THE PREPARATION OF *AVERRHOA BILIMBI*-DERIVED CARBON-TITANIA COMPOSITE AND ITS STRUCTURE-FUNCTION RELATIONSHIP IN PHOTOCATALYTIC AND CATALYTIC REACTIONS

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To my beloved father, Mohamed Yusoff, mother, Maznah Jusoh and all family members for their dua, love, support, encouragements and advices.

Verily after hardship comes ease (Quran 94:6)

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ABSTRACT

Nowadays, much interest has been shown in the synthesis of carbon-based titania due to its improved electronic properties and its efficiency in the photocatalytic and catalytic activities. In the meantime, cellulose has emerged as one of the promising sources of carbon. Therefore, in this research, a new approach in the preparation of cellulose-derived carbon/titania composite is introduced by using natural cellulosic material, namely *Averrhoa bilimbi* fruits or bilimbi, as the carbon source. The purpose of using bilimbi is to utilize its interconnected porous structures and hydrophilic properties, in order to obtain a good interfacial interaction between carbon and titania. The bilimbi was first freeze-dried before being impregnated with titanium isopropoxide as the titania precursor. Bilimbi/TiO_2 composite was then calcined at 200, 500 and 800°C in order to change the cellulosic material into carbon and subsequently formed cellulose-derived carbon (BDC)/TiO_2 composites. The interfacial interactions between carbon and titania were comprehensively studied through the changes in the physical and electronic properties. The composites were characterized using X-ray photoelectron spectrometer (XPS), X-ray diffraction (XRD) spectrometer, nitrogen adsorption-desorption analyser, Fourier transform infrared (FTIR) spectrometer, thermogravimetric analyser, photoluminescence spectrometer and UV-Visible diffuse reflectance (UV-Vis DR) spectrometer. The strong interfacial interaction between bilimbi and titania resulted in the changes on the surface area and the porosity. This suggested that the interconnected porous structures and the hydrophilicity of the freeze-dried bilimbi led to the good attachment and well distribution of titania particles on the bilimbi's surface. As the calcination temperature was increased, carbon was located at different locations. At calcination temperatures of 200 and 500°C, titania was at the interstitial titania lattice. However, as the calcination temperature was increased to 800°C, carbon substituted the oxygen atoms in the titania lattice as proved by the XPS analysis. This affected the phase transformation of titania from anatase (calcination at 500°C) to rutile (calcination at 800°C) and formed a mixture of anatase and rutile phases. Besides that, the band gap energies of the composites decreased from 3.2 to 2.9 eV with the increase of calcination temperature. Such changes did not occur in the synthesis of titania without bilimbi. The changes in the physical and electronic properties of the composites were then correlated to the photocatalytic and catalytic activities. The photodegradation of phenol under the irradiation of ultraviolet and visible lights was significantly improved by bilimbi/TiO_2 and BDC/TiO_2 composites. The formation of the mixture of anatase, rutile phases and the defect sites, as analysed by photoluminescence spectroscopy, reduced the rate of the electrons and holes recombination which consequently increased the photocatalytic activities of the composites. Meanwhile, the catalytic activity of the composites for the catalytic oxidation of styrene was not affected by the presence of carbon since the carbon did not change the titanium catalytic active sites. In conclusion, the amount and location of the carbon in bilimbi/TiO_2 composite, whether on the surface, interstitial, and substitution positions, were changed with the increase of calcination temperature and these changes affect the physical and electronic properties of the composites, and enhanced the photocatalytic activity of the composites.

ABSTRAK

Pada masa kini, banyak minat telah ditunjukkan dalam sintesis titania berasaskan karbon disebabkan oleh kebaikan sifat elektroniknya dan kecekapannya dalam aktiviti foto-pemangkinan dan pemangkin. Pada masa yang sama, selulosa telah muncul sebagai salah satu sumber karbon yang baik. Oleh itu, dalam kajian ini, satu pendekatan baharu dalam penyediaan komposit karbon berasaskan selulosa/titania diperkenalkan menggunakan bahan berselulosa, iaitu buah *Averrhoa bilimbi* atau bilimbi, sebagai sumber karbon. Tujuan penggunaan bilimbi adalah untuk menggunakan struktur berliang yang saling bersambung dan sifat hidrofiliknya untuk mendapatkan interaksi antara muka yang baik di antara karbon dan titania. Pertama, bilimbi dikering-sejuk beku sebelum pengisitepuan dengan titanium isopropoksida sebagai pelopor titania. Komposit bilimbi/TiO_2 kemudian dikalsin pada suhu 200, 500 dan 800°C untuk mengubah bahan selulosa kepada karbon dan seterusnya membentuk komposit karbon terbitan selulosa (BDC)/TiO_2. Interaksi antaramuka di antara karbon dan titania telah dikaji secara mendalam melalui perubahan sifat fizikal dan elektronik. Komposit telah dicirikan menggunakan spektrometer fotoelektron sinar-X (XPS), spektrometer pembelauan sinar-X (XRD), penganalisis penjerapan-penyaherapan nitrogen, spektrometer inframerah transformasi Fourier (FTIR), penganalisis termogravimetri, spektrometer fotopendarcahaya dan spektrometer pantulan serakan ultra lembayung-cahaya nampak (UV-Vis DR). Ikatan antara muka yang kuat di antara bilimbi dan titania menghasilkan perubahan pada luas permukaan dan juga keliangan. Ini mencadangkan bahawa struktur berliang yang saling bersambung dan sifat hidrofilik bilimbi kering-sejuk beku membawa kepada lekatan yang baik dan taburan zarah titania yang sekata di atas permukaan bilimbi. Apabila suhu pengkalsinan ditingkatkan, karbon terletak pada lokasi yang berlainan. Pada suhu pengkalsinan 200 dan 500°C, titania terlekat pada ruang antara kekisi titania. Walau bagaimanapun, apabila suhu pengkalsinan ditingkatkan kepada 800°C, karbon menggantikan atom oksigen di dalam kekisi titania seperti yang dibuktikan oleh analisis XPS. Ini telah memberi kesan kepada perubahan fasa titania daripada anatas (pengkalsinan pada 500°C) kepada rutil (pengkalsinan pada 800°C) dan membentuk campuran fasa anatas dan rutil. Selain itu, tenaga jurang jalur komposit berkurang dari 3.2 kepada 2.9 eV dengan peningkatan suhu pengkalsinan. Perubahan-perubahan ini tidak berlaku dalam sintesis titania tanpa bilimbi. Perubahan sifat fizikal dan elektronik komposit dikorelasikan dengan aktiviti fotopemangkinan dan pemangkin. Fotopemangkinan fenol di bawah penyinaran cahaya ultra ungu dan cahaya nampak menunjukkan penambahbaikan ketara oleh komposit bilimbi/TiO_2 dan BDC/TiO_2. Pembentukan campuran fasa anatas, rutil dan juga kecacatan tapak, seperti yang dianalisis oleh spektroskopi kefotopendarcahayaan, mengurangkan kadar penggabungan semula elektron dan lubang, justeru meningkatkan aktiviti fotopemangkinan komposit. Sementara itu, aktiviti pemangkinan komposit untuk pengoksidaan stirena bermangkin, tidak terjejas dengan kehadiran karbon memandangkan karbon tidak mengubah tapak aktif pemangkin titanium. Kesimpulannya, jumlah dan kedudukan karbon pada komposit bilimbi/TiO_2, samada pada permukaan, ruang-antara. dan juga tempat penggantian, berubah dengan pertambahan suhu pengkalsinan dan perubahan ini memberi kesan kepada sifat fizikal dan elektronik komposit, dan meningkatkan aktiviti fotopemangkinan komposit.

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%	-	Percentage
®	-	Registered
°C	-	Degree Celsius
2θ	-	Bragg angle
Å	-	Angstrom
a.u.	-	Arbitrary unit
BET	-	Brunauer-Emmet-Teller
BJH	-	Barret-Joyner-Halenda
c.a.	-	Circa
cm	-	Centimeter
cm^{-1}	-	Per centimeter
Cu Kα	-	X-ray diffraction from copper Kα energy levels
eV	-	Electron volt
FESEM	-	Field Emission Scanning Electron Microscopy
FTIR	-	Fourier-transform infrared
g	-	Gram
GC-FID	-	Gas chromatography-flame ionization detector
h	-	Hour(s)
H_2O_2	-	Hydrogen peroxide
K.M.	-	Kubelka-Munk
L	-	Liter
mg	-	miligram
min	-	Minute(s)

mL	-	Milliliter
nm	-	Nanometers
PL	-	Photoluminescence
ppm	-	Part per million
SEM	-	Scanning electron microscopy
TGA	-	Thermogravimetric analysis
UV	-	Ultraviolet
UV-Vis DR	-	Ultraviolet-visible diffuse reflectance
Wt%	-	Weight percent
XPS	-	X-ray photoelectron spectroscopy
XRD	-	X-ray diffraction
λ	-	Wavelength

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Titania is regarded as one of the most fascinating inorganic materials mainly due to its excellent physical and chemical properties, and its promising potential as the photovoltaic (Grätzel 2001), gas sensor (Varghese et al. 2003), electrochromic devices (Berger et al. 2009) and photocatalyst (Ohtani *et al*., 1997). However, despite these advantages, titania faces some drawbacks such as fast electron-hole pairs recombination and inactive under visible light irradiation (Linsebigler *et al*., 1995).

One of the ways to improve the functionality of titania is by the modification of titania with carbon to form carbon-based titania. Carbon nanotubes (CNT)-TiO_2 (Woan *et al*., 2009), multiwall-carbon nanotubes (MWCNTs)-TiO_2 (Tettey *et al*., 2010), fullerene-TiO_2 (Kamat *et al*., 1997; Wang *et al*., 2015), activated carbon-titania (Torimoto et al. 1997; Velo-Gala et al. 2017), carbon fibers (CFs)-TiO_2 (Teng et al. 2015), graphene-titania (Zhou et al. 2011; Khalid et al. 2013) and carbon-doped titania (Li et al. 2005) are among thousands of carbon-based titania materials that have been successfully synthesized in previous studies.

Towards the modifications, carbon has generally changed the electronic properties of titania by facilitating faster transport to the active sites on titania's surface, extending the light absorption to visible range, narrowing the band gap energy and suppressing the rate of the recombination of photo-induced electrons and holes (Palanivelu *et al*., 2007; Jeyalakshmi *et al.*, 2012; Teng *et al.*, 2014). Apart from that, it also changed the physical and structural properties of titania through the change in the lattice defects and impurities, particle size, bulk and surface crystal structure, including the morphology.

However, upon comprehensive reviews, one trend that can be seen is the different types of carbon have different characteristics that will reflect the properties of the carbon-based titania obtained. A slower recombination of electrons and holes in the CNT-TiO_2 composite was caused by the capability of CNT to act as the electron storage (Li et al. 2011). On the other hand, the efficient performance of graphene-TiO_2 composite was due to the graphene exhibiting strong charge mobility and high thermal conductivity (Khalid et al. 2013; Tan et al. 2013). Therefore, the selection of the type of carbon is crucial in designing an efficient catalyst.

In recent years, the attempt on using carbon from the natural sources in the synthesis of carbon-based titania became a topic of interest (Colmenares *et al*., 2016). Glucose (Zhang et al. 2016), starch (Tang et al. 2009) and chitosan (Shao et al. 2015) are the examples of the natural sources that have been used in the synthesis of carbon-based titania. Among all these different types of natural sources used, to date, only a few literatures have reviewed on the usage of cellulose as the carbon precursor in the synthesis of carbon-titania composite. Cellulose is foreseen as a good choice of carbon precursor because of the abundancy and the renewability of the cellulose promised the low cost and sustainable source of carbon materials. However, most of the reports about cellulose for the synthesis of titania are focused only on the use of cellulose as the template (Luo *et al*., 2013), the utilization of cellulose itself to form cellulose titania hybrids (Morawski et al. 2013) or the modification cellulose into the activated carbon before used in the synthesis of carbon based titania (Phan et al. 2006).

Based on the limited reports of cellulose as the in-situ carbon source, Liu *et al*. (2010) described that the synthesis of carbon-derived cellulose titania by employing filter papers as the carbon source through the decomposition of ultrathin titania film sol-gel process. The synthesized composite yielded a high specific surface area and showed good performance in the photodegradation of dyes and the photoreduction of silver cation to silver nanoparticles. On the other hand, Mohamed *et al.* (2016) and Mohamed *et al.* (2017a) reported the synthesis of carbon-doped mesoporous TiO_2 through the sol-gel method and the cellulose used is the regenerated cellulose membrane. The synthesized composite improved the photodegradation of methylene blue under the irradiation of visible light. Although these works have successfully proven the good effect of carbon derived from cellulose to the properties and the photocatalytic activity of titania, these works lacked the details on the interaction between carbon and titania, and the synthesized methods involved many synthesized steps, including the modification of cellulose into cellulose membrane.

Averrhoa bilimbi, or bilimbi (Figure 1.1) is one of the cellulosic materials available in nature. The fruits of the bilimbi, which is rich in water content, is expected to be highly porous and interconnected after the removal of water. In addition, bilimbi is expected to have a good hydrophilic feature due to the plenty of hydroxyl groups that are retained in the bilimbi. Therefore, considering all the concerns mentioned above, this research proposed the synthesis of cellulose-derived carbon/titania composite with bilimbi as the in-situ carbon source and the comprehensive studies on the interaction between carbon and titania particles. The target is achieved by the strategy to propose the interconnected porous structure of the bulk cellulosic materials. A bulk cellulosic material with highly interconnected pores, and rich with hydroxyl groups are expected to give accessibility for the titania precursor to diffuse into the porous structure, distribute well on the substrate surface and formed a strong interfacial interaction with the cellulose. Therefore, fitting the approach that was previously explained, the fruits of the *Averrhoa bilimbi* was chosen as the model material.

Figure 1.1 The image of the *Averrhoa bilimbi*'s fruits

1.2 Problem Statement

The abundant surface hydroxyl group in the cellulosic material is used as the strategy to anchor the titania particles. These hydroxyl groups can act as the sites for the attachment of titania particles (Colmenares *et al*., 2016). In the synthesis of bulk cellulose-titania, without surface modification, the titania attached have a tendency to form agglomeration and was not well dispersed (Teng et al. 2015). The probability of the titania particles to interact with carbon is low. Therefore, to uniformly disperse titania particles on the surface of bulk titania-cellulose without surface functionalization, remain a challenge and this challenge limits the utilization of cellulose as the carbon source in the synthesis of carbon-based titania.

In this research, in order to overcome this challenge, bilimbi has been used as the carbon source in the synthesis of carbon-titania composite. The water content of the bilimbi was first removed by freeze-drying method, leaving the bilimbi's structure to be porous. The bilimbi is then impregnated with the titania precursor by simple impregnation method. Following that, bilimbi-titania composite was carbonized at different calcination temperatures to form bilimbi-derived carbon titania composite. At low calcination temperature, it is expected to hold a strong interfacial between bilimbi and titania while at high calcination temperature, the bilimbi acted as the in-situ carbon source. By these factors, the physical and electronic properties of the bilimbi-TiO_2 will be improved and thus reflect the catalytic and photocatalytic performance. The interaction between carbon and titania was studied through the change of the physical and electronic properties.

The photocatalytic activities studied in this research is the photodegradation of phenol. Phenolic compounds are found to be the most organic pollutant found in wastewater and most of them generated from the coal and petrochemical industries (Busca et al. 2008). Uncontrolled phenolic pollutant introduced to wastewater lead to a cumulative hazardous effect on the environment. Even though there are many studies on the development of carbon-based titania as the photocatalyst to degrade the phenolic compounds, the improvement on the photocatalytic activity is still highly required. The catalytic reaction studied in this research is the oxidation of styrene. The oxidation of styrene by using aqueous hydrogen peroxide as the oxidant resulted to the production of styrene oxide, benzaldehyde and phenyl acetaldehyde that used as the chemical intermediates in the fine chemical industry (Lubis et al. 2012). Therefore, the catalytic oxidation of styrene is an important reaction organic synthesis. However, only a few researches were reported on the catalytic oxidation of styrene with carbon based titania as the catalyst.

Therefore, in this research, cellulose-derived carbon/titania composite prepared by the attachment of titania alkoxide on the surface of freeze-dried bilimbi and calcined at different temperature, affects the physical and electronic properties, including the photocatalytic and catalytic activities.

1.3 Motivation and Objectives of the Study

The aim of this research is to provide a comprehensive study on the effects of carbon to the changes in the properties (physical and electronic) of titania composite and the correlation between the properties of carbon-TiO_2 composite to its photocatalytic and catalytic activities. *Averrhoa bilimbi*, an example of highly interconnected porous and good hydrophilic cellulosic material, was used as the source of carbon since these characteristics are expected to improve the interaction of titania on the surface of the carbon. It is hypothesised that, with the use of interconnected porous carbon, it will prevent the aggregation of titania and therefore, provide a good interfacial interaction between titania particles and carbon. Moreover, the hydrophilicity of the material that was reflected from the abundant hydroxyl groups can enhance the attachment of titania particles. Hence, a good carbon-TiO_2 interaction is expected to be formed and subsequently change the physical and electronic properties of the carbon/TiO_2 composite.

In order to demonstrate the hypothesis, a systematic study has been carried out by varying the calcination temperature of bilimbi/TiO_2 composite. The calcination process will change the physical and electronic properties of the composite since the bilimbi was transformed into different forms and amount of carbon. It is expected that, at low temperature, the carbon in the bilimbi will change the physical properties of composite in terms of adsorption, whereby at high temperature, there is probability for carbon to substitute oxygen atoms in the titania lattice. The physical and electronic properties of the composite will change due to the interaction of carbon with TiO_2 and hence, improve their catalytic and photocatalytic activities.

In light of the issues mentioned above, this research is conducted based on the following objectives;

- To synthesize the carbon-based titania composite with natural cellulose, *Averrhoa bilimbi*, as the source of carbon
- To study the effect of calcination temperatures on the physical (surface and bulk) and electronic properties of the composite
- To study the photocatalytic and catalytic activities of the composite and the structure-activity relationship

1.4 Scope of the Study

This research is focused on understanding the changes in the physical and optical properties of the cellulose-derived carbon/TiO_2 composite when treated to different calcination temperatures and the structural-activity relationship of the composites. In order to accomplish the research's objectives, the scope of the study is designated into three parts, which are the preparation and synthesis of the carbon-TiO_2 composite, the characterization of the composite and the application of the composite in the photocatalytic and catalytic reactions.

Bilimbi is used as the model of the natural cellulose as main constituent in bilimbi is cellulose (67%), followed by 27% of hemicellulose and 13% of pectin (Muthu et al. 2016). The synthesis of carbon/TiO_2 composite was done by using the impregnation method. The raw bilimbi was first scoured and freeze-dried before being impregnated with titania alkoxide precursor. The bilimbi/TiO_2 was then calcined at 200, 500 and 800 °C, in order to see the effect of calcination temperatures on the physical and electronic properties of bilimbi/TiO_2 composite and to acquire a fully crystalline titania phase, which are believed to be active in the photocatalytic and catalytic reactions (Shamaila et al. 2011).

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