 2021). In addition, TiO_2 is an insulator, which means it does not conduct electricity and is suitable for electronic applications (A. Wu & Ren, 2020). Its photocatalytic activity makes it suitable for water treatment, and its mixed oxide with Fe(III)-Ti(IV) has shown good removal efficiency for arsenic. These unique properties make TiO_2 one of the most suitable metal oxides for various industrial and commercial uses (Samokhvalov, 2017).

2.2 Chicken Eggshell

Noviyanti et al., 2022 state that eggshell contained calcium carbonate ($CaCO_3$) and hydroxyapatite (HA). Recently, eggshell has attracted interest as a promising raw material for the synthesis of composites with a variety of applications (Noviyanti et al., 2022). For example, the sol-gel fabrication of TiO_2-Eggshell composites. The TiO_2-Eggshell composites may be used as a photocatalyst for the degradation of TC in the presence of solar light (Huang et al., 2021).

Based on Ummartyotin and Manuspiya (2018), eggshell waste has been offered as a source of the substance for photocatalytic applications that accelerate the pace of photoreaction. Photocatalysis has been utilized to eliminate organic pollutants from the water in advanced methods of oxidation. Some papers have been reviewed about the use of eggshell waste as a catalyst in different fields such as metal matrix composites, bioactive chemicals in anaerobic fermentation, and biodiesel manufacturing, and it is also used to treat water waste.

Furthermore, the eggshells' potential in biological and pharmacological applications has been examined. Eggshell membranes contain antibacterial and wound-healing characteristics, according to research. Moreover, because of its biodegradability and resemblance to the actual bones, eggshell-derived calcium is currently used for the manufacturing of calcium-containing products and skeleton scaffolds.

2.2.1 Properties of Chicken Eggshell

The structural integrity and protective qualities of chicken eggshells are a result of a variety of special qualities. There are some properties of chicken eggshells. The composition of chicken eggshell consist of 95% calcium carbonate ($CaCO_3$) and 5% of other minerals such as magnesium carbonate ($MgCO_3$), phosphorus and iron (Gautron et al., 2021). According to the Bartter et al. (2018), the eggshell have a high calcium content which is 380 mg of calcium/gram. Next, the thickness of the chicken eggshell. A chicken eggshell normally has a thickness of 0.3 millimetres. The breed of chicken, the size of the egg, and the environment in which the chicken was grown may all affect the thickness, though (Sun et al., 2012). The researchers state that 42 locations for each egg along the longitudinal and latitudinal axes were chosen, and thickness was measured using an eggshell thickness gauge at each position to calculate the overall variance in eggshell thickness. The thickness of the eggshell varied considerably (P 0.05) from blunt to sharp end. It was thinnest (0.341 -0.025 mm) around the blunt end and thickest (0.367 0.023 mm) towards the sharp end.

Furthermore, the eggshells from chickens are remarkable strong. They have a weight resistance of almost 100 times their own weight. This is due to the manner that the calcium carbonate crystals are organized in eggshells, which makes them incredibly robust. It is because, the outer layers of chicken eggs are stacked. The cuticle, a thin, waxy covering that helps shield the eggshell from germs and moisture, is the outermost layer. The outer membrane, a thin, flexible layer that aids in holding the eggshell together, is the inner layer.

According to the (Tullett & Burton, 1985), The porous nature of chicken eggshells allows water and air to travel through them. The development of the baby inside the egg depends on this porosity. The study discovered that reduced porosity eggshells lead to an increased retention of carbon dioxide within the egg, which is somewhat offset by an anticipated rise in blood bicarbonate levels. Based on Arzate-Vázquez et al. (2019), The mechanical characteristics of the eggshell are also influenced by its porosity.

2.2.2 Mechanical Properties of Eggshell

Eggshells act as a mechanical support system and a barrier against outside influences for growing embryos (Park & Sohn, 2018).

Table 2.1 Mechanical Properties of Animal's Eggshell

Animal	Eggshell Thickness (mm)	Young's modulus (GPa)	Compressive Strength (MPa)	Flexural Strength (MPa)
Chicken	0.3	10-14	100-120	10-14
Ostrich	0.6	7-10	150-200	15-20
Duck	0.4	12-15	100-120	12-15
Goose	0.5	10-13	100-120	10-13
Pigeon	0.2	7-10	50-60	7-10

Based on table 2.1, the Young's modulus of chicken eggshells is between 10 and 14 GPa, and they are rather thin. This indicates that they are slightly elastic as well as capable of withstanding compression and bending. In terms of tensile strength, they are not particularly strong (Chiang et al., 2021). The thickest animal eggshells are those of the ostrich, with a Young's modulus of 7–10

GPa. This indicates that they are quite sturdy and capable of withstanding compression and bending. They are not as robust as chicken eggshells, though, in terms of tensile strength.

Eggshells from ducks, geese, and pigeons have mechanical characteristics with those of chickens (J. Zhang et al., 2017). They all have a Young's modulus between 10 and 13 GPa and are all rather thin. This indicates that they are somewhat flexible and capable of withstanding compression and bending. In terms of tensile strength, they are not particularly strong.

Eggshells from chickens provide the finest overall mix of mechanical characteristics. They are relatively powerful while being relatively thin and flexible. They are therefore perfect for a range of uses, including the production of eggshell powder, membrane, and eggshell-based composites.

2.3 Method Used To Synthesize TiO_2-Eggshell

There are several methods for the synthesis of the composite eggshell mixed TiO2. The most popular is solid state, sol-gel, and hydrothermal method.

Table 2.2 Difference between Sol-Gel, Solid State, and Hydrothermal Method

Method	Sol-Gel	Solid State	Hydrothermal
Definition	The sol-gel technique is a more chemical (wet chemical) approach for producing different nanostructures, particularly	Solid-state synthesis is a process of synthesizing composite materials by grinding compounds of two or	Hydrothermal synthesis is a method of synthesizing inorganic materials in aqueous media above ambient

	metal oxide nanoparticles. In this procedure, the molecular precursor (typically a metal alkoxide) is dissolved in water or alcohol and then heated and stirred to form a gel by hydrolysis/alcoholysis (Bokov et al., 2021b).	more non-volatile solids and pelletizing and heating the materials (Solid State Synthesis, n.d.).	temperature and pressure. It involves growing single crystals in a nutrient and water solution in a steel pressure vessel called an autoclave. The process depends on the solubility of minerals in hot water under high pressure, and the solution forms a temperature gradient to grow the desired crystal(Pan et al., 2015).
Temperature °C	50- 80°C (depending on the specific materials and reaction conditions used.)	1000-1500°C (It's depending on the specific synthesis method and materials used.	100 – 250°C under the vapor pressure.

Application	Commonly used in various applications such as optics, electronics, energy and surface engineering, biosensors, and pharmaceuticals.	Typically used to produce high-quality single crystals, ceramics, and glasses.	Used to prepare materials with unique properties, such as zeolites, nanomaterials, and high-temperature semiconductors.

In the case of synthesizing TiO_2-Eggshell nanoparticles, the sol-gel method is suitable because it allows for precise control over the size, shape, and composition of the nanoparticles. The aqueous extract of eggshell waste can be used as a precursor for metal oxide nanoparticle synthesis (Ramya et al., 2022). The eggshell waste contains calcium carbonate ($CaCO_3$), which can be converted to calcium oxide (CaO) through calcination. The CaO can then be used as a precursor for the sol-gel synthesis of TiO_2 nanoparticles. The calcined eggshell can also serve as a support material for depositing TiO_2 nanoparticles with narrow size distribution (El-Kemary et al., 2018).

Furthermore, by controlling the temperature range and pressure throughout the synthesis process, the sol-gel approach allows for modifying the characteristics of the resultant materials (Haque et al., 2017). This is critical for optimizing the synthesis process and getting the ideal TiO_2-Eggshell nanoparticle characteristics. Overall, because of its accuracy, adaptability, and capacity to adjust the characteristics of the resultant materials, the process of sol-gel synthesis is a possible methodology for synthesizing TiO_2-Eggshell nanoparticles.

2.4 Calcination Temperature

Calcination is the method of heating an element to high temperatures either in or without any element of air or oxygen. Many materials, including ceramics, catalysts, and metal oxides, rely on this process. The temperature of the calcination is a crucial factor that impacts the end-product qualities of the material. The calcination temperature influences the material's crystal structure, phase composition, particle size, surface area, and shape. The particles could not completely crystallize at lower temperatures, resulting in amorphous or weakly crystalline materials. Particles may sinter or agglomerate at high temperatures, resulting in bigger particle sizes and a lower surface area (Kassa et al., 2022).

The calcination temperature also affects the material's specific surface area, pore size, and porosity. Porosity and surface area may be large at low temperatures due to the production of tiny particles and the elimination of volatile substances. The presence of pores can reduce at higher temperatures through sintering or the disappearance of reactive species. The pace of heating and cooling during calcination is also critical. Rapid heating and cooling can cause thermal shock and material fracture. Controlled heating and cooling can help prevent these problems and provide a more homogenous and stable material (Putz et al., 2019).

2.5 Limitations of Titanium Dioxide (TiO_2)

TiO_2 having a wide range of application in several sectors due to its distinctive qualities, which include a high refractive index, chemical stability, and photocatalytic activity, it is a desirable material for a variety of applications (Racovita, 2022). However, TiO_2 also have the limitations. Firstly, TiO_2 is limited photocatalytic efficiency. TiO_2 is well known for its photocatalytic abilities, however its effectiveness is constrained in several ways. TiO_2's photocatalytic activity can only occur under UV light due to the bandgap energy, which restricts its use in visible light. This limitation limits its potential for wider application in locations where visible light is the main energy source. Numerous studies are being conducted to improve the doping, composite creation, or structural alterations of TiO_2's photocatalytic performance (Anucha et al., 2022).

Next, TiO_2 has low electron-hole separation rate. According to the Nguyen et al. (2020), TiO_2 also has a low electron-hole separation rate, which has an impact on the efficiency of its photocatalytic activity. The production of reactive species is hampered by the reduction in charge transfer efficiency caused by the recombination of electron-hole pairs. To solve this problem, a number of methods have been suggested, including the addition of co-catalysts, surface alterations, and heterojunction forms. It is still difficult to achieve meaningful increases in electron-hole separation, though. According to the Chakhtouna et al. (2021), TiO_2 is not particularly stable in situations that are either acidic or alkaline. TiO_2 can deteriorate and lose its photocatalytic activity under these conditions. This may restrict the usage of TiO_2 in processes like water treatment where it will be exposed to acidic or alkaline conditions.

Finally, although titanium dioxide (TiO_2) has a number of beneficial qualities, it is important to understand its limits. For example, limited photocatalytic efficiency, low electron-hole separation rate, and not stable in acidic or alkaline conditions.

2.6 Characterization Study

Characterization studies are critical in establishing the chemical and physical properties of newly made catalysts. Using the chemical and physical characteristics of the material, researchers may acquire a deeper understanding of the synthesized material and assess its catalytic activity. It can be investigated by using XRD and UV-VIS characterization.

2.6.1 XRD Characterization

XRD method is commonly used to characterize the material's crystalline structure, preferred orientation and crystalline size. The diffraction of peaks is determined based on the crystalline structure of the specific materials (Trache et al., 2016). It is possible to identify a material's crystal structure by measuring the distinct diffraction angles, which are indicative of the material's crystal structure.

Since XRD is a non-destructive method, it does not harm the sample being examined. Additionally, it is a quick and simple approach to use. A wide range of materials, including metals, ceramics, polymers, and biological materials, are characterized using XRD (Heiney, n.d.). On length ranges between 0.1 and 100 nm, the XRD generates a diffraction pattern that does not visually reflect the underlying structure and offers details on the interior structure.

Figure 2.2 A Genetic X-ray Scattering Measurement (Heiney, n.d.).

A sample is exposed to an X-ray beam, and the dispersed intensity is calculated in relation to the direction of travel. Conventionally, the angle between the directions of the entering and exiting beams is referred to as 2θ. When Bragg's Law is met, constructive interference (higher scattered intensity) may be detected for the simplest sample, which consists of sheets of charge separated by distance, d.

$$n \lambda = 2 d \sin \theta \quad \text{Equation 1.1}$$

Here n is an integer (1, 2, 3, ...), λ is the wavelength of the x-ray beam, and θ is half the scattering angle 2 θ shown above.

Naturally, real materials are more complex, but the overall conclusion remains that there is a connection between the interparticle distances within the sample and the angles at which the scattered intensity is the maximum, with higher distances, d corresponding to lower scattering angles 2θ.

According to a study by Negoescu et al. (2020), XRD is an important technique for the characterization of TiO_2-based materials, including composites. Another study by Phromma et al. (2020) investigated the effect of different calcination temperature on the photocatalytic activity of TiO_2-based materials and found that XRD was useful for characterizing the crystal structure and phase composition of the materials. Overall, XRD provided valuable information about the crystal structure of the TiO_2-Eggshell composite and how it changed with varying calcination conditions.

This information can be useful for optimizing the synthesis and performance of the composite material.

2.6.2 UV-VIS Characterization

UV-Vis spectroscopy is an analytical method that compares the number of discrete wavelengths of UV or visible light absorbed or transmitted by a sample to the total number of discrete wavelengths absorbed or transmitted by the sample. Emitted by an untested sample These attributes are impacted by the sample's makeup and provide information about what is being examined and at what concentration (Tom, 2023).

In the instance of the TiO_2-Eggshell composite, UV-Vis spectroscopy may be utilized to assess its bandgap energy and optical characteristics, which are crucial aspects of its photocatalytic activity. They discovered that the absorbance and reflectance spectra of the composites changed with calcination temperature, with composites calcined at 500°C having the maximum photocatalytic activity.

Huang et al. (2021) used UV-Vis spectroscopy to explore the influence of calcination temperature on the bandgap energy of TiO_2-Eggshell composites. They discovered that when the calcination temperature increased, the bandgap energy of the composites reduced, indicating increased photocatalytic activity. Similarly, Bullo et al. (2021) employed UV-Vis spectroscopy to examine the optical characteristics of TiO_2-Eggshell composites discovered that the bandgap energy reduced as the calcination temperature increased, resulting in better photocatalytic activity.

2.6.3 TGA

Thermogravimetric Analysis (TGA) is employed as a technique for assessing changes in a sample's mass relative to temperature variations, offering insights into its thermal stability. The assessment of weight loss during heating is conducted by integrating an electronic microbalance with a temperature-controlled furnace. Several research studies have leveraged TGA to appraise the thermal stability of diverse materials (Al-Oqla et al., 2022). As indicated by Rami et al. (2021), this methodology generates a plot of temperature (or time) versus mass (or weight %), providing a means to investigate material mass loss attributed to processes like oxidation, degradation, or the release of volatiles within a specified temperature range.

2.7 Summary

Various type of metal oxide had been discussed in this paper to understand the properties and the characteristics of each metal oxide such as TiO_2, ZnO, SnO_2, and WO_3. Among of these metal oxide, TiO_2 is the most suitable metal oxide to use due to its high melting point, insoluble in water, insulator and other. Furthermore, the anatase TiO_2 is the best option for application in photocatalytic processes because anatase TiO_2 has a high energy band gap more than rutile.

Next, the eggshell is promising raw material to produce a good composites with different applications. There are three popular method that can be used to synthesis TiO_2-eggshell composites which is solid state, sol- gel, and hydrothermal method. In this project, the sol-gel method is used to investigate the effect of this method towards TiO_2-eggshell composite with different calcination. There are three characterization technique that can be used to characterize the TiO_2-eggshell composite which is XRD, TGA and UV-Vis spectroscopy.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

The chemical reagents used in this research is titanium dioxide powder (TiO_2), ethanol (C_2H_5OH), distilled water as a solvent and acid nitric (HNO_3) as catalyst. Waste chicken eggshells is collect from the local restaurant near to the University of Malaysia Kelantan (UMK) Jeli Campus in Jeli, Kelantan.

3.2 Methods

The method to prepare a TiO_2-Eggshell composite start with the extract the calcium precursor from the chicken eggshell and then, the synthesis of TiO_2-Eggshell using sol-gel method Lastly, the sample were calcined at different calcination temperature (400°C, 450°C, and 500°C) before characterized all the samples.

3.3 Research Flowchart

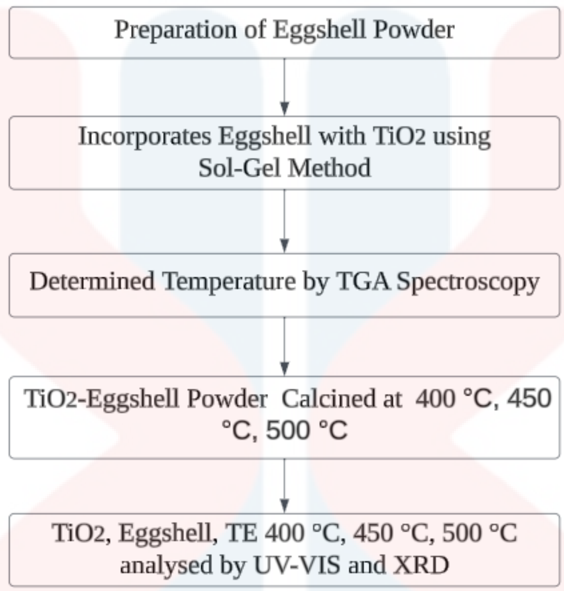

Figure 3.1 Research flow for TiO_2-Eggshell with Different Calcination Temperatures.

3.4 Extraction of Calcium Precursor from Chicken Eggshell

In this research, chicken eggshells are used as a source of calcium for synthesis of eggshell-TiO_2 via the sol gel method. Waste eggshells were thoroughly washed with water and cleaned with deionized water. Crushed the wash eggshell and put the small amount of crushed eggshell in crucibles before put in furnace as shoe. Then, the sample was dried at 900° C for 5h, ground into a fine powder using grinder or pestle and mortar and after that sieved with 100 µm sieve size. The decomposition of $CaCO_3$ to CaO is shown in equation (3.1).

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \text{Equation 3.1}$$

3.5 Sample Preparation

The synthesis of TiO_2-Eggshell composite were done via sol-gel method with the ratio 6:4. First, the 4g eggshell powder mixed together with 6g TiO_2 powder and put in the 100mL beaker. Then add 100 mL ethanol and stirred until the mixture of TiO_2-Eggshell powder dissolved. A few drop of nitric acid (HNO_3) were added into the solution of TiO_2 incorporated with Eggshell. 50 mL distilled water were added into the beaker and stirred for 3 hours to ensure the proper mixing and interaction between the eggshell and TiO_2 particles.

The sample were dried in an oven at 60 °C for about 2 hours in order to evaporate the solvent and to remove the organic residuals. The mixture of TiO_2-eggshell was ground using mortar and pestle before calcined for 4 hours with different temperatures which were 400, 450 and 500 °C. The obtained of TiO_2-eggshell powder were labelled as a TE 400, TE 450, TE 500 respectively.

3.6 Calcination Temperature of TiO_2-Eggshell powder

The powder of TiO_2 incorporates with Eggshell powder were calcined at different calcination temperature, 400 ˚C, 450 ˚C, and 500 ˚C respectively with 5 hours soaking time. Reference temperature as shown in Figure 3.2. Then, all the samples were analysed using UV-VIS spectrophotometer.

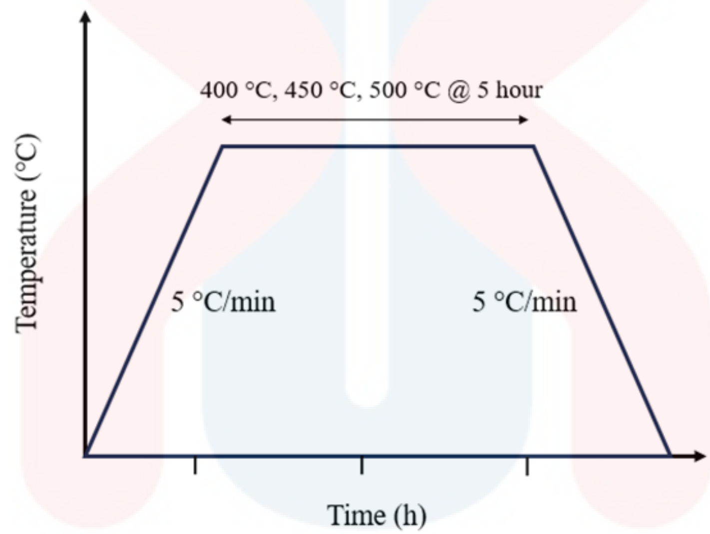

Figure 3.2 Calcination Temperature for TiO_2-Eggshell Powder Sample

3.7 Sample Characterization

The TGA/DSC 1-Thermogravimetric Analyzer, Mettler-Toledo, was used for thermal analysis. The structural of the composite powder have been evaluated using X-ray diffraction method (Bruker, model D2 Phaser) with the size step of 0.02° (2θ) at a fixed counting time of 71.6 s from 10° to 90°2θ. Next, all samples were analysed using Spectroquant Pharo 300 UV-Visible Spectrophotometer to determine the absorption spectra of all samples.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter were discussed about the different temperature to calcined the TiO_2- eggshell composite using TGA spectra. Then, UV-VIS spectroscopy was used to investigated the visible parts of the electromagnetic spectrum as well as identify the band gap. By using X-Ray Diffraction (XRD), the crystal structure properties , including crystallite size and lattice strain were discussed.

4.2 Determination of Calcination Temperature

Thermogravimetric Analysis (TGA) spectroscopy were conducted with the results are shown in Figure 4.1. TGA analysis was performed in temperature range between 30-1000°C at a heating rate of 10°C/min in the flow of pure nitrogen. Figure 4.2 represents the graph of catalyst weight versus temperature.

The TGA curves shows three stages of weight loss as temperature increases . The first one was observed between 39.07°C and 169.88°C which is 2.88% of weight loss, due to the loss of moisture in the nitrogen atmosphere from its surface. Then, the second weight loss occurred in the temperature range of 169.88°C to 376.62°C due to the transformation of $Ca(OH)_2$ to CaO with total weight loss was 3.12% . The final weight loss occurred in the range of 376.62°C to 577.57°C, due to the decomposition of TiO_2 itself with maximum weight loss 6.11%. However, over the 800°C, the sample weight increased might be due to the oxidation or the reaction with the crucible even though nitrogen was an inert atmosphere. The total weight loss of the TE sample was 12.11%. Based on the data provided by TGA analysis in Figure 4.1, the calcination temperature of TE were chosen as 400°C, 450°C and 500°C respectively.

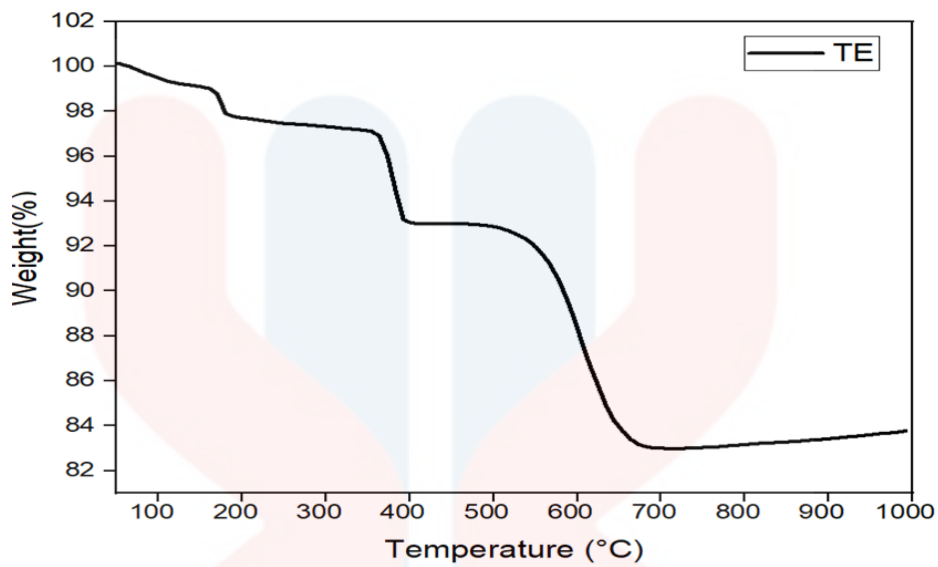

Figure 4.1 TGA analysis of TE (TiO_2-Eggshell) composites

4.3 Characterization Results of Ultra Violet Visible Spectrometer (UV-Vis Spectrometer)

The UV visible analysis were carried out in order to obtain the absorbance properties at specific wavelengths and the energy band gap of TiO_2-Eggshell samples with different calcination temperatures (400°C, 450°C, 500°C).

The absorbance spectra of TiO_2, Eggshell, TE 400°C, TE 450°C and TE 500°C at 300nm -800 nm shown in the Figure 4.2. The board absorption happened in the peak 400 to 450 nm with the optimum absorbance at 431 nm for sample TE 450°C among the other sample TE with different calcination temperature. For the pure TiO_2, the absorption peak was found at the 432 nm. Meanwhile, the pure eggshell displays weak absorption peak in the UV-visible region at 421 nm. The effect of calcined processed increase the absorption intensity in the range of 400-450 nm for the TE 450°C. However, TE 500°C sample has a lower absorbance compared to the TE 450°C.

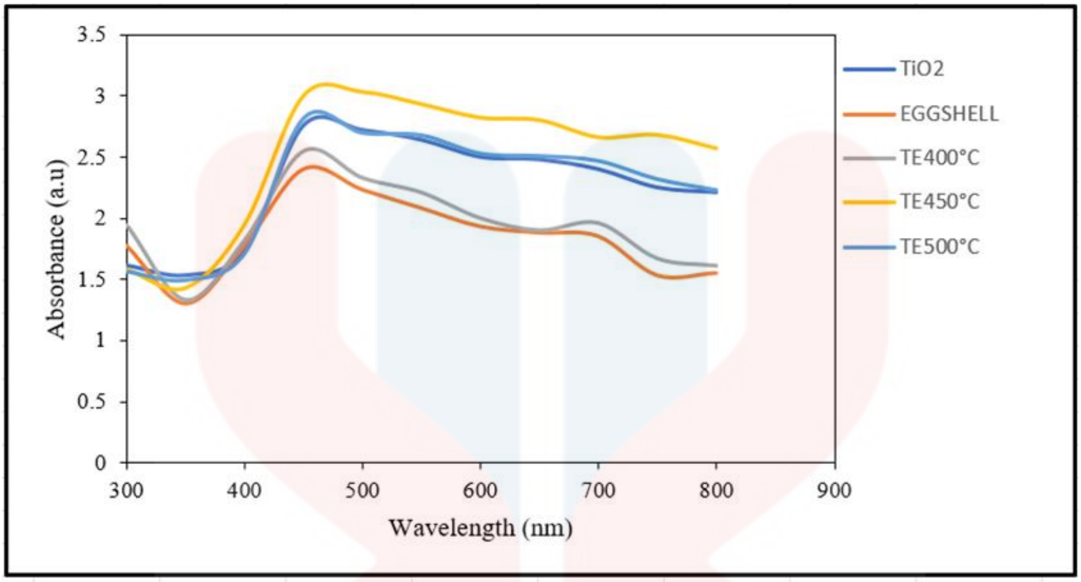

Figure 4.2 UV Visible absorption spectra of a) TiO_2 b) Eggshell c) TE 400°C d) TE 450°C e) TE 500°C

4.3.1 Band Gap Determination

The energy band gap of TiO_2, Eggshell and TiO_2-Eggshell (TE) with different calcination temperatures (400°C, 450°C and 500°C) was analysed via UV Vis spectrophotometer. According to Mursyalaat et al. (2023), the band gap (Eg) of this samples was calculated using the equation 4.1:

$$(\alpha h\nu) = k(Eg- h\nu)n \quad \text{Equation 4.1}$$

where :

α optical absorption coefficient

hv photon energy

Eg absorption coefficient

n constants (1/2 and 2 respectively for indirect and direct band gap)

This method was developed by Davis and Mott for semiconductor material to find the band gap using the Tauc plot. The table 4.1 shown the absorbance and photon energy of the TiO_2, Eggshell, and TE with different calcination temperatures (400°C, 450°C and 500°C).

Table 4.1 Absorbance and photon energy of TiO_2, Eggshell, TE 400°C, TE 450°C

Samples	Peak Absorption (nm)	Absorbance (a.u.)	Photon Energy (eV)
TiO_2	432	2.85	3.24
Eggshell	421	2.56	3.51
TE 400°C	426	2.67	3.48
TE 450°C	431	3.14	3.38
TE 500°C	435	2.91	3.25

Based on Table 4.1 above, TiO_2 expressed photon energy at peak absorption wavelength at 432 nm were 3.24 eV. According to Nair et al. (2022), the band gap of the typical TiO_2 crystal has been shown to be approximately 3.2 eV (UV absorption). The peak absorption wavelength of Eggshell was 421 nm which were the lowest wavelength compare to the other samples. Furthermore, TE 500°C is the highest peak absorption, at 435 nm. The energy band gap of eggshell were 3.51 eV. However, TE 500°C display the lowest photon energy among the TiO_2- Eggshell (TE) with different calcination temperature which were 3.25 eV compare to the TE 400°C and TE 450°C (3.48 eV and 3.38 eV).

The findings suggest a complex interaction between the optical characteristics of the TiO_2-Eggshell composite, the calcination temperature, and the incorporation of eggshell. The photon energy decreases with increasing calcination temperature, indicating a reduction in the superfluous band gap and boosting the composite's ability to absorb longer wavelength, lower energy photons. On the other hand, the TiO_2-Eggshell composites show greater band gaps regardless of the calcination temperature (400°C, 450°C and 500°C) when compared to the TiO_2 band gap. This suggests that adding eggshell expands the band gap by adding new energy levels or changing the electrical structure. Higher-energy photons are required to fill a bigger band gap, which triggers electron excitation across the gap and causes the absorption spectra to shift towards the ultraviolet (UV) and deep blue areas.

To sum up, the patterns found in band gaps and peak absorption wavelengths highlight the complex relationship between eggshell participation, calcination temperature, and the resulting optical characteristics. The TiO_2-Eggshell composites react in a complex way, allowing for accurate modifications in their optical properties depending on the conditions of synthesis. This opens up possibilities for modified uses in areas like photovoltaics and photocatalysis.

4.4 Structural and Properties of TiO_2-Eggshell Composites

Investigation of structural and properties was carried out by X-ray diffraction analysis. Figure 4.3 shown the diffraction spectra of each sample scanned at angle 2θ from 15 to 95° for of TiO_2, Eggshell, TE with different calcination temperatures, respectively at 400, 450 and 500 °C. For sample TE with calcination temperature 500°C, it have been recorded eight significant diffraction peaks at 2θ (25.271°, 38.509°, 47.980°, 53.761°, 54.994°, 62.010°, 73.856°) with delegated to the diffraction of lattice planes (0 1 1), (1 1 2), (0 2 0), (0 1 5), (1 2 1), (1 2 3), (2 2 0), and (0 1 7) planes respectively. This diffraction peaks were reflect to tetragonal anatase crystalline phase of TiO_2. According to Zheng et al. (2021), this value with the standard data Joint Committee on Powder Diffraction Standards (JCPDS) Card No. 21-1272).

Based on the differences in diffraction patterns it is known that the main diffraction peak of the anatase phase TiO_2 (0 1 1) was observed in all samples at the signals 25.271° except the Eggshell sample. The presence of the $Ca(OH)_2$ was not much as TiO_2 peaks in all sample due to the ratio of TiO_2-Eggshell (6:4).

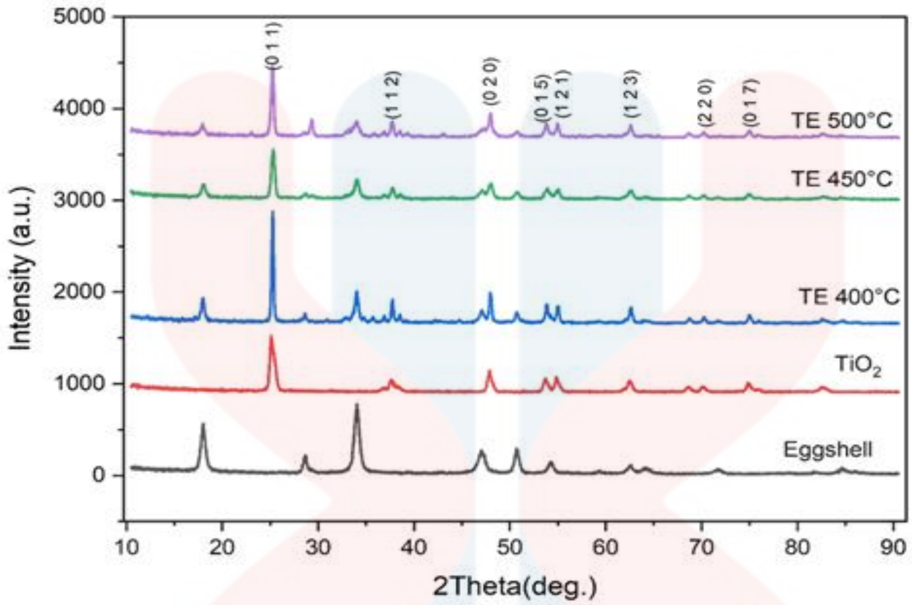

Figure 4.3 XRD spectra of TiO_2, Eggshell, TE 400 °C, TE 450 °C, TE 500 °C

The XRD spectra of eggshell resulted in a diffraction pattern as shown in Fig.4.4. The constituent of eggshell is mainly $Ca(OH)_2$, where the highest diffraction peaks exists at 2θ=34.101°. The XRD peaks of the $Ca(OH)_2$ appear at 2θ equal to 18.066°,28.675°, 34.101°, 47.145°, 50.798°, 56.201°, 64.223°, 64.298°,71.811°, and 84.916° which could delegated to the diffraction of (0 0 1), (1 0 0), (1 0 1), (1 0 2), (1 1 0), (0 0 3), (1 1 2), (1 0 3), (2 0 2), and (1 0 4) planes respectively. This demonstrated that $Ca(OH)_2$ with portlandite structure (hexagonal) with unit cell parameters (a=3.592 Å, c=4.906 Å). The diffraction patterns corresponding to the (0 0 1), (1 0 0), (1 0 1), and (1 0 2) planes are evident through peaks observed at 2θ angles of 18.066°, 28.675°, 34.101°, and 47.145°, respectively. The heightened intensity of these peaks in the XRD pattern signifies the prevalence of these planes in the analysed sample.

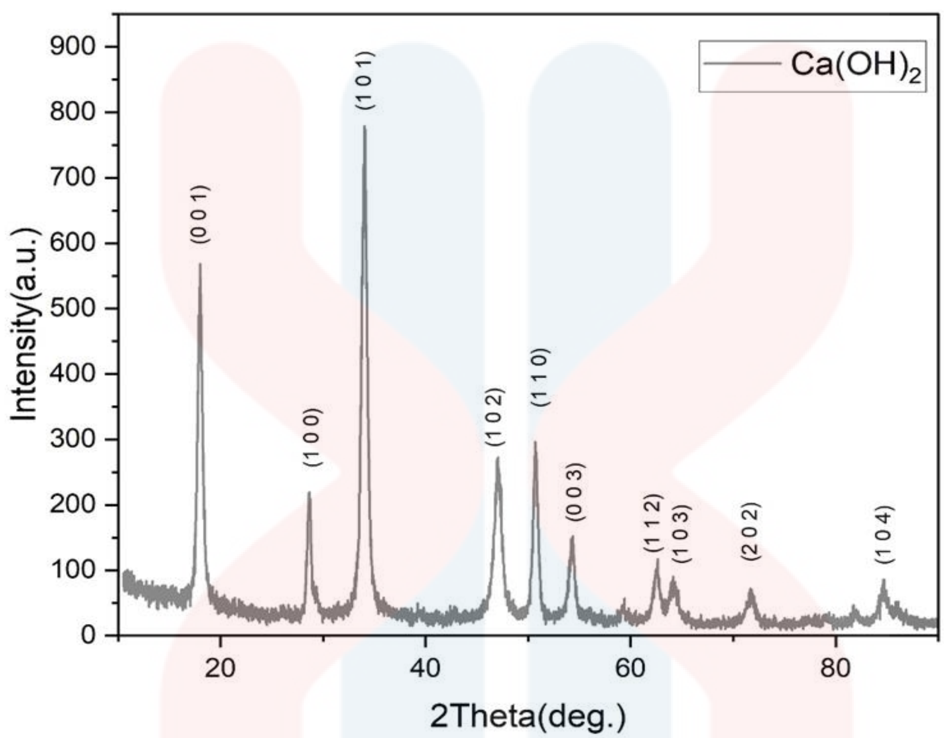

Figure 4.4 XRD spectra analysis for Eggshell ($Ca(OH)_2$)

The crystallize size of TiO_2-Eggshell with different calcination temperature (400, 450 and 500 °C) were calculated from the broadening of the diffraction line using Debye Scherrer's formula (Rahman et al., 2019);

$$D = K\lambda / \beta Cos\theta \quad \text{Equation 4.2}$$

Where D is the mean size of the crystallites (nm), K is the crystallite form variable and the appropriate approximation is 0.9 (Scherrer's constant) , λ wavelength (0.154060), β full width at the half maximum intensity (FWHM) in radians of the X-ray diffraction peaks and the Bragg angle is θ. The calculated crystallize size for TiO_2-Ehggshell with different calcination temperatures respectively 400, 450 and 500 °C were shown in the Table 4.2.

Table 4.2 Lattice Parameter, Average Crystallite Size and d-spacing of TiO_2-Eggshell with Different Calcination Temperature (400, 450 and 500 °C)

Samples	Average crystallite size, D (nm)	Cell Volume (Å^3)	a(Å)	c(Å)
Eggshell	16.86	54.82	3.59	4.91
TiO_2	18.29	136.27	3.76	9.51
TE400	27.80	136.30	3.76	9.51
TE450	23.10	136.27	3.76	9.51
TE500	27.06	136.27	3.76	9.51

Based on Table 4.2, the average size of TiO_2 without incorporating with eggshell particles was 18.29 nm. During this period, it was identified that the average crystallite sizes of TiO_2-Eggshell exhibited variation based on the calcination temperature TE 400°C,TE 450°C and TE 500°C, measuring 27.80 nm, 23.10 nm, and 27.06 nm. According to Hossain and Ahmed (2023), the average crystallite size is subject to variations influenced by both the calcination temperature and the specific conditions employed in the synthesis process. Elevated calcination temperatures have the potential to foster the enlargement of crystallites, thereby contributing to the observed differences in average crystallite size within TiO_2-Eggshell composites.

The mean size of the kelallite appeared to be affected by the eggshell particles added to TiO_2. In TiO_2 samples including eggshell particles, the average crystallite size is larger than in TiO_2 samples without eggshell particles (18.29 nm). This suggests that eggshell particles could act as sites of nucleation where TiO_2 crystallites develop. Eggshell particles, known for their high content of calcium and other minerals, possess a unique capability to act as primary sites for the initiation of TiO_2 crystal formation. This notion is based on the chemical affinity and surface characteristics inherent in eggshell particles.

According to Khalid et al. (2022), eggshells, abundant in calcium and diverse minerals, demonstrate a chemical compatibility with TiO_2, a semiconductor material. The noteworthy presence of calcium holds significance as it could create favourable conditions for the initial stage of crystal formation known as nucleation. The distinct chemical properties of calcium ions might play a facilitating role in the aggregation and arrangement of TiO_2 molecules, serving as nucleation centre's where crystalline structures begin to form and grow.

Overall, the analysis of the information highlights the effects of calcination temperature and eggshell particle inclusion on the average crystallite size of TiO_2. This important realization has the potential to greatly improve TiO_2-Eggshell material manufacturing activities, especially for uses like photoanode creation and photocatalytic processes in semiconductor applications.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study, the synthesis of TiO_2 powder was carried out in conjunction with Eggshell ($Ca(OH)_2$) powder at a ratio of 6:4 using the sol-gel method. The impact of different calcination temperatures, specifically 400 °C, 450 °C, and 500 °C, on the structural and morphological characteristics of the samples was investigated through TGA spectroscopy, UV-VIS spectrometer, and XRD analysis.

Thermogravimetric analysis (TGA) played a crucial role in assessing the thermal stability of the composite, aiding in the identification of an optimal calcination temperature range that preserves the structural integrity of TiO_2-Eggshell. Simultaneously, UV-VIS spectrophotometry provided a comprehensive understanding of the material's optical properties, encompassing band gap and absorbance—essential factors for determining potential applications. The UV-VIS analysis revealed absorption wavelengths within the range of 400 nm to 450 nm, with the TE 450°C sample exhibiting optimal absorbance at 3.14 a.u. Additionally, the band gap energies of all calcined temperature samples (400 °C, 450 °C, and 500 °C) ranged from 3.25 eV to 3.48 eV. XRD analysis, employed for the arrangement and classification of TiO_2 and Eggshell ($Ca(OH)_2$), demonstrated that TiO_2 possesses a tetragonal anatase structure, while eggshell (CaO) possesses a hexagonal portlandite structure.

In conclusion, the objectives of the study were successfully achieved, indicating that the incorporation of TiO_2 with Eggshell at different calcination temperatures (400 °C, 450 °C, and 500 °C) enhances TiO_2 performance in photocatalytic and photovoltaic activities. Notably, the TE 450°C composite emerged as the most suitable, characterized by a wider band gap (3.38 eV) compared to TiO2 alone (3.24 eV).

5.2 Recommendations

For future investigations, several recommendations are proposed. Firstly, employ transmission electron microscopy (TEM) or scanning electron microscopy (SEM) to scrutinize the surface area and morphology of the composite across different calcination temperatures. This exploration was anticipated to yield valuable insights into the structural evolution, offering potential implications for the photocatalytic activity of the material. Additionally, assess the photoanode activity through photoelectrochemical tests, providing conclusive evidence regarding the composite's efficacy as a photoanode for applications in solar cells and water splitting. Lastly, conduct a comprehensive examination of the photocatalytic activity of the samples under various conditions, including variations in light intensity, pH levels, and exposure to specific pollutants. This approach aims to achieve a profound understanding of the broader applications of the composite.

REFERENCES

Asim, N., Syuhami, M., Badiei, M., & Yarmo, M. A. (2014). WO3 modification by synthesis of nanocomposites. *APCBEE Procedia*, *9*, 175–180. https://doi.org/10.1016/j.apcbee.2014.01.031

Alhalili, Z. (2023). Metal Oxides Nanoparticles: General Structural Description, Chemical, Physical, and Biological Synthesis Methods, Role in Pesticides and Heavy Metal Removal through Wastewater Treatment. *Molecules*, *28*(7), 3086. https://doi.org/10.3390/molecules28073086

Al-Hamdi, A., Rinner, U., & Sillanpää, M. (2017). Tin dioxide as a photocatalyst for water treatment: A review. *Process Safety and Environmental Protection*, *107*, 190–205. https://doi.org/10.1016/j.psep.2017.01.022

Allen, N. S., Mahdjoub, N., Vishnyakov, V., Kelly, P., & Kriek, R. (2018). The effect of crystalline phase (anatase, brookite and rutile) and size on the photocatalytic activity of calcined polymorphic titanium dioxide (TiO 2). *Polymer Degradation and Stability*, *150*, 31–36. https://doi.org/10.1016/j.polymdegradstab.2018.02.008

Arzate-Vázquez, I., Méndez-Méndez, J. V., Flores-Johnson, E., Nicolás-Bermúdez, J., Chanona-Pérez, J., & Santiago-Cortés, E. (2019). Study of the porosity of calcified chicken eggshell using atomic force microscopy and image processing. *Micron*, *118*, 50–57. https://doi.org/10.1016/j.micron.2018.12.008

Bokov, D. O., Jalil, A. T., Chupradit, S., Suksatan, W., Ansari, M. J., Shewael, I. H., Valiev, G. H., & Kianfar, E. (2021). Nanomaterial by Sol-Gel Method: synthesis and application.

Advances in Materials Science and Engineering, *2021*, 1–21. https://doi.org/10.1155/2021/5102014

Bullo, T. A., Bayisa, Y. M., & Bultum, M. S. (2021). Optimization and biosynthesis of calcined chicken eggshell doped titanium dioxide photocatalyst based nanoparticles for wastewater treatment. *SN Applied Sciences*, *4*(1). https://doi.org/10.1007/s42452-021-04900-1

Camaratta, R., Lima, Á. N. C., Reyes, M., Hernández-Fenollosa, M., Orozco-Messana, J., & Bergmann, C. P. (2013). Microstructural evolution and optical properties of TiO2 synthesized by eggshell membrane templating for DSSCs application. *Materials Research Bulletin*, *48*(4), 1569–1574. https://doi.org/10.1016/j.materresbull.2012.12.047

Chiang, P., Tseng, Y., Wu, H., Tsao, S., Wu, S., Wang, W., Hsieh, H., & Juang, J. (2021). Elastic moduli of avian eggshell. *Biology*, *10*(10), 989. https://doi.org/10.3390/biology10100989

Dubey, R., Krishnamurthy, K. V., & Singh, S. (2019). Experimental studies of TiO2 nanoparticles synthesized by sol-gel and solvothermal routes for DSSCs application. *Results in Physics*, *14*, 102390. https://doi.org/10.1016/j.rinp.2019.102390

Dzinun, H., Khalid, N. H. A., & Hairom, N. H. H. (2022). Photocatalytic performance of TiO2/Eggshell composite for wastewater treatment. *Materials Today: Proceedings*, *65*, 3000–3006. https://doi.org/10.1016/j.matpr.2022.03.577

Eddy, D. R., Permana, M. D., Sakti, L. K., Sheha, G. a. N., Solihudin, Hidayat, S., Takei, T., Kumada, N., & Rahayu, I. (2023). Heterophase polymorph of TIO2 (Anatase, rutile, brookite, TIO2 (B)) for efficient photocatalyst: fabrication and activity. *Nanomaterials*, *13*(4), 704. https://doi.org/10.3390/nano13040704

Elbushra, H. A., Ahmed, M. A., Wardi, H., & Eassa, N. (2018). Synthesis and characterization of TiO2 using sol-gel method at different annealing temperatures. *MRS Advances*, *3*(42–43), 2527–2535. https://doi.org/10.1557/adv.2018.230

El-Kemary, M., El-Mehasseb, I. M., Shoueir, K. R., El-Shafey, S. E., El-Shafey, O. I., Aljohani, H. A., & Fouad, R. R. (2017). Sol-gel TiO2 decorated on eggshell nanocrystal as engineered adsorbents for removal of acid dye. *Journal of Dispersion Science and Technology*, *39*(6), 911–921. https://doi.org/10.1080/01932691.2017.1410829

Fischer, K., Gawel, A., Rosen, D. A., Krause, M., Latif, A. A., Griebel, J., Prager, A., & Schulze, A. (2017). Low-Temperature synthesis of Anatase/Rutile/Brookite TIO2 nanoparticles on a polymer membrane for photocatalysis. *Catalysts*, *7*(7), 209. https://doi.org/10.3390/catal7070209

Gautron, J., Stapane, L., Roy, N. L., Nys, Y., Rodríguez-Navarro, A. B., & Hincke, M. T. (2021). Avian eggshell biomineralization: an update on its structure, mineralogy and protein tool kit. *BMC Molecular and Cell Biology*, *22*(1). https://doi.org/10.1186/s12860-021-00350-0

Habte, L., Shiferaw, N., Mulatu, D., Thriveni, T., Ramakrishna, C., & Ahn, J. W. (2019). Synthesis of Nano-Calcium Oxide from Waste Eggshell by Sol-Gel Method. *Sustainability*, *11*(11), 3196. https://doi.org/10.3390/su11113196

Huang, Z., Wang, J., Yang, M., Qian, Q., Liu, X., Xiao, L., & Xue, H. (2021). Construction of TIO2-Eggshell for efficient degradation of tetracycline hydrochloride: sunlight induced In-Situ formation of carbonate radical. *Materials*, *14*(7), 1598. https://doi.org/10.3390/ma14071598

Hossain, M. S., & Ahmed, S. (2023). Easy and green synthesis of TiO2 (Anatase and Rutile): Estimation of crystallite size using Scherrer equation, Williamson-Hall plot, Monshi-

Scherrer Model, size-strain plot, Halder- Wagner Model. *Results in Materials*, *20*, 100492. https://doi.org/10.1016/j.rinma.2023.100492

Khalid, M., Jikan, S. S., Adzila, S., Yunus, Z. M., & Badarulzaman, N. A. (2022). Characterizations of Calcium Oxide from Calcined Eggshell Waste. *Key Engineering Materials*, *908*, 130–134. https://doi.org/10.4028/p-s8ckr0

Liang, Y., Sun, S., Deng, T., Ding, H., Chen, W., & Chen, Y. (2018). The preparation of TIO2 film by the Sol-Gel method and evaluation of its Self-Cleaning property. *Materials*, *11*(3), 450. https://doi.org/10.3390/ma11030450

Lim, S. P., Pandikumar, A., Lim, H. N., & Huang, N. M. (2016). Essential role of N and Au on TiO2 as photoanode for efficient dye-sensitized solar cells. *Solar Energy*, *125*, 135–145. https://doi.org/10.1016/j.solener.2015.12.019

Mursyalaat, V., Variani, V. I., Arsyad, W. O. S., & Firihu, M. Z. (2023). The development of program for calculating the band gap energy of semiconductor material based on UV-Vis spectrum using delphi 7.0. *Journal of Physics: Conference Series*, *2498*(1), 012042. https://doi.org/10.1088/1742-6596/2498/1/012042

Nair, R. V., Gummaluri, V. S., Murukeshan, V. M., & Vijayan, C. (2022). A review on optical bandgap engineering in TiO2nanostructures via doping and intrinsic vacancy modulation towards visible light applications. *Journal of Physics D: Applied Physics*, *55*(31), 313003. https://doi.org/10.1088/1361-6463/ac6135

Nguyen, T. P., Nguyen, D., Nguyen, V., Le, T., Vo, D. N., Trịnh, Q. T., Bae, S., Chae, S. Y., Kim, S. Y., & Van Le, Q. (2020). Recent advances in TIO2-Based photocatalysts for reduction of CO2 to fuels. *Nanomaterials*, *10*(2), 337. https://doi.org/10.3390/nano10020337

Noviyanti, A. R., Asyiah, E. N., Permana, M. D., Dwiyanti, D., Suryana, N., & Eddy, D. R. (2022). Preparation of Hydroxyapatite-Titanium Dioxide Composite from Eggshell by Hydrothermal Method: Characterization and Antibacterial Activity. *Crystals*, *12*(11), 1599. https://doi.org/10.3390/cryst12111599

Mursyalaat, V., Variani, V. I., Arsyad, W. O. S., & Firihu, M. Z. (2023). The development of program for calculating the band gap energy of semiconductor material based on UV-Vis spectrum using delphi 7.0. *Journal of Physics: Conference Series*, *2498*(1), 012042. https://doi.org/10.1088/1742-6596/2498/1/012042

Racovita, A. D. (2022). Titanium dioxide: structure, impact, and toxicity. *International Journal of Environmental Research and Public Health*, *19*(9), 5681. https://doi.org/10.3390/ijerph19095681

Raguram, T., & Rajni, K. S. (2022). Synthesis and characterisation of Cu - Doped TiO2 nanoparticles for DSSC and photocatalytic applications. *International Journal of Hydrogen Energy*, *47*(7), 4674–4689. https://doi.org/10.1016/j.ijhydene.2021.11.113

Rahman, M. U., Wei, M., Xie, F., & Khan, M. (2019). Efficient Dye-Sensitized Solar Cells Composed of Nanostructural ZnO Doped with Ti. *Catalysts*, *9*(3), 273. https://doi.org/10.3390/catal9030273

Shiferaw, N., Habte, L., Thriveni, T., & Ahn, J. W. (2019). Effect of eggshell powder on the hydration of cement paste. *Materials*, *12*(15), 2483. https://doi.org/10.3390/ma12152483

Tullett, S. G., & Burton, F. G. (1985). The effects of eggshell porosity on blood-gas and acid-base status of domestic fowl embryos within eggs of the same weight. *Comparative Biochemistry and Physiology Part A: Physiology*, *81*(1), 137–142. https://doi.org/10.1016/0300-9629(85)90279-8

Zheng, R., Wang, Z., Zhang, C., Chen, B., San, H., & Yu, H. (2021). Photocatalytic enhancement using defect-engineered black mesoporous TiO2/CeO2 nanocomposite aerogel. *Composites Part B: Engineering*, *222*, 109037. https://doi.org/10.1016/j.compositesb.2021.109037

APPENDIX A

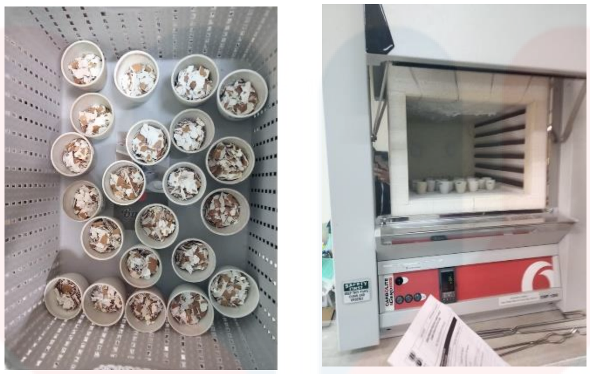

Figure A.1 Extraction of Calcium Precursor from Chicken Eggshell

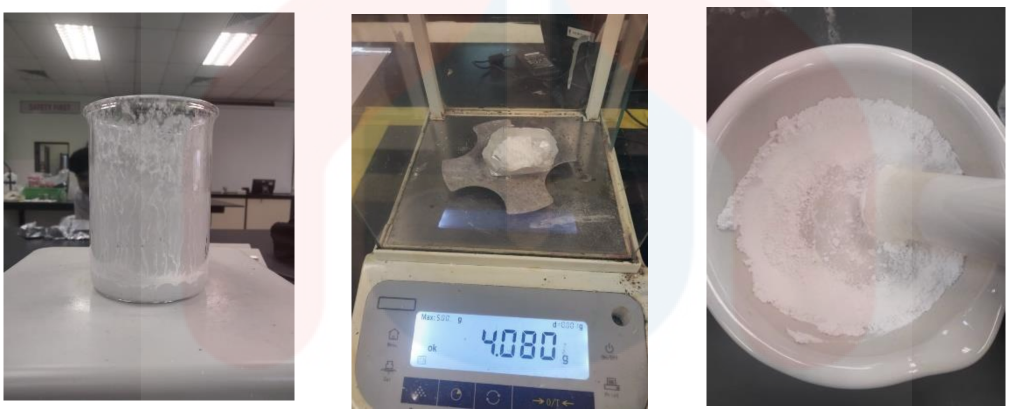

Figure A.2 Preparation of TiO_2-Eggshell using Sol-Gel Method

Figure A.3 Calcine TiO_2-Eggshell at Different Temperature

APPENDIX B

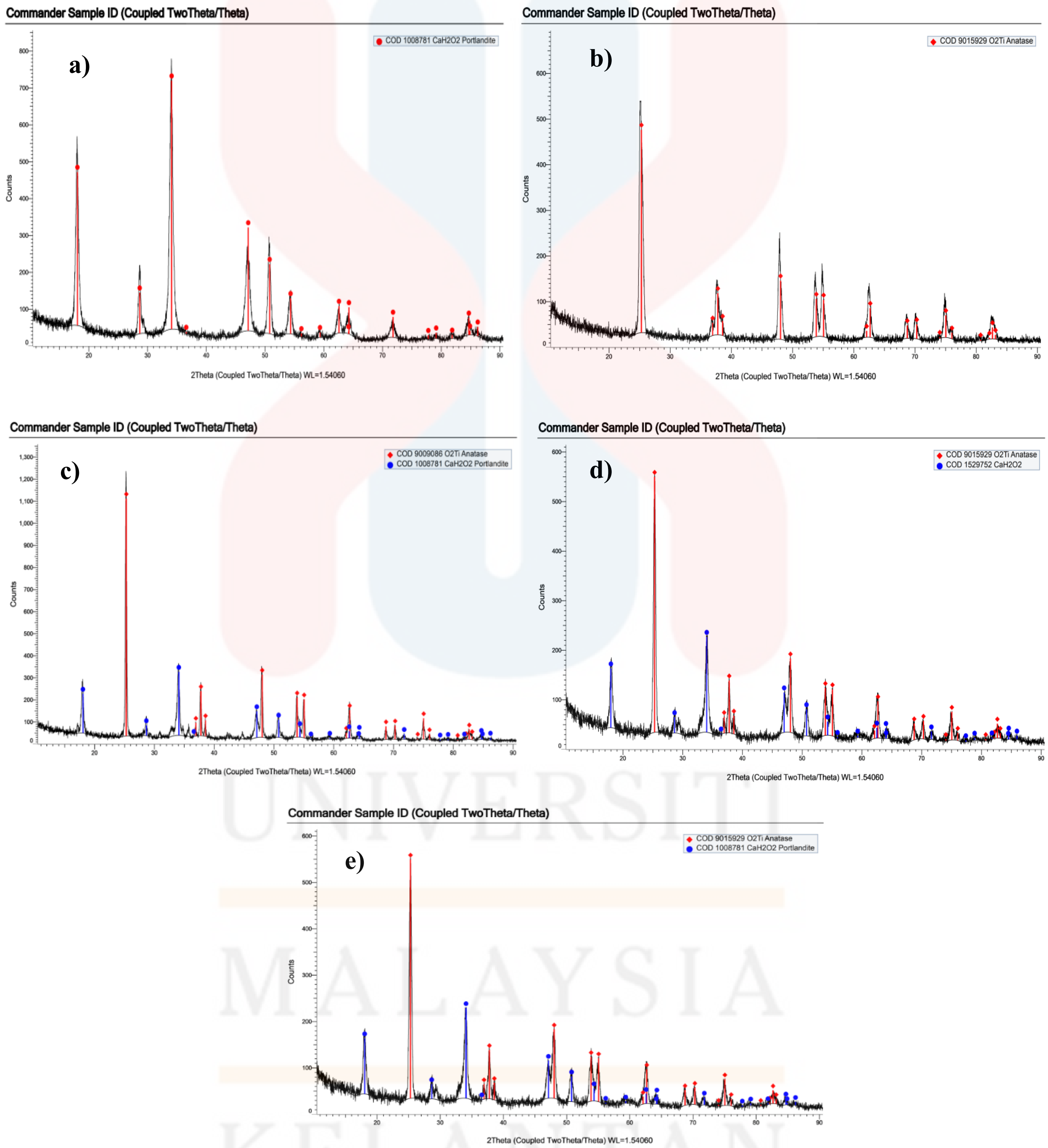

Figure B.1 XRD analysis for a) Eggshell b)TiO_2 c) TE 400 °C d) TE 450 °C e) TE 500 °C