EXTRACTION OF TITANIUM NANOPARTICLES FROM SYNTHETIC RUTILE VIA MODIFIED HYDROTHERMAL SYNTHESIS METHOD WITH A SILVER DOPED BY MOLTEN SALT PROCESS

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02nd March 2018 --------------------------------

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DEGREE : **MASTER OF ENGINEERING (ELECTRICAL)**

VIVA DATE : **04 OCTOBER 2017**

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ABSTRACT

In this research work, Titanium Dioxide (TiO_2) was synthesized from the synthetic rutile via a modified hydrothermal synthesis method and then was doped with a silver via a molten salt process. The main objectives in this research work are to find the optimum condition of high grade TiO_2 extraction and the optimum condition to extract the high crystalline Silver-Titanium (Ag-TiO_2). The high crystalline Ag-TiO_2 was extracted to improve its application for commercialize purpose especially in enhancing the fabricated solar cell efficiency industry. Firstly, we vary the molarity of acid sulfuric, treatment time, temperature and ratio in our modified hydrothermal synthesis method to synthesize the optimum condition to extract a high grade TiO_2 nanoparticles. After that, we characterize our samples using the Energy Dispersive X-ray spectroscopy (EDX), X-ray Diffraction spectroscopy (XRD), Field Emission Scanning Electron Microscope (FESEM) and High ResolutionTransmission Electron Microscopy (HRTEM). As the result, we found that, the optimum condition to extract the high grade TiO_2 was occurred at 2.2M acid molarity, 4 hours treatment time, 80^{o}C fixed temperature and 1:4 Na_2TiO_3:acid ratio at 600^{o}C calcination. Secondly, we vary the molarity of silver in our molten salt process to improve the nanocrystal crystallinity of Ag-TiO_2 via a doping method. We characterize our samples by using X-ray Diffraction (XRD), Surface Area BET (SBET), UV-Vis-NIR spectrophotometer (UV-Vis), Field Emission Scanning Electron Microscope (FESEM) and High Resolution Transmission Electron Microscopy (HRTEM). As the result, we found that, the optimum condition to extract the high purity and high crystallinity of Ag-TiO_2 were occurred at 1% and 5% of silver molarity at 600^{o}C calcination. Finally, we characterize the effectiveness of high crystalline Ag-TiO_2 by using a Methylene Blue Degradation (MBD) at Agensi Nuklear Malaysia. We were irradiated our samples with two types of light, which are visible light and Ultra Violet (UV) light. For the visible light irradiation, the high grade TiO_2 shows a 25% while the high crystalline 5% Ag-TiO_2 are 66% photodegradation performance. Besides that, for the UV light irradiation, the high grade TiO_2 shows a 50% while the high crystalline 5% Ag-TiO_2 are 75% photodegradation performance. This analyzation proves that, the nanocrystal crystallinity of Ag-TiO_2 was improved by adding the silver dopant via a molten salt doping process.

ABSTRAK

EKSTRAK TITANIUM DARIPADA SINTETIK RUTIL MELALUI KAEDAH "MODIFIED HYDROTHERMAL" DENGAN CAMPURAN SILVER MELALUI KAEDAH "MOLTEN SALT PROCESS"

Melalui Kajian ini, Titanium Dioxide (TiO_2) yang berkualiti tinggi telah di ekstrak daripada sintetik rutil melalui kaedah "modified hydrothermal synthesis method" dan kemudian dicampurkan dengan "silver" melalui kaedah "molten salt process" . Objektif utama dalam kajian ini adalah untuk mencari keadaan optimum dalam pengekstrakan TiO_2 yang berkualiti tinggi dan juga keadaan optimum untuk menghasilkan Silver-Titanium (Ag-TiO_2) pada fasa kristal yang tinggi. Ag-TiO_2 pada fasa kristal yang tinggi telah diekstrak untuk meningkatkan kegunaan TiO_2 agar dapat dikomersilkan secara meluas terutamanya dalam industri solar sel. Langkah pertama, molariti asid sulfurik, masa rawatan, suhu dan nisbah bagi kaedah "modified hydrothermal synthesis method" telah dijadikan pemboleh ubah dimanipuslasi untuk mencapai objektif pertama iaitu mencari keadaan optimum dalam pengekstrakan TiO_2 yang berkualiti tinggi. Selepas itu, kami mengenalpasti sampel kami menggunakan Energy Dispersive X-ray spectroscopy (EDX), X-ray Diffraction spectroscopy (XRD), Field Emission Scanning Electron Microscope (FESEM) and High ResolutionTransmission Electron Microscopy (HRTEM). Melalui keputusan yang kami perolehi, kami mendapati bahawa, keadaan optimum untuk mengekstrak TiO_2 yang berkualiti tinggi telah berlaku pada molariti asid sulfurik 2.2M, masa rawatan 4 jam, suhu tetap 80°C dan nisbah 1:4 Na_2TiO_3:asid pada penalaan 600°C. Langkah kedua, molariti silver dimanipulasikan dalam proses garam lebur untuk mendapatkan keadaan optimum bagi menghasilkan Silver-Titanium (Ag-TiO_2) pada fasa kristal yang tinggi. Seterusnya, sampel akan diuji menggunakan X-ray Diffraction (XRD), Surface Area BET (SBET), UV-Vis-NIR spectrophotometer (UV-Vis), Field Emission Scanning Electron Microscope (FESEM) and High Resolution Transmission Electron Microscopy (HRTEM). Melalui keputusan yang diperolehi, kami mendapati bahawa, pada molariti silver 1% dan 5%, Silver-Titanium (Ag-TiO_2) pada fasa kristal yang tinggi telah berjaya dihasilkan. Langkah kajian terakhir adalah menganalisis keberkesanan Ag-TiO_2 pada fasa kristal yang tinggi dengan menggunakan Degradasi Methylene Blue (MBD) di Agensi Nuklear Malaysia. Sampel telah diuji menggunakan dua jenis cahaya iaitu visible light dan Ultra Violet light (UV). Bagi visible light, kami mendapati, TiO_2 yang berkualiti tinggi menunjukkan 25% manakala 5% Ag-TiO_2 fasa kristal yang tinggi adalah 66% fotodegradasi. Selain itu, bagi Ultra Violet light (UV), kami mendapati, TiO_2 yang berkualiti tinggi menunjukkan 50% manakala 5% Ag-TiO_2 fasa kristal yang tinggi adalah 75% fotodegradasi. Analisis akhir ini membuktikan bahawa, kualiti nanokristal Ag-TiO_2 telah dipertingkatkan dengan penambahan dopan silver melalui melalui kaedah "molten salt process".

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Chapter 1 is comprised of the research background in subtopic 1.2 and consist of ilmenite waste management in Malaysia and titanium (TiO_2) as a photocatalyst material in 1.2.1 and 1.2.2 respectively. Further subtopics in this chapter 1 are problem statement, objectives, scope of work and thesis outline in 1.3, 1.4, 1.5 and 1.6 respectively. This chapter, followed by the literature review in chapter 2, methodology in chapter 3, result and discussion in chapter 4 and conclusion in chapter 5.

1.2 Research Background

The aim of this research works are to synthesize a high grade TiO_2 nanoparticles from the synthetic rutile Malaysia and improve its nanocrystal crystallinity. Therefore, in this research background, the synthetic rutile as the raw material and the application of high grade TiO_2 will be introduced in subtopic 1.2.1 and 1.2.2 respectively.

1.2.1 Synthetic Rutile from TOR Mineral Sdn Bhd, Malaysia

The synthetic rutile as the raw material in this research works were produced from a local ilmenite processing mineral company called TOR Mineral Sdn Bhd. Ilmenite mineral was obtained as a by-product from the Malaysian tin mining industry mainly found in Perak’s Kinta Valley. Figure 1.1 below shows the annual Malaysia tin production from 1970 to 2013.

From this figure, it significantly shows that at the end of the 19th century, Malaysia was produce a large number of tins which are around 70,000 to 60,000 tonnes of tin per year. During that century, Malaysia was became the world largest tin producer (Yap, 2007). Unfortunately, the total annual tin production was getting decrease and decrease until early the 20th century with only 4000 to 2000 tonnes of tin per year. However, this less production still can be beneficial to our economy by extracting a high grade and high commercial demand of TiO_2 from the synthetic rutile.

Year	Production (tonnes)	Average Price (RM$/kg)
1970	73,795	10.99
1975	64,364	15.94
1980	61,404	35.72
1985	36,884	29.67
1986	29,134	15.39
1989	32,034	23.09
1990	28,468	16.45
1991	20,710	15.05
1994	6,458	14.14
2000	6,307	20.45
2001	4,972	16.80*
2002	4,215	15.44*
2003	3,358	18.58*
2004	2,746	32.20*

Figure 1.1 : Malaysia tin production from 1970 to 200

Source : Yap (2007)

Figure 1.2 below shows the flow of ilmenite management in Malaysia. There are several locations of tin mining in Malaysia since the late of 18th century such as Larut Perak, Kinta Valley perak, Selangor and etc. The low grade mined tin called 'amang' were rewashed to produce a medium grade of tin. The medium grade of tin were then sell to the smelters factory with high price.

There are several smelting companies in Malaysia such as Datuk Keramat Smelter Sdn Bhd, Malaysia Smelting Corp. Bhd, Kilang Amang Onn Sdn Bhd and etc. The smelters factory is the mineral processing industry, which will smelting and treating the tin, rutile, ilmenite and etc. The high grade and pure ilmenite from smelter factory will then be sell to the mineral product specialist such as TOR Minerals Malaysia Sdn Bhd Company in the forms of block commonly known as ingot.

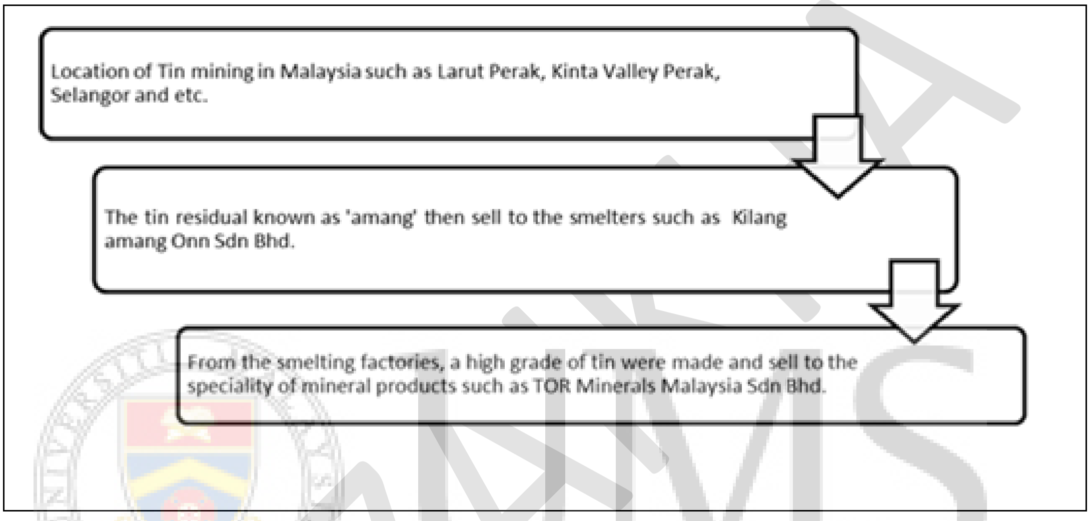

Figure 1.2 : Ilmenite waste management in Malaysia.
Source : Yap (2007)

1.2.2 Titanium Material

Nowadays, nanomaterial semiconductors are known as a great importance in our industrial world. A study by Hayle (2014) stated that the nanostructure science and technology is a major area of research and development activity that has been growing widely worldwide in the past decade. TiO_2 nanoparticles also known as Titanium (IV) oxide or titania is a semiconductor substance with a wide array of industrial applications. The TiO_2 particle size less than 100nm can be described as a nanoparticles TiO_2 (Teoh *et al.*, 2012). TiO_2 nanoparticles can be easily designed for various applications in many technological areas such as painting and coating, toothpaste and cosmetics, UV protection, photocatalysis components, solar cell and photovoltaics, sensors and others (W. Zhou et al., 2010)

According to H.K Shon (2007), the development of photocatalysis field was greatly assisted due to the development of semiconductor photochemistry knowledge since 1970 and 1980s. It discovered the excellent photocatalytic activity of TiO_2 to break down the organic compounds. Thus, since then, TiO_2 particles as a photocatalysis has been the attractive topic to study and explore due to its wide application on the elimination of hazardous pollutants in our environment, biosensors, medicine and pharmacy industry (Mahlambi *et al.*, 2015)

The active photocatalytic TiO_2 powder is able to decompose the polluted organic compound if we put it into the polluted air or water with the presence of sunlight illumination (Fujishima, 2000). TiO_2 has been studied and proved to be the most ideal photocatalyst due to several aspects such as high photoactivity, thermal and chemical stability, relatively inexpensive and non-toxicity (Castro et al., 2009)

1.3 Problem Statement

The TiO_2 extraction from the synthetic rutile in Malaysia via a modified hydrothermal synthesis method had been done by previous researcher (Mahdi *et al.*, 2012). However, they are only extracting a high grade TiO_2 with 96% purity and do not propose doping process with any metal or non-metal dopants. Therefore, the research gap in this research works is to synthesize a high grade TiO_2 nanoparticles at optimum condition and improve its nanocrystal crystallinity. The modification of TiO_2 synthesis method via a caustic hydrothermal method and the introduction of silver nitrate ($AgNO_3$) as a dopant agent via a molten salt doping process has been considered as an efficient method to produce a high industrial potential Ag-TiO_2 material in future.

1.4 Objectives

The main objectives of this study are:

1. To find the optimum condition to synthesize a high grade TiO_2 nanoparticles by varying the sulfuric acid molarity, temperatures, time and ratio.
2. To improve the nanocrystal crystallinity via a molten salt doping method by varying the molarity of Silver Nitrate ($AgNO_3$).

3. To study the photoactivity of high crystalline silver-titanium (Ag-TiO_2) nanoparticles compared to the high grade TiO_2.

1.5 Scope Of Work

The scope of work in this research work is divided into three main objectives; to find the optimum condition to synthesize a high grade TiO_2 nanoparticles by varying the sulfuric acid molarity, temperatures, time and ratio, to improve the nanocrystal crystallinity via a molten salt doping method by varying the molarity of Silver Nitrate ($AgNO_3$) and to study the photoactivity of high crystalline silver-titanium (Ag-TiO_2) nanoparticles compared to the high grade TiO_2.

The first objective, directed towards the synthesis process of high grade TiO_2 via a caustic hydrothermal decomposition. The optimum condition to synthesized the high grade TiO_2 is determined by varying the sulfuric acid molarity, temperatures, time and ratio. The Energy Dispersive X-ray spectroscopy (EDX), X-ray Diffraction spectroscopy (XRD) and Field Emission Scanning Electron Microscope (FESEM) are the characterization methods used to determine the optimum condition of our synthesized high grade TiO_2.

The scope of work for the second objective is focusing on the enhancement the nanocrystal crystallinity via a molten salt doping method by varying the molarity of Silver Nitrate ($AgNO_3$). A high crystallinity of Ag-TiO_2 material will be extracted and characterized by using X-ray Diffraction (XRD), Surface Area BET (S_{BET}), UV-Vis-NIR spectrophotometer (UV-Vis), Field Emission Scanning Electron Microscope (FESEM) and Transmission Electron Microscopy (TEM).

Finally, the third scope of work in this research work is to study the photoactivity of high crystalline silver-titanium (Ag-TiO_2) nanoparticles compared to the high grade TiO_2. The photoactivity of both samples were examined by using a methylene blue degradation in UV spectrometer at Agensi Nuklear Malaysia.