University Code: 10384

Student ID No.: 20420151154696

厦门大学

MASTER DEGREE THESIS

Methyl Orange degradation under visible Light over the heterojunction CuO/ZnO MPs prepared with precipitation assisted biosynthesis

By

HASSAN ABDULRAHEEEM MOHAMED MAHMOUD

(Sudan)

Supervisors:

Professor: Qingbiao Li

Assoc. Prof. Jiale HUANG

Major: Chemical Engineering

Date of Graduation: June, 2017

A THESIS SUBMITTED IN FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF ENGINEERING

DEPARTMENT OF CHEMICAL AND BIOCHEMICAL ENGINEERING

COLLEGE OF CHEMISTRY AND CHEMICAL ENGINEERING

厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下,独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果，均在文中以适当方式明确标明，并符合法律规范和《厦门大学研究生学术活动规范（试行）》。

另外，该学位论文为（**李教授教授**）课题（组）的研究成果，获得（**李教授教授**）课题（组）经费或实验室的资助，在（**李教授教授**）实验室完成。（请在以上括号内填写课题或课题组负责人或实验室名称，未有此项声明内容的，可以不作特别声明。）

声明人（签名）：**HASSAN ABDULRAHEEEM MOHAMED**

2017 年 6 月 4 日

厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

（　　）1.经厦门大学保密委员会审查核定的保密学位论文，于　　年　　月　　日解密，解密后适用上述授权。

（ √ ）2.不保密，适用上述授权。

（请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人（签名）：**HASSAN ABDULRAHEEEM MOHAMED**

2017 年 6 月 4 日

ACKNOWLEDGEMENTS

This thesis has been kept on track and been seen through to completion with the support and encouragement of numerous people. At the end I would like to thank all those people who made this thesis possible and an unforgettable experience to me.Truly, words are not enough to express my gratitude to all of them. I acknowledge the blessings of Almighty Allah for giving me the opportunity and strength to advance my academic and professional career in China.

First and foremost, I would like to express my overwhelming gratitude to my supervisor, Prof Qingbiao Li, for giving me the chance of working in his research group – thanks for giving me freedom for developing my research ideas, for showing me different ways to approach a research problem and the need to be persistent to accomplish any goal and for always being there whenever I need your help.

I pay special thanks to Assoc Prof. Huang Jiale for his keen interest, encouragement, and for His advice, excellent cordial relation, and constant intellectual support throughout this work.

I owe my sincere thanks to Dr. Tareque Odoom-Wubah, for his extensive discussions and valuable support during this work, he actually started an excellent work on the synthesis of the ZnO MFs providing the opportunity for me to continue.

I wish to extend my sincere thanks to all lecturers in the College of Chemistry and Chemical Engineering, Xiamen University for the knowledge imparted to me. I believe they are the driving force behind my achievement now and in the future.

I greatly acknowledge the facilities and financial support provided by the Government of the People's Republic of China and China Scholarship Council for giving me the opportunity to advance my studies in Xiamen University, China.

I offer my sincere wishes and thanks to all present and previous members of Professor Qingbiao Li's group for their cooperation and moral support.

I would like to acknowledge all friends, classmates and all students who in diverse ways contributed to the success of this work, especially Mr. Chika Okonkwo (Nigeria) for his great help, patience, and friendly attitude. I cannot forget, Damas (Rwanda) for his encouragement, moral and other support in a variety of ways.

Finally, my deepest debt of gratitude is to my entire family for their love and support. I must appreciate my brothers, my sisters and all my in – laws family for their guidance and encouragement. Most importantly, my father and mother, it was your dream which made my journey up to this possible – all I can say is, this small space is not enough to acknowledge your contributions up to this stage of my life . May Allah bless you all!!!

June, 2017.

ABSTRACT

Research on microstructures has become increasingly popular due to their peculiar physicochemical and catalytic features compared to bulk ones. The damaging effects of carbon-based contaminants particularly dyes have received important attention owing to its influence on human exists and the setting. Photocatalytic degradation of these color contaminants employing semiconductors has been proven as efficient means of eliminating these pollutants. Dissimilar semiconductors have been applied as a photocatalyst to remove these contaminants, amongst these materials; zinc oxide (ZnO) has attracted great attention because of its many superior properties. At room temperature ZnO a part from its wide band gap of 3.34 eV shows a large exciton binding energy of (60 meV) attractive for photocatalytic applications. ZnO due to its wide band hardly undergo degradation under visible light. However, doping with other metals or the formation of a heterojunction could improve its visible light application. Copper oxide (CuO), with a 1.2 eV narrow band gap and a variety of attractive physicochemical characteristic in several domains is reacted with ZnO to form a heterojunction through precipitation assisted biosynthesis method. However, previous works on producing heterojunction (CuO/ZnO) were limited to purely physical and chemical routes. Not only are these methods costly and require multiple reaction paths but they rely solely on the use of chemical substrates and environmentally unfriendly surfactants. Biological routes, on the other hand are classified as environmentally benign routes. Their limitations lie in their inability to effectively control the evolving morphology of nanomaterials. Compared to traditional chemical and physical methods or biological routes of fabricating CuO/ZnO MPs, a combined method founded on the use of plants extracts and some chemical methods have arisen as cost effective method to reach extremely steady and fewer toxic CuO/ZnO MPs at lower pH medium. In this thesis, we report the use of precipitation assisted by *Cinnamomum Campho*ra (*C. camphora*) leaf extract to synthesize CuO/ZnO MPs. The prepared CuO/ZnO MPs are characterized based on morphology, structure and optical properties. And the as-produced heterojunction CuO/ZnO MPs are applied as visible light photocatalyst to degreed methyl orange (MO). The detailed structural, compositional, and optical characterization of the as-produced CuO/ZnO MPs are evaluated by TEM, XRD, FT-IR, EDX, PL and UV Vis spectroscopy. Distinct CuO/ZnO MPs manufactured

by reacting 30 ml of aqueous Cu $(NO_3)_2.3H_2O$ and Zn $(NO_3)_2.6H_2O$ (0.1 M) with *Cinnamomum* camphora leaf extract (0.1 g/mL) at room temperature. Adjusting the pH of the mixture to 6 and annealed at 450 ºC for 4 h. The BET surface area was found 15 m^2/g. XRD analysis confirmed the purity and high crystalline nature of the CuO/ZnO MPs and EDX spectrum verified that pure CuO/ZnO was produced as it showed only peaks of Cu, Zn and O. Moreover, regulating the synthesis limits such as the forerunner concentration, amount of leaf extract, and pH of the reaction solution affected the morphology of the as-formed CuO/ZnO MPs. The analytical application of CuO/ZnO MPs presented outstanding photocatalytic performance for the degradation of methyl orange (MO). A catalyst filling of 0.05 g of CuO/ZnO MPs could degrade MO of initial concentration of 50 mg/L under 50 minutes under visible light irradiation. The obtained results proved that the as-produced heterojunction CuO/ZnO MPs has potential applications as an efficient photocatalyst with excellent efficiency for the photocatalytic assisted degradation of organic pollutants in aqueous solution under visible- light irradiation.

Keywords: Precipitation, assisted biosynthesis, Heterojunction Semiconductors, Photocatalytic degradation, Methyl orange, Microparticles, Visible light irradiation

摘要

与散装材料相比，纳米材料具有独特的物理、化学、视觉和催化性能，使得纳米材料的研究越来越普遍。碳基污染物尤其是染料对人类生存和环境的破坏性影响已受到人们的重视。以半导体为催化剂的光催化降解技术能有效地消除这些颜色污染物。众多的半导体可作为光催化剂来除去这些污染物，在这些材料中，ZnO 由于许多优异的性能引起了人们极大的关注。室温下，ZnO 宽带隙约为 3.34 eV，它的激子束缚能高达 60 meV，这对光催化应用是极其有吸引力的。由于 ZnO 具有较宽的带隙，其在可见光下光催化降解能力较弱。然而，往 ZnO 掺入其他金属元素或构建异质结可以提升其可见光的光催化性能。由于 CuO 具有较窄的带隙 (1.2 eV) 和特殊的物理化学性质，通过沉淀辅助生物合成法使其与 ZnO 形成异质构建具有可见光催化性能的催化剂具有较强的吸引力。此外，CuO/ZnO 复合纳米结构的异质结可能为各种新的应用铺平了道路，具有可观的应用前景。与传统的化学和物理方法制备的 CuO/ZnO 纳米颗粒相比，基于植物提取液和一些化学法组合的合成方法具有成本低廉，且能够在低 pH 介质中合成较稳定、毒性较小的 CuO/ZnO 纳米颗粒。在本文中，我们报道的是使用芳樟提取液沉淀辅助合成 CuO/ZnO 纳米颗粒，并对其形貌、结构及光学性能进行表征。本研究所资本的异质结 CuO/ZnO 纳米颗粒可作为可见光光催化剂应用于甲基橙中。CuO/ZnO 纳米颗粒的形貌结构，成分和光学特性通过 TEM，XRD，FT-IR，EDX，PL 和 UV-vis 等技术进行表征。实验表明，将 30 ml 0.1 M $Cu(NO_3)_2.3H_2O$ 和 $Zn(NO_3)_2.6H_2O$ 的混合物与 0.1 g/mL 芳樟提取液反应，将混合物的 pH 调节到 6，在 450 ºC 退火热处理 4 h，可合成不同的 CuO/ZnO 纳米颗粒。其比表面积为 15 m^2/g。XRD 分析证实了 CuO/ZnO 纳米颗粒的纯度和高结晶性，EDX 表明所制备的催化剂仅含有 Cu，Zn 和 O 的峰，证实合成了纯的 CuO/ZnO 纳米颗粒。此外本研究探讨了制备条件对催化剂催化性能的影响，比如先驱浓度，提取液的量以及影响合成 CuO/ZnO 纳米颗粒形貌的反应溶液的 pH。CuO/ZnO 纳米颗粒光催化性能测试表明，CuO/ZnO 纳米颗粒表现出优异的光催化降解甲基橙的活性。0.05 g CuO/ZnO 纳米颗粒的催化剂在可见光照射下接触 50 min 能够降解初始浓度为 50 mg/L 的甲基橙。因此，CuO/ZnO 纳米颗粒作为一种有效的催化材料，在可见光光催化降解水溶液中的有机污染物具有可观的应用前景。

关键词：沉淀，生物合成辅助，半导体异质结构，光催化降解，甲基橙，纳米颗粒，可见光照射

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES