ORGANIC POLLUTANT DEGRADATION AND HYDROGEN PRODUCTION USING $SrTiO_3$ PHOTOCATALYSTS

Tarawipa Puangpetch

A Dissertation Submitted in Partial Fulfilment of the Requirements
for the Degree of Doctor of Philosophy
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
and Case Western Reserve University
2011

Thesis Title: Organic Pollutant Degradation and Hydrogen Production Using $SrTiO_3$ Photocatalysts

By: Tarawipa Puangpetch

Program: Petrochemical Technology

Thesis Advisors: Prof. Sumaeth Chavadej
Prof. Susumu Yoshikawa
Asst. Prof. Thammanoon Sreethawong

Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

..... College Dean
(Asst. Prof. Pomthong Malakul)

Thesis Committee:

(Assoc. Prof. Sujitra Wongkasemjit) (Prof. Sumaeth Chavadej)

(Prof. Susumu Yoshikawa) (Asst. Prof. Thammanoon Sreethawong)

(Assoc. Prof. Pramoch Rangsunvigit) (Dr. Singto Sakulkhaemaruethai)

ABSTRACT

4791004063: Petrochemical Technology Program
Tarawipa Puangpetch: Organic Pollutant Degradation and Hydrogen Production Using $SrTiO_3$ Photocatalysts
Thesis Advisors: Prof. Sumaeth Chavadej, Prof. Susumu Yoshikawa, and Asst. Prof. Thammanoon Sreethawong, 160 pp.
Keywords: $SrTiO_3$/ Mesoporous Assembly/ Metal Loading/ Photocatalyst/ Pollutant Degradation/ Water Splitting/ Hydrogen Production

Pristine and metal-loaded mesoporous-assembled $SrTiO_3$ nanocrystal photocatalysts were successfully synthesized via the single-step sol-gel method with the aid of a structure-directing surfactant. The synthesis method provided the mesoporous-assembled $SrTiO_3$ nanocrystal photocatalysts with high purity, crystallinity, and homogeneity, as well as showed high reliability in photocatalyst reproduction. The synthesized photocatalysts were investigated their photocatalytic activity in both degradation of model organic pollutants and water splitting for hydrogen production with various hole scavengers. The results pointed out that the photocatalyst structure, in the form of a mesoporous assembly of $SrTiO_3$ nanocrystals, was found to be responsible for the enhancement of the photocatalytic activity of the $SrTiO_3$ photocatalysts. Some metals co-catalyst loading was found to enhance the photocatalytic hydrogen production activity of the mesoporous-assembled $SrTiO_3$-based photocatalyst. The enhancement in the photocatalytic hydrogen production activity depended on the electrochemical properties of the loaded metal type and the loading value. The 1 wt.% Au-loaded mesoporous-assembled $SrTiO_3$ photocatalyst was found to be the most effective photocatalyst for the hydrogen production from the photocatalytic water splitting.

บทคัดย่อ

ธรวิภา พวงเพ็ชร : การสลายสารมลพิษอินทรีย์และการผลิตก๊าซไฮโดรเจนด้วยตัวเร่งปฏิกิริยาแบบใช้แสงร่วมสตรอนเทียมไททาเนียมไตรออกไซด์ (Organic Pollutant Degradation and Hydrogen Production Using $SrTiO_3$ Photocatalysts) อ. ที่ปรึกษา: ศ. ดร. สุเมธ ชวเดช ศ. ดร. ซุซุมุ โยชิกาวา และ ผศ. ดร. ธรรมนูญ ศรีทะวงศ์ 160 หน้า

ตัวเร่งปฏิกิริยาแบบใช้แสงร่วมสตรอมเทียมไททาเนียมไตรออกไซด์ที่มีโครงสร้างรูพรุนในระดับเมโซพอร์จากการเกาะตัวกันของผลึกระดับนาโน (mesoporous-assembled $SrTiO_3$ nanocrystal photocatalysts) ทั้งที่ใส่และไม่ใส่โลหะตัวเร่งปฏิกิริยาร่วม สามารถสังเคราะห์ด้วยวิธีโซล-เจล แบบใช้สารลดแรงตึงผิวช่วยในการกำหนดโครงสร้างรูพรุน โลหะตัวเร่งปฏิกิริยาร่วมจะถูกใส่ในขั้นตอนเดียวกับการสังเคราะห์ตัวเร่งปฏิกิริยาสตรอมเทียมไททาเนียมไตรออกไซด์ (single-step sol-gel method with the aid of a structure-directing surfactant) การสังเคราะห์ด้วยวิธีการนี้จะได้ตัวเร่งปฏิกิริยาที่มีค่าความบริสุทธิ์ ความเป็นผลึก และความสม่ำเสมอของเนื้อสาร อยู่ในระดับสูง รวมทั้งให้ความแน่นอนในการสังเคราะห์ซ้ำ ความสามารถในการช่วยเร่งปฏิกิริยาของตัวเร่งปฏิกิริยาที่สังเคราะห์ขึ้นถูกทดสอบด้วยปฏิกิริยาการสลายสารมลพิษอินทรีย์ตัวอย่าง และปฏิกิริยาการแตกตัวของน้ำเพื่อการผลิตก๊าซไฮโดรเจนโดยใช้ตัวเก็บโฮล (hole scavenger) หลายชนิด ผลการทดสอบบ่งชี้ว่า โครงสร้างแบบรูพรุนในระดับเมโซพอจากการเกาะตัวกันของผลึกระดับนาโน สามารถช่วยเพิ่มความสามารถในการช่วยเร่งปฏิกิริยาของตัวเร่งปฏิกิริยาแบบใช้แสงร่วมสตรอมเทียมไททาเนียมไตรออกไซด์สำหรับทั้งสองปฏิกิริยาที่ทดสอบ โลหะตัวเร่งปฏิกิริยาร่วมบางชนิดสามารถช่วยเพิ่มความสามารถในการช่วยเร่งปฏิกิริยาของตัวเร่งปฏิกิริยาแบบใช้แสงร่วมสตรอมเทียมไททาเนียมไตรออกไซด์สำหรับปฏิกิริยาการแตกตัวของน้ำเพื่อการผลิตก๊าซไฮโดรเจน ความสามารถในการช่วยเพิ่มความสามารถในการช่วยเร่งปฏิกิริยาขึ้นกับคุณสมบัติทางไฟฟ้าเคมีของโลหะตัวเร่งปฏิกิริยาร่วม และปริมาณการใส่โลหะตัวเร่งปฏิกิริยาร่วมลงในตัวเร่งปฏิกิริยาแบบใช้แสงร่วมสตรอมเทียมไททาเนียมไตรออกไซด์ ตัวเร่งปฏิกิริยาแบบใช้แสงร่วมสตรอมเทียมไททาเนียมไตรออกไซด์ที่มีโครงสร้างรูพรุนในระดับเมโซพอจากการเกาะตัวกันของผลึกระดับนาโนที่ใส่โลหะทอง 1 เปอร์เซ็นต์โดยน้ำหนักเป็นโลหะตัวเร่งปฏิกิริยาร่วม เป็นตัวเร่งปฏิกิริยาที่มีประสิทธิภาพสูงสุดในการเร่งปฏิกิริยาการแตกตัวของน้ำเพื่อการผลิตก๊าซไฮโดรเจน

ACKNOWLEDGEMENTS

This thesis work is supported by a Project on Faculty Development in Shortage Area Scholarship (Thailand); Thailand Research Fund (TRF) and the Commission on Higher Education (Thailand); the Research Unit of Petrochemical and Environmental Catalysis, Chulalongkorn University (Thailand); the Sustainable Petroleum and Petrochemicals Research Unit, Center for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University (Thailand); and Institute of Advanced Energy, Kyoto University (Japan). This thesis work is partially funded by Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (PPT Consortium).

The author would like to express her sincere gratitude to Prof. Sumaeth Chavadej, Asst. Prof. Thammanoon Sreethawong, and Prof. Susumu Yoshikawa, her advisors, for their invaluable support, encouragement, supervision and useful suggestions throughout this research work. Their support and continuous guidance enabled the author to complete her work successfully.

She would like to express special thanks to Assoc. Prof. Sujitra Wongkasemjit, Assoc. Prof. Pramoch Rangsunvigit, and Dr. Singto Sakulkhaemaruethai for kindly serving on her thesis committee and their valuable suggestions throughout this study.

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

Furthermore, her sincere thanks go to her husband and sons, who shared their love and experiences with her.

Finally, she really would like to express her sincere gratitude to her parents for their love, understanding, and support throughout her life.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	xi
List of Figures	xii

CHAPTER		PAGE
I	**INTRODUCTION**	1
	1.1 Rationale and Problems	1
	1.2 Objectives	3
	1.3 Scope of Research Work	3
	1.4 References	5
II	**THEORETICAL BACKGROUND AND LITERATURE REVIEWS**	9
	2.1 Elementary Processes in Photocatalysis Using Semiconductors	9
	2.2 Photocatalytic Decomposition of Water for Hydrogen Production	12
	2.2.1 Thermochemical Water Splitting With the Sulfur-Iodine Cycle (S-I Cycle)	12
	2.2.2 Direct Water Splitting at High Temperatures Using a Mixed Conducting Membrane	12
	2.2.3 Water Electrolysis	13
	2.2.4 High Temperature Electrolysis or Steam Electrolysis	14
	2.2.5 Steam Reforming	15
	2.2.6 Photocatalytic Decomposition of Water	15

CHAPTER		PAGE
	2.3 Chemical Addition for H_2 Production Enhancement	19
	2.3.1 Hole Scavenger Reagent to Suppress Electron-Hole Recombination	19
	2.3.2 Chemical Additives to Suppress the Backward Reaction of H_2 and O_2	20
	2.4 Photocatalyst Modification for H_2 Production Enhancement	21
	2.4.1 Ion Doping	21
	2.4.1.1 Metal Ion Doping	21
	2.4.1.2 Anion Doping	22
	2.4.2 Metal or Co-Catalyst Loading	23
	2.4.3 Dye Sensitization	25
	2.4.4 Composite Semiconductor Photocatalysts	27
	2.4.5 Structure and Morphology Control of Photocatalysts	29
	2.5 Photocatalytic Degradation of Organic Pollutants	31
	2.6 References	36
III	**EXPERIMENTAL**	44
	3.1 Chemicals	44
	3.2 Photocatalyst Synthesis Methods	45
	3.3 Characterization Techniques	46
	3.4. Photocatalytic Activity Testing	49
	3.4.1 The Photodegradation of Methyl Orange	49
	3.4.2 The Photocatalytic Hydrogen Production	49
	3.5 References	52
IV	**SYNTHESIS AND PHOTOCATALYTIC ACTIVITY IN METHYL ORANGE DEGADRATION OF MESOPOROUS-ASSEMBLED $SrTiO_3$ NANOCRYSTALS PREPARED BY SOL-GEL METHOD WITH THE AID OF STRUCTURE-DIRECTING SURFACTANT**	53
	Abstract	53

CHAPTER		PAGE
	4.1 Introduction	53
	4.2 Experimental	55
	4.2.1 Materials	55
	4.2.2 Synthesis Procedure	56
	4.2.3 Characterization Techniques	56
	4.2.4 Photocatalytic Activity Testing	58
	4.3 Results and Discussion	59
	4.3.1 Effects of Synthesis Conditions	59
	4.3.2 Characterization Results	60
	4.3.3 Photocatalytic Activity Results	74
	4.4 Conclusions	79
	4.5 Acknowledgments	79
	4.6 References	80
V	**HYDROGEN PRODUCTION FROM PHOTOCATALYTIC WATER SPLITTING OVER MESOPOROUS-ASSEMBLED $SrTiO_3$ NANOCRYSTAL-BASED PHOTOCATALYSTS**	82
	Abstract	82
	5.1 Introduction	83
	5.2 Experimental	84
	5.2.1 Materials	84
	5.2.2 Synthesis Procedure of Mesoporous-Assembled $SrTiO_3$ Photocatalysts	85
	5.2.3 Photocatalyst Characterization Techniques	86
	5.2.4 Photocatalytic Water Splitting Experiments	87
	5.3 Results and Discussion	89
	5.3.1 Photocatalyst Characterization Results	89
	5.3.2 Effects of Type and Concentration of Hole Scavenger	95
	5.3.3 Effect of Pt Loading	98

CHAPTER		PAGE
	5.3.4 Effect of MeOH Volume Fraction and Reaction Temperature	100
	5.3.5 Photocatalyst Durability and Reuse	104
	5.4 Conclusions	107
	5.5 Acknowledgments	108
	5.6 References	109
VI	**HYDROGEN PRODUCTION OVER METAL-LOADED MESOPOROUS-ASSEMBLED $SrTiO_3$ NANOCRYSTAL PHOTOCATALYSTS: EFFECTS OF METAL TYPE AND LOADING**	112
	Abstract	112
	6.1 Introduction	112
	6.2 Experimental	114
	6.2.1 Materials	114
	6.2.2 Synthesis procedure of mesoporous-assembled $SrTiO_3$ photocatalysts	115
	6.2.3 Photocatalyst characterization techniques	115
	6.2.4 Photocatalytic hydrogen production system	116
	6.3 Results and discussion	117
	6.3.1 Characterization results	117
	6.3.2 Effect of metal loading on hydrogen production activity of the $SrTiO_3$-based photocatalysts	123
	6.3.3 Effect of photocatalyst dosage	126
	6.3.4 Effect of gas phase-to-liquid phase volumetric ratio	129
	6.4 Conclusions	129
	6.5 Acknowledgments	130
	6.6 References	131

CHAPTER		PAGE
VII	**HYDROGEN PRODUCTION OVER Au-LOADED MESOPOROUS-ASSEMBLED $SrTiO_3$ NANOCRYSTAL PHOTOCATALYST: EFFECTS OF MOLECCULAR STRUCTOR AND CHEMICAL PROPERTIES OF HOLE SCAVENGERS**	136
	Abstract	136
	7.1 Introduction	136
	7.2 Experimental	138
	7.2.1 Materials	133
	7.2.2 Synthesis procedure of photocatalysts	139
	7.2.3 Photocatalyst characterization techniques	139
	7.2.4 Photocatalytic hydrogen production system	140
	7.3 Results and discussion	141
	7.3.1 Photocatalyst characterization results	141
	7.3.2 Photocatalytic hydrogen production results	144
	7.4 Conclusions	150
	7.5 Acknowledgments	151
	7.6 References	152
VIII	**CONCLUSIONS AND RECOMMENDATIONS**	156
	8.1 Conclusions	156
	8.2 Recommendations	157
	CURRICULUM VITAE	**158**

LIST OF TABLES

TABLE		PAGE
2.1	Results of the $SrTiO_3$-based photocatalysts for photocatalytic decomposition of water for hydrogen production	33
2.2	Results of the $SrTiO_3$-based photocatalysts for photocatalytic decomposition of various pollutants	34
4.1	Thermal decomposition behaviors obtained from the TG-DTA analysis of photocatalysts prepared by using different solvents	62
4.2	Band gap wavelength (λ_g), the band gap energy (E_g), and crystallite size of $SrTiO_3$ synthesized by using different surfactants: LAHC, CTAB, and CTAC, commercial $SrTiO_3$ (Wako)	69
4.3	Band gap wavelength (λ_g), the band gap energy (E_g), and crystallite size of $SrTiO_3$ synthesized by using different LAHC-to-TIPT molar ratios: 0.25:1, 0.5:1, 0.75:1, and 1:1, as compared to commercial $SrTiO_3$ (Wako)	72
5.1	Physical and textural properties of all investigated photocatalysts	90
6.1	Textural properties of all studied photocatalysts from XRF, XRD, UV-visible spectroscopy, and N_2 adsorption–desorption analyses	120
7.1	Comparative results of specific H_2 production rate from the photocatalytic water splitting over various $SrTiO_3$-based photocatalysts	149

LIST OF FIGURES

FIGURE		PAGE
2.1	Electron-hole pair generation in a photo-irradiated n-type photocatalyst	9
2.2	The plot between the Kabelka-Munk function ($F(R)$) as a function of wavelength (λ, nm) and the band gap wavelength (λ_g) estimation	10
2.3	The concept of hydrogen production from direct water splitting at high temperatures using a mixed conducting membrane	13
2.4	The Hoffman electrolysis apparatus used in electrolysis of water	14
2.5	Schematic of high temperature electrolysis	15
2.6	Band gap energy of the photocatalyst	17
2.7	Band edge positions of semiconductors as determined in photoelectrochemical experiments with respect to a normal hydrogen electrode (NHE) as reference points, and the standard redox potentials of water in acidic	17
2.8	Mechanism of dye-sensitized photocatalysis under light irradiation	26
2.9	Electron injection in composite semiconductors	27
2.10	Cubic perovskite $SrTiO_3$	30
3.1	Schematic of the synthesis procedure	46
3.2	The plot between the Kabelka-Munk function ($F(R)$) as a function of wavelength (λ, nm) and the band gap wavelength (λ_g) estimation	48
3.3	The photocatalytic hydrogen production system used in this study	50

FIGURE **PAGE**

4.1 TG-DTA curves of the synthesized $SrTiO_3$ samples (zero gels) (LAHC as a structure-directing surfactant and a LAHC-to-TIPT molar ratio of 0.25:1) prepared by using different solvents: (a) EG, (b) EtOH, and (c) an EtOH/EG mixture (EtOH-to-EG volumetric ratio of 0.1:1) 61

4.2 XRD patterns of the synthesized $SrTiO_3$ (a calcination temperature of 700°C, a heating rate of 1°C min^{-1}, and a TIPT-to-LAHC molar ratio of 1:0.25) prepared with different solvents: EtOH, EG, and an EtOH/EG mixture (EtOH-to-EG volumetric ratio of 0.1:1), as compared to the commercial $SrTiO_3$ (Wako) 63

4.3 XRD patterns of the synthesized $SrTiO_3$ (EtOH as a solvent, a calcination temperature of 700°C, a heating rate of 1°C min^{-1}, and a surfactant-to-TIPT molar ratio of 0.25:1) using different surfactants: LAHC, CTAB, and CTAC, as compared to the commercial $SrTiO_3$ (Wako) 64

4.4 XRD patterns of the synthesized $SrTiO_3$ (EtOH as a solvent, a heating rate of 1°C min^{-1}, and a LAHC-to-TIPT of 0.25:1) calcined at different calcination temperatures 65

4.5 N_2 adsorption-desorption isotherms, specific surface area, and pore size distributions of (a) the commercial $SrTiO_3$ (Wako), and the synthesized $SrTiO_3$ (a calcination temperature of 700°C, a heating rate of 1°C min^{-1}, and a LAHC-to-TIPT molar ratio of 0.25:1) using different solvents: (b) EG, (c) EtOH, and (d) an EtOH/EG mixture 66

FIGURE		PAGE
4.6	N_2 adsorption-desorption isotherms, specific surface area, and pore size distributions of (a) the commercial $SrTiO_3$ (Wako), and the synthesized $SrTiO_3$ (EtOH as a solvent, a calcinations temperature of 700°C, a heating rate of 1°C min^{-1}, and a surfactant-to-TIPT molar ratio of 0.25:1) using different surfactants: (b) LAHC, (c) CTAB, and (d) CTAC	67
4.7	The plot between *F(R)* and λ of the $SrTiO_3$ samples (EtOH as a solvent, a calcination temperature of 700°C, a heating rate of 1°C min^{-1}, and a surfactant-to-TIPT molar ratio of 0.25:1) synthesized with different surfactants: LAHC, CTAB, and CTAC, as compared to the commercial $SrTiO_3$ (Wako)	69
4.8	(a) Pore size distribution and (b) specific surface area of the $SrTiO_3$ samples prepared with different LAHC-to-TIPT molar ratios using EtOH as a solvent, 700°C calcination temperature, and 1°C min^{-1} heating rate	71
4.9	Plot between *F(R)* and λ of the $SrTiO_3$ samples (EtOH as a solvent, a calcination temperature of 700°C, and a heating rate of 1°C min^{-1}) prepared with different LAHC-to-TIPT molar ratios, as compared to commercial $SrTiO_3$ (Wako)	72
4.10	TEM images of (a) the commercial $SrTiO_3$ (Wako), and the synthesized $SrTiO_3$ (EtOH as a solvent, a heating rate of 1°C min^{-1}, and a LAHC-to-TIPT molar ratio of 0.25:1) calcined at different calcination temperatures: (b) 600°C, (c) 650°C, and (d) 700°C	74

FIGURE		PAGE
4.11	(a) Time course of the percentage of methyl orange degradation over the synthesized $SrTiO_3$ photocatalysts and (b) the specific surface area and the pseudo-first-rate constant of the synthesized $SrTiO_3$ photocatalysts, as compared to the commercial $SrTiO_3$ (Wako). The synthesized $SrTiO_3$ photocatalysts were prepared under the optimum conditions (EtOH as a solvent, a heating rate of 1°C min^{-1}, and a LAHC-to-TIPT molar ratio of 0.25:1) at different calcination temperatures	76
4.12	(a) Time course of the percentage of methyl orange degradation over the synthesized $SrTiO_3$ photocatalysts and (b) the specific surface area and the pseudo-first-rate constant of the synthesized $SrTiO_3$ photocatalysts, as compared to the commercial $SrTiO_3$ (Wako). The synthesized $SrTiO_3$ photocatalysts were prepared under the optimum conditions (EtOH as a solvent, a calcination temperature of 700°C, and a heating rate of 1°C min^{-1}) at different LAHC-to-TIPT molar ratios	78
5.1	XRD patterns of the $SrTiO_3$ photocatalysts	90
5.2	TEM images of the $SrTiO_3$ photocatalysts: (a) commercial $SrTiO_3$, (b) pristine $SrTiO_3$, (c) 0.5 wt.% Pt-loaded $SrTiO_3$, and HRTEM images of the 0.5 wt.% Pt-loaded $SrTiO_3$ to show (d) d spacing of $SrTiO_3$ (110) and (e) d spacing of Pt^0 (111)	91
5.3	N_2 adsorption-desorption isotherm and pore size distribution (inset) of (a) the pristine mesoporous-assembled $SrTiO_3$ photocatalyst, (b) the 0.5 wt.% Pt-loaded $SrTiO_3$, and (c) the commercial $SrTiO_3$	93

FIGURE **PAGE**

5.4 Aggregated particle size distributions of the commercial $SrTiO_3$ and the mesoporous-assembled $SrTiO_3$ photocatalysts: pristine $SrTiO_3$ and 0.5 wt.% Pt-loaded $SrTiO_3$ 94

5.5 Deconvoluted Pt4f XPS spectra of the 0.5 wt.% Pt-loaded $SrTiO_3$ photocatalyst 94

5.6 Plot of (a) reflectance and (b) F(r) as a function of wavelength of the commercial $SrTiO_3$ and the mesoporous-assembled $SrTiO_3$ photocatalysts: pristine $SrTiO_3$ and 0.5 wt.% Pt-loaded $SrTiO_3$ 95

5.7 Dependence of H_2 production rate over the 0.5 wt.% Pt-loaded $SrTiO_3$ photocatalyst under UV irradiation on type and concentration of hole scavengers (studied conditions: 5 h irradiation time, 500 ml of aqueous solution, 0.5 g of photocatalyst, reaction temperature of 15°C) 96

5.8 Effects of the reactant system, the presence of a photocatalyst, and the reaction temperature on H_2 production (the overall rate of reaction at 5 h, 500 ml of solution, 0.5 g of 0.5 wt. % Pt-loaded $SrTiO_3$ photocatalyst, and UV irradiation). Note: the units of the H_2 production rate is μmol h^{-1} or μmol h^{-1} g_{cat}^{-1} in the case of no photocatalyst addition and in the case of photocatalyst addition, respectively 97

5.9 H_2 production rate under UV and visible light irradiation as a function of Pt loading over the synthesized $SrTiO_3$ (studied conditions: 5 h irradiation time, 500 ml of 50 vol.% MeOH aqueous solution, 0.5 g of photocatalyst, reaction temperatures of 45°C for UV irradiation and 30°C for visible light irradiation) 99

FIGURE **PAGE**

5.10 Dependences of H_2 production rate (a), H_2 production enhancement by MeOH (b), and apparent activation energy ($\hat{E}_a$) of the photocatalytic water splitting reaction (c) on the MeOH concentration and reaction temperature (studied conditions: 5 h irradiation time, 500 ml of solution, 0.5 g of 0.5 wt.% Pt-loaded $SrTiO_3$ photocatalyst, and UV irradiation) 103

5.11 Time course of (a) accumulative H_2 production and (b) instantaneous H_2 production rate over the 0.5 wt.% Pt-loaded $SrTiO_3$ photocatalyst under UV irradiation (studied conditions: 500 ml of 50 vol.% MeOH aqueous solution, 0.5 g of photocatalyst, and a reaction temperature of 45°C) 105

5.12 Time course of H_2 production over the fresh and spent 0.5 wt.% Pt-loaded $SrTiO_3$ photocatalyst under UV irradiation (studied conditions: 500 ml of 50 vol.% MeOH aqueous solution, 0.5 g of photocatalyst, and a reaction temperature of 45°C) 106

6.1 XRD patterns of the pristine and the 0.5 wt.% metal-loaded $SrTiO_3$ photocatalysts 118

6.2 Plot of the Kabelka–Munk function (F(r)) as a function of wavelength of the pristine and the 0.5 wt.% metal-loaded $SrTiO_3$ photocatalysts 121

6.3 N_2 adsorption–desorption isotherms of the pristine and the 0.5 wt.% metal-loaded $SrTiO_3$ photocatalysts: (a) unloaded, (b) Au, (c) Pt, (d) Ni, (e) Ag, (f) Ce, and (g) Fe 122

FIGURE **PAGE**

6.4 Dependence of H_2 production efficiency under (a) UV light irradiation and (b) visible light irradiation on type and quantity of metal loading (system conditions: 5 h irradiation time, 500 (UV) and 200 (visible) cm^3 of a 50 vol.% MeOH aqueous solution, and photocatalyst weight of 0.5(UV) and 0.2 (visible) g) 124

6.5 Dependence of H_2 production efficiency on (a) photocatalyst dosage (system conditions: 5 h irradiation time, 200 cm^3 of a 50 vol.% MeOH aqueous solution, photocatalyst weight of 0.1-1.5 g, 1 wt.% Au-loaded $SrTiO_3$ photocatalyst, and visible light irradiation) and (b) gas phase-to-liquid phase volumetric ratio (system conditions: 5 h irradiation time, 50 vol.% MeOH aqueous solution, photocatalyst dosage of 1×10^{-3} g cm^{-3}, photocatalyst weight of 0.05-0.6 g, 1 wt.% Au-loaded $SrTiO_3$ photocatalyst, and UV light irradiation) 127

7.1 XRD pattern of the 1 wt.% Au-loaded mesoporous-assembled $SrTiO_3$ photocatalyst 142

7.2 TEM image of the 1 wt.% Au-loaded mesoporous-assembled $SrTiO_3$ photocatalyst. 142

7.3 N_2 adsorption–desorption isotherms (a) and pore size distribution (b) of the 1 wt.% Au-loaded mesoporous-assembled $SrTiO_3$ photocatalyst. 143

7.4 Dependence of specific H_2 production rate on type and concentration of the hole scavengers (system conditions: 5 h irradiation time, 200 cm^3 of aqueous hole scavenger solution, 0.2 g of 1 wt.% Au-loaded mesoporous-assembled $SrTiO_3$ photocatalyst, and 45°C reaction temperature) 145

FIGURE **PAGE**

7.5 Dependence of specific H_2 production rate on initial solution pH value of the hole scavenger aqueous solution (system conditions: 5 h irradiation time, 200 cm^3 of aqueous hole scavenger solution, 2.5 vol.% of hole scavenger concentration, 0.2 g of 1 wt.% Au-loaded mesoporous-assembled $SrTiO_3$ photocatalyst, and 45°C reaction temperature) 147