

Status of thesis

Title of thesis

Development of Cu/TiO₂ Photocatalyst for Hydrogen
Production under Visible Light

I LEONG SIEW YOONG

hereby allow my thesis to be placed at the Information Resource Center (IRC) of
Universiti Teknologi PETRONAS (UTP) with the following conditions:

1. The thesis becomes the properties of UTP.
2. The IRC of UTP may make copies of the thesis for academic purposes only.
3. This thesis is classified as

Confidential

Non-confidential

If this thesis is confidential, please state the reason:

The contents of the thesis will remain confidential for _____ - _____ years.

Remarks on disclosure:

Endorsed by

Signature of Author

7, Persiaran Zarib 5,
Taman Pinji Mewah,
31500, Lahat, Perak

Date :

Signature of Supervisor

Department of Chemical Engineering
Universiti Teknologi PETRONAS
Perak

Date :

UNIVERSITI TEKNOLOGI PETRONAS

Approval by Supervisor (s)

The undersigned certify that they have read, and recommend to The Postgraduate Studies Programme for acceptance, a thesis entitled “**Development of Cu/TiO₂ Photocatalyst for Hydrogen Production under Visible Light**” submitted by **(Leong Siew Yoong)** for the fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

Date

Signature : _____

Main supervisor : _____

Date : _____

UNIVERSITI TEKNOLOGI PETRONAS

Development of Cu/TiO₂ Photocatalyst for Hydrogen Production

under Visible Light

By

Leong Siew Yoong

A THESIS

SUBMITTED TO THE POSTGRADUATE STUDIES PROGRAMME

AS A REQUIREMENT FOR THE

DEGREE OF MASTER OF SCIENCE

CHEMICAL ENGINEERING

BANDAR SERI ISKANDAR,

PERAK

MAY, 2009

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTP or other institutions.

Signature : _____

Name : LEONG SIEW YOONG

Date : _____

Acknowledgement

This dissertation was made possible by the help and support of many people. First of all, I would like to express my sincere gratitude and appreciation to my supervisor, Dr. Chong Fai Kait, for providing me with this unique research opportunity, and for her guidance and support all the way in my two years period of study and preparation of this thesis. Throughout my study and research project, she has constantly given me insightful advice. I have not only learnt from her but have also been inspired by her dedicated attitude to science. It has been a marvelous learning experience.

I would like to acknowledge all the staff members in the Chemical and Mechanical Engineering Department for their contributions to an active academic atmosphere. In addition, this research work was made possible by the generous financial support from the MOSTI (E-Science grant 03-02-02-SF0002).

Lastly, and most importantly, I felt very grateful to my parents for their unending support and love for the pursuit of my MSc. Thank you always for being there to support me.

ABSTRACT

Technologies for generating hydrogen from water using modified photocatalyst have drawn many attentions. In this study the photocatalysts for hydrogen generation were synthesized using two methods; complex-precipitation and wet impregnation method. Cu/TiO₂ with 2, 5, 10 and 15 wt% loading was prepared, dried and prior to calcination, thermal gravimetric analysis was carried out to determine their thermal stability. Based on the thermograms, the calcination temperature was estimated to be 300°C or higher. Therefore, the photocatalysts were calcined at 300°C, 400°C and 500°C for 30 min. The effect of transition metal loading and calcination temperatures on the photocatalytic activity was investigated. Photocatalytic activity was carried out under visible light illumination (500 W halogen lamp as the light source). The screening process is used to monitor the photocatalytic activities for hydrogen production in a multiport reactor containing of photocatalyst, water and methanol (as scavenger). The amount of hydrogen produced decrease as the calcination temperature increases for all the catalysts. The photocatalysts were also characterized using Temperature Programmed Reduction (TPR), Diffuse Reflectance UV-Vis (DR-UV-Vis), Field Emission Scanning Electron Microscope (FE-SEM), Fourier Transform Infrared (FTIR), X-ray Diffractometer (XRD) and surface area determination (BET). The results from TPR and XRD indicated that the only Cu species present was CuO supported on TiO₂. The SEM micrographs showed morphology of the prepared samples with particle size around 20 nm to 100 nm. The effect of transition metal loading was studied and found that incorporating with copper enhance the photocatalytic activity compared to TiO₂. However higher concentration of transition metal loading up to 15 wt% led to the decrement of the photocatalytic activity. The lower photocatalytic activity can be influence by the surface saturation of Cu which minimized the light penetration from reaching to the surface of the TiO₂. The incorporation of Cu transition metal had successfully shifted the TiO₂ band gap to a longer wavelength as evidence by DR-UV-Vis.

ABSTRAK

Teknologi untuk penghasilan hidrogen dari air dengan menggunakan modifikasi fotomangkin telahpun mendapat banyak perhatian. Fotomangkin Cu/TiO₂ yang telah disintesis menggunakan dua teknik iaitu pemendakan-kompleks dan impregnasi basah telah diaplikasikan dalam penyelidikan ini. Cu/TiO₂ dengan kandungan logam sebanyak 2, 5, 10 dan 15 wt% telah disediakan dan dikeringkan. Seterusnya, penentuan suhu penguraian menggunakan TGA yang dilakukan keatas fotomangkin segar sebelum meneruskan proses kalsinasi. Berdasarkan graf penguraian tersebut, suhu minimum bagi kalsinasi ialah 300°C dan ke atas. Seterusnya, fotomangkin dikalsin pada suhu 300°C, 400°C dan 500°C selama 30 min. Kegiatan fotoaktiviti untuk penghasilan hidrogen dijalankan di dalam multiport yang berisi fotomangkin, air dan metanol (sebagai bahan korban) di bawah sinaran lampu halogen 500 W sebagai sumber cahaya untuk semua fotomangkin. Kegiatan fotoaktiviti juga dijalankan tanpa menggunakan metanol sebagai eksperimen terkawal. Berdasarkan keputusan dari pengskrinan, fotoaktiviti optimum adalah bagi fotomangkin 10 wt% bagi kedua-dua kaedah. Pencirian fotomangkin Cu/TiO₂ ini telah dilakukan dengan menggunakan Penurunan Berprogramkan Suhu (TPR), Membaur Refleksi UV-Vis (DR-UV-Vis), Bidang Emisi Pengimbasan Elektron Mikroskop (FE-SEM), Fourier Transformasi Inframerah (FTIR), Pembelauan Sinar-X (XRD), teknik penjerapan fizik (BET) dan Analisa Terma Gravimetrik (TGA). Kesan penambahan kandungan Cu dan peningkatan suhu kalsinasi ke atas kegiatan fotoaktiviti tersebut disiasat. Fotoaktiviti penghasilan hidrogen bagi semua fotomangkin didapati menurun apabila suhu kalsinasi meningkat. Keputusan XRD yang diperolehi menunjukkan kehadiran spesies CuO sahaja. FE-SEM menunjukkan bahawa morfologi untuk butiran sampel adalah dalam julat sekitar 20 nm ke 100 nm. Kesan daripada penambahan Cu yang dikaji dan didapati bahawa aktiviti fotomangkin dipertingkatkan berbanding dengan TiO₂. Namun demikian, kandungan Cu yang berlebihan (15 wt%) mengakibatkan penurunan kegiatan fotomangkin. Penurunan fotoaktiviti disebabkan oleh kepekatan Cu yang terlalu tinggi dan seterusnya mengurangkan penembusan cahaya untuk sampai ke permukaan TiO₂. Penambahan Cu dari unsur peralihan menyebabkan pengurangan “band gap” berbanding dengan TiO₂ (3.2 eV) sepertimana yang telah

dibuktikan oleh DR-UV-Vis dan membolehkan fotomangkin yang telah dimodifikasi ini untuk menyerap lebih banyak cahaya tampak.

TABLE OF CONTENTS

STATUS OF THESIS	i
APPROVAL	ii
TITLE	iii
DECLARATION	iv
ACKNOWLEDGEMENT	v
ABSTRACT	vi
ABSTRAK	vii
TABLE OF CONTENTS	ix
LIST OF TABLES	xii
LIST OF FIGURES	xiii
LIST OF SYMBOLS	xv
LIST OF ABBREVIATIONS	xvi
CHAPTER ONE: INTRODUCTION	1
1.1 Hydrogen Production	1
1.2 Photocatalyst	4
1.3 Titanium Dioxide	6
1.4 Properties of Light	11
1.4.1 UV Light	11
1.4.2 Visible Light	12
1.4.3 Infrared Light	12
1.5 Objectives	13
CHAPTER TWO: LITERATURE REVIEW	14
2.1 Modification of Photocatalyst to Reduce TiO ₂ Band Gap	14
2.1.1 Transition Metal Incorporation	15

2.2	Addition of Sacrificial Reagent to Enhance Photocatalytic Acitivity	20
2.2.1	Addition of Electron Donors	21
2.3	Mechanism of Photocatalytic Water-splitting or Hydrogen Production	23
2.4	Band Gap Determination form Diffuse Reflectance Measurement	24
CHAPTER THREE: METHODOLOGY		26
3.1	Photocatalyst Preparation and Pretreatment	27
3.1.1	Preparation of Cu/TiO ₂ Photocatalyst by Complex-precipitation Method	27
3.1.2	Preparation of Cu/TiO ₂ Photocatalyst by Wet Impregnation Method	28
3.2	Characterization of Photocatalyst	29
3.2.1	Thermal Gravimetric Analysis (TGA)	30
3.2.2	Fourier Transform Infrared (FTIR)	30
3.2.3	Diffuse Reflectance UV-Vis (DRS)	30
3.2.4	Surface Area Determination	31
3.2.5	Field Emission Scanning Electron Microscope (FE-SEM)	31
3.2.6	Temperature Programmed Reduction (TPR)	32
3.2.7	X-ray Diffractometer (XRD)	32
3.3	Photocatalytic Activity	33
CHAPTER FOUR: RESULTS AND DISCUSSION		34
4.1	Activation of Photocatalyst	34
4.1.1	Thermal Gravimetric Analysis (TGA) of Uncalcined Cu/TiO ₂ Photocatalyst	34
4.1.2	Fourier Transform Infrared (FTIR) Spectra of Cu/TiO ₂ Photocatalyst	36

4.2	Photocatalytic Activity for Cu/TiO ₂ Photocatalyst	37
4.3	Photocatalyst Characterization	42
4.3.1	Field Emission Scanning Electron Microscope (FE-SEM) of Cu/TiO ₂ Photocatalyst	42
4.3.2	Surface Area of Cu/TiO ₂ Photocatalyst	44
4.3.3	Diffuse Reflectance UV Visible (DRS) Spectra of Cu/TiO ₂ Photocatalyst	45
4.3.4	Temperature Programmed Reduction (TPR) of Cu/TiO ₂ Photocatalyst	48
4.3.5	X-ray Diffractometer (XRD) of Cu/TiO ₂ Photocatalyst	51
CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS		55
5.1	Conclusion	55
5.2	Recommendations	56
REFERENCES		58
APPENDIX A: Calculation for 0.25 M NaOH		74
APPENDIX B: Calculation for Cu loading on TiO ₂		75
APPENDIX C: EDX Analysis		76
APPENDIX D: BET Results		77
APPENDIX E: XRD spectra results		81
APPENDIX F: Band gap estimation from DR-UV-Vis spectra results		85
APPENDIX G: FTIR spectra results		86

LIST OF TABLES

TABLE NO.	TITLE	PAGE
Table 1.1	Summary of main hydrogen production process	2
Table 1.2	Selected applications of photocatalysis	8
Table 1.3	Characteristic of Degussa P25	10
Table 1.4	Visible light wavelength and perceive colour	13
Table 3.1	List of chemicals used	26
Table 3.2	List of equipments used	27
Table 3.3	Summary of the materials used in Cu/TiO ₂ complex-precipitation	28
Table 3.4	Summary of the materials used in Cu/TiO ₂ wet impregnation	29
Table 4.1	Comparison of H ₂ production with and without methanol as scavenger	39
Table 4.2	Surface area of the photocatalysts	45
Table 4.3	Summary of the band gap energies estimated from UV-Vis data on the prepared samples compared to Degussa P25	48
Table 4.4	Summary of the hydrogen consumption and the reduction temperature of the samples	51
Table 5.1	Summary of the properties for the prepared photocatalyst	56

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
Figure 1.1	Basic principle of overall water splitting on a photocatalyst	3
Figure 1.2	Schematic illustrations of band structures of several semiconductor photocatalysts.	5
Figure 1.3	Crystal structure of TiO ₂ (a) anatase, (b) rutile and (c) brookite	6
Figure 1.4	Light spectrum	12
Figure 2.1	Visible-active photocatalysts obtained by doping to reduce band gap	16
Figure 2.2	Diffuse reflectance UV-Vis spectra of the TiO ₂ photocatalyst implanted with (a) V, (b) Cr, (c) Fe, (d) Ni and (e) Cr prepared by impregnation method	19
Figure 2.3	Schematic diagram for the photocatalytic H ₂ production	24
Figure 3.1	An overview of the characterization of the photocatalyst	29
Figure 3.2	Photocatalytic reaction set up	33
Figure 4.1	Thermal decomposition of uncalcined Cu/TiO ₂ catalyst using complex-precipitation and wet impregnation	35
Figure 4.2	The FTIR spectra of Cu/TiO ₂ catalyst prepared using complex-precipitation and wet impregnation	37
Figure 4.3	Comparisons of the Cu/TiO ₂ photocatalytic activity with various calcination temperatures	38
Figure 4.4	Schematic diagram for the mechanism of photocatalytic H ₂ production	41
Figure 4.5	The FE-SEM micrographs of the Cu/TiO ₂ and TiO ₂ photocatalyst	43
Figure 4.6	The DR-UV-Vis spectra of TiO ₂ and Cu/TiO ₂ prepared using complex-precipitation and wet impregnation methods	47
Figure 4.7	Plot of transformed Kubelka-Munk functions $[F(R).hv]^{1/2}$ vs hv for Cu/TiO ₂ and pure TiO ₂ samples to estimate band gap energies	48

Figure 4.8	TPR profile of 10 wt% copper loading with different calcinations temperature using (a) complex-precipitation and (b) wet impregnation method	50
Figure 4.9	Comparison of XRD diffractograms for (a) TiO ₂ , (b) 10CuGT3_30 and (c) 10CuT3_30.	53

LIST OF SYMBOLS

W	-	Watt
$h\nu$	-	Photon energy
e^-	-	electron
h^+	-	hole

LIST OF ABBREVIATIONS

TPR	-	Temperature Programmed Reduction
FTIR	-	Fourier Transform Infrared
DR-UV-VIS	-	Diffuse Reflectance UV visible
FE-SEM	-	Field Emission Scanning Electron Microscope
XRD	-	X-ray Diffractometer
BET	-	Brunauer-Emmet-Teller
TGA	-	Thermal Gravimetric Analyzer
R&D	-	Research and Development
C.B	-	Conduction band
V.B	-	Valence band
SAA	-	Specific surface area
K	-	Kelvin
nm	-	nanometer
mA	-	mili Ampere
kV	-	kilo Volt
KM	-	Kubelka-Munk