

ห้องสมุดงานวิจัย สำนักงานคณะกรรมการการวิจัยแห่งชาติ



E41070

CHARACTERIZATION OF MOLYBDENUM OXIDE  
NANOSTRUCTURE SYNTHESIZED BY  
HYDROTHERMAL METHOD

HATKAI SINAIME

MASTER OF SCIENCE  
IN CHEMISTRY

THE GRADUATE SCHOOL  
CHIANG MAI UNIVERSITY

MARCH 2011

600253545

ห้องสมุดงานวิจัย สำนักงานคณะกรรมการการวิจัยแห่งชาติ



**CHARACTERIZATION OF MOLYBDENUM OXIDE  
NANOSTRUCTURE SYNTHESIZED BY  
HYDROTHERMAL METHOD**

**HATHAI SINAIM**



**A THESIS SUBMITTED TO THE GRADUATE SCHOOL IN  
PARTIAL FULFILLMENT OF THE REQUIREMENTS  
FOR THE DEGREE OF  
MASTER OF SCIENCE  
IN CHEMISTRY**

**THE GRADUATE SCHOOL  
CHIANG MAI UNIVERSITY  
MARCH 2011**

**CHARACTERIZATION OF MOLYBDENUM OXIDE  
NANOSTRUCTURE SYNTHESIZED BY  
HYDROTHERMAL METHOD**

HATHAI SINAIM

THIS THESIS HAS BEEN APPROVED  
TO BE A PARTIAL FULFILLMENT OF THE REQUIREMENTS  
FOR THE DEGREE OF MASTER OF SCIENCE  
IN CHEMISTRY

**EXAMINING COMMITTEE**

**THESIS ADVISOR**

  
..... CHAIRPERSON  
Dr. Ponlayuth Sooksamiti

  
.....  
Assoc. Prof. Titipun Thongtem

  
..... MEMBER  
Assoc. Prof. Titipun Thongtem

  
..... MEMBER  
Prof. Dr. Somchai Thongtem

6 March 2011

© Copyright by Chiang Mai University

## ACKNOWLEDGEMENTS

I would like to express my sincere thanks and appreciation to Assoc. Prof. Titipun Thongtem, for my great opportunities of her supervision, valuable guidance, and encouragement throughout my study. Special thank to Prof. Dr. Somchai Thongtem and Dr. Ponlayuth Sooksamiti for their strong constructive valuable comments and serve in the examination committee, as well as Dr. Anukorn Phuruangrat for all assistance.

I gratefully acknowledge the Department of Chemistry, Faculty of Science, Chiang Mai University, Thailand for serving all the facilities, knowledge and valuable experience, including the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Graduate School of Chiang Mai University (CMU), and Nanoscience and Nanotechnology Center - CMU, for financial support throughout my study, including Electron Microscopy Research and Service Center - CMU for the electron microscopy analysis.

Finally, I like to give thank Mr. Somkiat Sinaim and Mrs. Hathairat Sinaim - my parents, and Ms. Prang Sinaim - my sister for their love, kindness, support and encourage to me all the time.

Hathai Sinaim

|                       |   |
|-----------------------|---|
| <b>Thesis Title</b>   | Characterization of Molybdenum Oxide<br>Nanostructure Synthesized by Hydrothermal<br>Method |
| <b>Author</b>         | Miss Hathai Sinaim  |
| <b>Degree</b>         | Master of Science (Chemistry)   |
| <b>Thesis Advisor</b> | Assoc. Prof. Titipun Thongtem   |

### ABSTRACT

**E** 41070

Orthorhombic molybdenum oxide ( $\alpha$ -MoO<sub>3</sub>) nanobelts were successfully synthesized by the 100-180 °C and 2-20 h hydrothermal reaction of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O solution containing 15 ml 2 M acid (HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> or HCl) with no surfactant and template adding. These products were characterized by X-ray diffraction, Fourier transform infrared and Raman spectroscopy, and electron microscopy. In the present research, the product synthesized by the 180 °C and 20 h hydrothermal reaction was  $\alpha$ -MoO<sub>3</sub> nanobelts with 10  $\mu$ m long and 200-250 nm wide, 3.75 eV band gap ( $E_g$ ), and the O<sub>2p</sub>→Mo<sub>4d</sub> charge transition at 437 nm. In addition, Ag nanoparticles were successfully composited on  $\alpha$ -MoO<sub>3</sub> nanobelts by sonochemical method of AgNO<sub>3</sub> containing in propylene glycol.

|                             |   |
|-----------------------------|---|
| ชื่อเรื่องวิทยานิพนธ์       | การหาลักษณะเฉพาะของ โครงสร้างนาโนโมลิบดีนัมออกไซด์ที่สังเคราะห์โดยวิธีไฮโดรเทอร์มอล |
| ผู้เขียน                    | นางสาวหทัย สีนอิม   |
| ปริญญา                      | วิทยาศาสตรมหาบัณฑิต (เคมี)  |
| อาจารย์ที่ปรึกษาวิทยานิพนธ์ | รศ. ธิติพันธุ์ ทองเต็ม  |

## บทคัดย่อ

**E 41070**

ได้สังเคราะห์โมลิบดีนัมออกไซด์โครงสร้างแบบอโธโรมบิก ( $\alpha\text{-MoO}_3$ ) สันฐานวิทยาแบบเข็มขนาดนาโนได้โดยปฏิกิริยาไฮโดรเทอร์มอลที่อุณหภูมิ 100-180 องศาเซลเซียสเป็นเวลานาน 2-20 ชั่วโมง ของ  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  ในน้ำ 15 มล ที่มีกรดความเข้มข้น 2 M ( $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  หรือ  $\text{HCl}$ ) ผสมอยู่ด้วย นำผลิตภัณฑ์ที่ได้ไปวิเคราะห์โดยเทคนิค เอกซ์เรย์ดิฟแฟรคชัน ฟลูเรียร์ทรานสฟอร์มอินฟราเรดและรามานสเปกโตรสโคปี และอิเล็กตรอนไมโครสโคปี ในงานวิจัยนี้พบว่าผลผลิตที่ 180 องศาเซลเซียส เป็นเวลา 20 ชั่วโมง เป็น  $\alpha\text{-MoO}_3$  มีสันฐานวิทยาเป็นเข็มขนาดนาโนยาว 10 ไมโครเมตร กว้าง 200-250 นาโนเมตรเมตร มีช่องว่างพลังงาน ( $E_g$ ) เป็น 3.75 eV ที่เกิดการทรานซิชันของประจุไฟฟ้าจาก  $\text{O}_{2p} \rightarrow \text{Mo}_{4d}$  ที่ 437 นาโนเมตร นอกจากนี้ยังได้สังเคราะห์วัสดุผสมโดยให้อนุภาคนาโน Ag เกาะบนโมลิบดีนัมออกไซด์โครงสร้างแบบอโธโรมบิก ( $\alpha\text{-MoO}_3$ ) ที่มีสันฐานวิทยาแบบเข็มขนาดนาโนโดยใช้สารละลายซิลเวอร์ไนเตรตในโพพิลีนไกลคอลโดยวิธีโซโนเคมีคอลได้สำเร็จ

**TABLE OF CONTENTS**

|   | Page |
|---|------|
| ACKNOWLEDGEMENTS                                  | iii  |
| ABSTRACT (ENGLISH)                                | iv   |
| ABSTRACT (THAI)                                   | v    |
| LIST OF TABLES                                    | viii |
| LIST OF FIGURES                                   | ix   |
| ABBREVIATIONS AND SYMBOLS                         | xii  |
| CHAPTER 1 INTRODUCTION                            | 1    |
| 1.1 Molybdenum Oxide (MoO <sub>3</sub> )          | 3    |
| 1.1.1 Physical Properties                         | 3    |
| 1.1.2 Structure                                   | 3    |
| 1.1.3 Application of MoO <sub>3</sub>             | 5    |
| 1.2 Powder Preparation                            | 6    |
| 1.2.1 Hydrothermal method                         | 6    |
| 1.2.2 Sonochemical method                         | 10   |
| 1.3 Ag Composite                                  | 11   |
| 1.4 Polyol Process: Reduction by Propylene Glycol | 12   |
| 1.5 Literature review                             | 13   |
| 1.6 Research objectives                           | 16   |

|  |    |
|--|----|
| CHAPTER 2 EXPERIMENTAL PROCEDURE   | 17 |
| 3.1 Chemical reagents and equipments   | 17 |
| 3.2 Synthesized methods  | 18 |
| 3.3 Characterization   | 23 |
| CHAPTER 3 RESULTS AND DISCUSSION   | 29 |
| 3.1 Molybdenum Oxide synthesized by a Hydrothermal method                                  | 29 |
| 3.2 Silver composite on Molybdenum Oxide nanobelts<br>synthesized by a Sonochemical method | 51 |
| CHAPTER 4 CONCLUSIONS  | 58 |
| REFERENCES   | 60 |
| APPENDICES   | 64 |
| APPENDIX A MoO <sub>3</sub> JCPDS used for the present research                            | 65 |
| APPENDIX B MoO <sub>3</sub> Material Safety Data Sheet                                     | 74 |
| CURRICULUM VITAE   | 79 |

**LIST OF TABLES**

| Table  | Page |
|--|------|
| 2.1 Experimental conditions for synthesizing of MoO <sub>3</sub> .   | 19   |
| 2.2 The gram of AgNO <sub>3</sub> and MoO <sub>3</sub> used for synthesis of Silver composite on Molybdenum Oxide nanobelts. | 21   |
| 3.1 The 1D $\alpha$ -MoO <sub>3</sub> nanostructures synthesized by hydrothermal reaction.                                   | 33   |
| 3.2 Raman vibration modes of $\alpha$ -MoO <sub>3</sub> nanobelts  | 39   |

**LIST OF FIGURES**

| Figure  | Page |
|---|------|
| 1.1 Orthorhombic crystal structure of MoO <sub>3</sub>  | 4    |
| 1.2 Monoclinic crystal structure of MoO <sub>3</sub>  | 4    |
| 1.3 Equipment of hydrothermal method 1) Stainless steel autoclave,<br>2) Precursor solution, 3) Teflon liner, 4) Stainless steel lid, 5) Spring | 7    |
| 1.4 Pressure temperature map of materials processing techniques   | 9    |
| 2.1 Schematic diagram for synthesis procedure of the MoO <sub>3</sub> using<br>Hydrothermal method.   | 20   |
| 2.2 Schematic diagram for synthesis Silver composite on<br>Molybdenum Oxide nanobelts by a Sonochemical method                                  | 22   |
| 2.3 X-ray Diffractometer  | 23   |
| 2.4 Fourier transform infrared spectroscopy   | 24   |
| 2.5 Raman spectroscopy  | 24   |
| 2.6 Scanning electron microscope  | 25   |
| 2.7 Transmission electron microscope  | 26   |
| 2.8 UV-visible spectrophotometer  | 27   |
| 2.9 Luminescence spectrometer   | 28   |
| 3.1 XRD pattern of $\alpha$ -MoO <sub>3</sub> nanostructure synthesized by hydrothermal<br>reaction at 180 °C for 20 h.                         | 29   |
| 3.2 SEM images of $\alpha$ -MoO <sub>3</sub> the low magnification  | 31   |

|   |    |
|---|----|
| 3.3 SEM images of $\alpha$ -MoO <sub>3</sub> the high magnification   | 31 |
| 3.4 TEM image(a), and (b-d) SEAD patterns at the 1, 2 and 3 areas of $\alpha$ -MoO <sub>3</sub> nanobelts.  | 34 |
| 3.5 FTIR spectra of $\alpha$ -MoO <sub>3</sub> nanobelts.   | 36 |
| 3.6 Raman spectra of $\alpha$ -MoO <sub>3</sub> nanobelts.  | 37 |
| 3.7 (a) UV absorbance, and (b) the $(\alpha h\nu)^2$ versus $h\nu$ plot of $\alpha$ -MoO <sub>3</sub> nanobelts.  | 41 |
| 3.8 PL emission of $\alpha$ -MoO <sub>3</sub> nanobelts at room temperature   | 43 |
| 3.9 XRD patterns of $\alpha$ -MoO <sub>3</sub> nanostructures under hydrothermal at (a) 120, (b) 140, (c) 160 and (d) 160 °C, respectively for 20 h.  | 44 |
| 3.10 SEM images of $\alpha$ -MoO <sub>3</sub> nanostructures under hydrothermal at (a) 120, (b) 140, (c) 160 and (d) 180 °C, respectively for 20 h.   | 45 |
| 3.11 XRD patterns of $\alpha$ -MoO <sub>3</sub> nanostructures under hydrothermal at 180 °C for (a) 2, (b) 5 (c) 10 and (d) 20 h, respectively.   | 46 |
| 3.12 SEM images of $\alpha$ -MoO <sub>3</sub> nanostructures under hydrothermal at 180 °C for (a) 2, (b) 5 (c) 10 and (d) 20 h, respectively.   | 47 |
| 3.13 XRD patterns of $\alpha$ -MoO <sub>3</sub> nanostructures under hydrothermal at 180 °C for 20 h using (a) HNO <sub>3</sub> , (c) HCl and (c) H <sub>2</sub> SO <sub>4</sub> , respectively.                    | 49 |
| 3.14 SEM images of $\alpha$ -MoO <sub>3</sub> nanostructures under hydrothermal at 180 °C for 20 h using (a) HCl and (b) H <sub>2</sub> SO <sub>4</sub> .   | 49 |
| 3.15 XRD patterns of $\alpha$ -MoO <sub>3</sub> /Ag composite under ultrasonic irradiation maintained at room temperature for 20 min with the coatings containing (a) 1 at.%, (b) 5 at.% and (c) 10 at.% of silver. | 51 |
| 3.16 SEM images and EDX spectra of $\alpha$ -MoO <sub>3</sub> /Ag composite under   | 53 |

ultrasonic irradiation maintained at room temperature for 20 min with the coatings containing (a) 1 at.%, (b) 5 at.% and (c) 10 at.% of silver.

- 3.17 TEM images of  $\alpha$ -MoO<sub>3</sub>/Ag composite under ultrasonic irradiation 54  
maintained at room temperature for 20 min with the coatings containing (a) 1 at.%, (b) 5 at.% and (c) 10 at.% of silver.
- 3.18 Raman spectra of  $\alpha$ -MoO<sub>3</sub>/Ag composite for the coatings containing 10 at.% of silver. 56
- 3.19 (a) UV absorbance, and (b) the  $(\alpha h\nu)^2$  versus  $h\nu$  plot of  $\alpha$ -MoO<sub>3</sub>/Ag composite for the coatings containing 10 at.% of silver. 57

## ABBREVIATIONS AND SYMBOLS

|       |   |
|-------|---|
| °C    | = degree celcius  |
| nm    | = nanometer   |
| µm    | = Micrometer  |
| mg    | = Milligram   |
| ml    | = Milliliter  |
| EDS   | = Energy Dispersive X-ray Spectroscopy                    |
| FT-IR | = Fourier-Transform Infrared Spectrometry                 |
| PL    | = Photoluminescence Spectrometry                          |
| SEM   | = Scanning Electron Microscopy                            |
| TEM   | = Transmission Electron Microscopy                        |
| XRD   | = X-Ray Diffraction Spectrometer                          |
| JCPDS | = The Joint Committee for Powder<br>Diffraction Standards |