

**SYNTHESIS OF CARBON MODIFIED TITANIUM DIOXIDE  
PHOTOCATALYSTS FOR REMOVAL OF PHENOL**

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**UNIVERSITI TEKNOLOGI MALAYSIA**

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SYNTHESIS OF CARBON MODIFIED TITANIUM DIOXIDE  
PHOTOCATALYSTS FOR REMOVAL OF PHENOL

MOHD HAYRIE BIN MOHD HATTA

A thesis submitted in fulfillment of the  
requirements for the award of the degree of  
Master of Science (Chemistry)

Faculty of Science  
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APRIL 2014

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*Special dedication to my beloved mom*  
**“SITI MAIMUNAH ABDUL RAHMAN”**

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## ABSTRACT

Titanium dioxide ( $\text{TiO}_2$ ) has been recognized as an excellent photocatalyst, but lack adsorption capability. One of the suitable approaches to solve the problem is to introduce carbon materials to  $\text{TiO}_2$ , through a simple process and only involve low cost precursors. In this study, carbon modified  $\text{TiO}_2$  was synthesized by using modified sol-gel method in the presence of acetyl acetone as the chelating ligand. Two carbon precursors of dichloromethane and carbon nanotubes (CNT) were used and the samples were denoted as DCM- $\text{TiO}_2$  and CNT- $\text{TiO}_2$ , respectively. X-ray diffraction patterns showed that the addition of dichloromethane induced the formation of rutile phase in  $\text{TiO}_2$ , while addition of CNT maintains the anatase phase of  $\text{TiO}_2$ . Scanning electron microscope and field emission scanning electron microscope revealed the unaffected morphology of  $\text{TiO}_2$  after addition of the carbon precursors. The presence of carbon species was confirmed by diffuse reflectance ultraviolet visible spectroscopy and elemental dispersive X-ray analysis especially on samples with high loading of carbon precursors. The photocatalytic removal of phenol was carried out under UV light irradiation at room temperature for 24 hours. It was confirmed that all DCM- $\text{TiO}_2$  and CNT- $\text{TiO}_2$  series showed better adsorption and photocatalytic activity than the  $\text{TiO}_2$ . The best catalyst for each series, which were 3% DCM- $\text{TiO}_2$  and 5% CNT- $\text{TiO}_2$ , gave 72% and 68% phenol removal, respectively, while  $\text{TiO}_2$  showed only 17% phenol removal. Adsorption was proposed to be the important factor for the high activity. Since 3% DCM- $\text{TiO}_2$  showed slightly faster rate constant than the 5% CNT- $\text{TiO}_2$ , it was proposed that the use of dichloromethane as carbon precursor and modified sol-gel as the simple method would be an alternative good method to prepare highly active carbon modified  $\text{TiO}_2$  photocatalysts.

## ABSTRAK

Titanium dioksida ( $\text{TiO}_2$ ) dikenali sebagai fotomangkin yang hebat tetapi kebolehan penjerapannya lemah. Salah satu teknik sesuai untuk menyelesaikan masalah tersebut ialah dengan memasukkan bahan karbon ke dalam  $\text{TiO}_2$  melalui proses pengubahsuaian yang mudah dan kos pemula yang rendah. Dalam kajian ini, karbon terubahsuai  $\text{TiO}_2$  telah disintesis melalui teknik sol gel yang diubahsuaikan dengan kehadiran asetil aseton sebagai ligan kelat. Dua pemula karbon iaitu diklorometana dan tiubnano karbon (CNT) telah digunakan dan masing-masing dilabelkan sebagai DCM- $\text{TiO}_2$  dan CNT- $\text{TiO}_2$ . Corak pembelauan sinar-X menunjukkan bahawa penambahan karbon mendorong pembentukan  $\text{TiO}_2$  fasa rutil manakala penambahan CNT masih mengekalkan fasa anatas  $\text{TiO}_2$ . Mikroskop imbasan elektron dan mikroskop imbasan elektron pancaran medan mengesahkan morfologi  $\text{TiO}_2$  tidak berubah selepas penambahan karbon. Kehadiran spesies karbon telah disahkan melalui spektroskopi pantulan serakan ultralembayung-cahaya nampak dan analisis tenaga sebaran sinar-X terutama bagi sampel yang mempunyai kandungan karbon yang tinggi. Penyingkiran fenol melalui teknik pemangkinan foto telah dijalankan di bawah sinaran UV pada suhu bilik selama 24 jam. Hasil eksperimen mengesahkan bahawa kedua-dua siri DCM- $\text{TiO}_2$  dan CNT- $\text{TiO}_2$  menunjukkan penjerapan dan aktiviti pemangkinan foto yang lebih baik daripada  $\text{TiO}_2$ . Mangkin terbaik bagi setiap siri iaitu 3% DCM- $\text{TiO}_2$  dan 5% CNT- $\text{TiO}_2$  masing-masing memberikan 72% dan 68% penyingkiran fenol sementara  $\text{TiO}_2$  hanya menyingkirkan 17%. Penjerapan dicadangkan sebagai faktor penting bagi mendapatkan hasil pemangkinan yang tinggi. Oleh kerana 3% DCM- $\text{TiO}_2$  menunjukkan kadar tindak balas yang lebih cepat daripada 5% CNT- $\text{TiO}_2$ , maka dicadangkan bahawa penggunaan diklorometana sebagai pemula karbon dan sol-gel terubah suai sebagai kaedah ringkas adalah kaedah alternatif yang baik dalam menyediakan karbon terubahsuai  $\text{TiO}_2$  yang aktif sebagai fotomangkin.

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## LIST OF ABBREVIATIONS

arb.u	-	Arbitrary unit
eV	-	Electron volt
h	-	hours
min	-	minutes
nm	-	Nanometers
Wt. %	-	Weight percents
K	-	Kelvin
kV	-	kilovolt
ppm	-	Part per million
DR UV-Vis	-	Diffuse Reflectance Ultra Violet-Visible
FTIR	-	Fourier Transform Infra-red
GC-FID	-	Gas Chromatography Flame Ion Detector
TGA	-	Thermogravimetric Analysis
XRD	-	X-ray Powder Diffraction
TEM	-	Transmission Electron Microscope
SEM	-	Scanning Electron Microscope
$\lambda$	-	Wavelength
$2\theta$	-	Bragg angle
CuK $_{\alpha}$	-	X-ray diffraction from copper K $_{\alpha}$ energy levels

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Background of Study

Recently, the applications of heterogeneous photocatalysis in water treatment have attracted global attention due to its effectiveness in degrading and mineralizing the organic pollutant (Grabowska, *et al.*, 2012). By far,  $\text{TiO}_2$  is the only photocatalyst applicable for industrial purpose at present and also probably in the future. This is due to the facts that  $\text{TiO}_2$  is an efficient photocatalyst with high stability and has low cost. More significantly, it has been used as a white pigment from ancient times, and thus, its safety to humans and the environment is guaranteed by history (Hashimoto, *et al.*, 2007). Photocatalytic degradation of organic pollutants using  $\text{TiO}_2$  has been proved to be most efficient method in the point of view of environmentally safe process (Chiou, *et al.*, 2007). However, there are certain disadvantages associated with the conventional  $\text{TiO}_2$  powder catalyst, especially its limitation in adsorption of organic compounds sufficiently when in hydrophobic conditions (Cao, *et al.*, 2010). In order to increase the efficiency of  $\text{TiO}_2$ , many works have been focused to modify  $\text{TiO}_2$  with carbon-based material such as activated carbon or carbon nanotubes (CNT) in order to increase the adsorption rate (Tryba, *et al.*, 2003).

Addition of activated carbon to  $\text{TiO}_2$  helped increasing its photocatalytic efficiency due to the large surface area of the composite catalyst, in which activated carbon acted as an adsorption trap to the organic pollutant before transferred to  $\text{TiO}_2$  surface, where the photocatalytic process occurred (Liu, *et al.*, 2007). However, the high cost of activated carbon in regeneration system make the activated carbon less

economically viable as even though the carbon successfully gave high percentage of phenol removal, the surface area of activated carbon reduced during the preparation process (Tryba, *et al.*, 2003). Incorporation of another type of carbon based material, *i.e.*, CNT into  $\text{TiO}_2$  also helped increasing the efficiency of  $\text{TiO}_2$  photocatalytic process due to its large surface area and better catalyst dispersion on CNTs (Chen, *et al.*, 2009). The important function of coupling  $\text{TiO}_2$  and CNTs was proposed to provide a synergistic effect, which can enhance the overall efficiency of photocatalytic process such as in the treatment of contaminated water (Zhang, *et al.*, 2009). However, unfortunately, the preparation of CNTs usually involves the use of expensive instruments, resulting in high cost of production entirely (Danafar, *et al.*, 2009). Therefore, instead of CNT modified  $\text{TiO}_2$ , different carbon modified  $\text{TiO}_2$  should be developed with simple method and low cost production.

Sol-gel method is one of the most widely used methods to prepare carbon modified  $\text{TiO}_2$ . In the preparation of carbon modified  $\text{TiO}_2$  via sol-gel method, the most crucial parameters that need to be considered are the uses of titania precursors as well as the calcination temperature. According to the previous literature, there are several titania precursors that have been used such as tetrabutyl orthotitanate (Tseng, *et al.*, 2006) and titanium tetrachloride (Konstantinova, *et al.*, 2007). It was reported that the different type of alkoxide used gave influence on the contents of produced carbon. There are alkoxides that produce low carbon contents but high surface area and vice versa (Lettmann, *et al.*, 2001). Therefore, the type of alkoxide used must be determined in order to produce  $\text{TiO}_2$  with high surface area and high carbon contents that will give high photocatalytic activity. Supporting this information, Treschev, *et al.* (2008) reported that the carbon contents gave influence on the crystallinity of the  $\text{TiO}_2$ . Lettmann *et al.* (2001) reported the carbonaceous species was produced by pyrolysis of the alcohols during the dissolution of various different alkoxides in responding alcohols. It was proved that carbonaceous species in the photocatalyst exhibited surprisingly a good long-time stability despite of the carbonaceous nature of the sensitising species. However, it must be taken into consideration that different alkoxides used gave different carbonaceous contents and differences surface area. Therefore, in the present study titanium tetraisopropoxide (TTIP) was used with expectation that it could provide high carbon contents as well

as high surface area that would lead to the increase in the photocatalytic activity of carbon modified TiO<sub>2</sub> photocatalysts.

Calcination temperature also is one of the important factors that will determine the nature of the sample contents. It was reported that the carbon modified TiO<sub>2</sub> prepared via different techniques affected the carbon contents in the photocatalyst (Konstantinova *et al.*, 2007). As example, the preparation of C-TiO<sub>2</sub> by hydrolysis of titanium tetrachloride and tetrabutyl ammonium hydroxide with different calcination temperatures and times gave different carbon contents. Calcination at 673.15 K for 1 hour and 623.15 K for 2 hour produces 2.5% and 0.48% carbon contents respectively. It was concluded that the optimum temperature and duration of calcination is required to control obtained TiO<sub>2</sub> with optimum carbon contents that can give high photocatalytic activity. Sakthivel and Kisch (2003) have also prepared the carbon modified TiO<sub>2</sub> by hydrolysis of titanium tetrachloride and tetrabutylammonium hydroxide at different calcination temperatures to investigate the properties of the formed carbon modified TiO<sub>2</sub>. It was found that the low carbon content (3% in TiO<sub>2</sub>), which was obtained at calcination temperature of 673.15 K for 15 minutes, increased the photocatalytic activity drastically with the rate of the reaction became 30 times higher than that of the unmodified TiO<sub>2</sub>. The used calcinations temperature should be controlled as the increase of calcination temperature will increase its crystallization, but the less active rutile phase of TiO<sub>2</sub> could be formed.

In sol-gel process, controlling the hydrolysis and condensation process would be the important factor to get the expected materials. Since titanium oxide precursors such as alkoxides and chlorides are very reactive, some papers reported the use of the chelating agent, *i.e.*, acetyl acetone to decrease the reactivity of the precursors (Yuliati, *et al*, 2006). It was proposed that the addition of the acetyl acetone resulted in a better dispersion of titanium oxide on silica matrix during the preparation of silica-titania photocatalysts by sol-gel method. The same concept should be applicable to prepare the carbon-containing TiO<sub>2</sub> since the hydrolysis of the titanium oxide precursor should be controlled so that there is sufficient time for carbon to be

dispersed in the titania matrix during sol-gel process. To the best of our knowledge, this strategy has never been applied to the preparation of the carbon modified  $\text{TiO}_2$  by sol-gel method. Therefore, in this study, we adopted the strategy for the first time to prepare the series of carbon modified  $\text{TiO}_2$  photocatalysts. As comparison, the series of CNT modified  $\text{TiO}_2$  was also prepared in this research. In addition, previous literature reported the successful production of CNT using dichloromethane as CNT precursor by adopting hydrothermal method in low temperature synthesis. The advantages of using dichloromethane as carbon precursor include the easiness to be reduced into carbon species and also considered as low-cost material. Thus, dichloromethane has been chosen as carbon precursor in this research as it offers low cost production entirely (Manafi, *et al.*, 2008).

Both of the prepared dichloromethane and CNT modified  $\text{TiO}_2$  series were applied for photocatalytic removal of phenol under UV light irradiation. Phenol has been recognized as the most common organic pollutants in wastewater. Industrial waste such as those from the oil waste, plastic, pharmaceutical and domestic wastewaters is the main source of introduction of phenol to water. Their presence in water supplies is noticed as a bad taste and odour. Therefore, the wastewaters containing phenolic compounds must be treated before their discharges into the water streams (Lin, *et al.*, 2009). Due to its toxicity even at low concentration and the nature of phenol that leads to formation of substituted compounds during disinfection and oxidation processes (Busca, *et al.*, 2008), many researchers focus on the finding and developing efficient techniques for phenol removal. Photocatalytic oxidation method has been proposed as one of the most efficient and environmentally safe processes to remove the phenol pollutants (Chun, *et al.*, 2000).

## 1.2 Statement of Problems

$\text{TiO}_2$  has been recognized as the most commonly used photocatalyst in removal of organic pollutants. However,  $\text{TiO}_2$  has limitation in its ability to adsorb organic pollutants. Therefore, modification of  $\text{TiO}_2$  with material having high

adsorption abilities is required in order to increase the photocatalytic efficiency of  $\text{TiO}_2$ . On the other hand, various carbon materials have been considered as good adsorbents. Carbon material such as CNT has been proposed to improve the photocatalytic activity of  $\text{TiO}_2$  by creating a synergic effect of adsorption and photocatalytic processes. Unfortunately, the high cost in production of CNT has limited its application and development of a low cost process by using low cost carbon material via simple method is remained as a challenge. Moreover, there is still lack of knowledge on designing  $\text{TiO}_2$  based photocatalyst with high adsorption capability without reducing its high photocatalytic activity. In this study, a new carbon based material synthesized from dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) was proposed to modify  $\text{TiO}_2$  by using an improved sol-gel method. In this study, dichloromethane has been chosen as carbon precursor since it is easily to be dispersed in the reaction medium. On the other hand, since dichloromethane is low cost and easily obtained, the uses of dichloromethane in this research contributed in the low cost preparation in production of carbon modified  $\text{TiO}_2$ . The series of prepared carbon modified  $\text{TiO}_2$  was then characterized in detail, tested for photocatalytic reaction, and compared to the prepared CNT modified  $\text{TiO}_2$ .

Sol-gel method has been recognized as a good method to prepare carbon modified  $\text{TiO}_2$ . While some studies to prepare silica titania photocatalysts showed the significance of controlling the hydrolysis process of the titanium oxide precursors, there is still no report on this point to prepare carbon modified  $\text{TiO}_2$ . Therefore, there is no clear understanding on the effect of carbon dispersion on  $\text{TiO}_2$  in the properties and the photocatalytic activity.

Phenolic compounds are found to be the most common organic pollutants found in wastewaters and most of them are generated from chemical and petroleum based industries. Uncontrolled phenolic compound introduced to wastewater caused a cumulative hazardous effect on the environment. Even though there are many studies on the development of  $\text{TiO}_2$  photocatalysts to degrade the phenolic compounds, the improvement in the photocatalytic activity of  $\text{TiO}_2$  is still highly required. In the present study, the prepared carbon and CNT modified  $\text{TiO}_2$  materials

were used to remove phenol under UV light irradiation. Some studies on the adsorption process and kinetic parts were also made to clarify the enhanced performance of the prepared materials.

### **1.3 Objective of the Study**

The objectives of this study are:

- a) To synthesize dichloromethane modified  $\text{TiO}_2$  (DCM- $\text{TiO}_2$ ) and CNT modified  $\text{TiO}_2$  using an improved sol gel method.
- b) To study the properties of the prepared DCM modified  $\text{TiO}_2$  and CNT modified  $\text{TiO}_2$ .
- c) To investigate the photocatalytic activity of the prepared DCM modified  $\text{TiO}_2$  and CNT modified  $\text{TiO}_2$  for degradation of phenol under UV light irradiation.

### **1.4 Scope of the Study**

In this study, two series of photocatalysts, which were DCM modified  $\text{TiO}_2$  and CNT modified  $\text{TiO}_2$  were synthesized by an improved sol-gel method. The first series was prepared using dichloromethane as the precursor of carbon with different amount of loading (1, 3, and 5 wt%), while the second series was prepared using the CNT. The CNT was only prepared by using catalytic chemical vapour deposition. For both series, the TTIP was used as the  $\text{TiO}_2$  precursor and hydrolysis process was controlled in the presence of acetyl acetone as the chelating ligand with mol ratio of TTIP to acetylacetone of 1 to 2. The calcination process was fixed at 773.15 K for 8 hours in air.

Both the prepared DCM and CNT modified  $\text{TiO}_2$  series were characterized by X-ray Diffraction (XRD) to investigate the structure and degree of crystallinity.



Diffuse Reflectance Ultraviolet-Visible Spectroscopy (DR UV-Vis) was used to determine the absorption spectra and band gap energy of the prepared photocatalysts. The band gap energy was only determined by Tauc Plot. Fourier Transform Infra-Red Spectroscopy was used to study the functional surface groups on the prepared photocatalysts. Scanning Electron Microscope (SEM) and Field Emission Scanning Electron Microscope (FESEM) were used to study the surface morphology of the prepared photocatalysts. Elemental analysis was determined from the Energy Dispersive X-ray Spectroscopy (EDX) attached to the FESEM. Thermal analysis was carried out by Thermal Gravimetric Analysis (TGA).

The photocatalytic activity of the prepared photocatalysts was tested for removal of phenol under UV light irradiation. The reactions were carried out at room temperature and closed reactor attached with a cooling water system. The reaction product and photocatalytic activity were analyzed by a gas chromatography equipped with a Flame Ionization Detector (GC-FID).

## **1.5 Significance of the Study**

The aim of this study is to increase the efficiency of the  $\text{TiO}_2$  by modify it with carbon materials. A new carbon precursor, which is dichloromethane, was proposed in this study. Furthermore, the slow hydrolysis due to the addition of chelating agent, acetyl acetone in the preparation process give sufficient time for dichloromethane to be dispersed in  $\text{TiO}_2$  was a new strategy adopted in this study. Therefore, this study will contribute on the fundamental knowledge on the material science, especially in the synthesis method and preparation of carbon modified  $\text{TiO}_2$ .

This study also highlighted the comparisons between the dichloromethane modified  $\text{TiO}_2$  and CNT modified  $\text{TiO}_2$  series in terms of properties and photocatalytic activity. It is expected that this study will catalyse the innovative finding on how to design good photocatalysts for removal of organic pollutants.

This study used photocatalytic removal of phenol as the model reaction. Since phenol is one organic pollutant that can be found in our environment, this research is also important for environmental study. This study will open the possibility to utilize the photocatalytic reaction method to solve the environmental problems relating to the organic pollutants as well as to promote the green technology by using clean and environmentally safe process.

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