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SYNTHESIS AND CHARACTERIZATION OF ZINC OXIDE/REDUCED GRAPHENE OXIDE HYBRID PHOTOCATALYSTS FOR DEGRADATION OF METHYL ORANGE

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By

MARILYN YUEN SOK WEN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Chair: Associate Professor Abdul Halim bin Abdullah, PhD
Faculty: Science

The recalcitrant nature and toxicity of organic pollutants in wastewater to mankind have led to extensive research on the usage of semiconductor based heterogeneous photocatalysis, in particular zinc oxide (ZnO). In this study, zinc oxide/reduced graphene oxide (ZnO/rGO) hybrid photocatalysts with varying graphene oxide (GO) to zinc salt volume ratio (0:100, 5:100, 10:100 and 20:100) were synthesized by precipitation method using zinc acetate dihydrate, ammonium hydroxide and graphene oxide (1 mg/mL) as precursors followed by thermal reduction. The product was denominated as ZnO, ZnO/rGO5, ZnO/rGO10 and ZnO/rGO20.

The samples were characterized using X-ray powder diffraction (XRD), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), raman spectroscopy and particle size analysis (PSA). Surface area and porosity analysis and the band gap energy of the photocatalysts were determined by the Brunauer-Emmett-Teller method (BET) and UV-visible spectroscopic analysis. The introduction of graphene into ZnO was found to alter the physicochemical properties of the ZnO particles by lowering its band gap energy, reducing both particle and pore sizes and increasing its specific surface area and pore volume.

The corresponding photocatalytic performance of the samples was then investigated by degrading methyl orange (MO) under UV light. The hybrid photocatalysts with ZnO particles decorated on the graphene sheet were found to achieve significant increased photocatalytic activity compared to ZnO with ZnO/rGO10 hybrid photocatalyst achieved fourfold enhancement in rate constant that of ZnO and about 40 % enhancement in the photocatalytic activity for the removal of 10 ppm MO within 3 hours. This was attributed to the presence of graphene that promotes efficient photoinduced charge separation by inhibiting the recombination of electron-hole pairs

and enhanced dye adsorptivity on the catalyst's surface via π-π interaction between MO and graphene sheet with delocalised conjugated π structure. Changes in textural properties and band gap energy of ZnO particles in the hybrid increased the light absorption and stronger adsorption of MO on the surface of the catalyst, thereby increasing its photocatalytic effciency. Increasing the GO content (ZnO/rGO20) however led to a decrement in photocatalytic activity by shielding the active sites on the surface of the catalyst, reducing light absorption.

The MO degradation was at its optimum with 96.78% of 10 ppm MO removed within 3 hours using 0.5 g of ZnO/rGO10 hybrid photocatalyst, obeying the pseudo-first-order kinetics according to the Langmuir-Hinshelwood model. The reusability of the ZnO/rGO10 hybrid photocatalyst was confirmed by retaining 83% of activity after four consecutive cycles.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

SINTESIS DAN PENCIRIAN HIBRID ZnO/rGO FOTOMANGKIN UNTUK DEGRADASI METIL JINGGA

Oleh

MARILYN YUEN SOK WEN

Disember 2017

Pengerusi: Professor Madya Abdul Halim bin Abdullah, PhD
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Sifat rekalsitran dan ketoksikanbahan pencemar organik yang terkandung dalam air sisa telah menyumbang kepada penyelidikan yang menyeluruh terhadap penggunaan foto pemangkinan heterogenous berasaskan semikonduktor, khususnya zink oksida (ZnO). Dalam kajian ini, foto pemangkin hibrid zink oksida/graphene oksida terturun (ZnO / rGO) dengan nisbah isipadu graphene oksida (GO) dan garam zink (0:100, 5:100, 10:100 dan 20:100) yang berbeza telah disediakan melalui kaedah pemendakan dengan menggunakan zink asetat dihidrat, amonium hidroksida dan graphene oksida (1 mg/mL) sebagai bahan pemula diikuti dengan proses reduksi haba. Produk-produk ini dinamakan sebagai ZnO, ZnO/rGO5, ZnO/rGO10 dan ZnO/rGO20.

Sampel-sampel tersebut telah dicirikan dengan menggunakan pembelauan sinar-X (XRD), mikroskopi pengimbasan elektron (FESEM), mikroskopi transmisi elekron (TEM) dan spektroskopi Raman. Luas permukaan dan tenaga jurang jalur fotomangkin telah ditentukan menggunakan kaedah Brunauer-Emmett-Teller (BET) dan analisis spektroskopi UV-sinar nampak. Kemasukan graphene dalam ZnO didapati mengubah ciri-ciri fizikokimia ZnO dengan menurunkan tenaga jurang jalur, mengurangkan saiz zarah dan saiz liang dan meningkatkan luas permukaan spesifik serta isipadu liang.

Prestasi sampel fotopemangkinan kemudiannya disiasat dengan fotodegradasi metil jingga (MO) di bawah sinaran cahaya UV. Pemangkin hibrid ZnO yang diletakkan atas lembaran graphene didapati mencapai aktiviti fotopemangkinan yang ketara berbanding dengan ZnO dengan fotopemangkin hibrid ZnO/rGO10 mencapai pemalar kadar empat kali ganda lebih tinggi daripada ZnO dan peningkatan 40% aktiviti fotopemangkinan dalam degradasi 10 ppm metil jingga dalam masa 3 jam. Ini disebabkan oleh pengenalan graphene yang mempromosikan kecekapan dalam pemisahan fotogenerasi caj dengan menghalang penggabungan semula pasangan elektron-lubang dan mengukuhkan penjerapan bahan pewarna pada permukaan pemangkin melalui interaksi π-π antara MO dan lembaran graphene yang berstruktur

dilokalisasi π. Perubahan tekstur dan tenaga jurang jalur ZnO dalam hibrid meningkatkan penyerapan cahaya dan penjerapan MO yang lebih kuat pada permukaan pemangkin, seterusnya meningkatkan kecekapan fotopemangkinan. Namun, peningkatan dalam kandungan GO (ZnO/rGO20) menyebabkan pengurangan aktiviti fotopemangkinan dengan menghalang tapak aktif pada permukaan pemangkin, mengurangkan penyerapan cahaya.

Degradasi optimum MO telah dicapai dengan 96.78% daripada 10 ppm MO digradasi dalam masa 3 jam dengan menggunakan 0.5 g fotopemangkin hibrid ZnO/rGO10. Fotopemangkinan ini mematuhi kinetik pseudo-tertib-pertama model Langmuir-Hinshelwood. Kadar kitar semula bagi fotopemangkin hibrid ZnO/rGO10 telah disahkan dengan pengekalan 83% aktiviti fotopemangkinan selepas empat kitaran.

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I certify that a Thesis Examination Committee has met on 7 December 2017 to conduct the final examination of Marilyn Yuen Sok Wen on her thesis entitled "Synthesis and Characterization of Zinc Oxide/ Reduced Graphene Oxide Hybrid Photocatalysts for Degradation of Methyl Orange" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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Committee: ______________________

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LIST OF ABBREVIATIONS

AOP	Advanced oxidation process
ZnO/rGO	Zinc Oxide/ Reduced Graphene Oxide Hybrid Photocatalysts
GO	Graphene Oxide
rGO	Reduced Graphene Oxide
MO	Methyl Orange
XRD	X-ray Powder Diffraction
JCPDS	Joint Committee on Powder Diffraction Standards
TEM	Transmission electron microscopy
FESEM	Field Emission Scanning Electron Microscopy
BET	Brunauer-Emmet-Teller Analysis
BJH	Barrett-Joyner-Halender Method
PSA	Particle Size Analysis
FWHM	Full Width at Half Maximum

CHAPTER 1

INTRODUCTION

1.1 Background

Water is a fundamental requirement for life. However, industrialization, urbanization and rapid growth of world population generate large amount of wastewater, causing environmental impact, particularly water pollution. It was reported that most of the natural resources of drinking water are found to be contaminated with diverse toxic materials and pathogenic microorganisms. According to a World Health Organization (WHO) report, water borne diseases kill nearly 12 million people every year (Baruah *et al.*, 2012). Statistic also shows that 700 million people across the globe face water scarcity, and it is estimated that this problem will touch 1.8 billion people by 2025. Hence, it is of utmost importance to maintain the sustainability of water resources.

Effluents discharged from textile industries and other dyeing industries such as cosmetic, leather, pulp and paper and plastic are among the key pollutants of the fresh water system as strong demand of dye in these industries contributes to enormous release of synthetic dyes into wastewater system. Senthilkumar and co-workers reported that a rough estimation of 7×10^5 tons of synthetic dyes and pigments is produced in a year globally (Senthilkumar *et al.*, 2014) but approximately 10-15% of the used dyes is lost during colouration process and is disposed into streams and rivers through waste (Haldorai & Shim, 2014). The World Bank also estimates that almost 10-15% of global industrial water pollution comes from the treatment and dyeing of textiles as the incomplete fixation of dye on textile during dyeing process results in coloured wastewater (Lee *et al.*, 2015b).

The first known use of dye by humans can be traced back to 4000 years ago in the wrappings of mummies in Egyptian tombs (Gordon & Gregory, 2012) where most of the dye was obtained naturally from sources like plants, insects and mollusks. In 1856, the first synthetic dye, mauveine was discovered by Henry Perkin (Venkataraman, 2012). Since then, synthetic dyes have been extensively used in various industries, including pulp and paper, paint, food processing, textile and pharmaceutical. Dyes can be categorized according to their solubility, where acid, mordant, metal complex, direct, basic and reactive dyes are examples of soluble dye while azoic, sulphur, vat and disperse dye are insoluble dyes. However, dyes are commonly classified into azo, anthraquinone, sulphur, indigoid, triphenylmethyl and phthalocyanine, emphasizing on the first two based on the presence of azo linkage and anthraquinone unit in the chemical structure. Azo dyes are normally strong and less expensive whereas anthraquinone dyes are relatively weak and costly (Gupta, 2009). According to Zangeneh and co-workers, more than half of all dyes used in various industries are azo dyes (Zangeneh *et al.*, 2015).

Most of the industrial used synthetic dyes are stable against light, temperature, chemicals and microbial attack (Li *et al.*, 2012). Its toxicity and carcinogenicity make it objectionable to both humans and aquatic lives. It was reported that dyes and pigments found in wastewater can cause skin ulceration, mucous membrane, dermatitis, perforation of nasal septum, severe respiratory tract irritation, haemorrhage and sharp diarrhea to human (Lavanya *et al.*, 2014). The colour pigments discharged into water may also upsets the natural growth cycle and biological metabolism process of aquatic organisms by interfering light penetration and reducing the solubility of gases (Lin *et al.*, 2012; Omar *et al.*, 2014). This would then cause serious impact to the aquatic ecosystem. Further, dyes can sequester metal, causing microtoxicity to fishes (Adegoke & Bello, 2015). As such it is important to treat wastewater containing dyes before it is introduced into water stream.

Over the years, several techniques have been employed on the remediation of coloured effluents. This includes chemical (i.e. electrochemical oxidation (Redha *et al.*, 2017; Singh *et al.*, 2016), ozonation (Manivel *et al.*, 2015), chlorination (de Oliveira *et al.*, 2012)), physical membrane filtration (Abdullah *et al.*, 2009), adsorption (El Haddad *et al.*, 2013), coagulation (Chafi *et al.*, 2011), flocculation, reverse osmosis, ion exchange (Kaith *et al.*, 2015)) and biological processes (Bera *et al.*, 2016). However, these are non-destructive techniques which can cause incompleteness of purification, thus, creating secondary pollution. As a result, expensive operations such as regeneration of adsorbent materials and post treatment of secondary waste are needed (Zangeneh *et al.*, 2015). Other major limitations include high operating cost, low removal efficiency and labour intensive operation (Ferreira *et al.*, 2014; Karthikeyan *et al.*, 2016). The drawbacks of some conventional treatment methods were listed in Table 1.1.

Table 1.1: A review on the drawbacks of conventional treatment methods for removing dyes.

Treatment Method	Drawbacks of treatment method	References
Filtration (microfiltration, ultrafiltration, nanofiltration, reverse osmosis)	Short membrane lifespan, costly membrane, residue (concentrated sludge) need to be further collected.	(Holkar *et al.*, 2016; Yagub *et al.*, 2014)
Coagulating/ flocculating agent ($Al^{3+}, Fe^{3+}, Ca^{2+}$ ions)	Large volume of concentrated sludge produced as final product, high chemical cost, pH dependent.	(Gupta, 2009; Singh *et al.*, 2015)
Oxidation (chlorine, hydrogen peroxide, Fenton reagent, ozonation)	Usage of chlorine gas produced organochlorine compounds, increasing the halogen content in wastewater. Fenton reagent required long reaction time and tight pH working range (pH 2-4). Generally formed sludge.	(Gupta, 2009; Hamoud *et al.*, 2017)
Electrochemical	Expensive energy cost, involve indirect oxidation with chlorinated organic and heavy metals that can cause pollution, sludge generation.	(Gupta, 2009; Saratale *et al.*, 2011)
Biological Treatment	Most dye have low biodegradability, requires long reaction time, production of toxic aromatic amines from the reduction of azo linkage of dye.	(Gupta, 2009; Zangeneh *et al.*, 2015)
Adsorption (activated carbon)	Failed to tolerate suspended solids in the influent stream as clogging occurs. Activated carbon need to be regenerated, adding cost to the process	(Zangeneh *et al.*, 2015)

Advanced oxidation processes (AOP), particularly semiconductor mediated photocatalysis served as a better alternative to the above conventional methods in removing non-biodegradable organic pollutants in water. Generally, photocatalysis involves the formation of strong oxidizing hydroxyl radicals responsible to attack the organic component without selectivity. The organic compound can then be mineralized into carbon dioxide, water and other non-toxic compound, without causing secondary pollution (Atchudan *et al.*, 2016; Moussa *et al.*, 2016). It is also an inexpensive process involving only stable photocatalytic materials and a natural or artificial light source (Gayathri *et al.*, 2014). Other advantages of photocatalysis are environmental and economical friendly (without using hazardous oxidants; e.g. ozone and chlorination), easy to handle and can perform at ambient temperature and pressure (Zangeneh *et al.*, 2015).

The photocatalytic process use in remediation of dye effluents is a heterogeneous process, involving the utilization of solid semiconductors such as titanium dioxide (TiO_2), zinc oxide (ZnO), cadmium sulphide (CdS), iron (III) oxide (Fe_2O_3) and tin dioxide (SnO_2) as they have excellent light absorption properties and charge transport characteristics. Among various semiconductors, zinc oxide has been a good candidate for photocatalytic application owing to its extraordinary properties including excellent optical and electrical properties, non-toxic, low production cost, ease of synthesis, high abundance, chemically stable, high photosensitivity, and most importantly, having a wide band gap (~ 3.37 eV) (Bera *et al.*, 2016; Moussa *et al.*, 2016). Generally, semiconductor photocatalyst with a band gap of approximately 1 to 4 eV is required for effective degradation of pollutants (Ameen *et al.*, 2012).

1.2 Problem Statement

Although ZnO has been reported as a good photocatalyst, its fast recombination of electron-hole pairs reduces its photocatalytic efficiency. To circumvent this limitation, ZnO can be modified by loading noble metals, doping with transition, alkaline and rare earth metal atoms and incorporation of electron accepting materials such as carbon nanotube and graphene based carbon.

Herein, ZnO is hybridised with reduced graphene oxide. Graphene is a two-dimensional (2D) carbon sheet with a single layer of sp^2 network of carbon atom. It has excellent conductivity, good chemical stability, mechanical flexibility, high mobility of charge carriers and high specific surface area (Wang *et al.*, 2012). The electron-acceptor and electron-transport properties of the above carbon based nanostructures help in promoting the migration of photogenerated electrons. This would then prolong the life times of electron-hole pairs thereby improving the photocatalytic efficiency of ZnO.

Methyl orange (MO), a common dyestuff widely used in the fabric industries is used as a model pollutant in this study due to its harmful effect to both human and aquatic life. Its strong absorption range at a wavelength of 380 nm to 750 nm with the maximum absorption at 464.3 nm is suitable to be investigated by photocatalysis under UV irradiation. Methyl orange is an azo compound which bear the functional group R-N=N-R' (Figure 1.1). It forms orange crystals and is commonly used as an acid-base indicator, due to the fact that its anion form is yellow (above pH 4.4) and its acid form is red (below pH 3.1). It has high molecular weight, with stable aromatic and cyclic structure which made it difficult to be removed.

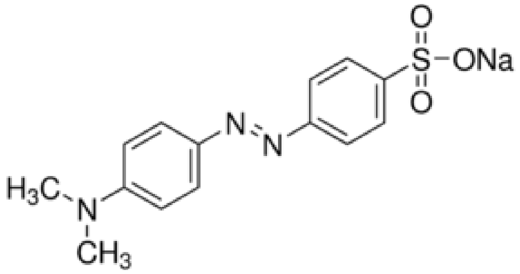

Figure 1.1: Chemical structure of methyl orange.

1.3 Scope of Work

In this study, both ZnO and zinc oxide/reduced graphene oxide (ZnO/rGO) hybrid photocatalysts with varied graphene oxide (GO) to Zn salt volume ratio were prepared using zinc acetate dihydrate and ammonia solution as precursors via precipitation method. The effect of doping reduced graphene oxide (rGO) on the physicochemical properties of ZnO was studied through characterization on the samples. Second, the corresponding photocatalytic efficiency of both ZnO and ZnO/rGO hybrid photocatalysts were compared by degrading MO under UV light. ZnO/rGO hybrid photocatalysts that achieved the best photocatalytic performance was then optimized by different operational parameters, including changing of photocatalyst dosage and changing of initial methyl orange concentration. Lastly, the recyclability and real wastewater removal efficiency of the photocatalyst were determined separately under optimum conditions.

1.4 Objectives

The aim of this study is to improve the photocatalytic efficiency of ZnO photocatalyst in degrading organic pollutant by changing the physicochemical properties of ZnO particles through hybridization with rGO.

The specific objectives of the study are outlined as below:

1. To prepare via precipitation method and characterize ZnO and ZnO/rGO hybrid photocatalysts.
2. To determine the efficiency of the photocatalysts prepared in degrading methyl orange (MO) under UV light.
3. To optimize the photocatalytic activity of the photocatalysts using different parameters.
4. To test the effectiveness of the photocatalysts in real wastewater.

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