# HYDROGEN PRODUCTION FROM WATER SPLITTING UNDER UV LIGHT IRRADIATION OVER Cu-LOADED MESOPOROUS-ASSEMBLED SrTi<sub>x</sub>Zr<sub>1-x</sub>O<sub>3</sub> AND SrTi<sub>x</sub>Si<sub>1-x</sub>O<sub>3</sub> NANOCRYSTAL PHOTOCATALYSTS



Pusratha Wongchanapai

A Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of Master of Science The Petroleum and Petrochemical College, Chulalongkorn University in Academic Partnership with The University of Michigan, The University of Oklahoma, Case Western Reserve University, and Institut Français du Pétrole 2012

551757

| Thesis Title:    | Hydrogen Production from Water Splitting under UV Light                        |
|------------------|--|
|                  | Irradiation over Cu-Loaded Mesoporous-Assembled                                |
|                  | $SrTi_{x}Zr_{1-x}O_{3}$ and $SrTi_{x}Si_{1-x}O_{3}$ Nanocrystal Photocatalysts |
| By:              | Pusratha Wongchanapai  |
| Program:         | Petrochemical Technology   |
| Thesis Advisors: | Prof. Sumaeth Chavadej   |
|                  | Assoc. Prof. Pramoch Rangsunvigit  |

Accepted by The Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

..... College Dean

è

(Asst. Prof. Pomthong Malakul)

**Thesis Committee:** 

Sumaeth Chuvadoj

(Prof. Sumaeth Chavadej)

Ramol 2

(Assoc. Prof. Pramoch Rangsunvigit)

····· apan

(Assoc. Prof. Apanee Leungnaruemitchai)

\_\_\_\_\_

(Dr. Tarawipa Puangpetch)

#### ABSTRACT

5371035063: Petrochemical Technology Program
Pusratha Wongchanapai: Hydrogen Production from Water Splitting
under UV Light Irradiation over Cu-Loaded Mesoporous-Assembled
SrTi<sub>x</sub>Zr<sub>1-x</sub>O<sub>3</sub> and SrTi<sub>x</sub>Si<sub>1-x</sub>O<sub>3</sub> Nanocrystal Photocatalysts
Thesis Advisors: Prof. Sumaeth Chavadej, and Assoc. Prof. Pramoch
Rangsunvigit 85 pp.
Keywords: Hydrogen production/ Mesoporous material / Perovskite/

Photocatalysis/ Water splitting

Nowadays, the global demand for energy is expected to increase, and the primary source of currently consumed energy is fossil fuels, e.g. petroleum oils, which cause global warming because fossil fuels produce a large amount of CO<sub>2</sub>. So, renewable and environmentally friendly energy resources are desirable and have tendency to increase in the future. Hydrogen has received great attention for use as an alternative and renewable energy source for internal-combustion engines and fuel cells. Photocatalytic water splitting can produce hydrogen by using solar light as an energy source and water as a feedstock. SrTiO<sub>3</sub> is one of the interesting photocatalysts due to its superior physicochemical properties, such as its excellent thermal stability, photocorrosion resistibility, and good structure stability as the host for metal ion doping. The purpose of this work was to optimize the composition of mesoporous-assembled SrTi<sub>x</sub>Zr<sub>1-x</sub>O<sub>3</sub> and SrTi<sub>x</sub>Si<sub>1-x</sub>O<sub>3</sub> nanocrystals, which were synthesized by a sol-gel process with the aid of a structure-directing surfactant for achieving the highest photocatalytic activity for hydrogen production from water splitting under UV light irradiation with methanol as a hole scavenger. The mesoporous-assembled SrTi<sub>0.93</sub>Zr<sub>0.07</sub>O<sub>3</sub> and SrTi<sub>0.95</sub>Si<sub>0.05</sub>O<sub>3</sub> photocatalysts calcined at 700 °C were found to show the better the photocatalytic hydrogen production activity than the other  $SrTi_xZr_{1-x}O_3$  and  $SrTi_xSi_{1-x}O_3$  photocatalysts. Moreover, the Cu loadings by photochemical deposition method were found to greatly enhance the photocatalytic activity of the SrTi<sub>0.93</sub>Zr<sub>0.07</sub>O<sub>3</sub> and SrTi<sub>0.95</sub>Si<sub>0.05</sub>O<sub>3</sub> photocatalysts.

# บทคัดย่อ

ภัสส์รฐา วงศ์ชนะภัย: การผลิตไฮโครเจนจากโมเลกุลของน้ำภายใต้สภาวะที่มีแสงโคย ใช้ตัวเร่งปฏิกิริยาสทอนเทียมไททาเนียมเซอร์โคเนตและสทอนเทียมไททาเนียมซิลิเกตที่มีขนาด อนุภาคผลึกและรูพรุนในระดับนาโนเมตรซึ่งถูกกระตุ้นด้วยคอปเปอร์ (Hydrogen Production from Water Splitting under UV Light Irradiation over Cu-Loaded Mesoporous-Assembled SrTi<sub>x</sub>Zr<sub>1-x</sub>O<sub>3</sub> and SrTi<sub>x</sub>Si<sub>1-x</sub>O<sub>3</sub> Nanocrystal Photocatalysts) อ. ที่ปรึกษา : ศ. คร. สุเมธ ชวเคช และ รศ. คร. ปราโมช รังสรรค์วิจิตร 85 หน้า

ในปัจจุบันความต้องการในการใช้พลังงานเพิ่มมากขึ้น และพลังงานที่สำคัญ คือ เชื้อเพลิงธรรมชาติ ได้แก่ น้ำมันปีโตรเลียมและถ่านหิน ซึ่งเป็นสาเหตุที่ทำให้เกิดภาวะโลกร้อน เพราะเชื้อเพลิงธรรมชาติทำให้เกิดก๊าซการ์บอนไดออกไซด์เป็นจำนวนมาก ไฮโดรเจนได้รับความ สนใจอย่างมากเพื่อใช้เป็นพลังงานทางเลือกใหม่และพลังงานทคแทนสำหรับเครื่องยนต์และเซลล์ เชื้อเพลิง ไฮโครเจนสามารถถูกผลิตได้จากแหล่งพลังงานที่สามารถหาได้อย่างไม่จำกัดได้แก่ น้ำ ้และแสงอาทิตย์ พร้อมกับตัวเร่งปฏิกิริยาแบบใช้แสงร่วมที่เหมาะสมเป็นตัวช่วยให้เกิดปฏิกิริยา ตัว ้เร่งปฏิริยาสทอนเทียมไททาเนตได้รับความสนใจเนื่องจากมีคุณสมบัติทางกายภาพและทางเคมีที่ เหมาะสม เช่น มีความเสถียรต่ออุณหภูมิ, มีด้านทานต่อการกัดกร่อน และมีโครงสร้างที่เสถียร สามารถโด๊ปโลหะอื่นๆ ลงไปได้ ในงานวิจัยนี้มุ่งเน้นศึกษาการปรับปรุงและพัฒนาความสามารถ ในการผลิตไฮโครเจนของตัวเร่งปฏิกิริยาแบบใช้แสงร่วมสตรอนเทียมไททาเนียมเซอร์โคเนตและ ้สตรอนเทียมไททาเนียมซิลิเกตที่มีขนาคอนุภาคผลึกและรูพรุนในระดับนาโนเมตร ในการทคลอง ้นี้ตัวเร่งปฏิกิริยาแบบใช้แสงร่วมถูกสังเคราะห์ขึ้นโดยกระบวนการโซล-เจลร่วมกับการใช้สารลด แรงตึงผิวเป็นตัวกำหนดโครงสร้าง จากผลการทดลองพบว่าตัวเร่งปฏิกิริยาแบบใช้แสงร่วม สตรอนเทียมไททาเนียมเซอร์โคเนตและสทอนเทียมไททาเนียมซิลิเกต ที่ประกอบด้วยอัตราส่วน ของไททาเนียมและเซอร์โคเนียมเท่ากับ 0.93:0.0.7 และอัตราส่วนของไททาเนียมและซิลิกอน เท่ากับ 0.95:0.05 ตามลำดับ ซึ่งถูกเผาที่อุณหภูมิ 700 องศาเซลเซียส ให้ผลในการผลิตไฮโครเจน ดีกว่าตัวเร่งปฏิกิริยาสตรอนเทียมไททาเนียมเซอร์โคเนตและและสทอนเทียมไททาเนียมซิลิเกตตัว ้อื่น การใส่คอปเปอร์แบบใช้แสงร่วมด้วยวิธีการยึดเกาะด้วยกระบวนการเคมีในปริมาณที่เหมาะสม บนตัวเร่งปฏิกิริยาดังกล่าวพบว่า อัตราการการเกิดไฮโดรเจนมีค่าเพิ่มขึ้น

#### ACKNOWLEDGEMENTS

This thesis work is funded by the Petroleum and Petrochemical College, and by the Center of Excellence on Petrochemical and Materials Technology, Thailand.

The author would like to express her sincere gratitude to Prof. Sumaeth Chavadej and Assoc. Prof. Pramoch Rangsunvigit for their invaluable guidance, understanding, and constant encouragement throughout the course of this research.

She would like to express special thanks to Assoc. Prof. Apanee Leungnaruemitchai and Dr. Tarawipa Puangpetch for kindly serving on her thesis committee. Their sincere suggestions are definitely imperative for accomplishing her thesis.

Her gratitude is absolutely extended to all staffs of the Petroleum and Petrochemical College, Chulalongkorn University, for all their kind assistance and cooperation.

Furthermore, she would like to take this important opportunity to thank all of her graduate friends for their unforgettable friendship.

Finally, she really would like to express her sincere gratitude to her parents and family for the love, understanding, and cheering.

### **TABLE OF CONTENTS**

| Title Page            | i   |  |
|-----------------------|-----|--|
| Abstract (in English) | iii |  |
| Abstract (in Thai)    | iv  |  |
| Acknowledgements      | v   |  |
| Table of Contents     | vi  |  |
| List of Tables        | ix  |  |
| List of Figures       | х   |  |
| CHAPTER               |     |  |
| I INTRODUCTION        | 1   |  |

| II | LITERATURE REVIEW                                    | 4  |
|----|--|----|
|    | 2.1 Hydrogen: Fuel of the Future                     | 4  |
|    | 2.2 Water Splitting: Hydrogen Generation Using Solar |    |
|    | Energy   | 5  |
|    | 2.2.1 Photocatalytic Reaction                        | 5  |
|    | 2.2.2 Splitting Water into Hydrogen                  | 7  |
|    | 2.2.3 Efficiency                                     | 9  |
|    | 2.2.4 Semiconductor                                  | 9  |
|    | 2.2.5 Types of Semiconductor Systems Proposed        |    |
|    | for Solar Water Splitting                            | 11 |
|    | 2.2.5.1 Semiconductor Solid State Photovoltaic       |    |
|    | Based Systems  | 11 |
|    | 2.2.5.2 Semiconductor Electrode Systems              | 12 |
|    | 2.2.5.3 Semiconductor Particle Systems               | 13 |
|    | 2.2.6 The Principle of Water Splitting Using         |    |
|    | Semiconductor Particle                               | 14 |
|    | 2.3 Photocatalyst                                    | 16 |

|     | 2.4. Titanium Oxide Photocatalyst                              | 17 |
|-----|--|----|
|     | 2.4.1 General Remarks  | 17 |
|     | 2.4.2 Crystal Structure and Properties                         | 18 |
|     | 2.4.3 Semiconductor Characteristic and                         |    |
|     | Photocatalytic Activity  | 20 |
|     | 2.5 Nano-Photocatalyst   | 22 |
|     | 2.5.1 General Remarks  | 22 |
|     | 2.5.2 Activity of Nano-Photocatalyst                           | 22 |
|     | 2.6 Chemical Additive for Enhancement of Photocatalytic        |    |
|     | H <sub>2</sub> Production                                      | 24 |
|     | 2.7 Metal Loading for Enhancement of H <sub>2</sub> Production | 26 |
|     | 2.8 Mixed Oxide System   | 27 |
|     | 2.9 Porous Material  | 30 |
|     | 2.10 Sol-Gel Process   | 31 |
|     |  |    |
| III | EXPERIMENTAL   | 35 |
|     | 3.1 Materials and equipment                                    | 35 |
|     | 3.1.1 Chemicals  | 35 |
|     | 3.1.2 Equipment  | 35 |
|     | 3.2 Methodology  | 36 |
|     | 3.2.1 Mesoporous-Assembled $SrTi_xZr_{1-x}O_3$ and             |    |
|     | $SrTi_xSi_{1-x}O_3$ Nanocrystal Photocatalyst Synthesis        |    |
|     | by a Sol-Gel Process with the Aid of                           |    |
|     | a Structure-Directing Surfactant                               | 37 |
|     | 3.2.2 Photocatalyst Characterizations                          | 39 |
|     | 3.2.3 Photocatalytic H <sub>2</sub> Production System          | 41 |
| IV  | RESULTS AND DISCUSSION   | 43 |
|     | 4.1 Photocatalyst Characteracterization Results                | 43 |
|     | 4.1.1 TG–DTA Results   | 43 |
|     |  |    |

|   | 4.1.2 N <sub>2</sub> Adsorption-Desorption Results | 47 |
|---|--|----|
|   | 4.1.3 XRD Results                                  | 52 |
|   | 4.1.4 UV-Visible Spectroscopy Results              | 58 |
|   | 4.1.5 SEM-EDX Results                              | 63 |
|   | 4.1.6 TEM-EDX Results                              | 67 |
|   | 4.1.7 Hydrogen Chemisorption Results               | 71 |
|   | 4.2 Photocatalytic Hydrogen Production Activity    | 72 |
|   | 4.2.1 Effect of Ti-to-Zr and Ti-to-Si Molar Ratio  | 72 |
|   | 4.2.2 Effect of Calcination Temperature            | 73 |
|   | 4.2.3 Effect of Cu Loadings                        | 74 |
| v | CONCLUSIONS AND RECOMMENDATIONS                    | 77 |
|   | 5.1 Conclusions                                    | 77 |
|   | 5.2 Recommendations                                | 77 |
|   | REFERENCES   | 78 |

CURRICULUM VITAE 85

### LIST OF TABLES

TABLE

| 2.1 | The band gap positions of some common semiconductor   |    |
|-----|---|----|
|     | photocatalysts  | 11 |
| 2.2 | Definitions about porous solids   | 30 |
| 4.1 | Thermal decomposition behavior results of the dried   |    |
|     | synthesized SrTiO <sub>3</sub> , SrZrO <sub>3</sub> , SrSiO <sub>3</sub> , SrTi <sub>0.93</sub> Zr <sub>0.07</sub> O <sub>3</sub> and |    |
|     | SrTi <sub>0.95</sub> Si <sub>0.05</sub> O <sub>3</sub> photocatalysts from TG–DTA analysis  | 46 |
| 4.2 | N <sub>2</sub> adsorption-desorption results of the synthesized   |    |
|     | mesoporous-assembled $SrTi_xZr_{1-x}O_3$ and $SrTi_xSi_{1-x}O_3$  |    |
|     | photocatalysts  | 51 |
| 4.3 | N <sub>2</sub> adsorption-desorption results of the synthesized Cu-   |    |
|     | loaded mesoporous-assembled $SrTi_{0.93}Zr_{0.07}O_3$ and   |    |
|     | SrTi <sub>0.95</sub> Si <sub>0.05</sub> O <sub>3</sub> photocatalysts   | 52 |
| 4.4 | Summary of XRD analysis of the synthesized mesoporous-  |    |
|     | assembled $SrTi_{0.93}Zr_{0.07}O_3$ and $SrTi_{0.95}Si_{0.05}O_3$ photocatalysts  | 57 |
| 4.5 | Summary of XRD analysis of the synthesized Cu-loaded  |    |
|     | mesoporous-assembled $SrTi_{0.93}Zr_{0.07}O_3$ and $SrTi_{0.95}Si_{0.05}O_3$  |    |
|     | photocatalysts  | 58 |
| 4.6 | Absorption onset wavelength and band gap energy results   |    |
|     | of the synthesized mesoporous-assembled $SrTi_xZr_{1-x}O_3$ ,   |    |
|     | $SrTi_xSi_{1-x}O_3$ photocatalysts without and with Cu loadings   |    |
|     | and calcined at various temperatures  | 62 |
| 4.7 | Cu dispersion results over theCu-loaded mesoporous-assembled  |    |
|     | $SrTi_{0.93}Zr_{0.07}O_3$ , and $SrTi_{0.95}Si_{0.05}O_3$ photocatalysts calcined at 700 °C   | 71 |

## LIST OF FIGURES

FIGURE

| 2.1  | Relative emissions of greenhouse gases (expressed in carbon             |    |
|------|---|----|
|      | units per km) for vehicles powered by today's internal                  |    |
|      | combustion engine using gasoline compared to vehicles                   |    |
|      | powered by fuel cells.  | 5  |
| 2.2  | Types of photocatalytic reactions: (a) photoinduced reaction            |    |
|      | and (b) photon energy conversion reaction.                              | 6  |
| 2.3  | Electrochemical cell, in which a $TiO_2$ electrode is connected         |    |
|      | with a Pt electrode.  | 8  |
| 2.4  | The structure of band gap energy.                                       | 10 |
| 2.5  | Schematic of (a) solid state photovoltaic cell driving a water          |    |
|      | electrolyzer and (b) cell with immersed semiconductor p/n               |    |
|      | junction (or metal/semiconductor Schottky junction) as one              |    |
|      | electrode.  | 12 |
| 2.6  | Schematic of liquid junction semiconductor electrode cell.              | 13 |
| 2.7  | Representation of semiconductor particulate systems for                 |    |
|      | heterogeneous photocatalysis.   | 14 |
| 2.8  | Reaction schematic for water splitting reaction over                    |    |
|      | semiconductor photocatalysts.   | 15 |
| 2.9  | Processes occurring in semiconductor photocatalyst under                |    |
|      | photoexcitation for water splitting reaction.                           | 16 |
| 2.10 | Band gap energy of the photocatalyst.                                   | 17 |
| 2.11 | Crystal structures of (a) anatase, (b) rutile, and (c) brookite.        | 18 |
| 2.12 | Photocatalytic hydrogen production over anatase/rutile $TiO_2$ under    |    |
|      | the mediation of $I^{-}/IO_{3}^{-}$ .                                   | 25 |
| 2.13 | A schematic of forming the BaTiO <sub>3</sub> nanoparticles.            | 33 |
| 3.1  | Synthesis procedure for mesoporous-assembled $SrTi_xZr_{1-x}O_3$ and    |    |
|      | $SrTi_xSi_{1-x}O_3$ photocatalysts: (a) without and (b) with Cu loading |    |
|      | by PCD method.  | 38 |

# FIGURE

| 3.2  | Setup of photocatalytic H <sub>2</sub> production system.   | 42 |
|------|---|----|
| 4.1  | TG-DTA curves of the dried synthesized (a) $SrTiO_3$ ,  |    |
|      | (b) $SrZrO_3$ , (c) $SrSiO_3$ , (d) $SrTi_{0.93}Zr_{0.07}O_3$ and (e) $SrTi_{0.95}Si_{0.05}O_3$   |    |
|      | photocatalysts.   | 44 |
| 4.2  | $N_2$ adsorption-desorption isotherms and pore size distributions   |    |
|      | (inset) of the synthesized (a) $SrTiO_3$ , (b) $SrTi_{0.93}Zr_{0.07}O_3$ ,  |    |
|      | (c) $SrTi_{0.95}Si_{0.05}O_3$ , (d) 0.25 wt.% Cu loaded $SrTi_{0.93}Zr_{0.07}O_3$ ,   |    |
|      | and (e) 0.75 wt.% Cu loaded $SrTi_{0.95}Si_{0.05}O_3$ photocatalysts calcined   |    |
|      | at 700 °C.  | 48 |
| 4.3  | XRD patterns of the synthesized (a) $SrTi_xZr_{1-x}O_3$ and   |    |
|      | (b) SrTi <sub>x</sub> Si <sub>1-x</sub> O <sub>3</sub> photocatalysts calcined at 700 °C for 4 h.   | 54 |
| 4.4  | XRD patterns of the synthesized $SrTi_{0.95}Si_{0.05}O_3$ photocatalysts  |    |
|      | calcined at various temperatures for 4 h.   | 55 |
| 4.5  | XRD patterns of the Cu-loaded synthesized (a) $SrTi_{0.93}Zr_{0.07}O_3$ and   |    |
|      | (b) SrTi <sub>0.95</sub> Si <sub>0.05</sub> O <sub>3</sub> photocatalysts with various Cu loadings calcined                                     |    |
|      | at 700°C for 4 h.   | 56 |
| 4.6  | UV-visible spectra of the synthesized mesoporous-assembled  |    |
|      | photocatalysts calcined at 700 °C: (a) SrTiO <sub>3</sub> and (b)-(f) SrTi <sub>x</sub> Zr <sub>1-x</sub> O <sub>3</sub> .                      | 60 |
| 4.7  | UV-visible spectra of the synthesized mesoporous-assembled  |    |
|      | photocatalysts calcined at 700 °C: (a) $SrTiO_3$ and (b)-(f) $SrTi_xSi_{1-x}O_3$ .  | 60 |
| 4.8  | UV-visible spectra of the synthesized mesoporous-assembled  |    |
|      | SrTi <sub>0.95</sub> Si <sub>0.05</sub> O <sub>3</sub> photocatalysts calcined at various temperatures.   | 61 |
| 4.9  | UV-visible spectra of the synthesized mesoporous-assembled  |    |
|      | photocatalysts calcined at 700 °C: (a) SrTi <sub>0.93</sub> Zr <sub>0.07</sub> O <sub>3</sub> ,   |    |
|      | (b) SrTi <sub>0.95</sub> Si <sub>0.05</sub> O <sub>3</sub> , (c) 1.25 wt.% Cu-loaded SrTi <sub>0.93</sub> Zr <sub>0.07</sub> O <sub>3</sub> ,   |    |
|      | and (d) 0.75 wt.% Cu-loaded SrTi <sub>0.95</sub> Si <sub>0.05</sub> O <sub>3</sub> .  | 61 |
| 4.10 | SEM images of the synthesized mesoporous-assembled photocatalysts   |    |
|      | calcined at 700 °C: (a) SrTi <sub>0.93</sub> Zr <sub>0.07</sub> O <sub>3</sub> , (b) 0.25 wt.% Cu-loaded  |    |
|      | SrTi <sub>0.93</sub> Zr <sub>0.07</sub> O <sub>3</sub> , (c) SrTi <sub>0.95</sub> Si <sub>0.05</sub> O <sub>3</sub> and (d) 0.75 wt.% Cu-loaded |    |
|      | $SrTi_{0.95}Si_{0.05}O_3$ .   | 64 |

## FIGURE

| 4.11 | SEM image and EDX area mappings of the synthesized 0.25 wt.%  |    |
|------|---|----|
|      | Cu-loaded mesoporous-assembled SrTi <sub>0.93</sub> Zr <sub>0.07</sub> O <sub>3</sub> photocatalyst           |    |
|      | calcined at 700 °C.   | 65 |
| 4.12 | SEM image and EDX area mappings of the synthesized 0.75 wt.%  |    |
|      | Cu-loaded mesoporous-assembled SrTi <sub>0.95</sub> Si <sub>0.05</sub> O <sub>3</sub> photocatalyst           |    |
|      | calcined at 700 °C.   | 66 |
| 4.13 | TEM images of the synthesized mesoporous-assembled photocatalysts   |    |
|      | calcined at 700 °C: (a) SrTiO <sub>3</sub> , (b) SrTi <sub>0.93</sub> Zr <sub>0.07</sub> O <sub>3</sub> , and |    |
|      | (c) $SrTi_{0.95}Si_{0.05}O_3$ .   | 68 |
| 4.14 | TEM image and EDX point mapping of the synthesized 0.25 wt.%  |    |
|      | Cu-loaded mesoporous-assembled $SrTi_{0.93}Zr_{0.07}O_3$ photocatalyst  |    |
|      | calcined at 700 °C.   | 69 |
| 4.15 | TEM image and EDX point mapping of the synthesized 0.75 wt.%  |    |
|      | Cu-loaded mesoporous-assembled $SrTi_{0.95}Si_{0.05}O_3$ photocatalyst  |    |
|      | calcined at 700 °C.   | 70 |
| 4.16 | Effect of Ti-to-Zr and Ti-to-Si molar ratio on specific hydrogen  |    |
|      | production rate over the synthesized mesoporous-assembled   |    |
|      | $SrTi_{x}Zr_{1-x}O_{3}$ and $SrTi_{x}Si_{1-x}O_{3}$ photocatalysts calcined at 700 °C.                        | 73 |
| 4.17 | Effect of calcination temperature on specific hydrogen production rate  |    |
|      | over the synthesized mesoporous-assembled $SrTi_{0.95}Si_{0.05}O_3$   |    |
|      | photocatalysts.   | 74 |
| 4.18 | Effect of Cu loading on specific hydrogen production rate over  |    |
|      | the synthesized mesoporous-assembled $SrTi_{0.93}Zr_{0.07}O_3$ and  |    |
|      | SrTi <sub>0.95</sub> Si <sub>0.05</sub> O <sub>3</sub> photocatalysts.  | 76 |