

การสังเคราะห์อนุภาคเงินนาโน โดยรีดักชันด้วยความร้อนของละอองเกลือเงิน

นายวีร์ พัฒนพิรเดช

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาเคมี ภาควิชาเคมี
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2550
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

SYNTHESIS OF SILVER NANOPARTICLES BY THERMAL REDUCTION
OF SPRAYED SILVER SALT

Mr. Wee Patanaperadej

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry

Department of Chemistry

Faculty of Science

Chulalongkorn University

Academic Year 2007

Copyright of Chulalongkorn University

501255

Thesis Title SYNTHESIS OF SILVER NANOPARTICLES BY THERMAL
 REDUCTION OF SPRAYED SILVER SALT

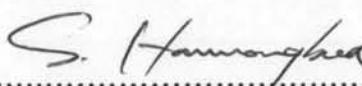
By Mr. Wee Patanaperadej

Field of Study Chemistry

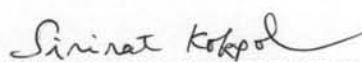
Thesis Advisor Rojrit Rojanathanes, Ph.D.

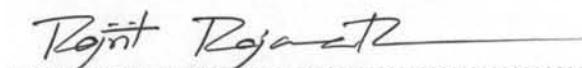
Thesis Co-advisor Associate Professor Sanong Ekgasit, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial
Fulfillment of the Requirements for Master's degree

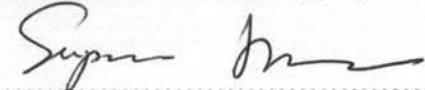
 Dean of the Faculty of Science
(Professor Supot Hannongbua, Ph.D.)

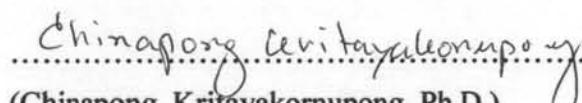
THESIS COMMITTEE

 Chairman
(Associate Professor Sirirat Kokpol, Ph.D.)

 Thesis Advisor
(Rojrit Rojanathanes, Ph.D.)

 Thesis Co-advisor
(Associate Professor Sanong Ekgasit, Ph.D.)

 Member
(Associate Professor Supason Wanichwecharungruang, Ph.D.)

 Member
(Chinapong Kritayakornupong, Ph.D.)

วิธี พัฒนาพิรเดช : การสังเคราะห์อนุภาคเงิน nano โดยการดักชันด้วยความร้อนของละอองเกลือเงิน
 (SYNTHESIS OF SILVER NANOPARTICLES BY THERMAL REDUCTION OF SPRAYED SILVER SALT) อ.ที่ปรึกษา: อ. ดร. ใจน์ฤทธิ์ ใจนันทน์, อ.ที่ปรึกษาร่วม:
 รศ. ดร.สนอง เอกสิทธิ์, 85 หน้า.

การสังเคราะห์อนุภาคเงิน nano โดยการดักชันด้วยความร้อนของละอองเกลือเงิน เป็นวิธีการรีดิวส์เกลือของเงินภายในละอองขนาดเล็ก เปรียบเสมือนเป็นอุปกรณ์ในการเกิดปฏิกิริยาขนาดเล็กระดับไมโครเมตร ทำให้สามารถสังเคราะห์อนุภาคเงิน nano ที่มีขนาดที่แน่นอนได้ สารตั้งต้นคือ ชิลเวอร์ไนเตรท กูลูโคส และสารละลายแอมโมเนียม วิธีการนี้สามารถสังเคราะห์อนุภาคเงิน nano ได้ในปริมาณมาก เนื่องจากเป็นกระบวนการที่สามารถสังเคราะห์ได้อายุต่อเนื่อง การวิเคราะห์ขนาด การกระจายตัวของอนุภาค และรูปร่างของอนุภาคเงิน nano ที่สังเคราะห์ได้โดยใช้ ยูวี-วิสิเบิล สเปกโตรมิเตอร์ และกล้องจุลทรรศน์เล็กตอนแบบทราบมิสชัน ได้ทำการศึกษาปัจจัยต่างๆเพื่อสังเคราะห์อนุภาคเงิน nano ที่มีขนาดเล็ก มีการกระจายตัวที่แนบและมีเสถียรภาพโดยไม่ต้องใช้สารคงสภาพ ซึ่งวิธีการนี้สามารถสังเคราะห์อนุภาคเงิน nano ทางกลมมีขนาดอยู่ในช่วง 10 ถึง 20 นาโนเมตร และมีการกระจายตัวของอนุภาคที่แนบ อนุภาคเงิน nano ที่สังเคราะห์ได้มีเสถียรภาพพอสมควร สามารถเก็บรักษาได้เป็นระยะเวลาประมาณ 1 เดือน โดยขนาดและการกระจายตัวของอนุภาคไม่เปลี่ยนแปลง

ภาควิชา	เคมี	ลายมือชื่อนิสิต	๙๙ พัฒนาใจนันทน์
ปีการศึกษา	2550	ลายมือชื่ออาจารย์ที่ปรึกษา	<i>Ramt Rama</i>

4872473923 : MAJOR CHEMISTRY

KEY WORD: SYNTHESIS/ SILVER NANOPARTICLES/ NEBULIZATION/
GLUCOSE REDUCTION

WEE PATANAPERADEJ: SYNTHESIS OF SILVER NANOPARTICLES BY
THERMAL REDUCTION OF SPRAYED SILVER SALT. THESIS ADVISOR:
ROJRIJ ROJANATHANES, PH.D., THESIS CO-ADVISOR: ASSOC. PROF.
SANONG EKGASIT, PH.D. 85 pp.

Silver nanoparticles were synthesized by thermal reduction of sprayed silver salt. This method is based on the reduction of silver salt in droplet as a micro-reactor that allows the synthesized particles of definite sizes. The precursor was the mixture of water, silver nitrate, glucose (reducing agent) and ammonia solution. This procedure is a continuous process that can be verified for mass scale production. The size, size distribution and morphology of the synthesized silver nanoparticles were characterized by UV-Visible spectroscopy, and transmission electron microscopy (TEM). The composition was varied in order to produce stabilized silver nanoparticles with a narrow size distribution without any stabilizer or capping agent. The results indicated the synthesized silver nanoparticles have spherical shape, small size with diameter of 10-20 nm with a narrow particle size distribution. The synthesized silver nanoparticles were fairly stable for a month without any stabilizer.

Department of study Chemistry

Student's signature Wee Patanaperaduj

Academic year 2007

Advisor's signature Boonit Rojanathane

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my thesis advisor, Dr. Rojrit Rojanathanes and my thesis co-advisor Associate Professor Dr. Sanong Ekgasit, for wholeheartedly provides the useful guidance, understanding, training and teaching the theoretical background and technical skills during my research.

I would like to thank Associate Professor Dr. Sirirat Kokpol, Associate Professor Dr. Supason Wanichwecharungruang, and Dr. Chinapong Kritayakornupong for usefully substantial suggestions as the thesis committee.

Exceptional acknowledgement to Dr. Nattaporn Pimpra of National Nanotechnology Center, Thailand (NANOTEC) for instrumental supported which is very useful in my research.

Gratefully thanks to Associate Professor Chuchaat Thammacharoen and Mr. Tewarak Parnklang for sparing time to read, recommend the wording and examine my thesis.

Warmest thanks to my friend, my colleagues and organization: the Sensor Research Unit (Thailand), Department of Chemistry, Faculty of Science, Chulalongkorn University, and all good friends for the suggestions and spiritual supports through out this research.

Above all, I am profoundly grateful to my parents and endearing family for all their love, understanding, support, and encouragement during the whole period of my study.

CONTENTS

	Page
ABSTRACT IN THAI.....	iv
ABSTRACT IN ENGLISH.....	v
ACKNOWLEDGEMENTS.....	vi
LIST OF FIGURES.....	xi
LIST OF TABLES.....	xvi
LIST OF ABBREVIATIONS.....	xvii
LIST OF SYMBOL.....	xviii
CHAPTER I INTRODUCTION.....	1
1.1 Synthesis of silver nanoparticles.....	1
1.2 The objectives.....	2
1.3 Scopes of research.....	3
CHAPTER II THEORETICAL BACKGROUND.....	4
2.1 Nanochemistry.....	4
2.2 Silver.....	5
2.3 Size effect in nanochemistry.....	7
2.3.1 Physical property: surface area.....	7
2.3.2 Optical property: absorption and scattering of light.....	7
2.3.3 Thermal property: melting point.....	10
2.4 Synthesis of silver nanoparticles.....	11
2.4.1 Chemical methods.....	12
2.4.2 Physical methods.....	20
2.4.3 Stabilizer.....	23

	Page
2.5 Nebulization (atomization)	25
2.5.1 Generation of droplets with jet nebulizer.....	25
2.5.2 Generation of droplets with ultrasonic nebulizer.....	27
2.6 Thermal reduction of sprayed silver salt	28
2.7 Characterization techniques.....	29
2.7.1 UV-Visible spectroscopy.....	29
2.7.2 Transmission electron spectroscopy.....	34
2.8 Antibacterial of silver nanoparticles.....	35
2.9 Effect of silver nanoparticles on human health.....	35
 CHAPTER III EXPERIMENT.....	 37
3.1 Equipment and Apparatus.....	37
3.1.1 Nebulizer.....	37
3.1.2 Heater.....	37
3.1.3 Temperature controller.....	38
3.1.4 Air compressor.....	39
3.2 Chemicals and material.....	39
3.3 Synthesis of silver nanoparticles by chemical reduction method...	40
3.4 Synthesis of silver nanoparticles by thermal reduction of sprayed silver salt.....	40
3.5 Preliminary study on the possibility of characterization technique (UV-Visible spectroscopy).....	43
3.6 Investigation of the various factors affecting the synthesis of silver nanoparticles by thermal reduction of sprayed silver salt.....	43
3.6.1 The concentration of silver nitrate.....	43
3.6.2 The concentration of glucose (reducing agents).....	43
3.6.3 The concentration of ammonia solution.....	43
3.6.4 Temperature in tubular reactor.....	44
3.6.5 Flow-rate in nebulizer.....	44

	Page
3.6.6 Type of carrier gas.....	44
3.7 Comparison of thermal reduction of sprayed silver salt, precursor injection, and precursor heating method.....	44
3.8 Long term stability of synthesized silver nanoparticles.....	45
3.9 Characterization of synthesized silver nanoparticles.....	45
3.9.1 UV-Visible spectroscopy.....	45
3.9.2 Transmission electron microscopy.....	47
CHAPTER IV RESULTS AND DISCUSSION.....	48
4.1 Synthesis of silver nanoparticles by chemical reduction method...	48
4.2 Synthesis of silver nanoparticles by thermal reduction of sprayed silver salt method.....	51
4.3 Preliminary study on the possibility of characterization technique.	54
4.4 Investigation of the various factors affecting the synthesis of silver nanoparticles by thermal reduction of sprayed silver salt method.....	57
4.4.1 The concentration of silver nitrate.....	57
4.4.2 The concentration of glucose (reducing agents).....	62
4.4.3 The concentration of ammonia solution.....	63
4.4.4 Temperature in tubular reactor.....	64
4.4.5 Flow-rate in nebulizer.....	67
4.4.6 Type of carrier gas.....	68
4.4.7 TEM images of synthesized silver nanoparticles by thermal reduction of sprayed silver salt method in optimized condition.....	70
4.5 Comparison of thermal reduction of sprayed silver salt method, precursor injection method, and precursor heating method.....	71
4.6 Long term stability of synthesized silver nanoparticles.....	76

	Page
CHAPTER V CONCLUSION.....	78
REFERENCES.....	80
CURRICULUM VITAE.....	85

LIST OF FIGURES

Figure	Page
2.1 Appearance of silver metal.....	5
2.2 Scheme illustration of electronic states of (A) bulk metal, (B) a large cluster, (C) dimer, and (D) atom	8
2.3 LSPR schematic illustration.....	9
2.4 Schematic illustration for Ag/Au core-shell nanoparticle-based detection probes: (A) without target, (B) with target at room temperature.....	9
2.5 Two approaches for synthesis of silver nanoparticles. A comparison of Top down method and Bottom up method.....	11
2.6 Proposed mechanism for formation of nanoparticles based on reduction, nucleation, and aggregation.....	13
2.7 Proposed model of interaction of citrate ion at the silver nanoparticles surface.....	15
2.8 Apparatus for synthesis of silver nanoparticles by electrochemical...	19
2.9 Schematic diagram for the preparation of silver nanoparticles by inert gas condensation method.....	20
2.10 Experimental set-up for colloid preparation by laser ablation in solution.....	21
2.11 Diagram of experimental apparatus for silver production by spray pyrolysis.....	23
2.12 Sketch of (A) electrostatic stabilization and (B) steric stabilization...	23
2.13 Schematic diagram of Hudson micro mist nebulizer.....	25
2.14 Absorption of a beam of light as it travels through a cuvette (b).....	29

Figure	Page
2.15 Calculated transmittance spectra of spherical silver nanoparticles in glass with increasing particle size at a fixed concentration = 500 $\mu\text{g}/\text{cm}^3$ and a sample thickness of $d = 1 \text{ mm}$. The particle size increases from $a = 10 \text{ nm}$ to $j = 100 \text{ nm}$ in steps of 10 nm.....	31
2.16 (A) Measured optical density (extinction) spectra of aggregated colloidal suspensions of silver nanoparticles with mean size = 27.4 nm and (B) Computed extinction efficiency spectra of a single silver particle (27.4 nm) and of three different aggregates with 5 particles.....	33
2.17 Schematic diagram of Transmission electron microscope (TEM) ...	34
3.1 MICRO MIST small volume (Hudson RCI) jet nebulizer	37
3.2 Microcomputer Based Temperature Indicating Controller FCR-13A	38
3.3 PID tuning.....	38
3.4 PUMA XM-2525.....	39
3.5 Schematic diagram of thermal reduction of sprayed silver salt.....	41
3.6 Apparatus for thermal reduction of sprayed silver salt.....	42
3.7 Ocean Optics Portable UV-Visible spectrometer.....	46
3.8 JEOL JEM-2010 analytical transmission electron microscope.....	47
4.1 UV-Visible extinction spectra of synthesized silver nanoparticles at various reducing agents: (a) ethylene glycol, (b) glycerol, (c) glucose, and (d) citrate.....	49
4.2 Photograph of synthesized silver nanoparticles reduced by various reducing agents: (a) ethylene glycol, (b) glycerol, (c) glucose, and (d) citrate.....	50
4.3 Thermal reduction of sprayed silver salt.....	51
4.4 UV-Visible extinction spectra of synthesized silver nanoparticles: (a) without ammonia solution, (b) with ammonia solution. Normalized spectra are shown in the inset.....	52

Figure	Page
4.5 UV-Visible spectra of synthesized silver nanoparticles measured at the reaction time: (a) 0 min, (b) 10 min., (c) 20 min., (d) 30 min., (e) 40 min., (f) 50 min., (g) 60 min. Normalized spectra are shown in the inset.....	53
4.6 Proposed interaction of carboxyl and the surface of silver nanoparticles.....	54
4.7 UV-Visible extinction spectra of trapping solution (a) and its diluted counterpart (b).....	55
4.8 UV-Visible spectra of (A) synthesized silver nanoparticles and precursor: (B) silver nitrate and glucose, (C) nebulized glucose, (D) glucose, (E) nebulized silver nitrate, (F) silver nitrate.....	56
4.9 UV-Visible extinction spectra of synthesized silver nanoparticles at various concentration of silver nitrate: (a) 0.3 mmol/L, (b) 0.5 mmol/L, (c) 0.7 mmol/L, (d) 1 mmol/L. Normalized spectra are shown in the inset.....	60
4.10 Proposed stabilizing mechanisms of silver nanoparticles.....	60
4.11 UV-Visible extinction spectra of synthesized silver nanoparticles with the silver nitrate concentration of (a) 1.0 mmol/L, and (b) 1.5 mmol/L.....	61
4.12 The UV-Visible extinction spectra of synthesized silver nanoparticles various concentration of glucose: (a) 0.001 mol/L, (b) 0.01 (mol/L), (c) 0.25 mol/L, (d) 0.5 mol/L, and (e) 0.75 mol/L.....	62
4.13 Schematic illustration of thermal reduction of sprayed silver method which have the silver nanoparticles in nebulizer reservoir...	63
4.14 The UV-Visible extinction spectra of synthesized silver nanoparticles varied concentration of ammonia solution: (a) 0.0011 mol/L, (b) 0.0110 mol/L, and (c) 0.1100 mol/L.....	64

Figure	Page
4.15 UV-Visible extinction spectra of synthesized silver nanoparticles of various temperatures in the tubular reactor: (a) 80°C, (b) 100°C, (c) 120°C, (d) 140°C, (e) 160 °C, (f) 180 °C, and (g) 200°C.....	65
4.16 Plot of intensity at absorption maxima (—■—) and peak area (—●—) against temperature.....	66
4.17 The UV-Visible extinction spectra of synthesized silver nanoparticles various flow-rates: (a) 4.5 L/min, (b) 3.5 L/min, and (c) 2.5 L/min.....	67
4.18 UV-Visible extinction spectra of synthesized silver nanoparticles under two different carrier gases: (a) air and (b) N ₂ . Normalized spectra are shown in the inset.....	69
4.19 Schematic illustration of dissolution and re-formation of synthesized silver nanoparticles which result the smaller particles...	70
4.20 TEM images of synthesized silver nanoparticles by thermal reduction of sprayed silver salt under an optimal condition.....	70
4.21 UV-Visible extinction spectra of synthesized silver nanoparticles by various synthesis methods: (a) thermal reduction of sprayed silver salt, (b) precursor injection, and (c) precursor heating method.....	71
4.22 Photograph of synthesized silver nanoparticles by various synthesis methods: (a) thermal reduction of sprayed silver salt, (b) precursor injection, and (c) precursor heating method.....	72
4.23 Schematic illustration of silver nanoparticles synthesis method: thermal reduction of sprayed silver salt, precursor heating method, and precursor injection method (●: silver nanoparticle and  : stabilized silver nanoparticle).....	74
4.24 UV-Visible extinction spectra of synthesized silver nanoparticles which measured as a function of time: (a) after synthesis, (b) two weeks later, (c) one month later, and (d) three months later.....	77

Figure	Page
4.25 Photograph of synthesized silver nanoparticles in water after three months. Red circle show the black powder of silver nanoparticles...	77

LIST OF TABLES

Table	Page
2.1 Classification of particles by their sizes.....	4
2.2 Physical properties of silver	6
2.3 Comparison of synthesis methods for silver nanoparticles.....	24
4.1 Condition in synthesis of silver nanoparticles by chemical reduction method	49
4.2 Theoretical prediction of size of synthesized silver nanoparticles at various in silver nitrate concentration.....	59

LIST OF ABBREVIATIONS

AgNO ₃	: silver nitrate
LSPR	: localized surface plasmon resonance
nm	: nanometer
DNA	: Deoxyribonucleic acid
Ag	: Argentum (silver)
Au	: Aurum (gold)
M	: Metal
PVP	: polyvinylpyrrolidone
SDS	: sodium dodecyl sulfate
FWHM	: Full width at half maxima
TEM	: Transmission electron microscopy
NIR	: near infrared
eV	: electron volt

LIST OF SYMBOL

A	: absorbance
ε	: absorption coefficient
b	: optical path length
c	: concentration
E	: redox potential of particles
E_{redox}	: solution potential
σ_{ext}	: extinction cross-section
σ_{sca}	: scattering cross-section
I_0	: intensity of incident beam
I	: intensity of transmitted beam
$^{\circ}\text{C}$: Celsius
V	: volume
ρ	: density