

FLOW-THROUGH REACTOR FOR PHOTOMEDIATED SYNTHESIS OF SILVER NANOPRISMS



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

Department of Chemistry

FACULTY OF SCIENCE

Chulalongkorn University

Academic Year 2021

Copyright of Chulalongkorn University

เครื่องปฏิกรณ์แบบไหลผ่านสำหรับการสังเคราะห์ที่ใช้แสงเป็นสื่อกลางของปรีซีมีระดับนาโนเมตรของ
โลหะเงิน



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาเคมี ภาควิชาเคมี
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2564
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

Thesis Title FLOW-THROUGH REACTOR FOR PHOTOMEDIATED
 SYNTHESIS OF SILVER NANOPRISMS

By Mr. Thanasit Laisanguangam

Field of Study Chemistry

Thesis Advisor Associate Professor KANET WONGRAVEE, Ph.D.

Accepted by the FACULTY OF SCIENCE, Chulalongkorn University in Partial
Fulfillment of the Requirement for the Master of Science

----- Dean of the FACULTY OF SCIENCE
(Professor POLKIT SANGVANICH, Ph.D.)

THESIS COMMITTEE

----- Chairman
(Professor VUDHICHAJ PARASUK, Ph.D.)

----- Thesis Advisor
(Associate Professor KANET WONGRAVEE, Ph.D.)

----- Examiner
(Associate Professor APICHAJ IMYIM, Ph.D.)

----- External Examiner
(Tewarak Panklang, Ph.D.)

ชนะเลิศ ไหลสงวนงาม : เครื่องปฏิกรณ์แบบไหลผ่านสำหรับการสังเคราะห์ที่ใช้แสงเป็นสื่อกลางของปรีซิมระดับนาโนเมตรของโลหะเงิน. (FLOW-THROUGH REACTOR FOR PHOTOMEDIATED SYNTHESIS OF SILVER NANOPRISMS) อ.ที่ปรึกษาหลัก : รศ. ดร.คณศ วังษ์ระวี

ปรีซิมระดับนาโนเมตรของโลหะเงิน (AgNPrs) ถูกนำไปประยุกต์ใช้อย่างกว้างขวางเนื่องจากมีสมบัติเชิงเคมีและสมบัติเชิงแสงที่โดดเด่น โดยสมบัติที่เป็นเอกลักษณ์ของปรีซิมระดับนาโนเมตรของโลหะเงิน คือมีปรากฏการณ์ทางแสงเฉพาะตัวโลคอลไลซ์เซอร์เฟซพลาสมอนเรโซแนนซ์ (LSPR) ซึ่งการเปลี่ยนแปลง LSPR ของ ปรีซิมระดับนาโนเมตรของโลหะเงินนั้นจะขึ้นอยู่กับขนาดและรูปร่างของอนุภาค นอกจากนี้การเปลี่ยนแปลงดังกล่าวยังสามารถสังเกตได้โดยตรงจากการเปลี่ยนแปลงสีของสารละลายด้วยตาเปล่า ด้วยเหตุนี้ AgNPrs จึงถูกนำมาประยุกต์ใช้เป็นตัวตรวจวัดทางเคมี (chemical sensors) ในหลากหลายด้าน เนื่องจากการเปลี่ยนแปลง LSPR ของปรีซิมระดับนาโนเมตรของโลหะเงินมีความไวในการตรวจสูง (sensitivity) และถูกปรับแต่งให้มีความเฉพาะ (selectivity) ต่อสารเป้าหมายได้ ผู้วิจัยจึงได้เสนอการสังเคราะห์ปรีซิมระดับนาโนเมตรของโลหะเงินโดยการใช้แสง (photochemical technique) กระตุ้นการเปลี่ยนรูปร่างของโลหะเงินจากทรงกลมระดับนาโนเมตรไปเป็นปรีซิมระดับนาโนเมตร ทดสอบโดยใช้แสงสีต่าง ๆ จากไดโอดเปล่งแสง (LEDs) การสังเคราะห์เริ่มต้นด้วยปฏิกิริยารีดักชันของซิลเวอร์ไอออน (Ag^+) และโซเดียมโบโรไฮไดรต์ ($NaBH_4$) ที่ทำหน้าที่เป็นตัวรีดิวซ์ (Reducing agent) เกิดเป็นอนุภาคระดับนาโนเมตรของโลหะเงินที่ถูกทำให้เสถียรด้วยซิเตรต การเปลี่ยนแปลงรูปร่างจะถูกกระตุ้นโดยการใช้แสงนั้นถูกควบคุมให้อยู่ภายใต้บรรยากาศไนโตรเจนเพื่อหลีกเลี่ยงปฏิกิริยาออกซิเดชันของออกซิเจน (O_2) กับโลหะเงิน การกระตุ้นด้วยแสงนั้นจะใช้ไดโอดเปล่งแสง (LED) แบบวงแคบที่ฉายแสงที่ 464 นาโนเมตร (สีน้ำเงิน) 513 นาโนเมตร (สีเขียว) และ 630 นาโนเมตร (สีแดง) พบว่าการเปลี่ยนแปลงรูปร่างจะเกิดขึ้นเมื่อฉายด้วยไดโอดเปล่งแสงที่ 514 นาโนเมตร (พลังงานมากกว่า 2.59 อิเล็กตรอนโวลต์) เท่านั้น ปรีซิมระดับนาโนเมตรของโลหะเงินที่ถูกสังเคราะห์ขึ้นมีสมบัติเชิงแสงแบบเอ้าท์ออฟเพลนควอดรูโพล (out-of-plane quadrupole) และอินเพลนไดโพล (in-plane dipole) นอกจากนี้ยังได้ศึกษาถึงผลกระทบของ pH และอัตราส่วนโมลของตัวทำปฏิกิริยา (Ag^+ , $NaBH_4$, Citrate) พบว่าการเปลี่ยนแปลงรูปร่างของอนุภาคเงินระดับนาโนโดยการฉายด้วยแสงเกิดขึ้นได้เมื่อระบบมีปริมาณ Ag^+ ที่เพียงพอ จากการใช้ระบบที่มีอัตราส่วนโมลของตัวรีดิวซ์ต่ำ ปรีซิมระดับนาโนเมตรของโลหะเงินที่ถูกสังเคราะห์ขึ้นมีเสถียรภาพสูงหลังจากเก็บที่อุณหภูมิ 4 องศาเซลเซียสในระบบปิดเพื่อป้องกันแสงจากภายนอกเป็นเวลาอย่างน้อย 45 วัน เครื่องปฏิกรณ์แบบไหลผ่านสำหรับการสังเคราะห์ที่ใช้แสงเป็นสื่อกลางของปรีซิมระดับนาโนเมตรของโลหะเงินถูกออกแบบและทดสอบการสังเคราะห์ปรีซิมระดับนาโนเมตรของโลหะเงินพบว่าอนุภาคที่ได้จากเครื่องปฏิกรณ์แบบไหลผ่านนั้นมีสมบัติเชิงแสงที่ไม่แตกต่างจากระบบการสังเคราะห์แบบดั้งเดิม

สาขาวิชา เคมี
ปีการศึกษา 2564

ลายมือชื่อนิสิต
ลายมือชื่อ อ.ที่ปรึกษาหลัก

6172130523 : MAJOR CHEMISTRY

KEYWORD: SILVER NANOPRISMS, FLOW-THROUGH REACTOR, PHOTOMEDIATED SYNTHESIS

Thanasit Laisanguangam : FLOW-THROUGH REACTOR FOR PHOTOMEDIATED SYNTHESIS OF SILVER NANOPRISMS. Advisor: Assoc. Prof. KANET WONGRAVEE, Ph.D.

Silver nanoprisms (AgNPrs) have been widely used due to their outstanding optical properties which is one of an important phenomenon that depends on their size, shape, and compositions with characteristic localized surface plasmon resonance (LSPR). The changes in LSPR of AgNPrs can be simply observed by the color changes of the AgNPrs colloidal solution, therefore, the AgNPrs have been mostly used as chemical sensors as they provide high sensitivity and capable to be functionalized to improve the detection selectivity. In this study, we report a photochemical technique to induce the shape conversion of the spherical silver nanoparticle to AgNPrs by light-emitting LED at several wavelengths. The synthesis reaction was simply started with the reduction of a silver ion and sodium borohydride (NaBH_4) as a reducing agent to generate silver nano-seeds stabilized by citrate. The reaction was controlled under a nitrogen atmosphere to avoid the oxidation reaction from oxygen. The reaction was then illuminated with narrowband Light Emitting Diode (LEDs) of 464 nm (blue), 513 nm (green), and 630 nm (red). It was found that the shape evolution was occurred when only LEDs source with 514 nm (> 2.59 eV) was used. The synthesized AgNPrs with out-of-plane quadrupole LSPR and in-plane dipole LSPR were obtained from the green LEDs. Effects of the pH and the mole ratio of the starting reagent (including Ag^+ : TSC: BH_4^-) were investigated. The shape conversion of AgNPs using light irradiation occurred when the system contains adequate amount of Ag^+ (low mole ratio of reducing agent). By monitoring their LSPR, the synthesized AgNPrs show good stability after storing at 4°C in closed vials to prevent the effect of external light for 45 days. Finally, the flow-through reactor for synthesis AgNPrs was designed and operated to synthesize the AgNPrs. It was found that the product (AgNPrs) from batch synthesis and flow reactor are similar by monitoring their LSPR.

Field of Study: Chemistry

Student's Signature

Academic Year: 2021

Advisor's Signature

ACKNOWLEDGEMENTS

I would like to express sincere gratitude to my thesis advisor, Associate Professor Dr. Kanet Wongravee for his kind and endure to my mistakes. He also provides useful guidance, understanding, training, and teaching the theoretical background and technical skills during my research.

I would like to thank Professor Dr. Vudhichai Parasuk, Associate Professor Apichat Imyim, and Dr. Tewarak Parnklang for usefully substantial suggestions as the thesis committee.

Warmest thanks to my friends, my colleagues and organization : Sensor Research Unit (SRU), Department of Chemistry, Faculty of science, Chulalongkorn University, and all good friends for the suggestions and spiritual supports throughout this research

I would like to thank the National Nanotechnology Center (NANOTEC) and the Department of Chemistry for their financial support.

Whatever shortcomings in the thesis remain, they are the sole responsibility of the author

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.

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

Thanasit Laisanguanngam

TABLE OF CONTENTS

	Page
.....	iii
ABSTRACT (THAI)	iii
.....	iv
ABSTRACT (ENGLISH)	iv
ACKNOWLEDGEMENTS	v
TABLE OF CONTENTS	vi
LIST OF TABLES	ix
LIST OF FIGURES.....	x
Chapter 1 Introduction	1
1.1 Silver nanostructure.....	1
1.1.1 Characteristics of silver nanoprisms	3
1.2 Fabrication of silver nanoprisms.....	6
1.2.1 Synthesis of AgNPs by chemical reaction.....	6
1.2.2 Nanosphere lithography.....	10
1.2.3 photo-mediated method.....	11
1.3 Objectives.....	17
1.4 Scope of the study	17
Chapter 2 Experimental	18
2.1.Chemicals and materials.....	18
2.2 LED.....	18
2.3 Synthesis of silver nanoprisms method under slow reduction of silver seeds ..	19

2.3.1 Preparation of silver seed under cold condition.....	19
2.3.2 Shape evolution to silver nanoprisms under LED illumination	20
2.4 Synthesis of silver nanoprisms method under normal reduction	21
2.4.1 Preparation of silver seed.....	21
2.4.2 Shape evolution to Silver nanoprisms under LED illumination.....	22
2.5 Flow-through reactor.....	22
2.5.1 Design of flow reactor	22
2.5.2 Synthesis silver nanoprisms by flow-through reactor.....	23
2.6 Characterization	24
2.6.1 UV-visible spectroscopy.....	24
2.6.2 Transmission electron microscopy.....	24
Chapter 3 Results and Discussion.....	26
3.1 Shape evolution of silver nanoprisms under slow reduction of AgNPs	26
3.1.1 Shape evolution of AgNPrs using the couple LEDs.....	30
3.1.2 Stability of the synthesized AgNPrs.....	32
3.2 Synthesis of silver nanoprisms method under normal reduction of AgNPs.....	34
3.2.1 Stability of the synthesized AgNPrs.....	38
3.2.2 Influences of synthesis parameters on the shape evolution of AgNPrs	39
3.2.3 Effects of residual silver ion concentration.....	45
3.3 Synthesis silver nanoprisms by flow-through reactor	47
Chapter 4 Conclusions.....	50
REFERENCES.....	53
VITA	58

LIST OF TABLES

	Page
Table 1.1 reducing agent, stabilizer, and TEM images of products from various chemical reduction method	9
Table 1.2 reducing agent, stabilizer, and TEM images of products from various photo-mediated method.....	16



LIST OF FIGURES

	Page
Figure 1.1 Schematic for low-dimensional nanostructure classification: zero dimension (0D), one dimension (1D), two dimension (2D), and three dimension (3D). The material includes examples for each dimension. [5]	3
Figure 1.2 The coupling phenomena between electromagnetic field and collective electron oscillation on the surface of metallic nanoparticle. [4]	4
Figure 1.3 The resonant plasmon modes involved in metal nanoplates are illustrated schematically. In (A) and (B), the dipolar in-plane and out-of-plane modes are depicted, respectively. In (C) and (D), the corresponding in-plane and out-of-plane quadrupolar modes are depicted. (E) type of facets on silver nano prisms	5
Figure 1.4 Simulations of the orientation averaged extinction effectiveness of perfect triangular nanoprisms using the discrete dipole approximation (DDA).	5
Figure 1.5 Pictures of silver sphere dispersions (yellow) and nanoplates; and b) UV-vis-NIR spectra of silver nanoprisms samples. Particle edge lengths increase from left to right in both cases.	6
Figure 1.6 Schematic illustration (A) colloidal crystal mask for synthesis by NSL (B) AgNPrs was synthesized by NLS. [23]	11
Figure 1.7 The growth mechanism in photomediated production of silver nanodecahedra and nanoprisms is depicted schematically. [13]	15
Figure 2.1 (A) experimental set up for measuring emission spectra of LEDs. (B) UV-Vis spectra of emission band (C) Emission energy of LEDs from Blue (464 nm), Green (514 nm), Red (630 nm), Pink (445nm, 635nm), and Daylight (445nm, 542nm) LED light source	19
Figure 2.2 Experiment setup for (A) silver seed preparation in cold temperature and (B) seed mediated growth using slow reduction.....	21
Figure 2.3 Experiment setup for silver seed preparation and photomediated growth under normal reduction.....	22
Figure 2.4 the design of the flow-through reactor	23

Figure 2.5 Flow-through reactor set up for silver seed preparation and synthesis AgNPrs by flow-through reactor	23
Figure 3.1 (A) UV-Vis spectra of emission band from Blue (464 nm), Green (514 nm), and Red (630 nm) LED light source (B) experimental set up for measuring emission spectra of LEDs.....	26
Figure 3.2 (A) show UV-Visible spectra of silver nanoparticles after illuminating with red LED (630 nm) and the color of solution at various illumination times (B) the λ_{\max} at various illumination times from 2-8 hours (C) TEM image of silver nanoparticle after illuminating with red LED for 8 Hours.....	27
Figure 3.3 (A) show UV-Visible spectra of silver nanoparticles after illuminate with green LED (514 nm) and color of solution at various illumination times (B) show trend of λ_{\max} of in-plane dipole LSPR at various illumination times (C) TEM image of silver nanoparticle after illuminating with green LED for 8 Hours.....	29
Figure 3.4 (A) show UV-Visible spectra of silver nanoparticles after illuminate with blue LED (464nm) and the color of solution at various illumination times (B) show trend of λ_{\max} of in-plane dipole LSPR at various illumination times (C) TEM image of silver nanoparticle after illuminating with blue LED for 8 Hours.....	30
Figure 3.5 (A) shows UV-Visible spectra of silver nanoparticles after illuminating with blue LED (464nm) (B) comparison of UV-Vis spectrum of silver nanoparticles that synthesized from daylight blue and green LED. UV-Vis spectrum of LED (C) Green and blue (D) daylight.....	31
Figure 3.6 (A) Shown All color of the LEDs from EVE in market (B) UV-Vis spectra of emission band (C) Emission energy of LEDs from Blue (464 nm), Green (514 nm), Red (630 nm), yellow(597nm), Pink (445nm, 635nm), and Daylight (445nm, 5642nm) LED light source.....	32
Figure 3.7 UV-vis spectra of the freshly prepared AgNPrs (gray spectrum) and the AgNPrs after kept at 4°C in dark container for 15 days	33
Figure 3.8 (A) UV-vis spectra of AgNPs after illumination with red LED (630 nm) with the inset Figures of the solution color at various times (0 – 10 hours). (B) plot of extinction λ_{\max} after illumination with red LED (C) TEM image of AgNPs after illumination with red LED for 10 hours.	35

Figure 3.9 (A)UV-vis spectrum of AgNPs after illumination with green LED (514 nm) and solution color at various times. (B) plot of λ_{\max} of out of plane quadrupole LSPR and extinction and (C) plot of λ_{\max} of in plane dipole LSPR and extinction after illumination with green LED at various times (D) TEM image of AgNPs after illumination with blue LED for 10 hours.....36

Figure 3.10 (A)UV-vis spectra of AgNPs after illumination with blue LED (464nm) and solution color at various times. (B) plot of λ_{\max} of out of plane quadrupole LSPR extinction and (C) plot of λ_{\max} of in plane dipole LSPR extinction after illumination with blue LED at various times (D) TEM image of AgNPs after illumination with blue LED for 10 hours.....38

Figure 3.11 (A) UV-vis spectrum of synthesized AgNPs were kept at 4°C at various times (B) plot of λ_{\max} extinction (C) the color of colloidal AgNPs were kept at various of time from 0-45 day.....39

Figure 3.12 Spectra of colloidal silver nanoparticles from various Ag^+ : citrate: NaBH_4 at 1:10:0.001 to 1:10:2 ratio (various only mole ratio of NaBH_4) before (A1) pH=7 (B1) pH=9 and after illuminated with green LEDs (514 nm) for 8 hours at (A2) pH=7 (B2) pH=9.....41

Figure 3.13 UV-Vis spectrum and Color of colloidal AgNPs at Ag^+ : Citrate : BH_4^- = (A) 1:10:0.001 at pH = 9 (B) 1:10:0.001 at pH = 9 after illumination with green LEDs (514 nm) at various times with TEM image for silver nano particles after illumination for 8 and 31 hours respectively.43

Figure 3.14 UV-Vis spectrum and Color of colloidal AgNPs at Ag^+ : Citrate : BH_4^- = (A) 1:10:0.001 at pH = 7 after illumination with green LEDs (514 nm) at various times with TEM image for silver nano particles after illumination for 8 hours.....45

Figure 3.15 (A) Experiment set up for spite test (B) show UV-Visible spectra of silver nanoparticles after spite with seed solution/ Ag^+ solution and illuminate with green (514 nm).....46

Figure 3.16 Comparison of temperature in reactor between fan turn on and turn off every 30 min.48

Figure 3.17 UV-Visible spectra of silver nanoparticles (Ag^+ : Citrate : BH_4^- = 1:10:0.001, pH 7) after illuminating with green LED (514nm) and color of solution at 2 and 4 hours after illuminating in flow-through reactor.....48

Figure 3.18 comparison of UV-Visible spectra of silver nanoparticles ($\text{Ag}^+ : \text{Citrate} : \text{BH}_4^- = 1:10:0.001$, pH 7) after illuminating with green LED (514nm) that were synthesized by batch and flow through reactor.....49



Chapter 1

Introduction

1.1 Silver nanostructure

Silver nanostructure is a silver metal structure with at least one dimension in the nanometer scale (1–100 nm). Silver nanostructure have been received intensive attention from the researcher around the world because it provides the distinctively outstanding chemical, physical, electronic, and optical properties which are different from the phenomena observed in the bulk form. AgNPs have various distinct and unusual physico-chemical properties that are not seen in their comparable bulk materials, thanks to their exceptionally high surface area to volume ratio. The fraction of atoms present on the surface of AgNPs provides these distinctive qualities, increasing the thermodynamic stability (phase transition) of NPs, whereas the presence of less atoms in bulk material results in a less marked phase transition upon temperature gradient.[1] Fundamental studies of the properties of silver nanostructures were carried out in the 1980s and 1990s to reveal that the silver nanostructure exhibits a extraordinary combination of valuable properties associated with the surface plasmon resonance (SPR). The SPR phenomenon was occurred based on the coupling between an external electromagnetic field and the collective electron oscillations in the conduction band of the metal in nanoscale. The localized surface plasmon resonance (LSPR) bands of AgNPs can be observed in the UV-visible region. In addition, the optical property is depending on size and shape of AgNPs.

This unique property is strongly related to color of the colloidal AgNPs solution.[2] Therefore, in early 1980s, the scientific and practical researches of the silver nanostructure was exclusively caused by the possibility of their uses as the substrate for surface enhanced Raman scattering. The good match between the laser light source in Raman spectrometer and LSPR band of the silver nanostructure will strongly enhance the Raman signals of organic molecules closed to the metal surface. [3, 4] Moreover, antibacterial properties of the silver nanostructure has also been discovered.

Nanostructures can be classified in general based on their dimension. A nanoscale scale exists in each of the three directions (x, y, and z) in a zero-dimension (0D) material, but only in two directions in a one-dimension (1D) material. A nanometer-scale exists exclusively in one direction in a two-dimensional (2D) structure. Even though their dimensions are greater than 100 nm, three-dimensional (3D) nanostructures are included in this classification because they are built in a hierarchical design with 0D, 1D, and 2D nanostructures that grow in all directions.[5] The examples of each type were shown in Figure 1.1. In the study, only two dimensions of the silver nanostructure in either plate or prism shape has been investigated.

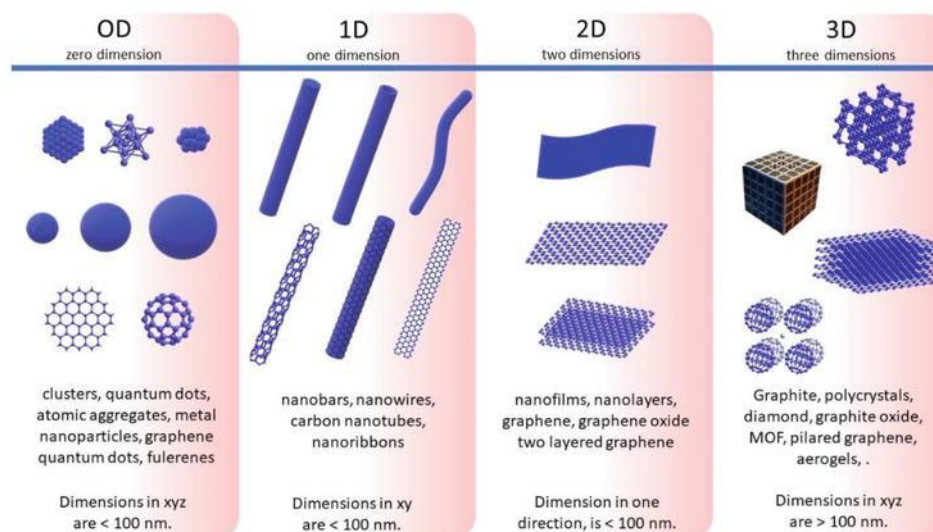


Figure 1.1 Schematic for low-dimensional nanostructure classification: zero dimension (0D), one dimension (1D), two dimension (2D), and three dimension (3D). The material includes examples for each dimension. [5]

1.1.1 Characteristics of silver nanoprisms

Silver nanoprisms (AgNPrs) are one of 2D nanomaterials. The optical property of AgNPrs is one of the key properties of the nanostructure as they provide strong localized surface plasmon resonance (LSPR) in visible regions.[2] This phenomenon can be observed by either UV-visible spectrometer or naked eye. The LSPR of AgNPrs greatly depends on their size and shape which relates to the refractive index of the metal and the surrounding medium. [6] The changes in shape and size of AgNPrs could reflect to the shift of LSPR which can be easily observed by the color changes of AgNPrs colloidal solution. Therefore, the AgNPrs have been mostly used as chemical sensors in various applications, such as biosensing [7, 8], trace analysis [9, 10], and medical diagnosis [11, 12] because they provide high sensitivity and capable to be functionalized to improve the detection selectivity.

When light strikes a small metallic nanoparticle, the oscillating electric field causes the conduction electrons to oscillate coherently. Figure 1.2 depicts this schematically. When the electron cloud is moved relative to the nuclei, a restoring force emerges due to Coulomb interaction between electrons and nuclei, causing the electron cloud to oscillate relative to the nuclear framework. This phenomena was called Localized surface plasmon resonance (LSPR). The oscillation frequency is determined by four factors: the density of electrons, the effective electron mass, and the shape and size of the charge distribution.[4]

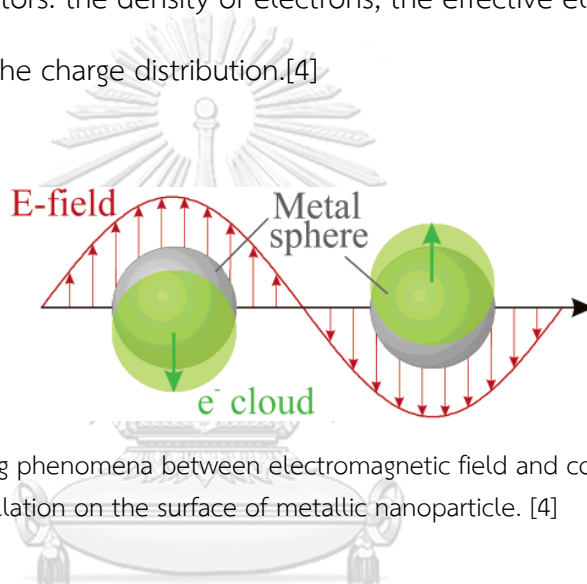


Figure 1.2 The coupling phenomena between electromagnetic field and collective electron oscillation on the surface of metallic nanoparticle. [4]

In the case of triangular nanoplates, it has been shown that both in-plane and out-of-plane excitations can lead to dipolar and quadrupolar resonances theoretically (Fig. 1.3). The simulation of extinction spectra was demonstrated in Figure 1.4. From the extinction spectra, the out of plane quadrupole LSPR band around 340 nm depend on ration between lateral dimensions and thickness (aspect ratio). The in-plane dipole LSPR around 600-800 nm by this band will red-shift as the edge length (lateral size) increase as shown in Figure 1.5. The out of plane dipole and in plane quadrupole modes around 470 and 410, respectively, are not well described. From Figure 1.4E, silver nanoprisms have only two types of facet which

are $\{111\}$ as blue, and $\{110\}$ as orange color. $\{111\}$ facet have lower surface energy than $\{110\}$ facet [13].

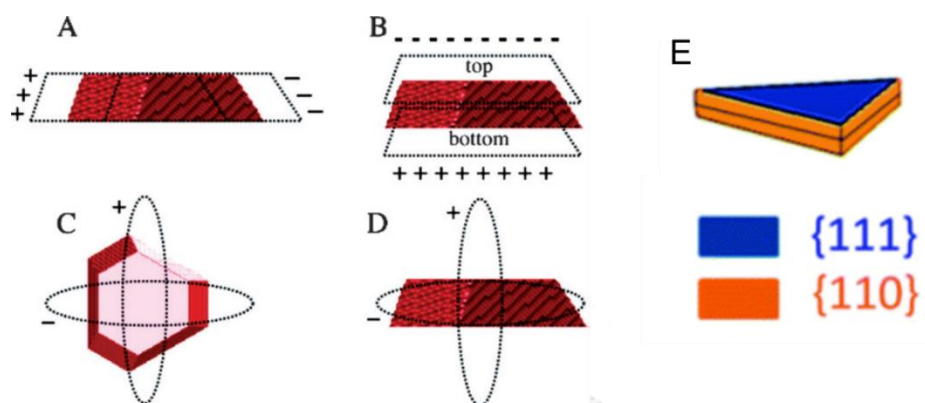


Figure 1.3 The resonant plasmon modes involved in metal nanoplates are illustrated schematically. In (A) and (B), the dipolar in-plane and out-of-plane modes are depicted, respectively. In (C) and (D), the corresponding in-plane and out-of-plane quadrupolar modes are depicted. (E) type of facets on silver nano prisms

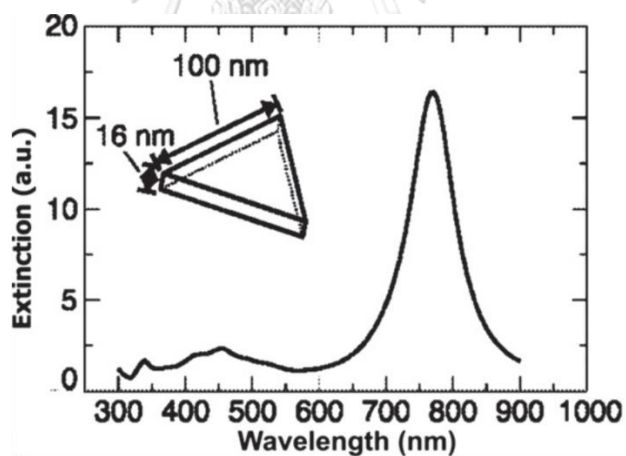


Figure 1.4 Simulations of the orientation averaged extinction effectiveness of perfect triangular nanoprisms using the discrete dipole approximation (DDA).

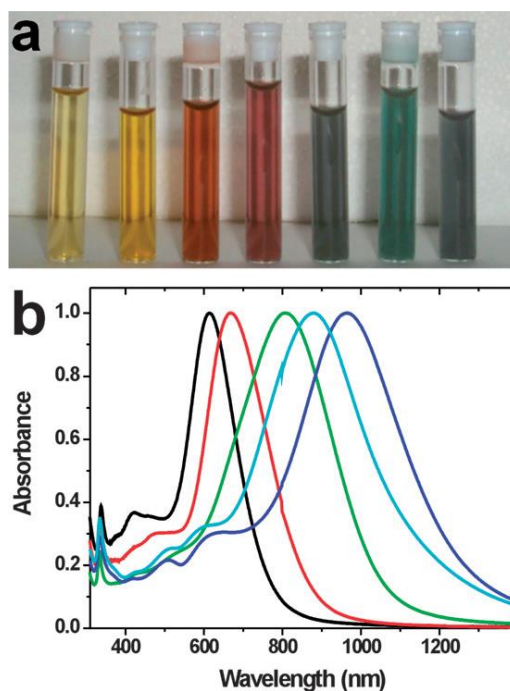


Figure 1.5 Pictures of silver sphere dispersions (yellow) and nanoplates; and b) UV-vis-NIR spectra of silver nanoprisms samples. Particle edge lengths increase from left to right in both cases.

1.2 Fabrication of silver nanoprisms

There are several methods to fabricate the AgNPrs with tunable LSPR bands. The robust methods involve the chemical reaction, lithography, and light-mediated methods.

1.2.1 Synthesis of AgNPrs by chemical reaction

To synthesize the AgNPrs by chemical reaction, the reaction usually started with the reduction of silver ions into silver spherical seed using the strong reducing agent, such as sodium borohydride (NaBH_4). Then, seed mediation and shape evolution of the generated silver seed was induced by shape converting agents, e.g. hydrogen peroxide (H_2O_2) together with the suitable stabilizer such as starch, bis(p-sulfonato phenyl)phenylphosphine (BSPP) and polyvinylpyrrolidone (PVP) as listed in Table 1.1.

Chen and Carroll [14] reported a solution phase method for reducing silver ions (Ag^+) on silver seeds in the presence of cetyltrimethylammonium bromide (CTAB) micelles using a mild reducing agent (ascorbic acid). The main disadvantage of this approach is the limited yield of nanoplates and non-uniform particles of varying size and shape. The preferential adsorption of CTAB on the (111) plane of the silver seeds, as well as the production of silver bromide in contact with the seeds, was discovered to play a significant role in nanoplate synthesis.

Pastoriza-Santos et al. [15] developed a straightforward method for producing truncated AgNPs by boiling AgNO_3 in N,N-dimethylformamide (DMF) in the presence of poly(vinylpyrrolidone) (PVP). Surprisingly, the initial concentration of both AgNO_3 and PVP has a significant role in defining the final morphology. The hypothesized mechanism called for the production of small silver spheres, which would then aggregate and recrystallize into particles with well-defined edges via a melting-like process.

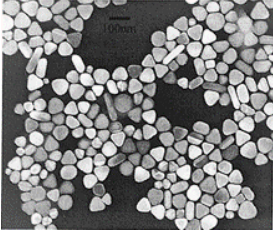
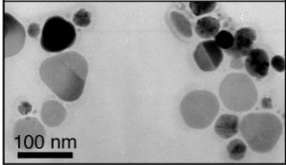
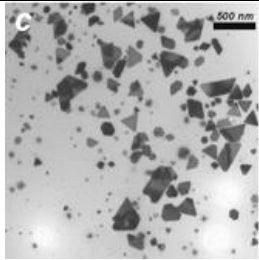
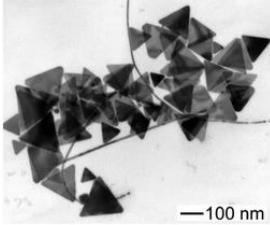
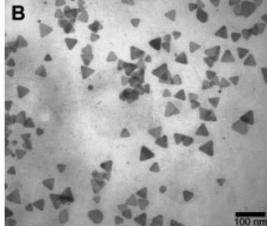
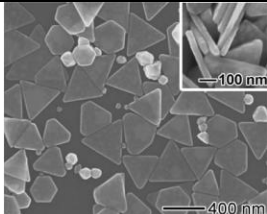
Sun et al. [16] suggested a photoinduced technique for the synthesis of sharp tip AgNPs, in which an aqueous dispersion of tiny spherical nanoparticles (3.5 nm) was refluxed in the presence of sodium citrate and PVP. The primary function of PVP was to maintain silver seeds with diameters smaller than a minimum size necessary for morphological change, but the presence of citrate was essential to trigger nanoplate development by preferential binding onto (111) planes. Furthermore, Sun et al [17] propose the synthesis of high purity AgNPs by heating an aqueous solution of AgNO_3 and PVP at 60°C without the presence of citrate to stimulate nanoplate formation.[18, 19] In this case, PVP adsorption is used to protect the particles from agglomeration as well, but the PVP hydroxyl end groups are thought to reduce Ag^+ at

such a slow rate that particle growth becomes kinetically controlled, favoring triangular shapes. The ability to control particle edge lengths between 50 and 350 nm by adjusting the reaction time was reported, while the thickness was always around 5 nm.

Métraux et al.[20]. proposed the preparation of silver nanoplates with control over the edge length. The conversion of AgNPs into AgNPrs with NaBH₄ and H₂O₂, in the presence of PVP and citrate, and in the absence of light, is the basis of this method. The concentration of NaBH₄ was found to have a significant impact on the conversion of silver nanoparticles into AgNPrs, controlling the edge length, thickness, and tip sharpness of the final products. Citrate was discovered to be essential for the formation of AgNPrs, while PVP appeared to act as a stabilizer.

From the literature review, chemical method can be divided to two steps. First step is seed preparation by reducing silver ion (Ag⁺) in solution to silver nanosphere (seeds) with reducing agent such as ascorbic acid, hydrazine, NaBH₄, etc. Second step is shape conversion by chemical reagent such as H₂O₂. But this method required the polymeric stabilizer such as CTAP, PVP, and AOT. Due to these stabilizers as a result the synthesized nanoparticles hard to surface modification.

Table 1.1 reducing agent, stabilizer, and TEM images of products from various chemical reduction method

Author	Reducing agent	Stabilizer	Product
S. Chen (2002) [14]	ascorbic acid	CTAB	
M. Maillard (2003) [21]	hydrazine	bis(2-ethyl-hexyl) sulfosuccinate (AOT), isooctane, water reverse microemulsions	 c
P. Santos (2002)[15]	N,N-dimethylformamide (DMF)	poly(vinylpyrrolidone) (PVP)	 c
Y. Sun (2003)[16]	NaBH ₄	sodium citrate and PVP	 — 100 nm
G. S. Métraux (2005)[20]	NaBH ₄	sodium citrate and PVP	 B — 100 nm
I. Washio (2006) [19]	The hydroxyl end groups of PVP	PVP	 — 400 nm

1.2.2 Nanosphere lithography

Nanosphere lithography (NSL) is a physical technique used to create AgNPs by controlling the growth step of silver atoms into the designed block. Van Duyne et al. [22, 23] developed NSL as a multi-step process. and produces surface-confined nanoparticle arrays with good control over shape, size, and interparticle spacing, but the particles can be lifted from the substrate and dispersed in a solvent. The first step is the self-assembly of D-diameter monodisperse polystyrene spheres to form a two-dimensional colloidal crystal deposition mask. Due to capillary forces, the simplest NSL scenario involves the solvent evaporation of the nanosphere solution, which results in the formation of a monolayer of hexagonal close-packed nanospheres patterned on the substrate (Figure 1.6A). The typical defect free domain sizes are in the 10–100 nm² range, though Giersig et al. [24] have reported variations of this strategy resulting in much larger ordered areas. Following mask fabrication, a silver film with a fixed mass thickness of d_m is deposited by thermal evaporation through the nanosphere mask. The nanosphere mask is simply removed from the sample after metal deposition by sonicating it in a solvent, resulting in AgNPs ordered arrays on the substrate (Figure 1.6B). Van Duyne et al.[25] recently reported that monodispersed AgNPs synthesized by NSL can be discharged into solution due to the NPs' weak adherence to the glass. Prior to release, the NPs must be asymmetrically functionalized with a capping agent to prevent particle aggregation in the solvent. Unfortunately, particle break-up was detected as a result of the usage of sonication in the release step, restricting the process's uses.

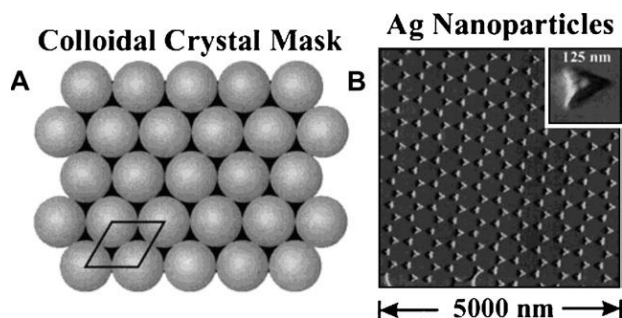


Figure 1.6 Schematic illustration (A) colloidal crystal mask for synthesis by NSL (B) AgNPrs was synthesized by NLS. [23]

1.2.3 photo-mediated method

The photo-mediated method was also used to generate the AgNPrs. This method gives accurate size and shape of AgNPrs as it uses the external energy from various light source to control the chemical reaction.

Jin et al. [26] developed the photoinduced aggregation method, which involved converting citrate-capped Ag spherical nanoparticles (seeds, 10 nm) into larger triangular particles (edge length around 100 nm) by irradiating the small seeds with visible light using a conventional fluorescent tube in the presence of bis(p-sulfonatophenyl)phenylphosphine dihydrate dipotassium (BSPP). After that Gehlen et al. [27] reported that replacing BSPP with poly(vinylpyrrolidone) (PVP) resulted in the formation of Ag AgNPrs as well.

Sun et al. [17] asserted that, while PVP was responsible for generating well-dispersed and small Ag seeds, citrate ions were the critical chemical species in promoting the morphological transition from spherical to AgNPrs, implying that a combination of chemical and photochemical processes were at work. Their rationale was based on a preferential interaction of citrate ions with the {111} facets of silver

nanocrystals, which resulted in the platelike morphology during particle creation by inhibiting development on the {111} plane.

Xue's group reported an alternative way to control the nanoprism fusion process, by adjusting the pH of the solution and thus the attraction/repulsion between particles, [28] , as well as the formation of silver triangles by aggregation of small silver particles on gold nanoparticles during irradiation with a laser beam at 550 nm, so that the gold surface plasmon is preferentially excited at the start of the aggregation process. [29]

Bastys et al. [30] reported a later report that modified the photoinduced approach by illuminating the Ag seeds with low intensity light emitting diodes (LEDs). The ability to create silver nanoprisms with dimensions resulting in high absorption coefficients well within the NIR region was the key addition of this work in comparison to earlier published results. Using LEDs with emission bands at 518 nm and 653 nm, respectively, particles having intense in-plane dipole bands at 1037 nm and 1491 nm were generated.

Rocha and Zanchet recently shown that particle size may be adjusted by changing the light wavelength, although particle thickness is independent of illumination conditions, as previously seen in the photoinduced aggregation approach [27]. Furthermore, these authors [31] confirmed some aspects of the growth mechanism proposed by Maillard et al. [14] and discovered that the origin of anisotropic growth is not related to LSPR excitation, but rather to intrinsic characteristics of the seeds, such as structural defects or the capping agent. [32]

H. Wang et al propose a photomediated synthesis is a reliable, high yield method to produce a variety of morphologies of silver nanoparticles. Their method can synthesize silver nanoprisms and nanodecahedra with tunable sizes via control of the reaction temperature (5°C, 10°C, 20°C, 30°C, and 40°C) and the irradiation wavelength (478nm, 503 nm, 523 nm, and 590 nm). They use NaBH₄ as reducing agent and only sodium citrate as stabilizer. The results showed that shorter excitation wavelengths and lower reaction temperatures result in high yields of nanodecahedra, while longer excitation wavelengths and higher reaction temperatures result in the formation of nanoprisms. They also propose mechanism for the growth condition of silver nanoparticles (Figure1.7).

(#1) The mechanism for the growth starting with chemical reduction of silver ion to silver nano seeds by NaBH₄.

(#2) When silver nanoparticles are irradiated, they enter short-lived excited states (Ag* intermediates) and then assemble form planar twinned seeds. Planar twinning seeds are changed competitively into small silver nanoprisms or five-fold twinning seeds. Plasmon excitation by irradiation light provides the energy barrier for conversion.

(#3) The lower excitation energies (low $h\nu$ indicated by red arrow) resulting in at a longer wavelength are unable to efficiently overcome the energy barrier for conversion of planar structure seeds to five-fold twinning seeds, so nanoprisms were the only products with 590 nm irradiation even at lower reaction temperature.

(#4) High excitation energies (high $h\nu$ shown by blue arrow) at a short wavelength can overcome both energy barriers for planar and five-fold twinning seeds, allowing nanoprisms and nanodecahedra to develop. Because the energy of

nanoprisms and nanodecahedra fluctuates with size throughout the reaction, Alternatively, Ag^+ ions can be selectively reduced on distinct faces, resulting in differing selective deposition rates for Ag on different faces.

(#5) The Ag Growing on {110} facets of The small size AgNPrs and results in the formation of nanoprisms,

(#6) {111} deposition, on the other hand, results in the production of nanodecahedra. The expansion of a single stable twin plane can result in the expansion of additional twin planes, such as a five-fold twinning plane.

(#7) Under the right conditions, silver nanoparticles with a planar structure can be converted into five-fold twinning particles, but the process is irreversible. Twin plane structures are demonstrated to grow into thermodynamically stable five-fold twinning structures. The quick reaction rate at higher temperatures promotes the formation of nanoprisms by preferential Ag deposition on planar structures in a kinetics-controlled mode, whereas slower rates produce thermodynamically favored nanodecahedra.[13]

From various of photo-mediated method to synthesis AgNPrs. This method gives good accurate size and shape but require polymeric stabilizer. And all of these literature syntheses in batch, so it cannot do continuous synthesis and hard to upscale of the batch. So, we are interested to develop flow-through reactor for synthesis silver nanoprisms.

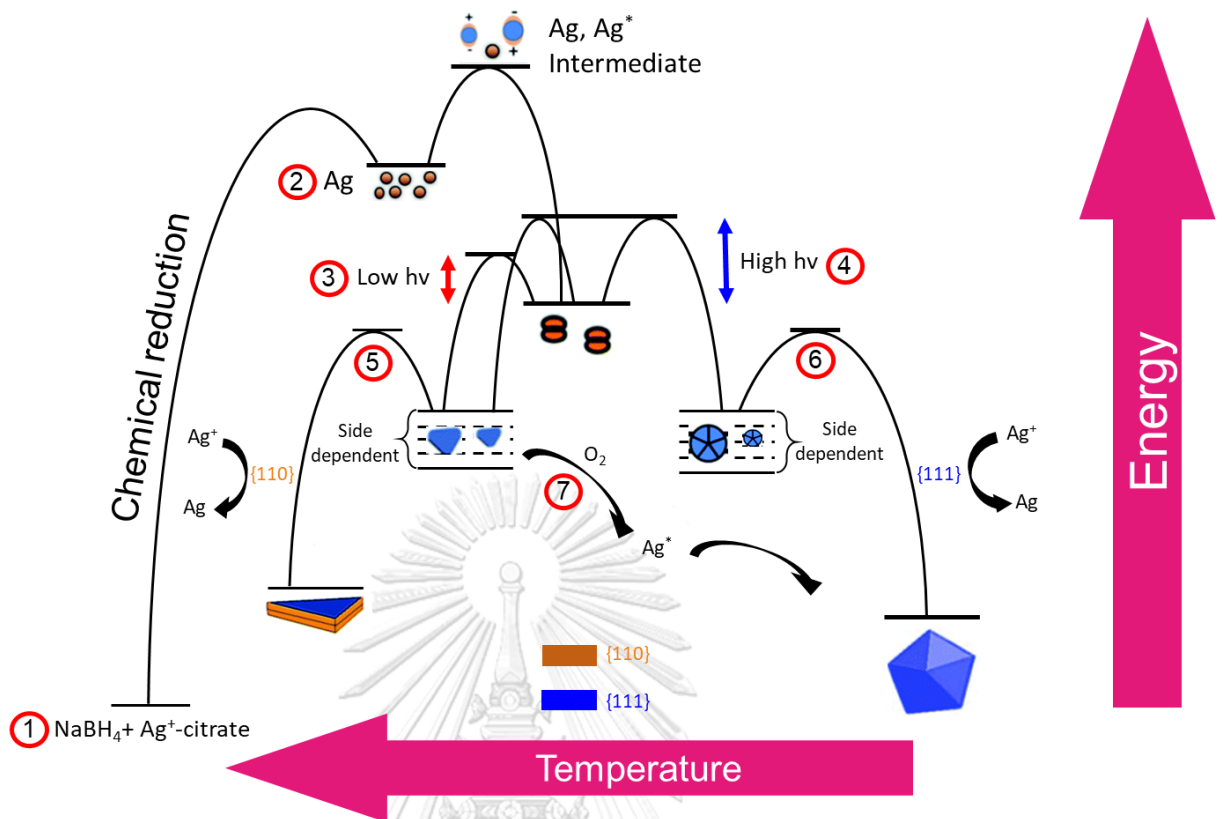
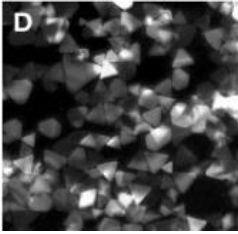
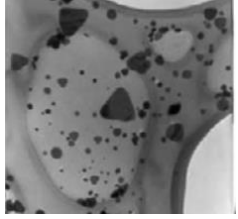
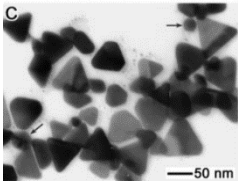
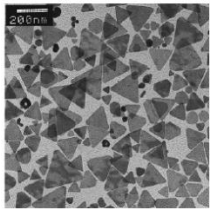
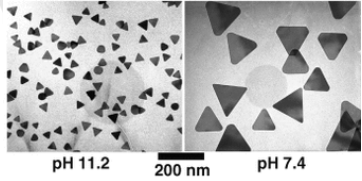


Figure 1.7 The growth mechanism in photomediated production of silver nanodecahedra and nanoprisms is depicted schematically. [13]

Table 1.2 reducing agent, stabilizer, and TEM images of products from various photo-mediated method

Author	Reducing agent/ Stabilizer	Light source	Product
R. Jin (2001) [26]	NaNH ₄ / BSPP	40 W fluorescent tube	
M. H. Gehlen. (2003) [27]	NaNH ₄ / BSPP, PVP	20 W fluorescent lamps	
Y. Sun (2003) [17]	NaNH ₄ / PVP	Halogen lamp	
V. Bastys (2006) [30]	NaNH ₄ / citrate, PVP	LEDs (518 nm,641 nm,653 nm), cool-white fluorescent tubes	
C. Xue (2007) [28]	NaNH ₄ / Citrate, BSPP	150-W halogen lamp coupled with an optical bandpass filter (550 ±20 nm).	

1.3 Objectives

The objective of this research is to synthesize silver nanoprisms (AgNPrs) by using a flow-through reactor. The reactor used the photo-mediation method without any use of a polymeric stabilizer. Optimize The mole ratio between silver ion source, reducing agent, and citrate.

1.4 Scope of the study

1. Flow-through reactor using photo mediation method by using LEDs as a light source. The temperature in the reactor was controlled by a fan. And the peristaltic pump to control the flow rate of the reactor.

2.Synthesize silver nanoprisms using citrate as a stabilizer.

3.The parameter optimized were pH, Ag^+ : TSC: NaBH_4 ratio, inducing energy

(λ_{max} of LEDs).

Chapter 2

Experimental

2.1. Chemicals and materials

- 2.1.1 Silver nitrate (AgNO_3 , Thomas baker, AR)
- 2.1.2 Sodium borohydride (NaBH_4 , Acros organic, AR)
- 2.1.3 Trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, Carlo erba, AR)
- 2.1.4 Ammonia (NH_3 , MERCK, AR)
- 2.1.5 LEDs (EVE lightning LED stripe, 7.5 W/m)
- 2.1.6 UV-visible spectrometer reflection probe (ocean optic USB2000+UV-vis)
- 2.1.7 Transmission Electron Microscope (JEM 2100 Electron microscope)
- 2.1.8 UV-visible spectrometer (Thermo Scientific™ GENESYS™ 10S)
- 2.1.9 IV Tube (NIPRO IV set)
- 3.1.10 Peristaltic pump (INTLLAB DP-385 Peristaltic Liquid Pump)

2.2 LED

Five meters of LED stripe (EVE) with power of 7.5 w/m including Blue (464 nm), Green (514 nm), Red (630 nm), Pink (445nm, 635nm), and Daylight (445nm, 542nm) were used in the study as light source. The UV-Vis spectra of emission band were measured by UV-vis spectrometer with reflection mode. The set up for emission spectrum acquisition was shown in Figure 2.1A. Figure 2.1B reveal the emission spectra of the LED. The emission energy of each LEDs were calculated using Planck's equation (as shown in Figure 2.1C) with equal to 2.67 eV, 2.41 eV, 1.97 eV, 2.79 eV & 1.95 eV, and 2.79 eV & 2.29 eV for the Blue, Green, Red, Pink, and Daylight

LED, respectively. The LEDs can be divided to two categories which are single emission (blue, green, and red) and couple emission (pink and daylight).

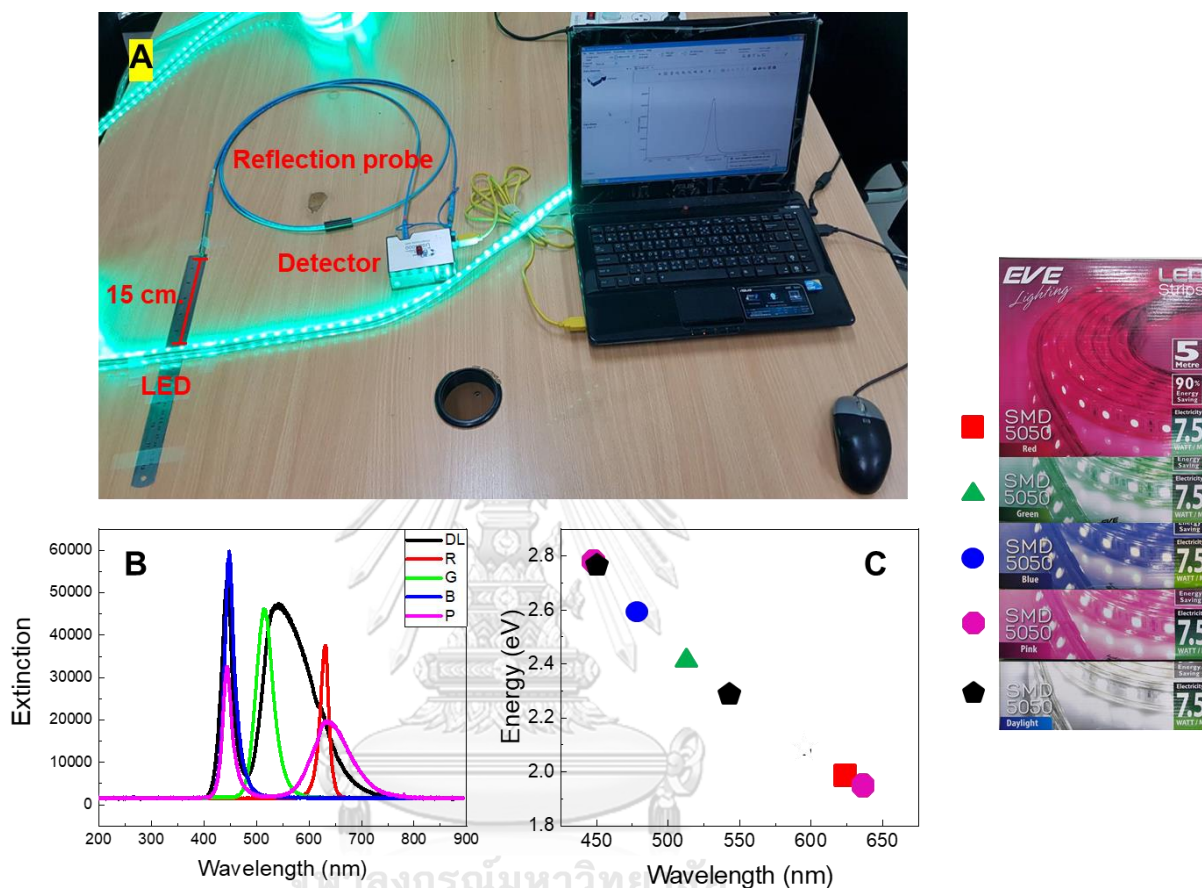


Figure 2.1 (A) experimental set up for measuring emission spectra of LEDs. (B) UV-Vis spectra of emission band (C) Emission energy of LEDs from Blue (464 nm), Green (514 nm), Red (630 nm), Pink (445nm, 635nm), and Daylight (445nm, 542nm) LED light source

2.3 Synthesis of silver nanoprisms method under slow reduction of silver seeds

2.3.1 Preparation of silver seed under cold condition

To prepare silver seed solution, 88 ml of Milli-Q water was firstly bubbled with N_2 for 30 min. to remove the dissolved oxygen. Then, the deoxygenated Milli-Q water was further used the solvent. Silver nitrate ($AgNO_3$) solution (1 mL, 10 mM) and

trisodium citrate (TSC) solution (10 mL, 10 mM) were mixed in a 250 mL Erlenmeyer flask. The mixture solution was constantly stirred in an ice bath for 30 min under N_2 gas. The scheme of the setup for silver seed preparation is shown in Figure 2.2A. After 30 min, the solution was then mixed with the freshly prepared sodium borohydride ($NaBH_4$) solution (1 mL, 10 mM) and stirred for 2 min. The colorless solution immediately turned to yellow. The solution called silver seed solution prepared with mole ratio of $AgNO_3$: TSC: $NaBH_4$ equal to 1: 10: 1. This ratio was further optimized for investigating the shape evolution process.

2.3.2 Shape evolution to silver nanoprisms under LED illumination

To fabricate the silver nanoprisms using LED illumination, 5 ml of the prepared silver seed solution was transferred a 5 mL vial. Then, the seed solution was illuminated with LED stripe (EVE, power of 37.5 W) for 8 hours under controlled temperature of the system with water bath. N_2 gas was constantly flowed to prevent the unnecessary oxidation by oxygen gas during the illumination (Figure 2.2B). To adjust the illuminated energy, several LEDs with different wavelengths were used to investigate the effects of energy in shape evolution of silver nanoprisms.

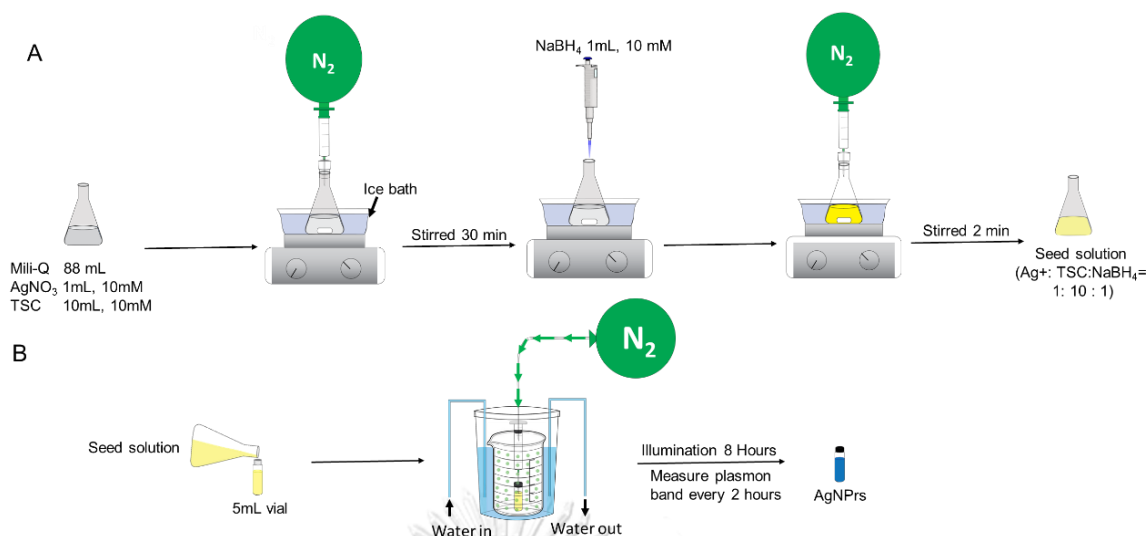


Figure 2.2 Experiment setup for (A) silver seed preparation in cold temperature and (B) seed mediated growth using slow reduction.

2.4 Synthesis of silver nanoprisms method under normal reduction

2.4.1 Preparation of silver seed

To prepare silver seed solution, the Milli-Q water was initially bubbled with N₂ gas, and the water was further used as the solvent. Silver nitrate (AgNO₃) solution (1mL, 10mM), and trisodium citrate (TSC) solution (10mL, 10mM) were mixed in a 100 mL Erlenmeyer flask covered with aluminum foil. The mixture was then adjusted to pH = 9 using ammonia (10 %v/v) and was stirred for 30 min as shown in Figure 2.3. After 30 min, the solution was mixed with the freshly prepared sodium borohydride (NaBH₄) solution (1mL,10mM) and stir for 2 min. The color of the solution was immediately changed from colorless to light-yellow. The solution called silver seed solution prepared with mole ratio of AgNO₃: TSC: NaBH₄ equal to 1: 10: 1. This ratio was further optimized for investigating the shape evolution process.

2.4.2 Shape evolution to Silver nanoprisms under LED illumination

To fabricate the silver nanoprisms using LED illumination, the prepared silver seed solution 5 mL was transferred in a 5 mL vial. Then, the seed solution was illuminated with green-LED stripe with emission wavelength of 514 nm (EVE, power of 37.5 W) for 8 hours with constantly flow N_2 gas to prevent the unnecessary oxidation by oxygen gas during the illumination (Figure 2.3).

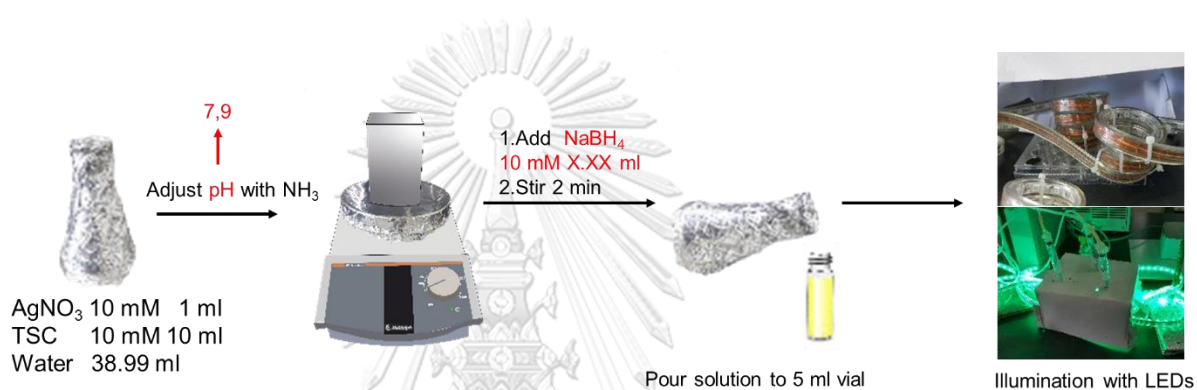


Figure 2.3 Experiment setup for silver seed preparation and photomediated growth under normal reduction

2.5 Flow-through reactor

2.5.1 Design of flow reactor

The flow-through reactor was designed to have major 4 components including peristaltic pump, tube, LEDs chamber, and beaker to stock the solution of silver nanoprisms. The process starting with preparation of the seed solution in beaker and then the solution was flowed through a clear tube (PVC) by peristaltic pump with constant flow rate of 15 mL/min though the LEDs chamber illuminated with green LED (540 nm, 60 W). The flow process was constantly continued for 4 hours.

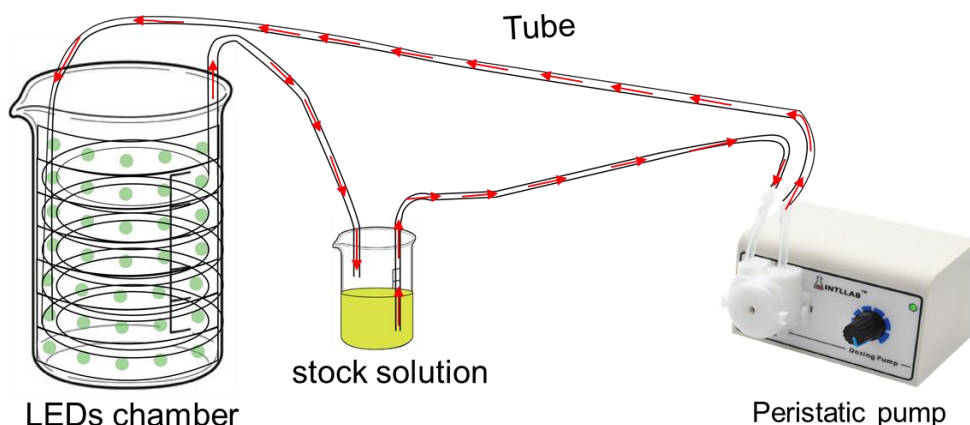


Figure 2.4 the design of the flow-through reactor

2.5.2 Synthesis silver nanoprisms by flow-through reactor

The silver seed solution was prepared following the section 2.4.1. Prepare the seed solution in 40 mL beaker. The seed solution was injected in the flow tube using peristaltic pump with constant flow rate of 15 mL/min. The seed solution was flowed through the LED chamber using green-LED (540 nm, 37.5 W) for 4 hours under the temperature controlled by ventilating fan as shown in Figure 2.5.

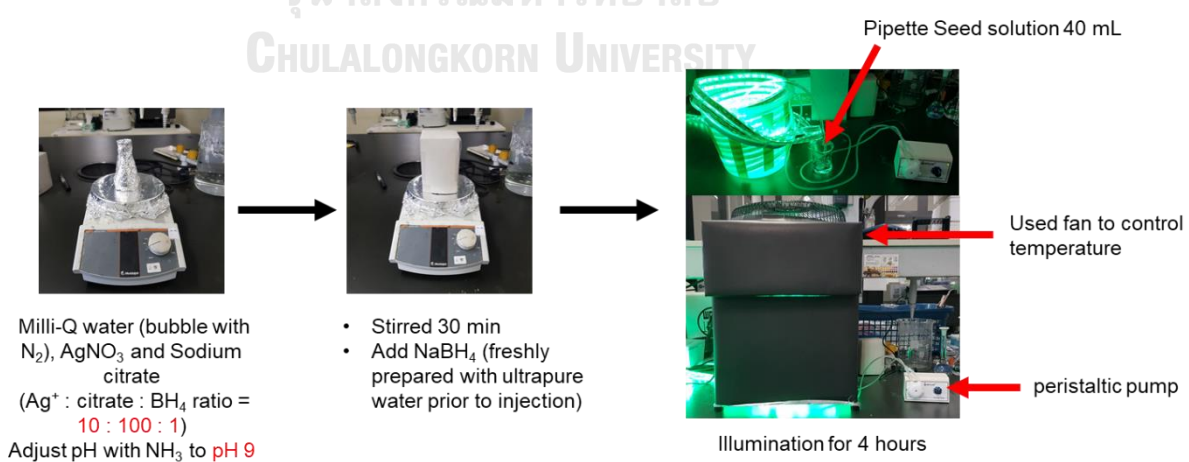


Figure 2.5 Flow-through reactor set up for silver seed preparation and synthesis AgNPrs by flow-through reactor

2.6 Characterization

2.6.1 UV-visible spectroscopy

UV-Visible spectroscopy is the most commonly used technique for characterizing nanoparticles. The approach measures the amount of light that passes through samples and onto the detector. The extinction spectra of AgNPs can be examined using the absorption band in the visible region using the UV-visible absorption technique. Because of the relationship between the shape and size of nanoparticles and LSPR, changes in shape and size of nanoparticles affect the absorbance spectra in UV-visible method. Due to concentration of colloidal AgNPs from synthesis method light skirt under slow reduction of silver seeds, Synthesis method under normal reduction, and Synthesis by flow-through reactor are 0.1 mM, 0.2 mM, and 0.2 mM respectively. And the colloidal products from those synthesis methods are transparent solution. So, the colloidal AgNPs can be used to measure UV-vis spectra directly. First, colloidal AgNPs was pipetted to 1 mL plastic cuvette. After that measure the UV-vis spectra from UV-visible spectroscopy.



2.6.2 Transmission electron microscopy

Transmission electron microscopy (TEM) was an effective method for investigating the size, size distribution, and morphology of MNPs. The approach employs an accelerated electron generated in vacuum, bent at a slight angle by the atoms of the samples, and transmitted through the samples. These deflected electrons are magnified by a magnetic lens, resulting in a bright field on a fluorescent screen. The preparation of TEM sample starting with centrifuge 1 ml colloidal AgNPs at 15000 rpm for 15 min. Second, pipette the pellet of AgNPs at the bottom for 10

μL to another centrifuge tube and dilute to 1 mL with MQ-water. After that put grid on Petri dish and drop 9 μL of MQ-water on grid. Next drop the diluted solution to MQ-water on grid. Finally close the Petri dish and let solution dry in vacuum. The sample is ready for take a TEM image.



Chapter 3

Results and Discussion

3.1 Shape evolution of silver nanoprisms under slow reduction of AgNPs

In the section, the shape evolution of silver nanoprisms (AgNPs) was controlled and induced by the external energy from the irradiation of narrow band LEDs. Firstly, the reflection mode of the UV-vis spectrometer was used to reveal the emission wavelength of each LED as shown in Figure 3.1. It can be seen that LED sources give a single narrow emission band at 464 nm, 514 nm and 630 nm corresponding to blue, green, and red LED color, respectively. From the emission band, the blue LED gives the highest energy equal to 2.59 eV, while the green and red LED give 2.42 eV and 1.97 eV, respectively. These LEDs can give a stable light intensity for at least 8 hours. Therefore, the shape conversion can undergo the identical irradiated energy from LED through the whole experiment.

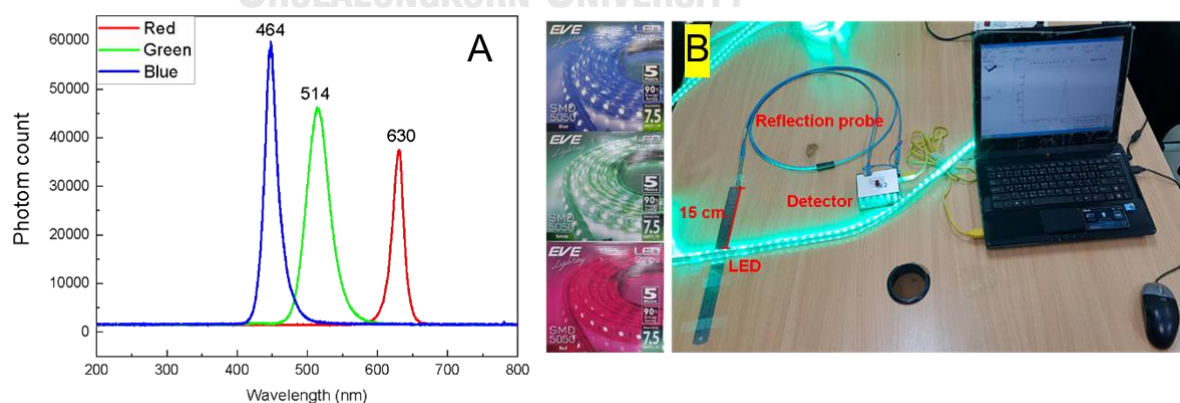


Figure 3.1 (A) UV-Vis spectra of emission band from Blue (464 nm), Green (514 nm), and Red (630 nm) LED light source (B) experimental set up for measuring emission spectra of LEDs.

After illuminating the silver seed solution prepared using cool condition with the red LED (630 nm, 1.97 eV) which exhibits the lowest energy compared to the other LEDs, it was found that the LSPR band was observed and unchanged at ~400 nm. The intensity of the LSPR fluctuated during the first two hours after the irradiation as shown in Figure 3.1A. The LSPR band was slightly red-shifted from 401 nm (starting point) to 410 nm (after 8 hours). There is no appearance of the characteristic LSPR bands that represent the longitudinal and aspect ratio of the particles. The observation suggests that the silver particles were still in spherical shape and were not transformed to prism shapes. The morphology of silver particles was investigated using TEM as shown in Figure 3.2C. Only spherical silver particles were observed with the various sizes. From the results, it can be concluded that the shape evolution of the silver particles cannot be induced by the red LED as it might support low energy which is not adequate to overcome barrier energy of the shape evolution.

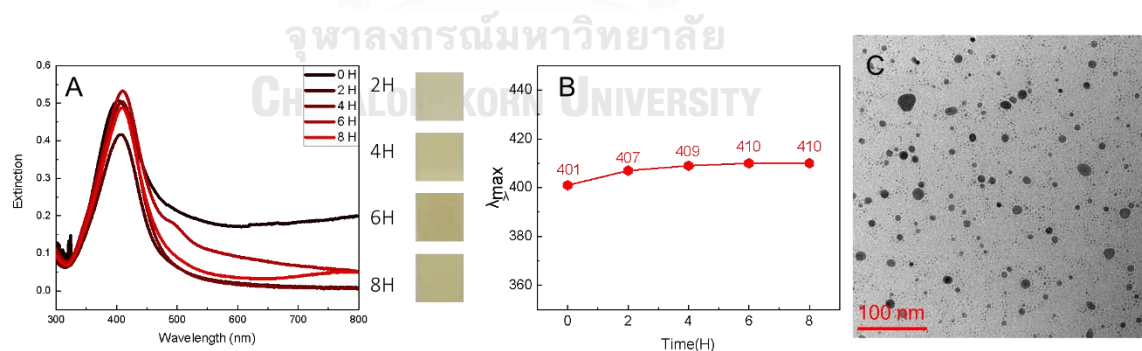


Figure 3.2 (A) show UV-Visible spectra of silver nanoparticles after illuminating with red LED (630 nm) and the color of solution at various illumination times (B) the λ_{\max} at various illumination times from 2-8 hours (C) TEM image of silver nanoparticle after illuminating with red LED for 8 Hours.

In the next study, the higher energy green LED was used instead of the red-LED to investigate the effects of external energy to the shape evolution process of the silver particle from spherical shape to prism shape. The colloidal silver solution with characteristic LSPR at 400 nm (spherical shape) representing as yellow was distinctively changed to blue colloidal solution after illuminating the seed solution with the green LED (514 nm, 2.42 eV) for 8 hours as shown in Figure 3.3. After illumination with the green-LED for 2 hours, the intensity of the LSPR band at 400 nm of silver nanosphere dramatically decreased, while a new set of LSPR bands at 330 nm and 600 nm were newly appeared. This is a strong evidence suggesting that the spherical shape of silver particles were converted into the prism structure as a new LSPR band at 330 nm (out of plane quadrupole LSPR) relating to the aspect ratio and LSPR band at 580 nm (in-plane dipole LSPR) corresponding lateral size of AgNPrs emerged. The intensity of in-plane dipole LSPR continuously increased. After irradiation for long period of time, the out of plane LSPR band was blue-shifted with the declining of the LSPR band at 400 nm, while the out of plane quadrupole at 330 nm was insignificantly changed. The observations suggest that the AgNPrs becomes smaller and also thinner because the aspect ratio was kept constant. The observed LSPR bands were in good agreement with TEM image that the transformation of spherical silver nanoparticles to the AgNPrs were completed using the illumination of green LED of 514 nm for at least 4 hours.

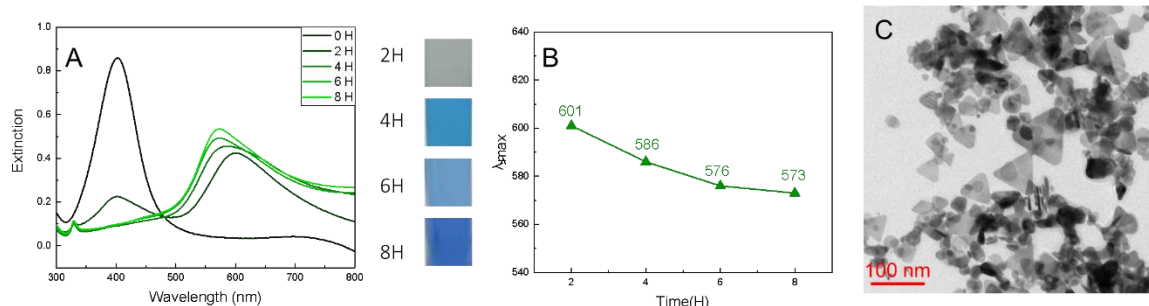


Figure 3.3 (A) show UV-Visible spectra of silver nanoparticles after illuminate with green LED (514 nm) and color of solution at various illumination times (B) show trend of λ_{max} of in-plane dipole LSPR at various illumination times (C) TEM image of silver nanoparticle after illuminating with green LED for 8 Hours.

In the case of using blue-LED, the colloidal solution with characteristic LSPR at 400 nm (spherical shape) was changed to the dark yellow after illuminating the solution with the blue LED (464 nm, 2.59 eV) for 8 hours as shown in Figure 3.3. After illumination with blue LED for 2 hours, the LSPR band of the starting colloidal solution at 400 nm of silver nanosphere vanish and a strong LSPR bands at 480 nm were appeared. However, the LSPR band at ~ 330 nm (out of plane quadrupole LSPR) is not well-defined. This suggests that the nanoparticles do not contain the structure with aspect ratio which is crucial characteristic for prism structure. Therefore, the spherical silver particles could possibly be transformed to rod structure which provide only lateral dimension but not aspect ratio. It was found that the intensity of in-plane dipole LSPR was continuously increased and was blue-shifted over incubation time. The characteristic LSPR bands are in good agreement with the TEM images that silver nanosphere transform to various shapes of silver nanostructure including rod (majority one), plate, and prism. From shape evolution process using the blue LED, it generates a various shape of nanostructure as the energy from the blue LED (464nm) is too high to overcome the reaction energy barrier. Therefore, the

shape evolution could go through several growth-mediation pathways not only transform to the nanoprisms but also to other shapes.

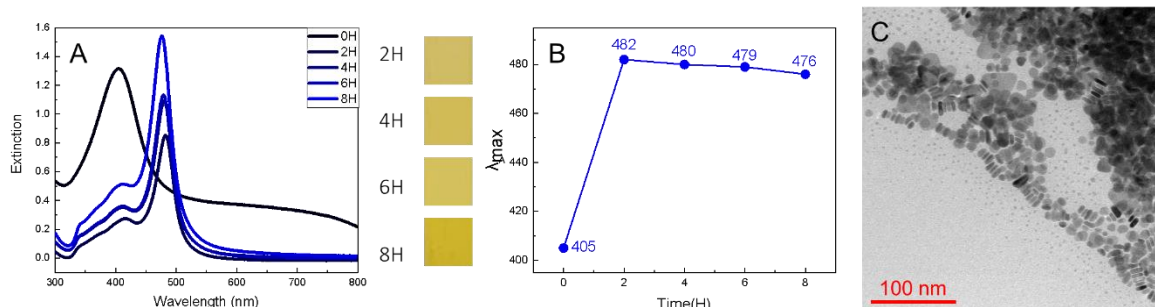


Figure 3.4 (A) show UV-Visible spectra of silver nanoparticles after illuminate with blue LED (464nm) and the color of solution at various illumination times (B) show trend of λ_{\max} of in-plane dipole LSPR at various illumination times (C) TEM image of silver nanoparticle after illuminating with blue LED for 8 Hours.

3.1.1 Shape evolution of AgNPRs using the couple LEDs

In the section, we would like to elucidate whether the shape evolution of silver nanosphere to silver nanoprisms could be precisely controlled by only the illumination of LED. To prove our hypothesis, the couple wavelength LED (daylight: blue 445 nm, 2.79 eV and green 542 nm, 2.29 eV) was used as the light source. If the shape evolution could be controlled by only LEDs, the products which originated by using each LEDs should be equally mixed. The shape evolution was monitored by the LSPR bands. At the starting point, the yellow colloidal solution with characteristic LSPR at 400 nm (spherical shape) was changed to the gray solution after illuminating the seed solution with the daylight LED for 8 hours as shown in Figure 3.4. It could be seen that the LSPR band at 400 nm of silver nanosphere is vanished, and a new spectrum contain two significant LSPR bands at 480 nm, and 580 nm was developed. The products using daylight LEDs provide the mixed LSPR bands at indistinguishable

positions with the product generated using the individual blue and green LED as shown in Figure 3.4B. This is a strong evidence suggesting that size and shape of silver nanostructures could be precisely controlled by the external energy from LED illumination.

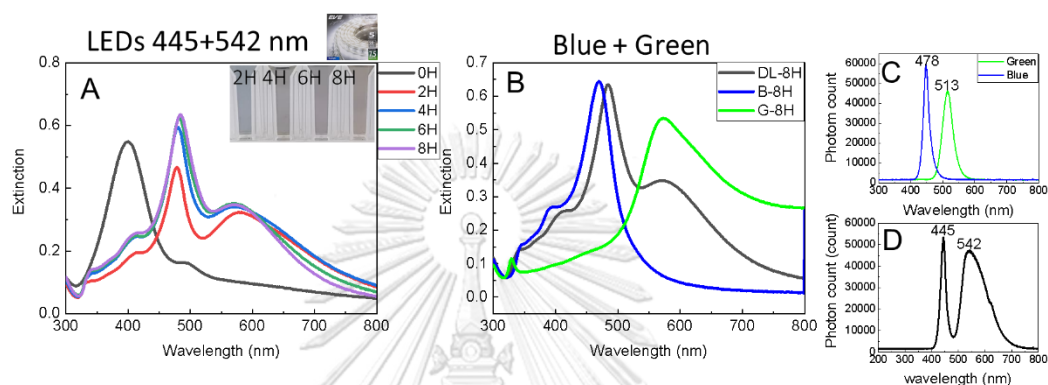


Figure 3.5 (A) shows UV-Visible spectra of silver nanoparticles after illuminating with blue LED (464nm) (B) comparison of UV-Vis spectrum of silver nanoparticles that synthesized from daylight blue and green LED. UV-Vis spectrum of LED (C) Green and blue (D) daylight.

All color of the LEDs from EVE in market which are blue, green, yellow, red, daylight, and pink. From the previous results, the lowest energy that can induce shape evolution of AgNPs to AgNPrs is 2.42 eV from green (514nm) as shown in small square in Figure 3.6B. After this section we used on single emission LEDs that have proper energy to induce shape evolution of AgNPs to AgNPrs which is only green (514nm). Due to the energy from other LEDs (above 2.59eV) can induce shape evolution not only to AgNPrs but also to other shape such as rod.

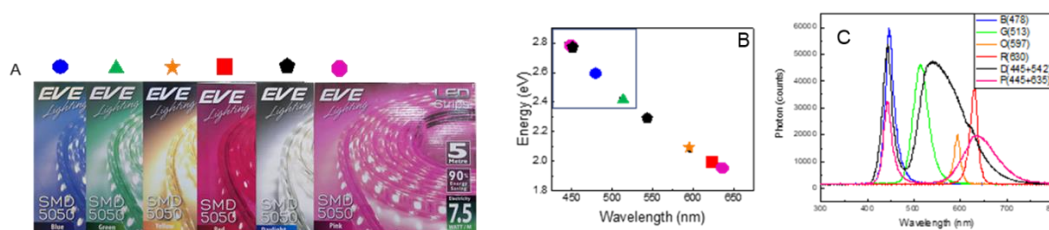


Figure 3.6 (A) Shown All color of the LEDs from EVE in market (B) UV-Vis spectra of emission band (C) Emission energy of LEDs from Blue (464 nm), Green (514 nm), Red (630 nm), yellow(597nm), Pink (445nm, 635nm), and Daylight (445nm, 5642nm) LED light source

3.1.2 Stability of the synthesized AgNPrs

The stability test is crucial as there is no additional stabilizer in our developed synthesis protocol. To elucidate the stability of the synthesized AgNPrs, the AgNPr products were stored at 4°C in closed vials to prevent the effect of external light for 15 days. Then, the stability of the colloidal solution of the silver nanoparticles was observed by the position and intensity of LSPR bands. The LSPR patterns of the product using green, red and daylight LED are insignificantly changed after storing for 15 days. It shows good stability over time. However, it was found that the in-plane dipole LSPR band of the product using blue LED was blue-shifted from 480 nm to 450 nm but out of plane quadrupole provides insignificant changes. As the blue LED provides the highest energy, it possibly enforces the shape evolution pathway to transform the silver seeds to the thermodynamically unstable products (structures have energy greater than seed solution), so after storing for 15 days, the product possibly reverses to the large seed structure.

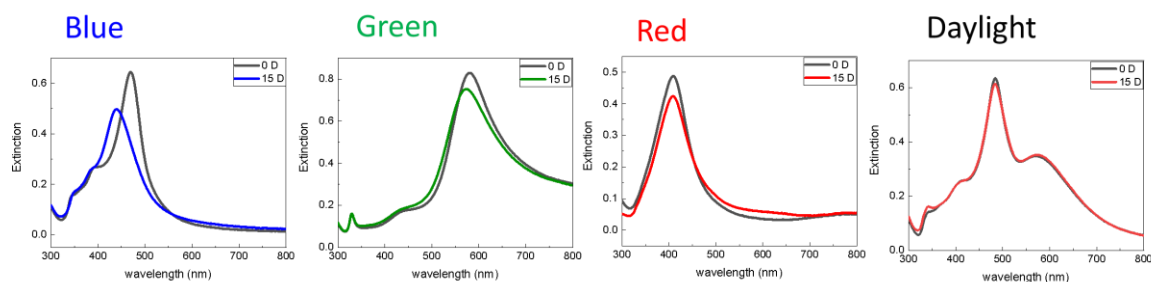


Figure 3.7 UV-vis spectra of the freshly prepared AgNPs (gray spectrum) and the AgNPs after kept at 4°C in dark container for 15 days

This work demonstrates the optimized conditions to fabricate silver nanoprisms (AgNPs) using photoinduced method without any additional polymeric stabilizer. The silver nanoprisms was generated from the silver seed by illuminating external energy from LED. The effects of the wavelengths (energy) from LED with various emitting wavelengths (energy) were investigated. It was found that only LED give higher energy than 2.4 eV will induce the shape evolution of silver nanosphere, while LED with lower energy (<2.4 eV) cannot be used for the shape transformation of silver nanoprisms. UV-vis spectrometer and TEM were used to monitor size and shape of the products. Surprisingly, only green LED (514 nm, 2.42 eV) could be used to generate the AgNPs with the two distinguished characteristic LSPR bands of lateral dimension (in-plane dipole at 570 nm) and aspect ratio (out-of-plane quadrupole at 330 nm) after 8 hours of the illumination. Shape evolution of the silver seeds was not completed by using the red LED because it provides insufficient energy, while shape transformation using blue LEDs give some thermodynamically unstable structures which could be possibly reversed to the starting seed. The AgNPs from red, green and daylight LED show very good stability, while the products from the blue LED were unstable. However, the method provide the cricial weakpoint as the silver seed has to prepared under slow reduction using low temperature (control by

ice bath). It is further difficult to be developed to be used in a flow reactor as temperature has to be controlled. Therefore, we will propose an alternative way to synthesize the silver nanoprisms by preparing silver seed solution under room temperature which will be discussed in the next section.

3.2 Synthesis of silver nanoprisms method under normal reduction of AgNPs

The previous method for synthesis AgNPs used ice bath for control rate of reduction of AgNPs. Due to the condition, it is quite complicated and difficult to control in the further flow process in flow reactor. Therefore, we proposed the alternative method to generate AgNPs at room temperature (28 °C). The parameters including the energy of light source (LED), mole ratio of reactants (Ag^+ , NaBH_4 and Citrate) and pH on the shape evolution of AgNPs were systematically investigated.

After illuminating the silver seed solution prepared using normal reduction condition with the red LED (630 nm, 1.97 eV) which exhibits the lowest energy compared to the other LEDs, it was found that the LSPR band was observed at ~400 nm without any significant changes. The intensity of the LSPR fluctuated during the first two hours after the irradiation and then color of the colloidal solution becomes darker after illumination for 2 hours as shown in Figure 3.8A. The extinction λ_{max} was slightly red shifted from 410 nm to 420 nm. However, the characteristic LSPR band of the aspect ratio for the AgNPs which is out of plane quadrupole around 350 nm cannot be observed. After illumination for 6 hours found the new LSPR band around 800 nm which might relate to large aggregates of the AgNPs. The observation on the LSPR is in good agreement with TEM image (Figure 3.8C) which exhibit only the

spherical silver nanostructure. From the results, it can be concluded that the shape evolution of the silver particles cannot be occurred by using the red LED because the energy of the red LED may be inadequate to overcome barrier energy of the shape evolution step.

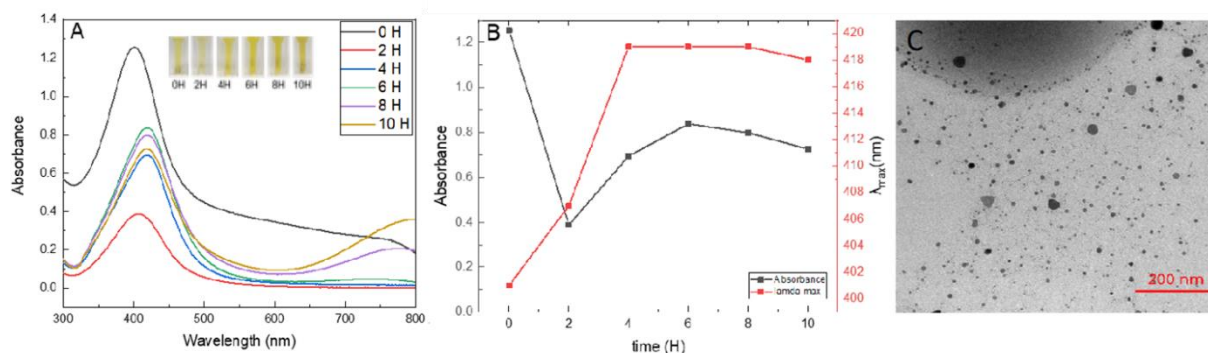


Figure 3.8 (A) UV-vis spectra of AgNPs after illumination with red LED (630 nm) with the inset Figures of the solution color at various times (0 – 10 hours). (B) plot of extinction λ_{max} after illumination with red LED (C) TEM image of AgNPs after illumination with red LED for 10 hours.

In the next study, the higher energy from the green LED was used instead of the red-LED to investigate the effects of external energy to the shape evolution process of the silver particle from spherical shape to prism. The colloidal silver solution with characteristic LSPR at 400 nm (spherical shape) representing as yellow was distinctively changed to green and then blue after illuminating the seed solution with the green LED (514 nm, 2.42 eV) for 10 hours as shown in Figure 3.9A. After illumination with the green LEDs for 4 hours the LSPR band of silver nano sphere at 400 nm is significantly decrease with generation of the new LSPR band at 340 nm and ~580 nm. This is strong evidence suggesting that the spherical shape of silver particles were transformed to the prism structure. A new LSPR band at 340 nm (out of plane quadrupole LSPR) relates to the aspect ratio of the particle and LSPR band at 580 nm (in-plane dipole LSPR) represents the lateral size of AgNPs. It was found

that the LSPR band of in-plane dipole LSPR is red-shifted (Figure 3.9C), while the extinction LSPR band of out of plane LSPR is unchanged (Figure 3.9B). The observations suggest that the lateral size of the AgNPs becomes larger and also thicker because the aspect ratio kept constantly. From TEM image, the synthesized AgNPs is in irregular plate shape including tri-angular, spherical prisms etc. The results encourage that the transformation of spherical silver nanoparticles to the AgNPs were achieved using the illumination of green LED of 514 nm

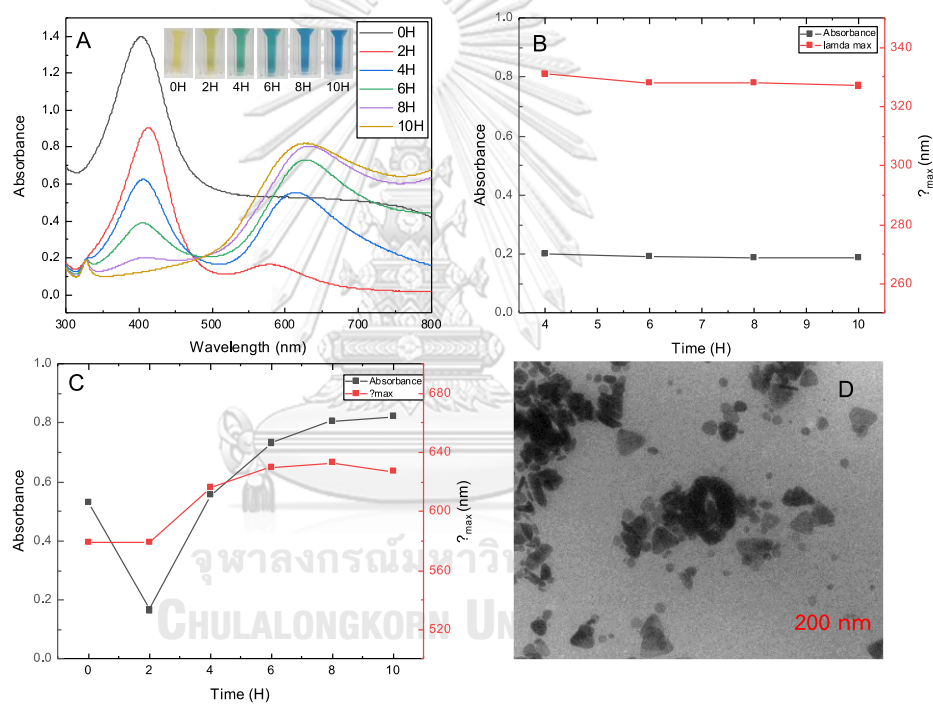
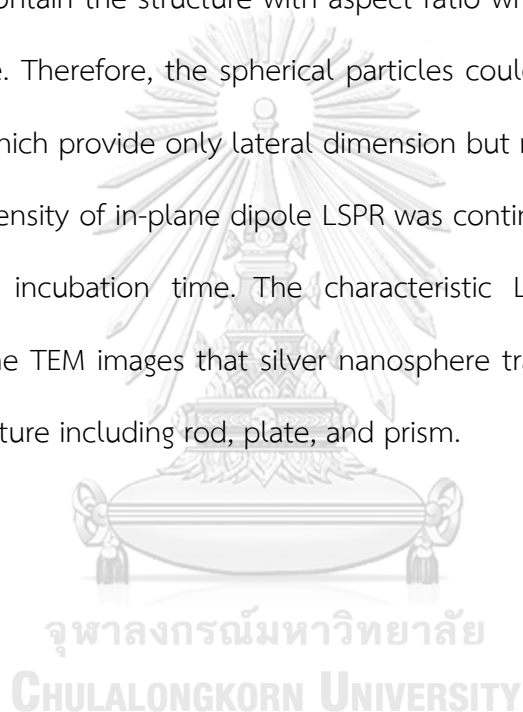


Figure 3.9 (A) UV-vis spectrum of AgNPs after illumination with green LED (514 nm) and solution color at various times. (B) plot of λ_{max} of out of plane quadrupole LSPR and extinction and (C) plot of λ_{max} of in plane dipole LSPR and extinction after illumination with green LED at various times (D) TEM image of AgNPs after illumination with blue LED for 10 hours.

After illuminating the silver seed solution with the blue LED (464 nm, 2.59 eV), the colloidal solution of AgNPs changes from yellow to red orange according to the duration of illumination as shown in Figure 3.10. After illumination with the blue LED for 2 hours, the LSPR band of the starting colloidal solution at 400 nm trends to vanish and a new LSPR bands at 440 nm is occurred. However, the out-of-plane quadrupole LSPR band at ~330 nm is not well-defined. This suggests that the particles do not contain the structure with aspect ratio which is crucial characteristic for prism structure. Therefore, the spherical particles could possibly be transformed to rod structure which provide only lateral dimension but not the aspect ratio. It was found that the intensity of in-plane dipole LSPR was continuously increased and was blue-shifted over incubation time. The characteristic LSPR bands are in good agreement with the TEM images that silver nanosphere transform to various shapes of silver nanostructure including rod, plate, and prism.



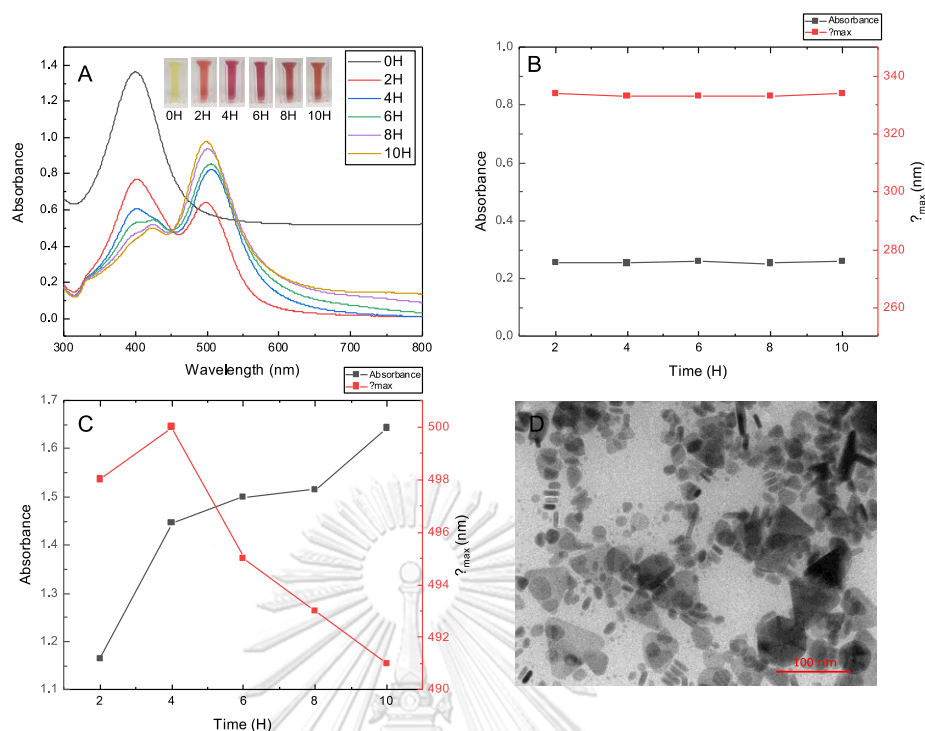


Figure 3.10 (A) UV-vis spectra of AgNPs after illumination with blue LED (464nm) and solution color at various times. (B) plot of λ_{max} of out of plane quadrupole LSPR extinction and (C) plot of λ_{max} of in plane dipole LSPR extinction after illumination with blue LED at various times (D) TEM image of AgNPs after illumination with blue LED for 10 hours.

3.2.1 Stability of the synthesized AgNPs

The synthesized AgNPs were kept at 4 °C with no exposure to external light. The LSPR extinction bands of the AgNP solution were monitored at the storage day of 3-45 days. After that, the extinction spectra of synthesized AgNPs were measured after illumination with red (630nm), green (514nm), and blue (464nm). It was found that the extinction spectra λ_{max} does not have any significant change even when they were kept for 45 days (Figure 3.11). The results suggest that the synthesized AgNPs are highly stable for at least 30 days before using when they were kept in dark and cold condition.

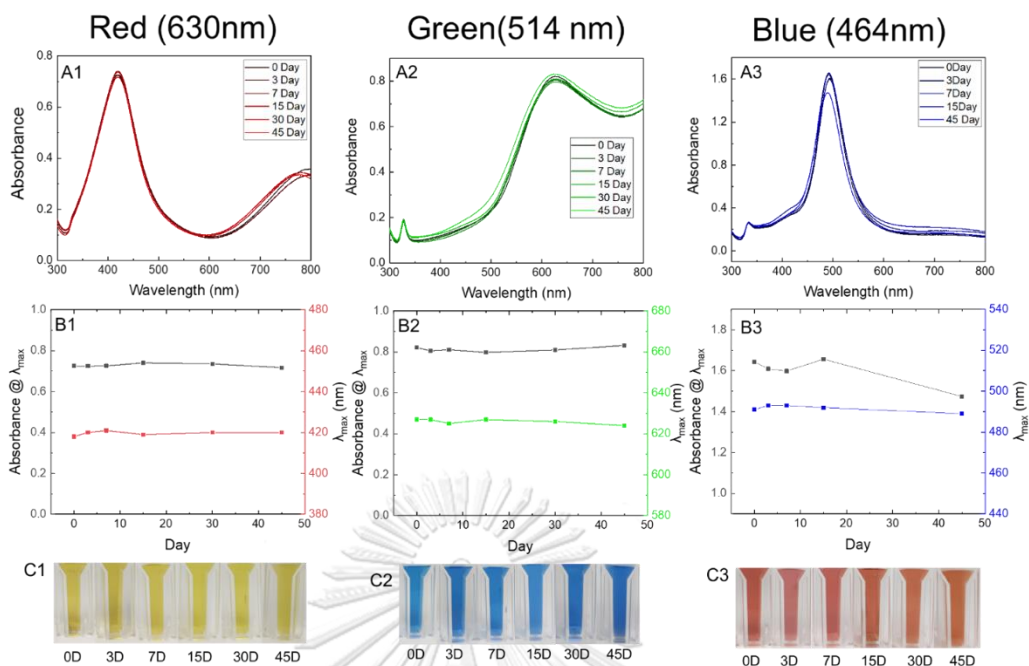


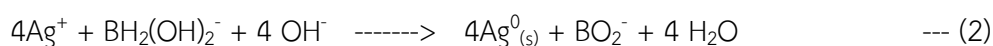
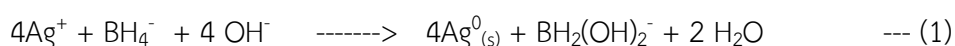
Figure 3.11 (A) UV-vis spectrum of synthesized AgNPs were kept at 4°C at various times (B) plot of λ_{max} extinction (C) the color of colloidal AgNPs were kept at various of time from 0-45 day

3.2.2 Influences of synthesis parameters on the shape evolution of

AgNPrs

In this section, the parameters of the mole ratios of the reactants and pH were systematically investigated. From the previous section, the reduction rate of AgNPs in the first step is crucially affected to the size and shape of the final product (AgNPrs).

The chemical reduction equations between Ag^+ and BH_4^- as a reducing agent are shown below



It could be seen that the reduction rate depends on the concentration of reducing agent (BH_4^-) and pH of the solution. The higher concentration of the reducing agent, the higher reduction rate. Moreover, the higher pH of the reaction, the higher reduction rate occurs. Therefore, the small particle size of AgNPs will be generated with the high reduction rate, while the larger particle size of AgNPs will be obtained with the low reduction rate. In the section, the parameters of the mole ratio of Ag^+ : Citrate: BH_4^- ratio and also pH of the reaction were optimized. The mole ratio was controlled by fixing the ratio between Ag^+ : Citrate to 1:10 with the various ratio of BH_4^- from 0.001 to 2 to control the reduction rate. Moreover, the reactions were performed within pH = 7 and pH = 9 to reveal the effect of pH on the nucleation step. From the previous section, it was found that only the green LED can induce the shape evolution of silver nanoprisms. Therefore, only green LED was used in further experiments as the light illumination source to keep the constant external energy to the reaction.

The extinction LSPR band before illumination at pH 7 (Figure 3.12A1) and pH 9 (Figure 3.12B1) are unchanged even the various BH_4^- mol ratios have been used. Only the extinction intensity increases when the higher mole ratios has been used. It obviously shows that the high amount of reducing agent, the larger amount of silver particle occurs. Interestingly, the full width at half maximum (FWHM) of the silver seed generated at pH 7 and pH 9 is significantly different. At pH 7, the FWHM of the silver seeds are larger when the higher mole ratio of BH_4^- were used. On the hand, the FWHM of the silver seeds are remain constant for all ratios using the reduction condition at pH 9. This suggests that the size of the silver seeds could be well controlled at alkaline condition due to the high reduction rate. After illumination the

seed solution for 8 hours, it could be seen that the spherical silver seed could be transformed to prism structure when the low mole ratio of BH_4^- were used. With low mole ratio of BH_4^- , the in-plane dipole LSPR can be observed for pH 7 (Figure 3.12A2) and pH 9 (Figure 3.12B2). These LSPR bands relate to the lateral size of AgNPs. However, only the solution at pH = 9 obviously provides the out-of-plane quadrupole LSPR at 335 nm (Figure 3.12B2) which is the characteristic band for aspect ratio of AgNPs. On the other hand, there is no shape evolution on the starting silver seed prepared at the higher mole ratio of BH_4^- . These results suggest that, the shape conversion of AgNPs using light irradiation can occur when the system contains extra Ag^+ .

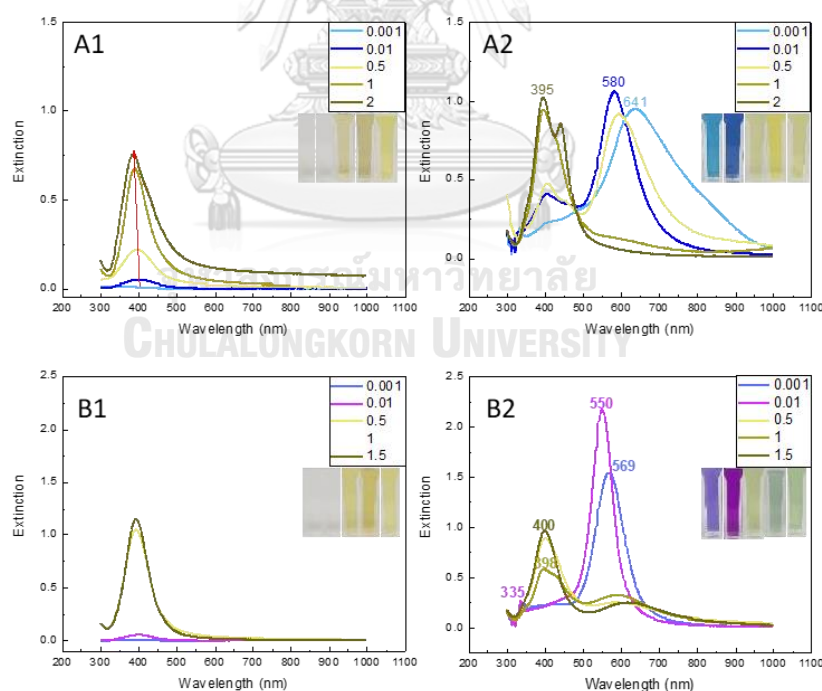


Figure 3.12 Spectra of colloidal silver nanoparticles from various Ag^+ : citrate: NaBH_4 at 1:10:0.001 to 1:10:2 ratio (various only mole ratio of NaBH_4) before (A1) pH=7 (B1) pH=9 and after illuminated with green LEDs (514 nm) for 8 hours at (A2) pH=7 (B2) pH=9

Because of this reason, we further investigate by comparing the shape evolution of the AgNPs synthesized from different conditions at mole ratio of Ag^+ : citrate: NaBH_4 equal to 1: 10: 0.001 and 1: 10: 0.05 at pH9. Figure 3.13A shows the extinction spectra of the synthesized AgNPs at NaBH_4 ratio = 0.001. The In-plane dipole LSPR can be observed at 581 nm after illumination for 2 hours and then was blue-shifted to 573, and 569 nm, respectively. Moreover, the out of plane LSPR can be observed at 339 nm after illumination for 2 hours and does not change even after illumination for 8 hours. This is strong evidence suggesting that the synthesized silver nanoparticles were growth in both direction of the lateral size and thickness of the AgNPs. The obtained LSPR bands are in good agreement with the color the colloidal solution which changes from colorless to purple, and darker purple overtime. The TEM images (Figure3.13A) show the shape of synthesized AgNPs. which contains of the majority of the silver nanoplates and silver nanoprisms

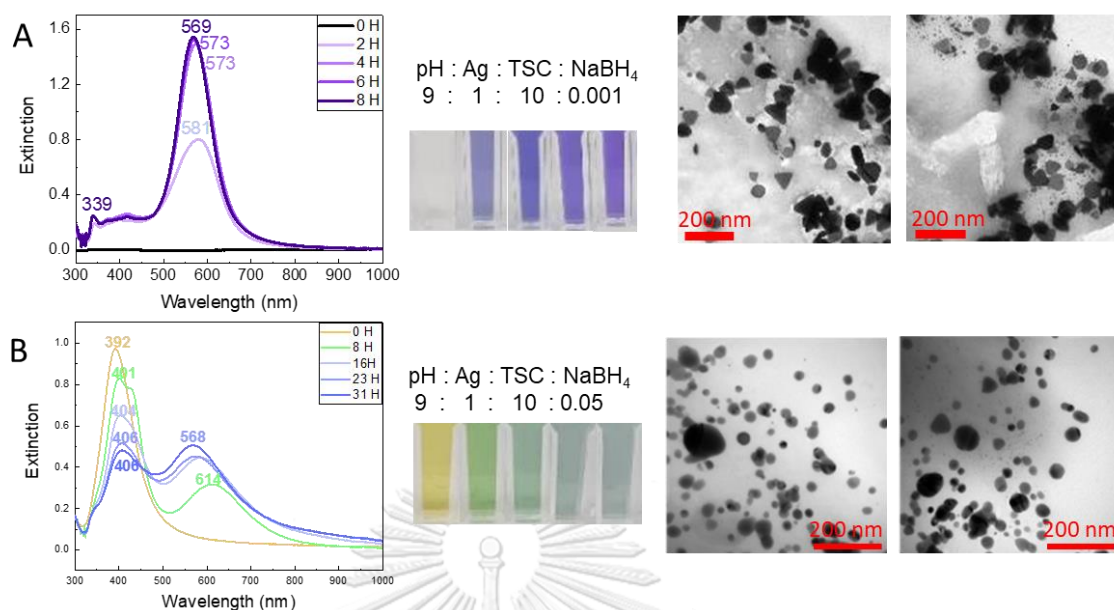


Figure 3.13 UV-Vis spectrum and Color of colloidal AgNPs at $\text{Ag}^+ : \text{Citrate} : \text{BH}_4^- =$ (A) 1:10:0.001 at pH = 9 (B) 1:10:0.001 at pH = 9 after illumination with green LEDs (514 nm) at various times with TEM image for silver nano particles after illumination for 8 and 31 hours respectively.

In case of increasing the mole ratio of BH_4^- to 0.05, the concentration is approximately higher than the previous experiment for 50 times. Figure 3.13B demonstrates the extinction spectra of AgNPs colloidal solution which no appearance of the out of plane quadrupole. Therefore, the shape conversion of the silver seeds to AgNPs has not occurred even the system was illuminated for 8 hours. In the case, the illumination process was prolonged from 8 hours to 16, 23, and 31 hours, respectively. After increasing the illumination time, the colloidal solution color changes from yellow to green and then blue, respectively. It seems that the shape evolution seemed take place. However, from UV-vis spectra, the in-plane dipole LSPR occurs at 568 nm while no observation on the out of plane quadrupole LSPR. TEM image of the colloidal solution collected at 31 hours of illumination shows the large spherical shape of AgNPs which could be represented

the particle shape as either large sphere or large thick plate. It is difficult to determine directly from TEM images. From the results, it could suggest that the concentration of silver species including silver seeds and Ag^+ are an crucial factor to control the growth process. In case of high concentration of the reducing agent (BH_4^-), the generation of silver seed favorably occurred. Therefore, there is less amount of Ag^+ presented in the solution. As the growth reaction was controlled by illuminating light only, the amount of Ag^+ before illumination is limited. In the growth process, the Ag^+ ion species is required in the shape transformation. In the photochemical technique [13], O_2 is typically required to oxidatively dissolve the Ag nanoparticles in order to generate additional Ag^+ , resulting in an Ag^+/Ag nanoparticles copresence environment and therefore a longer growth of the nanoprisms. When utilizing a low concentration of the reducing agent, it is plausible to assume that O_2 is unnecessary in a stepwise reduction approach since there is enough residual Ag^+ for the formation of the nanoprisms.

From the last session, we notice that the amount of residual Ag^+ after seed generation is strongly affected to the final product of AgNPrs. Therefore, in this process, the synthesis condition was controlled to pH 7 (reduce rate of seed generation) with the low mole ratio of BH_4^- at 0.001. Figure 3.14 demonstrates the extinction spectra of the AgNPrs colloidal after illumination with green LEDs (514nm) for 2 hours. The extinction of the in plane dipole and out of plane quadrupole LSPR can be observed at 636 and 333 nm, respectively. Then, the in-plane dipole LSPR was red-shifted to 653 nm with unchanged out of plane quadrupole after illumination for 4 hours. This observation suggests that in first 4 hours the AgNPrs are growth at lateral size and thickness equally. TEM image of the colloidal solution

collected at 8 hours of illumination shows the large AgNPrs with sharp edge. It provides the bigger size compared with the particle synthesized at pH 9 because there is less amount of silver seeds (due to the slow reduction rate) and high amount of residual Ag^+ to be used in the growth process. It shows that the silver ion species is the crucial factor for the shape evolution of AgNPrs for photo-mediation, therefore, the effect of Ag^+ on the growth process was further investigated in the next section.

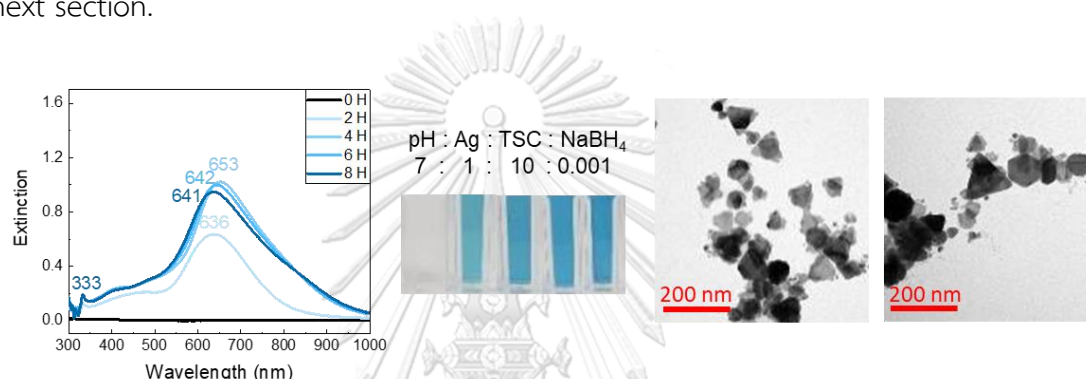


Figure 3.14 UV-Vis spectrum and Color of colloidal AgNPs at $\text{Ag}^+ : \text{Citrate} : \text{BH}_4^- = (A) 1:10:0.001$ at $\text{pH} = 7$ after illumination with green LEDs (514 nm) at various times with TEM image for silver nano particles after illumination for 8 hours.

3.2.3 Effects of residual silver ion concentration

From the previous result, the Ag^+ in the system is crucial to shape conversion of AgNPrs. The experiment was designed to use the synthesized condition of mole ratio ($\text{Ag}^+ : \text{Citrate} : \text{BH}_4^- = 1: 10: 0.001$) at $\text{pH} 7$. After the AgNPrs was obtained by irradiate with green LEDs for 8 hours. The solution was equally separated to one with the spiked silver seed and another one with the spike Ag^+ ion. Then, the colloidal solution was prolonging with light irradiation for 2 hours. Figure 3.15A and extinction spectra was monitored. From Figure 3.15B, it was found that the extinction spectra of the system (with the spiked silver seed) is insignificantly changed. This suggests that the growth process cannot be occurred with the additional silver seed in the system.

On the other hand, the system (with the spiked Ag^+) show the distinctive spectra with the redshift of in-plane dipole LSPR from 580 nm to 603 nm and dramatically increased intensity. This shows that the AgNPrs was continuously grown with the larger size on the lateral size and high number of particles. This observation is significant to be developed as an alternative method to extend the particle size of the existed AgNPrs using photo-mediation. It could be done by simply add Ag^+ in the system. However, it should be aware that the amount of silver ion might not be completely converted to AgNPrs. However, this problem can be simply clarified by add more reducing agent (NaBH_4). If there is no silver ions in the collodiation solution, the LSPR of silver seed at 400 nm will not be occurred.

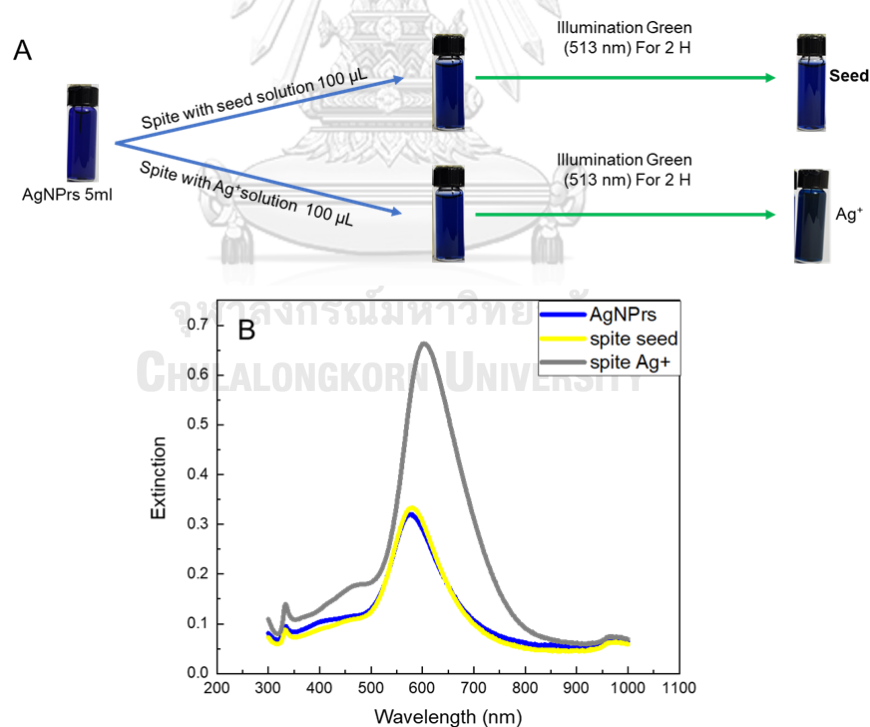


Figure 3.15 (A) Experiment set up for spite test (B) show UV-Visible spectra of silver nanoparticles after spite with seed solution/ Ag^+ solution and illuminate with green (514 nm)

3.3 Synthesis silver nanoprisms by flow-through reactor

Our design of flow-through reactor uses small transparent PVC tube in illumination step. Because the tube increases emitting area to the colloidal solution so the light (energy) from LEDs can emit to solution thoroughly. In the reactor also have a fan in our setup. The performance of the fan was demonstrated in Figure 3.16. From the result show that the fan can reduce temperature from around 70 °C (off) to around 40 °C (on). From H. Wang's work [13] the condition that suitable for the synthesis of AgNPrs was the temperature range at 20-40 °C and the emitting wavelength of 523 and 590 nm. We used beaker to stock the colloidal solution. In this work, we use only 40 mL of the colloidal for synthesis in flow-through reactor. If we increase amount of the stock colloidal the illumination must keep longer. The synthesis of silver nanoprisms method under normal reduction was applied to flow reactor that control temperature with fan and used green LEDs (514nm) for induce shape conversion and use the system have $\text{Ag}^+ : \text{Citrate} : \text{BH}_4^- = 1:10:0.001$ at pH 7. From Figure 3.17 found that AgNPs occur shape conversion because the characteristic LSPR band of AgNPrs which are in-plane dipole and out of plane quadrupole can be observe at 636 nm, and 334 nm respectively after illumination for 4 hours when compared to the batch synthesis our flow reactor also gave similar result. Therefore, that AgNPrs can be synthesized by our flow-through reactor. When comparing UV-Visible spectra of silver nanoparticles that were synthesized by batch and flow through reactor (Figure 3.18). From the extinction spectra the in-plane dipole LSPR from batch and flow through reactor can be observed at 641 and 639 respectively. The out of plane quadrupole from batch and flow through reactor can be observed

at 333 and 334 respectively. These two characteristic LSPR no significant difference. That is strong evidence suggesting that our flow through reactor gives the same AgNPs as batch synthesis. The reactor can reduce the time to synthesize and increase production volume.

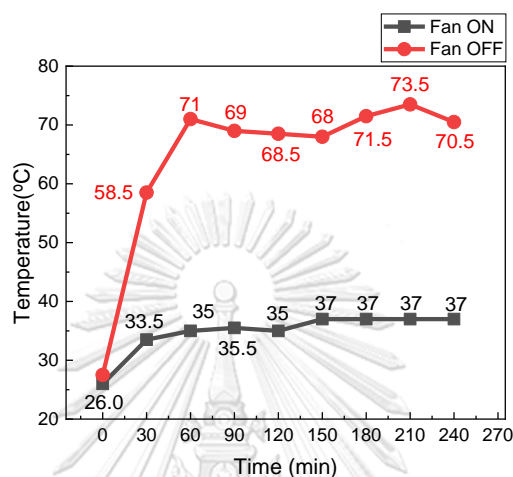


Figure 3.16 Comparison of temperature in reactor between fan turn on and turn off every 30 min.

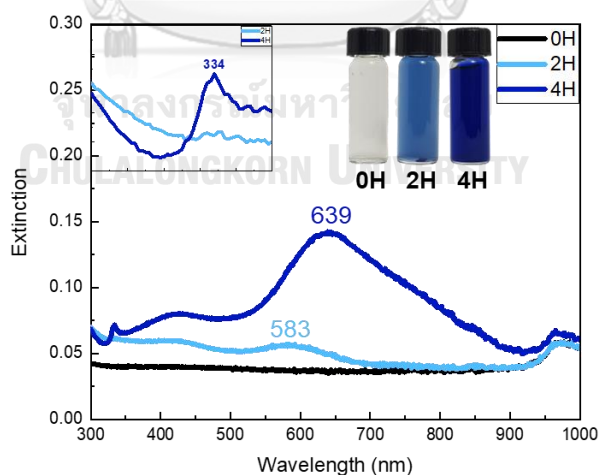


Figure 3.17 UV-Visible spectra of silver nanoparticles ($\text{Ag}^+ : \text{Citrate} : \text{BH}_4^- = 1:10:0.001$, pH 7) after illuminating with green LED (514nm) and color of solution at 2 and 4 hours after illuminating in flow-through reactor

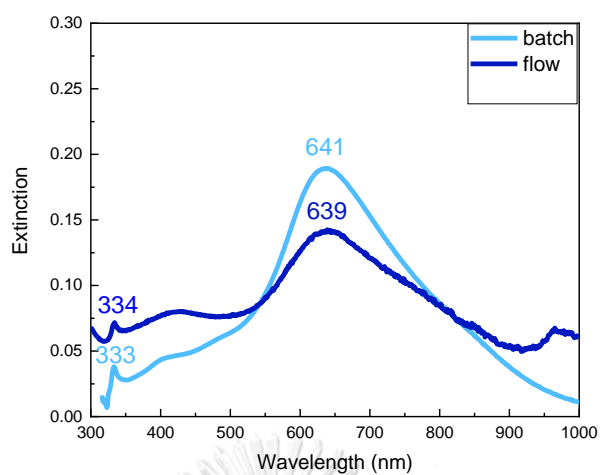


Figure 3.18 comparison of UV-Visible spectra of silver nanoparticles ($\text{Ag}^+ : \text{Citrate} : \text{BH}_4^- = 1:10:0.001$, pH 7) after illuminating with green LED (514nm) that were synthesized by batch and flow through reactor.

Chapter 4

Conclusions

Silver nanoprisms (AgNPrs) were mostly used as the chemical sensors in various application because they could provide the strong localized surface plasmon resonance (LSPR) in visible region which highly sensitive to their size and shape. There are several methods e.g. chemical reduction, seed mediation, and using shape converting agent to fabricate AgNPrs with controllable LSPR (size and shape). By these methods, the growth mechanism were generated thought kinetic model (the fastest route) which difficult to be controlled. Moreover, some methods required the long chain polymeric stabilizer which is difficult to perform further surface modification. Therefore, in the study, we propose the fabrication of AgNPrs using photo-mediation on the silver seed without polymeric stabilizer.

The silver seed was prepared by using silver nitrate as the silver source and sodium borohydride as the reducing agent with citrate as the stabilizer. Then, the shape evolution of the silver seed to AgNPrs was performed using the photo-mediation under the LED irradiation. The effects of the light source energy were investigated by varying the LEDs from 446 nm (2.67 eV) to 630 nm (1.97 eV). It was found that the shape evolution was occurred when LEDs source with > 2.41 eV was used. This suggests that the external light source should provide the energy to overcome the reaction energy barrier. Interestingly, only the green LEDs (2.41 eV) could induce the shape evolution of the silver seed to AgNPrs which could be monitored by the presence of characteristic band at ~ 330 nm (out of plane quadrupole LSPR) relating to the aspect ratio and LSPR band at 600 nm (in-plane

dipole LSPR) corresponding lateral size of AgNPrs. From TEM images, they suggest that the shape evolution could go through several growth-mediation pathways not only transform to the nanoprisms but also to other shapes. To prove of the growth model, the couple wavelength LED (daylight: blue 445 nm, 2.79 eV and green 542 nm, 2.29 eV) was used instead of the single narrow band LED. It was found that the mixed LSPR bands were observed at indistinguishable extinctions with the product generated using the individual blue LED and green LED. This observation is a strong evidence suggesting that size and shape of silver nanostructures could be precisely controlled by the external energy from LED illumination. From the process, the synthesized AgNPrs show good stability as monitored by their LSPR after storing at 4°C in close vials to prevent the effect of external light for 45 days.

Moreover, effects of the pH and the mole ratio of the starting reagent (including Ag^+ : TSC: BH_4^-) were revealed. From the chemical reaction between silver ions and the reducing agent (BH_4^-), the reduction rate of the silver seeds depends on the concentration of reducing agent (BH_4^-) and pH of the solution. The higher concentration of the reducing agent and the higher pH will provide the higher reduction rate. The mole ratio of BH_4^- was varied from 0.001 to 2 with the constant ratio of Ag^+ :TSC at 1:10. There is no shape evolution on the starting silver seed prepared at the high mole ratio of BH_4^- . These results suggest that the shape conversion of AgNPs using light irradiation can occur when the system contains adequate amount of Ag^+ . Then, the flow reactor will used the optimized parameter which are illumination wavelength from green LEDs (514 nm, 2.59 eV) for induce shape evolution, Ag^+ : TSC: $\text{BH}_4^- = 1:10:0.001$ at pH 7. It was found that AgNPs occur shape conversion because the characteristic LSPR band of AgNPrs which are in-plane

dipole and out of plane quadrupole can be observe at 636 nm, and 334 nm respectively after illumination for 4 hours when compared to the batch synthesis our flow reactor also gave similar result. That is evidence suggest that our flow through reactor give the same AgNPrs as batch synthesis.



REFERENCES

Uncategorized References

1. Pareek, V., R. Gupta, and J. Panwar, *Do physico-chemical properties of silver nanoparticles decide their interaction with biological media and bactericidal action? A review*. Mater Sci Eng C Mater Biol Appl, 2018. **90**: p. 739-749.
2. Kelly, K.L., et al., *The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment*. The Journal of Physical Chemistry B, 2003. **107**(3): p. 668-677.
3. Creighton, J.A., C.G. Blatchford, and M.G. Albrecht, *Plasma resonance enhancement of Raman scattering by pyridine adsorbed on silver or gold sol particles of size comparable to the excitation wavelength*. Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics, 1979. **75**(0): p. 790-798.
4. Lee, P.C. and D. Meisel, *Adsorption and surface-enhanced Raman of dyes on silver and gold sols*. The Journal of Physical Chemistry, 1982. **86**(17): p. 3391-3395.
5. María, L.G.B., et al., *Low Dimensional Nanostructures: Measurement and Remediation Technologies Applied to Trace Heavy Metals in Water. Trace Metals in the Environment*. New Approaches and Recent Advances. Vol. 1-24. 2020.
6. Aherne, D., et al., *Optical Properties and Growth Aspects of Silver Nanoprisms Produced by a Highly Reproducible and Rapid Synthesis at Room Temperature*. Advanced Functional Materials, 2008. **18**(14): p. 2005-2016.
7. Fan, M., et al., *Silver Nanoparticles on a Plastic Platform for Localized Surface Plasmon Resonance Biosensing*. Analytical Chemistry, 2010. **82**(15): p. 6350-6352.
8. Gao, C., et al., *Highly Stable Silver Nanoplates for Surface Plasmon Resonance Biosensing*. Angewandte Chemie International Edition, 2012. **51**(23): p. 5629-5633.

9. Chen, L., et al., *Highly Sensitive and Selective Colorimetric Sensing of Hg²⁺ Based on the Morphology Transition of Silver Nanoprisms*. ACS Applied Materials & Interfaces, 2013. **5**(2): p. 284-290.
10. Huber, J. and K. Leopold, *Nanomaterial-based strategies for enhanced mercury trace analysis in environmental and drinking waters*. TrAC Trends in Analytical Chemistry, 2015. **80**.
11. Kim, J.-Y. and J.-S. Lee, *Synthesis and Thermodynamically Controlled Anisotropic Assembly of DNA–Silver Nanoprisms for Diagnostic Applications*. Chemistry of Materials, 2010. **22**(24): p. 6684-6691.
12. Lee, S.H. and B.-H. Jun, *Silver Nanoparticles: Synthesis and Application for Nanomedicine*. International Journal of Molecular Sciences, 2019. **20**(4): p. 865.
13. Wang, H., et al., *Kinetic effects in the photomediated synthesis of silver nanodecahedra and nanoprisms: combined effect of wavelength and temperature*. Nanoscale, 2014. **6**(13): p. 7295-7302.
14. Chen, S., Z. Fan, and D.L. Carroll, *Silver Nanodisks: Synthesis, Characterization, and Self-Assembly*. The Journal of Physical Chemistry B, 2002. **106**(42): p. 10777-10781.
15. Pastoriza-Santos, I. and L.M. Liz-Marzán, *Synthesis of Silver Nanoprisms in DMF*. Nano Letters, 2002. **2**(8): p. 903-905.
16. Sun, Y., B. Mayers, and Y. Xia, *Transformation of Silver Nanospheres into Nanobelts and Triangular Nanoplates through a Thermal Process*. Nano Letters, 2003. **3**(5): p. 675-679.
17. Sun, Y. and Y. Xia, *Triangular Nanoplates of Silver: Synthesis, Characterization, and Use as Sacrificial Templates For Generating Triangular Nanorings of Gold*. Advanced Materials, 2003. **15**(9): p. 695-699.
18. Xiong, Y., et al., *Poly(vinyl pyrrolidone): A Dual Functional Reductant and Stabilizer for the Facile Synthesis of Noble Metal Nanoplates in Aqueous Solutions*. Langmuir, 2006. **22**(20): p. 8563-8570.
19. Washio, I., et al., *Reduction by the End Groups of Poly(vinyl pyrrolidone): A New and Versatile Route to the Kinetically Controlled Synthesis of Ag Triangular*

- Nanoplates*. *Advanced Materials*, 2006. **18**(13): p. 1745-1749.
20. Métraux, G.S. and C.A. Mirkin, *Rapid Thermal Synthesis of Silver Nanoprisms with Chemically Tailorable Thickness*. *Advanced Materials*, 2005. **17**(4): p. 412-415.
 21. Maillard, M., S. Giorgio, and M.-P. Pileni, *Tuning the Size of Silver Nanodisks with Similar Aspect Ratios: Synthesis and Optical Properties*. *The Journal of Physical Chemistry B*, 2003. **107**(11): p. 2466-2470.
 22. Hulteen, J.C. and R.P.V. Duyne, *Nanosphere lithography: A materials general fabrication process for periodic particle array surfaces*. *Journal of Vacuum Science & Technology A*, 1995. **13**(3): p. 1553-1558.
 23. Haynes, C.L. and R.P. Van Duyne, *Nanosphere Lithography: A Versatile Nanofabrication Tool for Studies of Size-Dependent Nanoparticle Optics*. *The Journal of Physical Chemistry B*, 2001. **105**(24): p. 5599-5611.
 24. Rybczynski, J., U. Ebels, and M. Giersig, *Large-scale, 2D arrays of magnetic nanoparticles*. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2003. **219**(1): p. 1-6.
 25. Haes, A.J., et al., *Solution-Phase, Triangular Ag Nanotriangles Fabricated by Nanosphere Lithography*. *The Journal of Physical Chemistry B*, 2005. **109**(22): p. 11158-11162.
 26. Jin, R., et al., *Photoinduced Conversion of Silver Nanospheres to Nanoprisms*. *Science*, 2001. **294**(5548): p. 1901-1903.
 27. Machulek Junior, A., H. Paulo Moisés de Oliveira, and M. Henrique Gehlen, *Preparation of silver nanoprisms using poly(N-vinyl-2-pyrrolidone) as a colloid-stabilizing agent and the effect of silver nanoparticles on the photophysical properties of cationic dyes*. *Photochemical & Photobiological Sciences*, 2003. **2**(9): p. 921-925.
 28. Xue, C. and C.A. Mirkin, *pH-Switchable Silver Nanoprism Growth Pathways*. *Angewandte Chemie International Edition*, 2007. **46**(12): p. 2036-2038.
 29. Xue, C., et al., *Plasmon-Driven Synthesis of Triangular Core-Shell Nanoprisms from Gold Seeds*. *Angewandte Chemie International Edition*, 2007. **46**(44): p. 8436-8439.

30. Bastys, V., et al., *Formation of Silver Nanoprisms with Surface Plasmons at Communication Wavelengths*. *Advanced Functional Materials*, 2006. **16**(6): p. 766-773.
31. Rocha, T.C.R., et al., *Formation Kinetics of Silver Triangular Nanoplates*. *The Journal of Physical Chemistry C*, 2007. **111**(7): p. 2885-2891.
32. Rocha, T.C.R. and D. Zanchet, *Structural Defects and Their Role in the Growth of Ag Triangular Nanoplates*. *The Journal of Physical Chemistry C*, 2007. **111**(19): p. 6989-6993.





จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

VITA

NAME Thanasit Laisanguanngam

DATE OF BIRTH 16 August 1995

PLACE OF BIRTH Angthong, Thailand

INSTITUTIONS ATTENDED 2017 Bachelor of Science in Chemistry,
Chulalongkorn University, Thailand

HOME ADDRESS 531, 5, Nongmakamong, Danchang, Suphanburi, 72180,
Thailand,

PUBLICATION Conference:
February 13-14,2020 Pure and Applied Chemistry
International Conference 2020 (PACCON 2020), Thailand
February 23-26,2021 International Union of Materials
Research Societies- International Conference in Asia
(IUMRS-ICA 2020)