

SYNTHESIS AND CHARACTERIZATION OF HKUST-1/TiO<sub>2</sub> THIN FILM

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THIS DISSERTATION IS SUBMITTED AS A PARTIAL REQUIREMENT TO OBTAIN  
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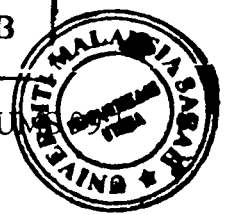
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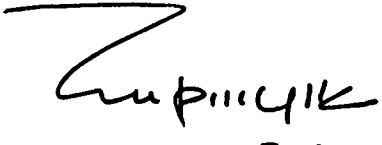
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## ABSTRACT

High electron-hole recombination ratio and low surface area have always been the major problems of TiO<sub>2</sub> thin film. This study focuses on the effect of HKUST-1 towards photocatalytic efficiency TiO<sub>2</sub> thin film. The HKUST-1/TiO<sub>2</sub> thin film was prepared by dip-coating a Duran glass tube in a TiO<sub>2</sub> precursor sol-gel, followed by drying in oven at 150 °C and calcination at 550 °C. The TiO<sub>2</sub> coated Duran glass tube was then dipped into a mixture of TiO<sub>2</sub> precursor sol-gel and HKUST-1 powder to form a HKUST-1/TiO<sub>2</sub> thin film. Crystal phase of HKUST-1 and anatase TiO<sub>2</sub> were both confirmed by powder XRD. The morphology of HKUST-1/TiO<sub>2</sub> thin film showed an unevenly distributed HKUST-1 powder on the surface of TiO<sub>2</sub> thin film. Study of photocatalytic performance revealed that HKUST-1/TiO<sub>2</sub> thin film layer was able to degrade 4.5 % of 5 ppm of methyl orange (MO) solution in 3 hours under the UV-A irradiation while the bare TiO<sub>2</sub> thin film was able to degrade 49.5 % of MO under same condition. The low photodegradation efficiency of HKUST-1/TiO<sub>2</sub> thin film may due to the absence of anatase TiO<sub>2</sub> on the surface of thin film, trapped guest molecules in HKUST-1 cavities and uneven distribution of HKUST-1 on the thin film. Besides, terminating species at the surface of HKUST-1 might be dominated by the BTC<sup>3-</sup> that gives rise to the negative surface of HKUST-1. This repels MO molecules and therefore hindered the reaction between thin film and MO molecules.

# **SINTESIS DAN PENCIRIAN PENYALUTAN HKUST-1 DENGAN FILEM TIPIS TiO<sub>2</sub>**

## **ABSTRAK**

*Penyesatan gabungan semula h<sup>+</sup> dan e<sup>-</sup> yang tinggi dan luas permukaan yang rendah sentiasa menjadi masalah utama filem tipis TiO<sub>2</sub>. Kajian ini member tumpuan terhadap kesan HKUST-1 atas kecekapan pemangkinan foto filem tipis TiO<sub>2</sub>. Filem tipis HKUST-1/TiO<sub>2</sub> telah disediakan dengan celup-salut satu tiub kaca Duran dalam larutan TiO<sub>2</sub> sol-gel, kemudian dikeringkan dalam ketuhar pada suhu 150 °C dan pengapuran dijalankan pada suhu 550 °C. Tiub kaca Duran dengan lapisan kot TiO<sub>2</sub> telah dicelupkan ke dalam campuran yang mengandungi TiO<sub>2</sub> sol-gel dan serbuk HKUST-1 untuk menghasilkan satu filem tipis HKUST-1/TiO<sub>2</sub>. Tahap hablur HKUST-1 dan TiO<sub>2</sub> fasa anatas kedua-dua telah disahkan dengan XRD. Morfologi filem tipis HKUST-1/TiO<sub>2</sub> menunjukkan taburan serbuk HKUST-1 yang tidak serata atas permukaan filem tipis TiO<sub>2</sub>. Kajian daripada pemangkinan foto menunjukkan bahawa filem tipis HKUST-1/TiO<sub>2</sub> dapat menyingkirkan 4.5 % daripada larutan 5 ppm metal oren (MO) yang dijalankan selama 3 jam di bawah penyinaran UV-A manakala filem tipis TiO<sub>2</sub> semata-mata cuma dapat menyingkirkan sebanyak 49.5 % daripada MO bawah keadaan yang sama. Kecekapan fotodegradasi filem tipis HKUST-1/TiO<sub>2</sub> yang rendah mungkin disebabkan oleh ketidakhadiran TiO<sub>2</sub> fasa anatas atas permukaan filem tipis, molekul tetamu yang terperangkap dalam kaviti HKUST-1 dan taburan HKUST-1 yang tidak serata atas filem tipis. Di samping itu, sepsis atas permukaan HKUST-1 mungkin dikuasai oleh BTC<sup>3-</sup> yang menghasilkan permukaan negatif HKUST-1. Ini akan menyingkirkan molekul MO dan seterusnya menghalang reaksi antara filem tipis dan molekul MO.*

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## LIST OF SYMBOLS AND ABBREVIATIONS

HKUST-1	Copper (II) benzene-1,3,5-tricarboxylate
AOPs	Advanced oxidation processes
GAC	Granular activated carbon
UV	Ultraviolet
TGA	Thermogravimetric analyzer
DSC	Differential scanning calorimeter
XRD	X-ray diffractometer
SEM	Scanning electron microscopy
UV-Vis	UV-Vis spectrophotometer
E-beam	High Energy Electron Beam Irradiation
$h^+$	Photoactivated holes
$e^-$	Photoactivated electrons
DDT	Dichlorodiphenyltrichloroethane
IUPAC	International Union of Pure and Applied Chemistry
MOFs	Metal organic frameworks
BTC	Benzene-1,3,5-tricarboxylate
Cp	Heat capacity
TBOT	Tetrabutylorthotitanate
MO	Methyl orange
D%	Percent of Degradation of MO Sample Solution



## CHAPTER 1

### INTRODUCTION

#### 1.1 Advanced Oxidation Processes (AOPs)

Over the past few decades, advanced oxidation processes (AOPs) have attracted significant attention as an alternative to conventional methods of water treatments. Conventional methods like air stripping, granular activated carbon (GAC) adsorption, resin sorption are phase-transfer processes; on the other hand, biological treatment is only applicable for biodegradable contaminated wastewater. Unlike those processes, AOPs are destructive processes which destroy the contaminants directly in the water through chemical transformation instead of simply transferred them from liquid phase into a gas phase or solid phase (Kommineni *et al.*, 2000). This makes AOPs earned the credit of "water treatment processes of the 21<sup>st</sup> century" (Munter, 2001). The principle of AOPs is to mineralize numerous pollutants into ultimately less toxic substances like carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O) or transform non-biodegradable compounds into harmless compounds that could be further biodegraded (Munter, 2001; Stasinakis, 2008). Generally, AOPs refer to the processes that involve ozone (O<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), and/or ultraviolet (UV) light. They also refer to a more general group of processes which may also involve titanium dioxide (TiO<sub>2</sub>) catalysts, electron beam irradiation and Fenton's reaction (Kommineni *et al.*, 2000). All these processes are characterized by same features for example production of highly reactive hydroxyl radical ( $\bullet\text{OH}$ ) and superoxide anion (O<sub>2</sub> $\bullet^-$ ) (Han *et al.*, 2009). In this study, TiO<sub>2</sub> catalysis with UV is focused.



## 1.2 Titanium Dioxide (TiO<sub>2</sub>) Powder

In 1970s, heterogeneous photocatalytic oxidation process has been developed as one of the novel AOPs (Han *et al.*, 2009). TiO<sub>2</sub> as an oxide semiconductor catalyst, has been proven to be the most widely used in water treatment processes because of the strong oxidizing strength, relatively low toxicity, long-term photostability, highly oxidizing photogenerated holes and highly potential to produce radicals (Han *et al.*, 2009; Santhanalakshmi and Komalavalli, 2012). Also, it is relatively inexpensive and commercially available (Stasinakis, 2008). TiO<sub>2</sub>/UV light process also caught a lot of attention due to ambient conditions required for the operation, lack of mass transfer limitation and possible use of solar irradiation (Stasinakis, 2008).

Even though TiO<sub>2</sub> powder seem to be a good candidate for photocatalysis oxidation, it has several limitations must be worked out to optimize the performance of the techniques (Kalra *et al.*, 2011). First, the wavelength spectrum of TiO<sub>2</sub> needs to be widened for photonic activation. Secondly, the structure in the catalyst composition should be stabilized. Next, the hole-electron recombination must be reduced and the adsorption of organic molecules must be increased. Hence, chemically impregnated (doped) or physically implanted with other materials have been developed to improve the photoactivity of TiO<sub>2</sub> powder (Vogelpohl and Kim, 2004). Doping of TiO<sub>2</sub> powder with other elements can narrow the band gap; scavenge excited electrons or holes and enhance the specific surface area that will then solve the limitations of TiO<sub>2</sub>/UV light process (Stasinakis, 2008).

TiO<sub>2</sub> powder catalyst must be stirred during the reaction and it has to be separated from treated water after each run. To recover the highly dispersed and suspended catalyst, processes like sedimentation, centrifugation and filtration are necessary for the system. These separation processes are not only time consuming but also become less efficient as the powder size of TiO<sub>2</sub> diminished. It is because when the powder become smaller, they become easier to penetrate through filtration materials and stay suspended in the water causing clogging of filter membranes (Malato *et al.*, 2003).

### 1.3 Titanium Dioxide (TiO<sub>2</sub>) Thin Films

To overcome the problems, immobilization of TiO<sub>2</sub> powder has been introduced. TiO<sub>2</sub> powder are bounded on solid supports or form thin solid films (Tennakone *et al.*, 1997; Kumara *et al.*, 1999; Karches *et al.*, 2002). However, the immobilized TiO<sub>2</sub> largely reduced the surface area that exposed to UV light. This makes the photocatalytic efficiency of TiO<sub>2</sub> thin films much lower than the TiO<sub>2</sub> powder (Arabatzis *et al.*, 2002). Besides the reduced surface area, narrow corresponding wavelength range and high electron-hole recombination ratio also further reduce the photocatalytic performance of the system of the TiO<sub>2</sub> thin films (Arabatzis *et al.*, 2003).

In order to improve the efficiency of the material, TiO<sub>2</sub> thin films have been modified by doping noble metals, transition metals or non-metals on it. The doping process has altered both of the surface features and surface chemistry, hindered the photo-generated electron hole recombination, accelerated the photoexcitation and formation of oxidizing species (Arabatzis *et al.*, 2003; Arabatzis *et al.*, 2003). This study focuses on enhancing the degradation efficiency of TiO<sub>2</sub> thin film by coating with nanoporous materials.

### 1.4 HKUST-1

HKUST-1, a three-dimensional nanoporous cubic framework, has also known as Cu-BTC or MOF-199. It was first discovered and synthesis in 1999 (Chui *et al.*, 1999). HKUST-1 has caught a significant attention since then. It was popular in catalysis, separation and storage application. HKUST-1 also shows a great interest in preferential adsorption of quadruple molecules as well as heterogeneous catalysis (Li *et al.*, 2009). This make the HKUST-1 has a high potential to improve the efficiency of TiO<sub>2</sub> on photocatalytic degradation process.

## 1.5 Objectives

The objectives of this study are:

- i. to prepare HKUST-1 coated  $\text{TiO}_2$  thin film composite.
- ii. to characterize HKUST-1/ $\text{TiO}_2$  thin film using XRD, SEM, TGA and DSC.
- iii. to examine the photocatalytic activity of HKUST-1/ $\text{TiO}_2$  composite toward degradation of methyl orange.

## 1.6 Scope of study

This study involves preparation and characterization of HKUST-1/ $\text{TiO}_2$  thin film by dip-coating method. It was started with the synthesis of  $\text{TiO}_2$  thin film through the sol-gel method followed by calcination at 550 °C. The obtained  $\text{TiO}_2$  thin film was then dipped into the HKUST-1/ $\text{TiO}_2$  solution in order to obtain the HKUST-1/ $\text{TiO}_2$  composites.

The identification and morphology of HKUST-1/ $\text{TiO}_2$  composites was characterized under the x-ray diffractometer (XRD) and scanning electron microscope (SEM). Thermogravimetric analyzer (TGA) and differential scanning calorimeter (DSC) were used to characterize the thermal stability of HKUST-1 crystals. Photocatalytic activity of the prepared composites was tested using 5 ppm methyl orange solution for 3 hours. Degree of degradation of methyl orange solution was then studied using the UV-Vis spectrophotometer.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Advanced Oxidation Processes (AOPs)

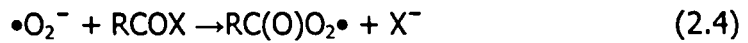
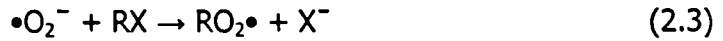
In 1987, the AOPs concept was established by Glaze *et al.*, he defined AOPs as “near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radical ( $\bullet\text{OH}$ ) in sufficient quantity to effect water purification”. AOPs are generally refer to those aqueous oxidation processes that are based on the intermediacy of reactive species such as  $\bullet\text{OH}$  and superoxide anion ( $\bullet\text{O}_2^-$ ) radicals in the mechanism, resulting in the almost complete degradation of the target pollution compound, including a variety of xenobiotics and micropollutants (Andreozzi *et al.*, 1999; Esplugas *et al.*, 2002). The radicals react rapidly and non-selectively with nearly all electron rich organic compounds. It can completely remove refractory organics and reduce the toxicity of effluent (Stasinakis, 2008).

Several possible mechanisms might happen during the AOPs such as oxygen reduction reaction (Equation 2.1 and 2.2) (Shao *et al.*, 2006).



The  $\bullet\text{O}_2^-$  is also able to oxidize many organic compounds via a complicated deprotonation-oxidation mechanism. The  $\bullet\text{O}_2^-$  ion is a supernucleophile which can be origin of destructive processes initiated by the splitting-off of various carbon-oxygen (C-O) and carbon-halogen (C-X) bonds (Equation 2.3 and 2.4) (Zhang *et al.*, 2008). R in the equations refers to hydrocarbon chain in the compounds.

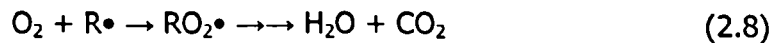




The common reactions of  $\bullet\text{OH}$  are hydrogen abstraction (Equation 2.5), radical addition (Equation 2.6) and electron transfer (Equation 2.7) (Stasinakis, 2008).



The reaction between molecular oxygen and peroxy radicals may generate organic radicals which initiate chain reactions of oxidative degradation and eventually form  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and inorganic salts (Equation 2.8). Hydrogen gas ( $\text{H}_2$ ) might be produced as a by-product when the electron reacts with the proton ion. (Equation 2.9) (Zhang *et al.*, 2008).



The  $\bullet\text{OH}$  and  $\bullet\text{O}_2^-$  radical can be produced by using one or more primary oxidants like  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$  or oxygen ( $\text{O}_2$ ) and/or with the help of energy sources such as UV light and electron beam radiation or catalysts such as  $\text{TiO}_2$  and heterogeneous photocatalysts (Kalra *et al.*, 2011). Table 2.1 showed the types of AOPs system of established technologies and emerging technologies. Emerging technologies stated here as technologies that have very limited full-scale applications (Kommineni *et al.*, 2000).

**Table 2.1:** Types of AOPs (Kommineni *et al.*, 2000).

<b>Established Technologies</b>	<b>Emerging Technologies</b>
Hydrogen Peroxide/Ozone (H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> )	High Energy Electron Beam Irradiation (E-beam)
Ozone/Ultraviolet Irradiation (O <sub>3</sub> /UV)	Sonication/Hydrodynamic Cavitation
Hydrogen Peroxide/Ultraviolet Irradiation (H <sub>2</sub> O <sub>2</sub> /UV)	TiO <sub>2</sub> -catalyzed UV Oxidation (TiO <sub>2</sub> /UV)
	Fenton's Reaction (H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup> /UV, H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup> )

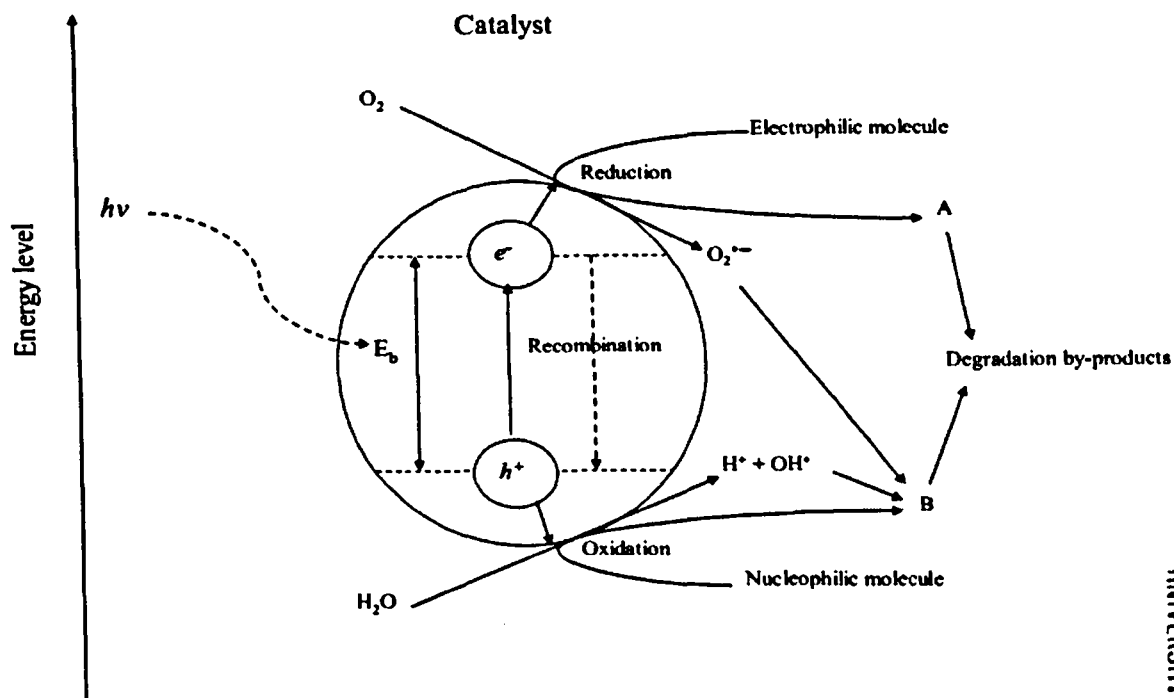
These combinations can highly accelerate the generation of •OH and •O<sub>2</sub><sup>-</sup> radical. In general, the ability to generate •OH and •O<sub>2</sub><sup>-</sup> is proportional to the effectiveness of an AOP. Thus, many studies are done to find out the most efficient oxidation system choice or design for different industries wastewater (Munter, 2001).

However, despite all the advantages, AOPs are still much less well understood in the complex chemical and physical processes compare to conventional methods. There are several limitations and challenges need to be overcome and solved in full-scale applications. The knowledge of background water quality effects on contaminant removal for AOPs is still very limited (Kommineni *et al.*, 2000). Highly reactive and relatively short half-life •OH and •O<sub>2</sub><sup>-</sup> radicals made it difficult to measure the methods of chemical reactions, spin-trap and direct detection (Zhang *et al.*, 2008). Since the oxidation processes are non-selective, therefore there is a significant amount of potential interference which is unpredictable. To overcome these limitations, higher chemical dosages or more energy may be required which may also lead to increase in cost (Kommineni *et al.*, 2000).

### **2.1.1 TiO<sub>2</sub>-UV Catalyzed Oxidation (TiO<sub>2</sub>/UV)**

TiO<sub>2</sub>/UV is a photocatalytic oxidation which the semiconductor is photoexcited through absorption of electromagnetic radiation (Munter, 2001). TiO<sub>2</sub>, as a semiconductor, only generates the photoactivated holes ( $h^+$ ) and electrons ( $e^-$ )

when absorbs light energy more than or equal to energy band gap (See Figure 2.1) (Santhanalakshmi and Komalavalli, 2012).

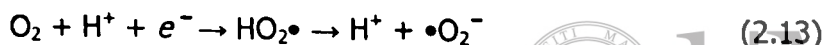


**Figure 2.1:** Photocatalytic oxidation mechanisms of  $\text{TiO}_2$  (Chong *et al.*, 2010).

When  $\text{TiO}_2$  is activated by UV light, the valence band electrons are excited to conduction band and electron vacancies, or holes, are created (Equation 2.10) (Kommineni *et al.*, 2000). Both photogenerated  $h^+$  and  $e^-$  are assumed to react with electrophilic and nucleophilic molecules absorbed on the photocatalyst surface, inducing reduction or oxidation respectively, producing activated and unstable products (Equation 2.11 and 2.12) (Chong *et al.*, 2010).



The excited-state electrons are capable of initiating a wide range of chemical reaction and able to interact with surface absorbed oxygen molecules and proton ions to form  $\bullet\text{O}_2^-$  ions (Equation 2.13) and  $\text{H}_2\text{O}_2$  molecules (Equation 2.14) (Kommineni *et al.*, 2000).





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