Controlled Transformation of Nanoparticles with Tunable Surface Plasmon Resonance

Nimer Murshid
nimermurshid@yahoo.ca

Follow this and additional works at: https://scholars.wlu.ca/etd

Part of the Materials Chemistry Commons, Other Chemistry Commons, and the Physical Chemistry Commons

Recommended Citation
https://scholars.wlu.ca/etd/1623

This Thesis is brought to you for free and open access by Scholars Commons @ Laurier. It has been accepted for inclusion in Theses and Dissertations (Comprehensive) by an authorized administrator of Scholars Commons @ Laurier. For more information, please contact scholarscommons@wlu.ca.
Controlled Transformation of Nanoparticles with Tunable Surface Plasmon Resonance

by

Nimer Murshid

Bachelor of Science in Chemistry, University of Jordan, 1993
Master of Curricula and Teaching Methods, Amman Arab University, 2007

THESIS
Submitted to the Department of Chemistry
in partial fulfillment of the requirements for
Master of Science in Chemistry
Wilfrid Laurier University
2013

© Nimer Murshid 2013
Abstract

This thesis reports key findings in the synthesis and transformation of silver nanoparticles (AgNPs) with pentagonal symmetries. The main focus of the thesis work is on the synthesis of silver decahedral nanoparticles (AgDeNPs) and their transformation into larger AgDeNPs and silver pentagonal rod nanoparticles (AgPRNPs). In another direction, produced AgNPs were stabilized by gold plating. In a one-stage photochemical synthesis of AgDeNPs (pentagonal bipyramid, J\textsubscript{13} solid), oxidative etching by hydrogen peroxide was implemented to achieve complete conversion of the small silver platelet precursor NPs. For convenient laboratory synthesis of high-purity size-selected AgDeNPs, we have also adapted LEDs as a light source and documented optimal exposure time, LED power, and wavelength range. In the absence of platelet impurities, AgDeNPs produced by the new-generation procedure could be conveniently re-grown into larger sizes using silver ions as a precursor. Thermal one-dimensional regrowth of new-generation AgDeNPs into AgPRNPs has been reliably accomplished with the precise variation in rod length (by varying amounts of added silver) and width (by using different seed AgDeNPs). Chemical stability of prepared AgNPs was improved by deposition of a uniform thin layer of gold at the surface with the controlled slow rate. The produced gold-plated silver nanoparticles (Au@AgNPs, shell@core) were found to be stable in such aggressive chemical environment as: 1.5 M NH\textsubscript{3}, 0.5 M H\textsubscript{2}O\textsubscript{2}, and 150 mM NaCl solutions, where AgNPs were degraded in several minutes. Furthermore, strong SPR and surface uniformity of AgNPs have been advantageously preserved after gold plating. With the reported reproducible synthetic protocols that can be readily
implemented in any chemistry laboratory, AgDeNPs and AgPRNPs will serve as a versatile plasmonic platform with a precisely tunable surface plasmon resonance (SPR) from ca. 430 nm (rounded AgDeNPs) to 1100+ nm (longitudinal SPR of longer AgPRNPs). This plasmonic platform should be useful and advantageous for diverse range of applications, especially plasmonic sensing and surface-enhanced Raman spectroscopy (SERS).
Acknowledgements

At the outset I thank God for giving me the opportunity to complete this work while taking care of my lovely family.

First of all, I would like to extend my thanks to Dr. Vladimir Kitaev for accepting me in his group and for his friendly and continuously (24/7) support, guidance and patience throughout the last two years. I wish you knew Arabic so I can express my feeling better for you. I would also like to express my appreciation to the first person whom I have met at Laurier and who gave me continuous support and courage, Dr. Masoud Jelokhani-Niaraki. Great thanks to Dr. Scott Smith who gave me, after meeting him, the inspiration to work hard to attend Laurier, as well as, for his support in my first course in my degree. I would like to thank my thesis committee Dr. Ken Maly and Scott Smith as well for their invaluable discussion and feedback. Great thanks to Dr. Xiaosong Wang for offering me the PhD position in his group next year, which is the driving force for completing my thesis on time.

Special thanks to Dilyn Keogh and Matt McEachran for their valuable notes and preliminary finding which were beneficial for me to start my projects. Also, I would like to thank all of my current and former lab members, Kyle Bachus, Danielle Macoretta, Alanna Mceneny, Mary Samimi, Nicole Cathcart, Krysten Hobbs, Matthew Eade, and Tomendro Subedi for providing me the friendly working atmosphere.

This thesis is dedicated to my wife Rana and my children Lara, Osama, and Razan for their support, wishes and the stress that they felt due to our relocation.
# Table of Contents

List of Tables .......................................................................................................................... viii

List of Figures ......................................................................................................................... ix

List of Abbreviations ............................................................................................................. xii

**Chapter 1** General Introduction.................................................................................... 1

1.1 Introduction ...................................................................................................................... 2

1.2 References ....................................................................................................................... 9

**Chapter 2** Optimized Synthetic Protocol for Preparation of Versatile Plasmonic Platform Based on Silver Nanoparticles with Pentagonal Symmetries ......................... 14

2.1 Introduction ..................................................................................................................... 15

2.2 Key synthetic protocols ................................................................................................. 15

2.2.1 New generation of one-stage AgDeNP synthesis ....................................................... 17

2.2.2 Large decahedral silver nanoparticles .................................................................... 19

2.2.3 Pentagonal rod silver nanoparticles (AgPRNPs) .................................................... 21

2.3 Optimization of the synthesis and discussion of the key parameters ...................... 22

2.3.1 New-generation synthesis silver decahedral nanoparticles .................................... 22

2.3.1.1 Effect of the light exposure source .................................................................... 22

2.3.1.2 Effect of citrate .................................................................................................. 25

2.3.1.3 Effect of hydrogen peroxide ............................................................................. 26

2.3.1.4 Effect of borohydride ....................................................................................... 27

2.3.1.5 Effect of arginine ............................................................................................. 27
Chapter 3 Gold-Plated Silver Nanoparticles with Superior Stability and Plasmon Resonance

3.1 Introduction..............................................................................................................74
3.2 Results and discussion............................................................................................75
  3.2.1 Optimized gold plating protocol.........................................................................75
  3.2.2 Chemical stability................................................................................................77
  3.2.3 Effect of gold percentage (Au%)..........................................................................78
  3.2.4 Effect of reducing and complexing agents.........................................................80
3.3 Conclusion..............................................................................................................82
3.4 Supporting Information (SI†)..................................................................................83
  3.4.1 Experimental Section.........................................................................................83
    3.4.1.1 Reagents........................................................................................................83
    3.4.1.2 Synthesis of silver decahedral nanoparticles...............................................83
    3.4.1.3 Synthesis of silver pentagonal rod nanoparticles........................................84
    3.4.1.4 Synthesis of gold coated AgDeNPs...............................................................84
    3.4.1.5 Characterization.............................................................................................84
  3.4.2 Supplementary Figures.......................................................................................85
3.5 References..............................................................................................................95
Chapter 4  Conclusions and Other Projects Performed for Future Work

4.1 Conclusion

4.2 Other projects

4.2.1 Synthesis and Characterization of Polystyrene Latex at Room Temperature Using Green Initiator System

4.2.2 Is PVP a Miracle Reagent for Stabilization and Formation of Nanoparticles with {100} Facets?

4.2.3 Silica Encapsulation of MNPs for the Formation of Metallodielectric Arrays

4.3 Manuscripts summary

Appendix A
List of Tables

2.1 Optimal amounts of the reagents used in the synthesis of AgDeNPs..........................46

2.2 Maximum SPR wavelength and synthesis conditions of larger AgDeNPs .................46

2.3 Optimal amounts of Ag⁺ and SPR peaks for AgPRNPs with different length.............47

A.1 Chemical information table for synthesis of polystyrene latex.............................117
List of Figures

1.1 Schematic illustration that summarizes the preparation stages of AgNPs ..........8

2.1 Detailed schematic representation of the synthesis of AgNPs........................16
2.2 Representative UV-vis spectra and EM images of AgNPs and AgPRNPs.............17
2.3 UV-vis spectra and EM/AFM images of different AgNPs and AgPRNPs..............20
2.4 Effect of light exposure on the morphology and SPR of AgNPs.........................24
2.5 UV-vis spectra and EM images of AgPRNPs with different width.......................34
2.6 Optical photographs of the setups used in AgNP synthesis.............................48
2.7 Illustration of the major steps in the optimized AgDeNP synthesis.....................49
2.8 UV-vis spectra of the optimized AgDeNPs and AgPRNPs.................................50
2.9 Effect of AgDeNP size on SPR maxima and UV-vis spectra............................51
2.10 UV-vis spectra of AgPRNPs prepared using different amounts Ag⁺..................52
2.11 The effect of the amount of added Ag⁺ on the average length and λ_max............53
2.12 Emission spectra of different LEDs and UV-vis spectra of prepared AgNP........54
2.13 Emission spectra of different LEDs and TEM images of prepared AgNP..........55
2.14 UV-vis spectra of AgDeNP development using different light sources.............56
2.15 Modeling of the spectral component analysis using SIMPLISMA syntax............56
2.16 UV-vis spectra and TEM images illustrate the effect of citrate on AgDeNPs........57
2.17 UV-vis spectra and TEM images illustrate the effect of H₂O₂ on AgDeNPs...........58
2.18 UV-vis spectra and TEM images illustrate the effect of NaBH₄ on AgDeNPs.......59
UV-vis spectra and TEM images illustrate the effect of arginine on AgDeNPs..

UV-vis spectra and TEM images illustrate the effect of PVP on AgDeNPs.

UV-vis spectra and TEM image of AgDeNPs synthesized using PSS.

UV-vis spectra and TEM image of AgDeNPs synthesized using chloride.

UV-vis spectra and TEM images of AgDeNPs with gold as doping metal.

UV-vis spectra and TEM images illustrate the effect of pH on AgDeNPs.

TEM images of AgDeNPs with different size prepared using different LEDs.

Dependence of wavelength maxima of SPR peaks on AgPRNP dimensions.

Experimentally and expected average length of AgPRNP as a function of Ag⁺.

UV-vis spectra and TEM images of AgPRNPs prepared at different temp.

Effect of temperature on the time of the development of AgPRNPs.

Effect of citrate concentration on AgPRNP synthesis.

TEM images demonstrating the high yield and shape selectivity of AgDeNPs.

Schematic illustration of preparation, TEM images, and UV-vis spectra of Au@AgNPs.

Stability of the Au@AgDeNPs in different aggressive environments.

Effect of Au% on the prepared Au@AgDeNPs.

Effect of citrate addition on synthesis of 60% Au@AgDeNPs.

UV-vis spectra of the 10% Au@AgDeNPs using different rate of gold addition.

TEM images of AgDeNPs and Au@AgDeNPs.

EDX spectra and analysis of the Au@AgDeNPs.
3.8 Stability of uncoated AgDeNPs in H₂O₂ solution monitored by UV-vis spectra....88
3.9 TEM images illustrate stability of Au@AgDeNPs in H₂O₂ NaCl solutions.............89
3.10 UV-vis spectra and TEM image of Au@AgDeNPs treated in arginine solution.....90
3.11 Stability of gold plated pentagonal rods in H₂O₂ monitored by UV-vis spectra....91
3.12 Effect of Au% on SPR maxima and optical properties of Au@AgDeNP solution..92
3.13 TEM images of Au@AgNPs prepared with different reducing reagents..........93
3.14 TEM images of 80% Au@AgNPs prepared with and without citrate............94

4.1 Representative UV-vis spectra of AgDeNPs and AgPRNPs with tunable SPR.....98
4.2 Representative TEM images of AgDeNPs, Au@AgDeNPs, and Au@AgPRNPs.....99
4.3 Schematic illustration showing preparation of Au@AgDeNPs ......................99
4.4 Representative EM images of the prepared PS latex .............................101
4.5 Effect of the total PVP concentration on the average size of PS latex........101
4.6 Optical microscopy images of the prepared PS lattices films......................102
4.7 TEM image and schematic of silica encapsulation of the Au@AgDeNPs.......103
4.8 UV-vis spectra and EM images of AgPRNPs prepared using different steric stabilizers........................................................................................................104

A.1 Schematic representation of the stages of free-radical polymerization...........108
A.2 Schematic representation of the methods of free-radical polymerization.......109
A.3 Schematic representation of the emulsion polymerization stages.................110
A.4 Experimental setup for synthesis of polystyrene latex...............................119
# List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgDeNP</td>
<td>Silver decahedral nanoparticle</td>
</tr>
<tr>
<td>AgNP</td>
<td>Silver nanoparticle</td>
</tr>
<tr>
<td>AgPRNP</td>
<td>Silver pentagonal rod nanoparticle</td>
</tr>
<tr>
<td>Au@AgDeNP</td>
<td>Gold-plated silver decahedral nanoparticle</td>
</tr>
<tr>
<td>Au@AgNP</td>
<td>Gold-plated silver nanoparticle</td>
</tr>
<tr>
<td>Au@AgPRNP</td>
<td>Gold-plated silver pentagonal rod nanoparticle</td>
</tr>
<tr>
<td>AuNP</td>
<td>Gold nanoparticle</td>
</tr>
<tr>
<td>CTAB</td>
<td>Cetyltrimethylammonium bromide</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-dispersive X-ray</td>
</tr>
<tr>
<td>EM</td>
<td>Electron microscopy</td>
</tr>
<tr>
<td>Fcc</td>
<td>Face centered cubic</td>
</tr>
<tr>
<td>LED</td>
<td>Light-emitting diode</td>
</tr>
<tr>
<td>MNP</td>
<td>Metal nanoparticle</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>PAA</td>
<td>Polyacrylic acid</td>
</tr>
<tr>
<td>PNP</td>
<td>Plasmonic nanoparticle</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PSS</td>
<td>Poly (sodium 4-styrene sulfonate)</td>
</tr>
<tr>
<td>PVP</td>
<td>Polyvinylpyrrolidone</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SERS</td>
<td>Surface-enhanced Raman spectroscopy</td>
</tr>
<tr>
<td>SI</td>
<td>Supporting information</td>
</tr>
<tr>
<td>SPR</td>
<td>Surface plasmon resonance</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TEOS</td>
<td>Tetraethyl orthosilicate</td>
</tr>
<tr>
<td>UV-vis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>vis-NIR</td>
<td>Visible-near infrared2</td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$</td>
<td>Maximum absorbance wavelength</td>
</tr>
</tbody>
</table>
Chapter 1
General Introduction
Chapter 1

General Introduction

1.1 Introduction

Nanoscience is one of today’s most inspiring competitive interdisciplinary fields. It provides integration and unification rather than division between chemistry, physics, biology, engineering and medicine. Nanotechnology, promised by nanoscience, is manufacturing of devices, machines or products based upon nanoscale constituents. Nanochemistry is naturally concerned with the chemistry aspects of the nanoscience being involved in the synthesis and self-assembly of building blocks with at least one spatial dimension in the nanometer range. Controllably tailoring nanomaterial parameters, such as: surface, size, shape, and defect, can tune their properties for prospective applications.

Metal nanoparticles (MNPs) have attracted scientific attention for hundreds of years due to their intrinsic catalytic, electronic, magnetic and optical properties. MNPs are considered as metal nanocrystals that have at least one dimension ranging from 1 to 100 nm.

Plasmonic metal nanoparticles (PNPs), in particular silver and gold NPs, have proven to serve as a versatile platform for a range of diverse applications including catalysis, solar cells, sensors, especially sensors based on surface plasmon resonance and surface enhanced Raman scattering (SERS). PNPs are
distinct in their properties both from bulk materials and smaller superatomic metal clusters\textsuperscript{1,15,16} in displaying surface plasmon resonance (SPR). The SPR energy (wavelength) of PNP\textsubscript{s} is a function of nanoscale confinement, as a result SPR can be advantageously manoeuvred\textsuperscript{1,17} through several NP parameters including composition, size, and morphology.\textsuperscript{1,18,19,1,20,1,21} Silver features the highest energy of $d$-$sp$ transitions among coinage metals that enables SPR of silver nanoparticles (AgNP\textsubscript{s}) to span through the entire visible range into NIR (ca. 395 nm to 1300+ nm).\textsuperscript{1,20} Owing to their advantageous properties, AgNP\textsubscript{s} were synthesized in different morphologies including prisms,\textsuperscript{1,7,1,20} cubes,\textsuperscript{1,22} octahedra,\textsuperscript{1,23} bars,\textsuperscript{1,24} rods,\textsuperscript{1,25,1,26} wires,\textsuperscript{1,27} nanoflowers,\textsuperscript{1,28} and particles with concaved-surfaces.\textsuperscript{1,29} Several approaches to synthetic size and shape control of AgNP morphologies include systematic investigations of reducing agents,\textsuperscript{1,30} capping agents,\textsuperscript{1,31} synthetic parameters,\textsuperscript{1,32} and photochemical transformation pathways.\textsuperscript{1,25,1,32,1,34}

Metal decahedral nanoparticles (MDeNPs) feature the most compact pentagonal twinned morphology with $D_{5h}$ symmetry. Decahedra are pentagonal bipyramids (Johnson solid $J_{13}$). AgDeNPs are enclosed with ten (111) triangular facets of face center cubic (fcc) close packed lattice. A decahedral particle can be also represented as consisting of five tetrahedra twinned together by faces leaving a twinned defect gap of $7.35^\circ$.\textsuperscript{1,35,1,36} Gold decahedral nanoparticles (AuDeNPs) were first described as multiple twinned morphologies in the pioneering work of Ino and Ogawa at an earlier stage of gold film formation on alkali halide crystals and by evaporation in ultrahigh vacuum.\textsuperscript{1,37,1,38}
Several approaches have been subsequently developed to produce, transform and characterize MDeNPs.\textsuperscript{1,26,1,39,1,41,1,44} A synthetic protocol to prepare high-quality monodisperse shape-selected gold decahedral nanoparticles in DMF,\textsuperscript{1,39} and subsequent detailed studies of their plasmonic properties have been reported by Liz-Marzán’s group.\textsuperscript{1,40,1,41} Lombardi and co-workers reported the first feasible approach to the synthesis of silver decahedral nanoparticles (AgDeNPs) by using a 476.5-nm monochromatic laser light (decahedral particles were described as pentagons and produced as a mixture with other pyramidal particles).\textsuperscript{1,42} In a further development, silver decahedra were produced using blue 465-nm LED with a yield of about 90\% (with a significant contribution of tetrahedral morphologies) and FWHM of the SPR band of the prepared AgDeNPs of ca. 50 nm.\textsuperscript{1,43} AgDeNPs have been photochemically produced by our group with very good shape selectivity, using a metal halide lamp equipped with a blue filter as a light source.\textsuperscript{1,44} Yoon and co-workers reported synthesis of AgDeNPs in DMF through the proposed stepwise growth of tetrahedral NPs; the resulting decahedral NPs were produced as a mixture with triangular and hexagonal platelets, as well as with quasi-spherical morphologies, with the decahedra yield of ca. 35-50\%.\textsuperscript{1,45} Huang and co-workers recently reported one-pot synthesis of AgDeNPs using seedless photo-assisted citrate reduction under blue LED excitation with the yield of decahedral particles exceeding ca. 85\%; the remaining shapes being platelets and tetrahedra.\textsuperscript{1,46} All of these studies did not provide a reliable route for the preparation of AgDeNPs with high-quality shape selection, eliminating the presence of other morphologies, especially platelets/prisms. The key influence of even a minor fraction of platelet impurities is in
the transformation of AgDeNPs into other shape-selected morphologies with tunable SPR bands, where AgDeNPs serve as seed particles, for which the purity (absence of other seeds, such as small platelet AgNPs) is crucial.

When AgDeNPs undergo anisotropic one-dimensional elongation, the morphology is transformed from decahedra enclosed with ten {111} triangular facets into pentagonal rod nanoparticles (AgPRNPs) enclosed with five {100} side facets and preserved ten {111} capping facets. Metal nanorods and nanowires with pentatwinned symmetry have been synthesized using various approaches. A synthetic protocol to prepare gold nanorods in presence of a cationic surfactant, cetyltrimethylammonium bromide (CTAB), has been reported by Wang’s group. This method has been adopted by El-Sayed’s group to prepare gold nanorods with different controlled aspect ratios. Murphy and co-workers used the seed regrowth approach in the presence of CTAB to prepare silver and gold cylindrical nanorods with various aspect ratios (4.6 to 18). Mann and co-workers reported a seed-mediated synthetic protocol for gold nanorods with pentatwinned symmetry directed by CTAB that stabilizes {100} and {110} facets. Xia’s group reported a polyol synthetic protocol to prepare pentagonal silver nanowires on a large scale by using ethylene glycol at high temperature (160 °C) as a thermal reducing agent for silver ions in the presence of poly vinylpyrrolidone (PVP) as {100} facet stabilizer. AgPRNPs have been prepared by our group using thermal regrowth of decahedra in the presence of citrate as a thermal reducing agent. Good control over the length and long-range self-assembly have been demonstrated. Mirkin and co-workers recently reported
photochemical synthesis of silver rod NPs by SPR excitation of AgNP seeds using LEDs with the wavelength ranging from 600 and 750 nm.\textsuperscript{1.25} The aspect ratios of the prepared rods have been tailored through the excitation wavelengths.\textsuperscript{1.25} The key factor in controlling the quality of the rod MNPs is in the purity (both in size and in shape) of the precursor NP seeds.\textsuperscript{1.54}

Strong and sharp SPR of silver makes AgNPs potentially more advantageous compared to AuNPs for application based on plasmonic sensing and surface enhanced Raman spectroscopy (SERS). Despite these advantages, many applications of AgNPs, especially in biological systems, are limited due to their low stability in different detrimental environments, e.g. in presence of chloride ions that are common in physiological fluids.\textsuperscript{1.55} At the same time, AuNPs feature much better stability, but their major drawback is dampened plasmonic peaks below ca. 650 nm due to d-sp transitions in the visible. Despite the SPR disadvantage, AuNPs remain the only choice of PNPs for a wide range of biomedical applications.\textsuperscript{1.56}

In the above context, production of stable PNPs with strong SPR is essential for versatile applications. Several approaches to protect the surface of AgNPs by deposition a layer of silica\textsuperscript{1.57,1.58} or gold\textsuperscript{1.59,1.60} have been reported. Due to galvanic replacement, deposition of Au at the surface of AgNPs commonly results in silver oxidation and dissolution of AgNPs resulting in hollow gold particles without retaining the advantageous SPR characteristics of silver.\textsuperscript{1.61,1.62,1.63} Controllable deposition of the gold at the edges of silver decahedral nanoparticles to produce ultrathin gold nanoframes
was previously reported by our group. The key to form a uniform thin protective layer of gold at the surface of AgNPs is to avoid galvanic replacement. Xue’s group produced gold coating on silver nanoprisms using hydroxylamine as a reducing agent, and Yin’s group recently reported a synthetic protocol to prepare stable silver nanoplatlets through reducing the reduction potential of the gold salt by complexation with iodide ions in presence of diethyl amine. Both approaches rely on use of extra reagents and appreciably complex to readily adapt for silver morphologies other than nanoprisms. With the complexity of the reported procedures, there is a need for simple and reliable protocols for gold plating to readily attain these particles for use in diverse applications.

The main projects of this thesis were focused on synthesis and controlled transformation of PNPs (silver and gold-plated silver NPs) with pentagonal symmetry. Synthetic methods employed in this work were a combination of chemical, photochemical and thermal processes in aqueous solution.

The second chapter of this thesis includes the main body of the research work. The objective of this project is summarized schematically in Figure 1.1. The most significant stage in this project starts by the optimization of reproducible synthetic protocol to produce photochemically monodisperse AgDeNPs. Subsequently, produced AgDeNPs will be transformed photochemically into larger AgDeNPs or thermally into AgPRNPs with controllably varied dimensions. Key new developments that we report include the use of oxidative etching by hydrogen peroxide, adaptation of LEDs for versatile photochemical transformations, and efficient regrowth of AgDeNPs using silver ions as a precursor.
Figure 1.1 Schematic illustration that summarizes preparation stages of AgDeNPs and AgPRNPs with different dimensions (see also Figure 1.3 for representative EM images).

The research work in Chapter 3 describes feasible synthetic protocol to improve the stability of AgNPs by the uniform deposition of thin surface coating of gold. The main objective of this project is to prepare Au@AgNPs (shell@core) with high stability in most of the aggressive environments while preservation of the strong plasmonic properties of AgNPs.

Concluding Chapter 4 summarizes the results of the main two projects described in Chapters 2 and 3 and presents a brief description of the other significant projects that have been an important part of my thesis work. The summary of the manuscripts published and in preparation that are based on the thesis work is prepared in the end of the chapter.
1.2 References


[1.39] I. Pastoriza-Santos, A. Sánchez–Iglesias, F. J. García de Abajo, L. M. Liz-Marzán, 


Chem. Lett.* **2010**, *1*, 874.

**2007**, *111*, 14962.

**2009**, *25*, 3802.


Chapter 2
Optimized Synthetic Protocol for Preparation of Versatile Plasmonic Platform Based on Silver Nanoparticles with Pentagonal Symmetries
Chapter 2

Optimized Synthetic Protocol for Preparation of Versatile Plasmonic Platform

Based on Silver Nanoparticles with Pentagonal Symmetries

2.1 Introduction

This chapter describes the optimized synthetic procedures to reproducibly prepare, in high yield and with high shape selectivity (ca. 99.7%), silver decahedral and pentagonal rod nanoparticles with controllably varied dimensions. Key new developments that we report include the use of oxidative etching, adaptation of LEDs for versatile photochemical transformations, and efficient regrowth of AgDeNPs using silver ions as a precursor. We provide detailed experimental protocols for scientists to conveniently prepare these AgNPs with pentagonal symmetry and tailored plasmonic bands in common laboratory settings and to use them as a versatile plasmonic platform for diverse applications. Finally, the effect of various synthetic parameters and key reagents is described and discussed in detail to add to an existing body of knowledge on control of silver nanoparticle morphologies.

2.2 Key synthetic protocols

Figure 2.1 presents the schematics of the new-generation protocols to produce AgDeNPs photochemically and subsequently transform them either into larger AgDeNPs by photochemical regrowth or into AgPRNPs by thermal regrowth.
Figure 2.1 Schematic representation of the optimized photochemical synthesis of AgDeNPs, their photochemical regrowth into larger AgDeNPs, and thermal transformation into AgPRNPs. The colors in the schematic are chosen to closely represent the actual colors of AgNP solutions during the synthesis.

Representative UV-vis spectra and electron microscopy images of the resulting plasmonic AgNPs are shown in Figures 2.2a and 2.2b,c, respectively.
Figure 2.2 (a) Representative UV-vis spectra of as prepared AgNPs, measured in a 0.5-cm path length cell, of (1) AgDeNPs synthesized using 449±2 nm LED, (2) large AgDeNPs regrown on 505±2 nm LED (cyan), (3) pentagonal silver nanorods with an average length of 115±5 nm. (b) Transmission electron microscopy (TEM) image of synthesized AgDeNPs, using royal blue LED ($\lambda_{\text{max}} = 449±2$ nm), with the largest dimension across the pentagonal rim of 41±2 nm. (c) Scanning electron microscopy (SEM) image of AgPRNPs with the average length 115±5 nm. The scale bar is 100 nm for all images.

2.2.1 New generation of one-stage AgDeNP synthesis

Synthesis of AgDeNPs starts with the reduction of silver ions by sodium borohydride to generate primary precursor AgNPs. Citrate and PVP serve as charge and steric stabilizers of AgNPs, respectively. Arginine is used as a photochemical promoter and to halt the growth of silver platelets/prisms in the system\textsuperscript{2,1} (see Experimental Section). The new-generation synthetic procedure introduces oxidative etching by hydrogen peroxide as an important refining step to assist formation of stable decahedral morphologies and to achieve complete conversion of the precursor AgNPs, which are predominantly small platelets.\textsuperscript{2,1} The etching of less stable precursor AgNPs is
schematically depicted in Figure 2.1 as elimination of silver atoms with the higher surface energy, shown as blue spheres. We have also adapted light emitting diodes, LEDs, as a versatile efficient light source for photochemical transformations.\textsuperscript{2,2,3,2,4} We have found that royal blue LEDs (\(\lambda_{\text{max}} = 449\pm2\) nm) serve as an optimal light source to produce high-quality AgDeNPs with the largest dimension across the pentagonal rim of 41\(\pm2\) nm. Using 1-W royal blue LEDs together with hydrogen peroxide as a refining agent, the exposure time for ca. 15 ml of precursor AgNP solution in a 20-ml cylindrical vial required for complete conversion to decahedra is ca. 14 hrs (see Experimental Section, Figure 2.6a and 2.7), which is convenient overnight exposure. Crucially, oxidative etching by hydrogen peroxide assured full elimination of precursor platelet AgNPs and allowed to achieve their complete conversion into AgDeNPs. The presence of platelet AgNPs even at very low levels (not detectable by UV-vis spectra and hardly detectable by electron microscopy imaging) was found to be highly detrimental for the AgDeNP regrowth to pentagonal rods and especially for the regrowth to larger AgDeNPs using silver ions as a direct silver precursor, which could not be accomplished in our previous work.\textsuperscript{2,1} UV-vis spectra of AgDeNPs produced using a new-generation protocol (spectrum \(c\) in Figure 2.2a; see also Figure 2.8a in SI) with the maximum wavelength of the strongest SPR at 475 \(\pm\) 2 nm and prominently narrow HWHM of the peak at 15 nm (0.082 eV HWHM at 2.62 \(\pm\) 0.01 eV peak) is indicative of highly monodisperse AgDeNPs and can be compared to HWHM of ca. 25 nm reported by our group previously.\textsuperscript{2,1} Low size-dispersity (ca. 4.5\% standard deviation from average) and excellent shape selection is also corroborated by TEM and SEM images (Figure 2.2b and 2.3c respectively; also see
Figure 2.31 in SI). As prepared aqueous dispersions of AgDeNPs are chemically and colloidally stable for at least 4 years in ambient conditions; their zeta potential of \(-41 \pm 10\) mV is indicative of efficient charge stabilization provided by citrate ions.

2.2.2 Large decahedral silver nanoparticles

Achieving complete conversion of precursor AgNPs to AgDeNPs by oxidative etching allowed us to accomplish direct regrowth using silver ions as a precursor. It should be noted that we have not been able to achieve this regrowth with our previously reported AgDeNPs.\(^2\) It took us appreciable time to realize that even seemingly “unnoticeable” by UV-vis and EM amounts of platelet AgNPs are highly detrimental for the AgDeNP regrowth. The small AgNPs serve as very efficient growth centers that lead to the formation of fast growing platelets during the regrowth process. AgDeNPs prepared using optimized oxidative etching have minimal amounts of platelets, so the regrowth of these AgDeNPs could be accomplished photochemically by the slow addition of citrate-stabilized silver ions using either blue (\(\lambda_{\text{max}} = 472 \pm 2\) nm) or cyan (\(\lambda_{\text{max}} = 505 \pm 2\) nm) LEDs, as shown schematically in Figure 1a. UV-vis spectra and EM images of larger AgDeNPs are shown in Figure 2.3a and 2.3c,d respectively. The summary of the sizes and SPR maxima of large AgDeNPs prepared with different amounts of silver ions and light sources is presented in Table 2.2 and Figure 2.9 in SI.
Figure 2.3 (a) Normalized UV-vis spectra of (1) AgDeNPs synthesized using 449±2 nm LED and their regrowth using (2) 472±2 nm LED (blue) and (3) 505±2 nm LED (cyan). (b) UV-vis spectra, measured using a 0.5-cm path length cell of (1) seed AgDeNPs, and AgPRNPs with the length of (2) 97±4 nm; (3) 115±5 nm; (4) 147±6 nm; (5) 175±7 nm. SEM and TEM images of synthesized AgDeNPs with the largest dimension across the pentagonal rim of (c) 41±2 nm; (d) 51±4 nm and (e) 75±5 nm. (f) Atomic force microscopy (AFM) 4×4 µm topography image of AgPRNPs deposited on a silver-coated glass slide. (g) and (h) SEM images of AgPRNPs with the average length of (g) 120±5 nm and (h) 354±30 nm. The scale bar is 100 nm for all images.
2.2.3 Pentagonal rod silver nanoparticles (AgPRNPs)

Using AgDeNPs prepared by the new-generation procedure using oxidative etching was instrumental for the improvement of the reproducibility of previously reported rod regrowth procedure.\textsuperscript{2,5} In this procedure, as shown schematically in the bottom part of Figure 2.1, AgDeNPs are transformed thermally, by one-dimensional growth initiated at the pentagonal twinned defect,\textsuperscript{2,5,2,6} forming five new \{100\} side facets while retaining ten \{111\} capping facets of the decahedral seeds. Initial stages of the rod regrowth lead to more isotropic particles since the growth direction is along the shorter axis of the decahedra. In particular, using the amount of silver ions added less than two-times relative to the amount of silver present in the regrown AgDeNP seeds produced AgPRNPs with a blue-shifted single peak relative to the SPR of AgDeNP seeds (Figure 2.10 in SI). The single peak with the smallest SPR maxima at ca. 417 nm (Figure 2.10 and 2.11b in SI) has been achieved by using ca. 110\% of added silver ions relative to that present in the original AgDeNP solution. The subsequent increase in the amount of added silver ions results in more anisotropic particles (rods) with a corresponding red shift of the maximum of the longitudinal SPR mode (Figure 2.3b and 2.10 in SI) and an increased average length of synthesized AgPRNPs that could be readily varied from ca. 50 nm to >500 nm (48 ± 2 nm to 450 ± 30 nm is shown in Figure 2.11a in SI). Furthermore, our improvements in the synthesis of monodisperse large AgDeNPs enabled us to produce AgPRNPs of different widths varying from 35 to 75 nm (Figure 2.5). AFM and SEM images of these synthesized monodisperse AgPRNPs are shown in Figures 2.3f and 2.3g,h, respectively.
2.3 Optimization of the synthesis and discussion of the key parameters

Optimization of the synthesis of AgDeNPs, their further photochemical regrowth to larger decahedra, and thermal regrowth to pentagonal rods involved systematic variation of multiple synthetic parameters. Below we discuss the role of key parameters for all the synthetic protocols described.

2.3.1 New-generation synthesis silver decahedral nanoparticles (AgDeNPs)

2.3.1.1 Effect of the light exposure source

Upon silver reduction with borohydride, the produced precursor NP solution contains largely ill-defined small platelets with some amount of decahedral and quasi-spherical AgNPs (Figure 2.1).\textsuperscript{2,1} It is difficult to estimate precisely the amount of AgDeNPs in the reactive precursor NPs; it can be gauged approximately from TEM images as less than 1% (by number of particles). The photochemical transformation of the precursor AgNPs, which is enhanced by the oxidative etching, involves selective growth of the most stable AgNPs (AgDeNPs in our case) in appropriately chosen conditions (photochemical exposure and enhanced red-ox equilibrium with hydrogen peroxide and citrate). It has been reported by several groups that photochemical reduction of silver ions at AgNP surface is promoted by light excitation.\textsuperscript{2,7,2,8,2,9} The excitation of surface plasmon resonance (SPR) activates the photochemical reducing agent (citrate) to reduce silver ions to metallic silver at the energized AgNP surface.\textsuperscript{2,9} In the presence of AgNP seeds, SPR excitation reduces the activation energy required for the reduction of silver ions with citrate.\textsuperscript{2,10} Excitation of SPR effectively induces electron
holes ("hot holes") at the surface of AgNPs,\textsuperscript{2,11,2,12} so the photochemical reduction can be described as a charge transfer between the adsorbate (citrate and Ag\textsuperscript{+}) and the "hot holes".

Our photochemical growth of precursor AgNPs into AgDeNPs has been accomplished in presence of both a reducer (citrate) and an oxidative etching agent (hydrogen peroxide). Unstable AgNP morphologies have been etched by hydrogen peroxide into silver ions which then were stabilized and reduced by citrate at the surface of plasmonically excited growing AgDeNPs. The wavelength of the light used for this photochemical transformation has been found to affect both the size and shape of the resulting particles.\textsuperscript{2,2,3,2,13} Unlike more conventional sources of light exposure, LEDs feature fairly narrow emission spectra (Figure 2.12 in SI). Selective SPR excitation of specific AgNPs in a precursor solution can control the growth of the AgNPs into desired morphologies (AgDeNPs using royal blue LEDs in our case).\textsuperscript{2,1,2,2}

Figures 2.4a,b show schematic representation of AgNP morphologies (based on electron microscopy imaging) synthesized using LEDs with different wavelengths with the corresponding UV-vis spectra of AgNPs. AgDeNPs have been successfully produced with a good yield and shape selectivity using LEDs with emission $\lambda_{\text{max}}$ ranging from ca. 425 to 475 nm. In this range of excitation wavelengths, AgNPs with decahedral morphology were the most stable. Consequently, as shown in Figure 2.4c, other morphologies (platelets and quasi-spherical AgNPs) were oxidized (etched) and the
produced silver ions were then reduced onto the surface of AgDeNPs as the most stable morphology under these conditions.

**Figure 2.4 (a)** Effect of the LED maximum wavelength on the morphologies of photochemically developed AgNPs. **(b)** UV-vis spectra, measured in a 0.5-cm path length cell, of AgNP solutions synthesized using LEDs with \( \lambda_{\text{max}} \) of (1) 417; (2) 435; (3) 449; (4) 474; (5) 499; (6) 505 and (7) 520 nm. **(c)** Schematic representation of the effect of light exposure in photochemical formation and growth of AgDeNPs. Background colors in schematic (a) are the photographed colors of synthesized AgNP solutions.

The SPR of growing platelets is selectively excited relative to AgDeNPs when using LEDs with the excitation wavelength larger than ca. 500 nm. Under these conditions, platelet morphology was found to become predominant AgNPs (Figure 2.13h in SI).\(^{2,2,7,2,8,2,13}\) On the other hand, SPR of quasi-spherical seeds is selectively excited using excitation wavelength shorter than ca. 425 nm, which then yields rounded and truncated AgNPs (Figure 2.13c,d in SI).
Royal blue LED ($\lambda_{\text{max}} = 449\pm2$ nm) has been found to serve as the best light source to prepare AgDeNPs with the highest shape and size selectivity (see Figure 2.4 and 2.13 in SI). To investigate the effect of the irradiation wavelength on the kinetics of the development of AgDeNPs, we compared a royal blue LED ($\lambda_{\text{max}} = 449\pm2$ nm), a blue LED ($\lambda_{\text{max}} = 472\pm2$ nm), and a high intensity metal halide lamp with a blue filter cut off at ca. 450 nm as photochemical light sources. Figure 2.14 in SI presents the results of the development of AgDeNPs monitored by UV-vis spectroscopy. It has been observed that unreacted precursor platelets that contaminate AgDeNPs can be correlated with a red shift (typically to ca. 520 nm) of the SPR band during the early stages of the development (first 10-15 minutes of the light exposure). The most pronounced SPR red shift was observed for the LED with $\lambda_{\text{max}} = 472\pm2$ nm, whilst this red shift was smaller for the blue-filtered metal halide lamp and the smallest for the LED with $\lambda_{\text{max}} = 449\pm2$ nm. To assist our analysis of SPR spectra, we have utilized simple-to-use interactive self-modeling mixture analysis (SIMPLISMA) computational syntax that was adapted from a Windig’s program.\textsuperscript{2,14} As shown in Figure 2.15 in SI, the smallest amount of platelets with the SPR band at ca. 520 nm was observed for AgDeNPs that were synthesized using the LED with $\lambda_{\text{max}} = 449\pm2$ nm. These AgDeNPs also featured the highest spectral purity, as indicated by the main plasmon band at ca. 475 nm, and convincingly corroborated by EM images.

2.3.1.2 Effect of citrate

Trisodium citrate served as a multifunctional reagent in the synthesis of AgDeNPs. In addition to stabilization of $\{111\}$ facets,\textsuperscript{2,15,2,16} citrate is known to form
chelate complexes with silver ions which is likely an important factor during nucleation and shape-refining process.\textsuperscript{2,17,2,18,2,19} As it was discussed for the effect of light exposure, citrate also plays an important role as a photochemical reducing agent.\textsuperscript{2,10} The optimized molar ratio of citrate-to-silver used in our new protocol was found to be 12-14 compared to the previously used ratio of 18-18.5. Using lower molar ratios of citrate to silver (< 9) resulted in truncated decahedral particles with high polydispersity and aggregated AgNPs (see spectrum and image \textsuperscript{1} in Figure 2.16 in SI). For higher molar ratios of citrate to silver (> 36) highly truncated and polydisperse AgDeNPs have been produced as well (see spectrum and image \textsuperscript{2} in Figure 2.16 in SI).

\textbf{2.3.1.3 Effect of hydrogen peroxide}

The optimized total concentration of hydrogen peroxide in the synthesis of the new-generation AgDeNPs was found to be quite high at 0.20 M (see Figure 2.7 in SI). There are two reasons to explain such high concentration. The first is that hydrogen peroxide is a neutral reagent that reacts slowly with the reducing agents, such as citrate and borohydride. The second is that peroxide is actively decomposed to oxygen and water at the metallic silver surface that commonly manifests in our synthesis by bubble evolution when AgNPs become sufficiently large (darker yellow-orange from pale yellow; see Figure 2.7 in SI). From a synthetic point of view, high peroxide concentration was found to be essential for the efficient oxidative etching where all of the less stable morphologies (platelets, quasi-spherical and other ill-defined particles) were dissolved. Using lower amounts of hydrogen peroxide (< 0.15 M) was noticeably less effective for the refinement of the formation of AgDeNPs, while small platelets and large decahedral...
particles were produced as impurities (see spectra and image ① in Figure 2.17 in SI). At the same time, using higher amounts of hydrogen peroxide (> 0.25 M) resulted in increased truncation and polydispersity of the synthesized AgDeNPs (see spectrum and image ② in Figure 2.17 in SI) due to significant dissolution of the decahedral seeds in the precursor solution.

2.3.1.4 Effect of borohydride

The optimized total concentration of sodium borohydride was found to be ca. 1.3 mM, which corresponds to the molar ratio of 10 to 1 relative to silver ions. Using higher molar ratios (e.g. 16 to 1) of borohydride delayed nucleation and produced reddish precursor AgNPs which then converted to larger less monodisperse AgDeNPs upon light exposure (see spectrum and image ② in Figure 2.18 in SI). On the other hand, using lower molar ratios of borohydride to silver (5 to 1) resulted in higher polydispersity of AgDeNPs and formation of platelets and distorted particles (see spectrum and image ① in Figure 2.18 in SI). AgNPs prepared using the molar ratio of borohydride to silver (less than 5) were dissolved by hydrogen peroxide into silver ions during the oxidative etching step.

2.3.1.5 Effect of arginine

Arginine slows down the growth of larger platelets in the precursor AgNPs through its relatively strong binding to AgNP surface. During light exposure, arginine also seems to improve the uniform growth of the AgDeNPs, possibly by complexing silver and binding to citrate complexes to reduce their negative charge and enhance their reactivity. The total optimal concentration of arginine was found to be 0.016 mM.
In the absence of arginine, a mixture of aggregated and ill-defined AgNPs was produced (see spectrum and image ① in Figure 2.19 in SI). With the increasing concentration of arginine to the optimal level, the SPR spectra of synthesized AgDeNPs become more developed and better resolved (Figure 2.19 in SI). At the same time, truncation of AgDeNPs was noticeably increased for higher than optimal arginine concentrations (see spectrum and image ④ in Figure 2.19 in SI).

2.3.1.6 Effect of steric stabilizers

As a steric stabilizer, polyvinylpyrrolidone (PVP) is commonly used to improve colloidal stability of AgNPs.\textsuperscript{2,15,2,20} The best shape selectivity and size distribution of AgDeNPs have been achieved at optimum PVP total concentration in solution of 0.048 mM (expressed in terms of monomer units). Using no PVP or lower than optimal concentrations lead to the reduced AgDeNP stability; as a result, aggregated ill-defined large AgNPs were produced (see spectrum and image ① in Figure 2.20 in SI). Although PVP is a steric stabilizer and is instrumental to improve stability and monodispersity of MNPs,\textsuperscript{2,21} higher concentrations of PVP (> 0.8 mM) caused increased polydispersity of the AgDeNPs with the presence of distorted decahedral particles (see spectrum and images ② and ③ in Figure 2.20 in SI). A likely cause of the distorted shapes is that the binding of an excess PVP at the AgNP surface prevents uniform growth of AgNPs.

As a suitable alternative to PVP, poly (sodium 4- styrene sulfonate), PSS, was successfully used in the high-yield synthesis of monodisperse AgDeNPs. Using royal blue LEDs and similar synthetic conditions, AgDeNPs with SPR maxima at ca.468 nm and the largest dimension across the pentagonal rim of 35±5 nm were produced, which is
smaller compared to 41±2 nm for the AgDeNPs stabilized using the optimal PVP concentration. The optimal total concentration of PSS has been found to be essentially the same as for PVP (ca. 0.048 mM by monomer units). AgDeNPs synthesized using PSS have well-defined UV-vis spectra (Figure 2.21a in SI) that are indicative of NPs with very low size-dispersity, which is also corroborated by TEM imaging (Figure 2.21b in SI).

2.3.1.7 Effect of chloride ions

Addition of chloride ions to the AgDeNP synthesis before or shortly after reduction forced nucleation and severely reduced the number of developing AgNP seeds. The seed development was less affected when chloride was added after the refining step, which is indicative that the seeds become more stable after oxidative etching with hydrogen peroxide. AgDeNPs prepared using chloride ions with total concentration of ca. 0.064 mM, which corresponds to the molar ratio of 1 to 2 relative to silver ions, were highly truncated and distorted (Figure 2.22 in SI).

2.3.1.8. Effect of doping with gold ions

Although we could produce monodisperse decahedral particles using lower amounts of gold relative to silver (up to ca. 1 mol. %), no significant difference compared to AgDeNPs prepared without gold has been observed. At the same time, using higher amounts of gold (>1 mol. %) resulted in increased AgDeNP polydispersity accompanied with the presence of truncated AgNPs. UV-vis spectra and TEM images of AgDeNPs synthesized using different percentage of gold are shown in Figure 2.23 in SI.
2.3.1.9 Effect of pH

The development of AgDeNPs was found to be dependent on pH of the solution. When pH increased above 7.5 (Figure 2.24a,c-e in SI) AgNP formation slowed down at early stages of the development, which resulted in incomplete conversion of AgNP seeds to decahedral nanoparticles. This observation can be possibly attributed to the lower redox potential of hydrogen peroxide in basic aqueous solutions. At pH lower than 7, truncated decahedral particles were produced (Figure 2.24b,g in SI). The optimal pH for the AgDeNPs synthesis was found to be ca. 7.5 (Figure 2.24f in SI), which was the pH used in our new optimized synthetic protocol.

2.3.2 Photochemical regrowth to large silver decahedral nanoparticles (Large AgDeNPs)

The successful achievement of complete conversion of precursor AgNPs into AgDeNPs allowed us to accomplish direct regrowth using silver ions as a simple precursor. Such regrowth process could not be performed using the previously prepared AgDeNPs, for which we had to use small platelet AgNPs as a precursor. Optimization of the new AgDeNP regrowth process has been attained by the systematic investigation of the effect of light exposure sources, and the balance of the amount of added silver ions with the speed of the silver precursor addition. We have found silver ions complexed with citrate (Ag⁺/citrate) to be an optimal precursor which worked well for slow addition to the solution of the AgDeNP seeds upon light exposure. Stabilized silver ions were photochemically reduced at the excited AgDeNP surface. To produce larger AgDeNPs, light sources with a longer wavelength compared to that used to prepare the
original AgDeNPs (ca. 449 nm) were required. We have successfully optimized the regrowth protocol using blue LEDs ($\lambda_{\text{max}} = 472 \pm 2$ nm) and cyan LEDs ($\lambda_{\text{max}} = 505 \pm 2$ nm). The ranges of optimal molar ratios of precursor silver ions relative to the amount of silver present in the regrown AgDeNP seeds were found to be 0.9-1.8 and 2-7 for blue and cyan LEDs, respectively. Together with the amount of added silver ions and the LED wavelength, the speed of addition was found to be a key factor to attain uniform regrowth without secondary nucleation. The speed of addition of silver ions was optimized for each particular combination of the percentage of added silver ions and LED wavelength (Table 2.2 in SI). For example, AgDeNPs with the SPR maximum of 488 nm and the largest dimension across the pentagonal rim of 51±4 nm were produced by dispensing silver ions with the rate of 0.77 µmol/hr using the blue LED; whereas, AgDeNPs with the SPR maximum of 510 nm and the largest dimension across the pentagonal rim of 75±5 nm were achieved by dispensing silver ions with the rate of 0.26 µmol/hr using the cyan LED. Overall, large monodisperse AgDeNPs with an average size from ca. 45 nm to 100 nm (Figure 2.9 in SI) have been produced in this regrowth process. Using the blue LEDs, AgDeNPs with the main SPR maxima ranging from 485 nm to 505 nm could be produced, while using the cyan LEDs, SPR maxima of AgDeNPs could be tailored from 505 nm to 540 nm. The SPR maxima of regrown AgDeNPs were typically red-shifted by 20-30 nm relative to that of the LED irradiation wavelength. At the same time, AgDeNPs with high polydispersity and presence of quasi-spherical particles have been produced when using violet LEDs ($\lambda_{\text{max}} = 409 \pm 4$ nm) for the regrowth. Polydisperse AgDeNPs with platelet AgNP impurities were the result of the
decahedra regrowth using green LEDs ($\lambda_{\text{max}} = 520 \pm 5$ nm). Detailed information on the optimized amounts of added silver, speed of addition, and SPR of the regrown AgDeNPs is provided in Table 2.2 in SI. Corresponding UV-vis spectra and TEM images of AgDeNPs regrown using different LEDs are presented in Figures 2.9a and 2.25, respectively.

2.3.3 Thermal growth of silver pentagonal rod nanoparticles (AgPRNPs)

Thermal transformation of AgDeNPs into AgPRNPs has been successfully and reproducibly demonstrated for different length and width of AgPRNPs using the new generation of AgDeNPs. Further optimization of the thermal growth of AgPRNPs has been accomplished by the systematic investigation of the effects of the amount of added silver, size of regrown AgDeNPs, regrowth temperature, and concentrations of reducing and stabilizing reagents.

2.3.3.1 Effect of the amount of added silver ions

Figure 2.10 and 2.11b in SI show the effect of the percentage of added silver ions on the SPR spectra of regrown AgPRNPs. Using amount of added silver ions up to twice as less relative to the silver present in seed AgDeNPs transformed SPR of AgDeNPs into a single blue-shifted peak. A single SPR peak with the shortest wavelength of the maximum at ca. 417 nm has been produced in AgPRNP growth using 110% of added silver ions relative to the silver present in AgDeNP seeds (Figure 2.10 and 2.11b in SI). The longitudinal peak of AgPRNPs starts to be defined when the amount of added silver ions exceeds more than two times (200%) of that present in the AgDeNP seeds. It has been clearly observed, as shown in Figures 2.3b, 2.11 and 2.26a, that both the average
length and primary (longitudinal) SPR peaks maxima of prepared AgPRNPs increase upon increasing the percentage of added silver ions, which enables us to produce AgPRNPs with precisely tailored SPR bands. To accomplish precise AgPRNP growth, it is important to quantify the amount of silver present in AgDeNP seeds (e.g. after centrifugation and concentration) that can be conveniently done by UV-vis spectroscopy through monitoring the intensity of the strongest SPR peak. Figure 2.27 in SI presents the dependence of the experimental average length of the prepared AgPRNPs on the percentage of added silver ions relative to that present in the original AgDeNP solution, together with the calculated AgPRNP length based upon geometric considerations of transformations of Johnson solid $J_{13}$ to pentagonal rods. In general, the experimental average length of synthesized AgPRNPs has been found to be higher for the larger rod length ($> 130$ nm), which can be attributed to the partial loss of the AgDeNP seeds in the long regrowth process.

### 2.3.3.2 Effect of AgDeNPs size

Using new synthetic protocols allowed us to prepare high-quality AgDeNPs of different sizes that could be successfully regrown into AgPRNPs of different width (which was considerably limited in our previously reported rod regrowth).\(^2\) During the one-dimensional growth of AgPRNPs, the average width of the synthesized AgPRNPs remains the same as the largest dimension across the pentagonal rim of the AgDeNP seeds. AgPRNPs with the width of 41±2 nm were successfully produced by thermal
regrowth of the optimized one-stage AgDeNPs with the largest dimension across the pentagonal rim of 41±2 nm (Figure 2.2d, 2.3f,g and image ② in Figure 2.5).

**Figure 2.5** UV-vis spectra normalized by the transverse peak absorbance (top panel) and EM images (four bottom panels) of AgPRNPs with an average width of (1) 35; (2) 41; (3) 51; (4) 75 nm. All scale bars are 100 nm for all images.
AgPRNPs with larger width (ca. 50-75 nm) were synthesized using larger AgDeNPs that have been produced using photochemical regrowth of the optimized AgDeNPs (spectra and images ③ and ④ in Figure 2.5). Thinner AgPRNPs (ca. 35 nm) were prepared using AgDeNPs that have been synthesized using either PSS instead of PVP or LEDs with the wavelength maxima of ca. 435 nm instead of ca. 449 nm (spectra and image ① in Figure 2.5). Figure 2.5 and 2.26b illustrate the effect of the AgPRNP width on the secondary (transverse) SPR peaks. The wavelength of the transverse SPR peak maximum increased as expected, with the increase in the width of the AgPRNPs.

2.3.3.3 Effect of temperature

During the thermal transformation of AgDeNPs into AgPRNPs, heating at the constant controlled temperature of 98 °C has been found to be optimal for uniform regrowth and full conversion of added silver ions into AgPRNPs. To fully investigate the effect of the regrowth temperature on the transformation, we have first determined the time required for the complete development of AgPRNPs at different temperatures by monitoring UV-vis spectra during the transformation (Figure 2.10 and 2.6c in SI). The time of the development was increased upon decreasing regrowth temperature: decreasing temperature from 98 °C to 75 °C resulted in an increased development time of from 20 to 180 minutes (Figure 2.29 in SI). Polydispersity of AgPRNPs appreciably increased at temperatures approaching 80 °C. At temperatures lower than 80 °C, significant amounts of untransformed decahedral particles were observed (Figure 2.28 in SI).
2.3.3.4 Effect of citrate

During the regrowth of AgDeNPs into AgPRNPs, trisodium citrate is used to charge-stabilize growing AgPRNPs, particularly the ten \{111\} capping facets. In addition to its stabilization role, citrate functions as a thermal reducing agent. Omitting sodium citrate from the synthetic protocol prevents reduction of silver ions, resulting in the arrest of AgPRNP production, whilst truncated AgDeNPs were observed as a main reaction product (Figure 2.30b in SI). The optimal total concentration of citrate in the solution has been found to be ca. 4.5 mM. Using lower than optimal citrate concentrations leads to reduced preservation of \{111\} pentagonal cap facets, resulting in rounded rods (Figure 2.30c in SI). Using higher citrate concentrations (>6 mM) causes non-uniform reduction of silver ions and likely the secondary nucleation in the system by reduction of silver ions in the solution rather than exclusively on the surface of the growing AgPRNPs. As a result, ill-shaped morphologies were produced in addition to AgPRNPs (Figure 2.30d in SI). UV-vis spectra of AgPRNPs synthesized using different citrate concentrations are shown in Figure 2.30a in SI.

2.3.3.5 Effect of PVP

During the one-dimensional growth of AgPRNPs, PVP is commonly used to stabilize the five developing \{100\} side facets.$^{2,15,2,20}$ The optimal total concentration of PVP for our regrowth has been found to be 0.10 mM (by monomer units). At the same time, we could successfully prepare AgPRNPs with an average length less than ca. 400 nm without PVP addition; relying on the residual amount of PVP that is already present in concentrated precursor AgDeNPs (ca. 0.6 µM by monomer units). PVP addition was
found to be more crucial for the synthesis of longer AgPRNPs (>500 nm). On the other hand, AgPRNPs could also be successfully synthesized by thermal regrowth of AgDeNPs that were synthesized using PSS as an alternative stabilizer.

2.4 Conclusion

A new-generation photochemical synthetic protocol to produce AgDeNPs with a 99.7% yield of decahedral particles and excellent size-dispersity (ca. 4.5% standard deviation from average) implementing oxidative etching and LEDs is described with the detailed discussion of synthetic parameters. New developments enabled us to extend the control in photochemical regrowth of AgDeNPs into larger decahedral particles, as well as thermal transformation into AgDeNPs with a tunable width and length. Feasible reliable synthetic protocols to prepare AgNPs with pentagonal symmetry and precisely manoeuvrable SPR through the entire visible spectrum should be valuable for scientists working with a wide range of applications from optical to biochemical and medical.

2.5 Experimental Section

2.5.1 Reagents

Silver nitrate (99.9%), hydrogen peroxide (30-32 wt.% solution in water (ca. 10.4 M), semiconductor grade, 99.99%), L-arginine (TLC, 98%), sodium citrate tribasic dihydrate (99%), and sodium borohydride (99%), were supplied by Aldrich and used as received, polyvinylpyrrolidone (PVP, Mw = 40K) was supplied by Caledon. High-purity deionized water (> 18.4 MΩcm) was produced using Millipore A10 Milli-Q.
2.5.2 Instrumentation

UV-vis spectra were recorded using both an Ocean Optics QE65000 fiber-optic UV-vis spectrometer and a Cary 50 UV-vis spectrometer. Both TEM and SEM imaging were performed with a Hitachi S-5200 using a copper grid with a formvar/carbon film (FCF-200, Electron Microscopy Science). Zetasizer S (Malvern Instruments) was used to measure both zeta potentials and to estimate hydrodynamic particle sizes. Topography imaging of AgNPs were acquired using Omegascope SL AFM/Raman microscope (AIST-NT). AgNPs were centrifuged using a Clinical 100 Centrifuge (VWR). Controlled uniform heating for the synthesis of pentagonal rods was performed using a Heidolph MR 3004 safety heater with an aluminum heating block (VWR). For slow controlled addition, a KDS100 syringe pump (KDS scientific) was used. Light exposure has been performed using a setup of 1-watt 350 mA LEDs (LEDs Super Bright) powered by a TDC LED driver operating at 350 mA constant current (Figure 2.6a in SI) and a high intensity metal halide lamp with a blue filter cut off at ca. 450 nm.

2.5.3 Synthesis of decahedral silver nanoparticles (AgDeNPs)

To a 20-mL vial containing 14.00 mL of high-purity deionized water, the following solutions were added in the listed order: 0.520 mL of 0.050 M sodium citrate (1.679 mM total concentration in solution), 0.0150 mL of 0.050 M PVP (0.048 mM total concentration of monomer units), 0.050 mL of 0.005 M L-arginine (0.016 mM), 0.400 mL of 0.050 M silver nitrate (0.13 mM total concentration in solution), and freshly prepared 0.200 mL of 0.100 M sodium borohydride (1.3 mM total concentration in solution). The
content of the vial was mixed using a magnetic stir bar (8 by 1.5 mm) with the stirring speed of 600 rpm. Upon borohydride addition, a pale yellow solution is first formed, which then turns to bright yellow upon continuing stirring for ca. 45 minutes. Subsequently, 0.300 mL of ca. 10.4 M hydrogen peroxide (0.20 M total concentration in reaction mixture) was added to the bright yellow solution upon continuous stirring until bubble evolution vanishes. The bright yellow-orange precursor solution produced was then exposed to royal blue LED ($\lambda_{\text{max}}$ = 449±2 nm) for 14 hrs. The LEDs setup is shown in Figure S1a. UV-vis spectra and photographs of the colour progression of the reaction mixture throughout the synthesis are presented in Figure 2.7. The optimal amounts of reagents used in the synthesis of AgDeNPs are summarized in Table 2.1. A more detailed description of the synthetic protocols is also provided in SI (section 2.7).

**2.5.4 Synthesis of large decahedral silver nanoparticles**

To a 20-mL vial containing 3.00 mL of previously prepared AgDeNPs upon stirring at 200 rpm using a magnetic stir bar (8 by 1.5 mm), and exposed to blue LED ($\lambda_{\text{max}}$ = 472±2 nm), 3.00 mL of freshly prepared aqueous solution containing 0.077 mL of 0.005 M silver nitrate, 0.300 mL of 0.05 M sodium citrate and 2.623 ml of water were dispensed at a constant rate during 30 minutes. The reaction vial then remained exposed to light for 3 more hours. When cyan LEDs ($\lambda_{\text{max}}$ = 505±2 nm) were used as a light source, a higher silver concentration was used (0.231 mL of 0.005 M silver nitrate instead of 0.077 mL) with a dispensing time of 3 hours. The synthesis setup is described
in Figure 2.6d-g in SI. The summary of the optimal concentrations and addition times used for the regrowth of AgDeNPs into larger sizes are presented in Table 2.2 in SI.

2.5.5 Synthesis of silver pentagonal rod nanoparticles (AgPRNPs)

First, concentrated AgDeNPs were prepared as following: as-synthesized dispersions of AgDeNPs were centrifuged at 4,000 g for 30 minutes, the supernatant was removed and the centrifuged particles dispersed in deionized water to one fifth of their original volume prior to the centrifugation (during the centrifugation process, up to ca. 15% of the original AgDeNP seeds can remain in the supernatant). Then 0.720 mL of 0.050 M sodium citrate and 0.135 mL of 0.050 M PVP were added to a 20-mL vial containing 6.00 mL of deionized water. The mixture was heated, using a heater with an aluminum heating block (VWR), at a controlled temperature near boiling (most commonly at 98 °C) for 10 minutes. In the next step, 1.00 ml of previously concentrated AgDeNP dispersion followed by a first portion of 0.005 M silver nitrate (typically 0.300 ml to 0.500 ml) were added to the heated solution. Then after an additional 10 minutes of heating, the second portion of silver nitrate was added and the reaction mixture was continuously heated for 10 more minutes. The heating setup and the progression of colour changes during the synthesis are described in Figure 2.6b,c in SI. The summary of the optimal conditions for the preparation of AgPRNPs and the range of their tunable SPR peaks are provided in Table 2.3 in SI.
2.6 Supporting Information (SI):

Experimental details, description of several additional experimental series by UV-vis spectroscopy, electron microscopy, and optical photography and tables that summarize the effect of the variation of synthetic parameters.

2.6.1 Supplementary experimental section:

2.6.1.1 Apparatus setup

**Light exposure setup.** AgDeNPs were produced using a setup for light exposure, as illustrated in Figure 2.61a, that consists of the following components:

- High power 1 Watt 449±2 nm royal blue 350 mA LED with 100 degree light emitting angle.
- TDC power LED drive operating at a constant 350 mA current is typically used to drive three 1 Watt LEDs in series simultaneously
- 30 degree clear lens (Cree XR series XLamp)
- Aluminum foil for covering vials during the light exposure and a piece of Teflon, as a thermal insulator, mounted underneath of LEDs.
- For the synthesis of larger AgDeNPs, blue LED (\(\lambda_{\text{max}}=472\pm2\) nm) and cyan LED (\(\lambda_{\text{max}}=505\pm2\) nm) were used. Figure 2.6d shows synthesis setup and the color of solutions for the regrowth of larger AgDeNPs.
**Heating setup.** Decahedral AgNPs can undergo thermal transformation into AgPRNPs using a controlled uniform heating setup (Figure 2.6b) which consists of the following components:

- Heidolph MR 3004 safety heater (another heater with controlled temperature can be used)
- Aluminum heating block for 20.0 mm vials was used to insure uniform heating (no stirring was used)

### 2.6.1.2 Detailed Synthetic Procedures

**Synthesis of optimized decahedral silver nanoparticles (AgDeNPs).** (see Figure 2.6, 2.7 and Table 2.1)

- Place a 20-mL vial containing 14.0 mL of high-purity deionized water and a magnetic stir bar (8 by 1.5 mm) on a magnetic stirring plate and set stirring speed at 600 rpm
- To the 20-mL vial, add the following solutions in the listed order:
  - 0.520 mL of 0.050 M sodium citrate
  - 0.0150 mL of 0.050 M (monomer unit concentration) PVP
  - 0.050 mL of 0.005 M L-arginine
  - 0.400 mL of 0.050 M silver nitrate
  - 0.200 mL of 0.100 M sodium borohydride (freshly prepared)
- Continue stirring until the color of the reaction solution turns from pale to bright yellow; ca. 40-50 minutes is typically required.
• To the bright yellow solution, add 0.300 mL of 10.4 M hydrogen peroxide (stored in a fridge), then continue stirring until bubble evolution vanishes; ca. 15-20 minutes is usually needed.

• Cap the vial and expose it to royal blue LED (\(\lambda_{\text{max}} = 449\pm 2\) nm) light for 14 hours.

**Synthesis of large decahedral silver nanoparticles (Large AgDeNPs)**

• To a 20-mL vial containing 2.62 mL of high-purity deionized water, add 0.300 mL of 0.05 M sodium citrate and 0.077 mL of 0.005 M silver nitrate to yield a total volume of 3.0 mL. Then fill a 5.0-mL syringe with the prepared solution.

• Mount a blue LED (\(\lambda_{\text{max}} = 472\pm 2\) nm) setup on a magnetic stirring plate and set the stirring speed at low (200 rpm).

• Onto the LED setup, mount a 20-ml vial containing 3.0 ml of previously prepared AgDeNPs solution equipped with a magnetic stir bar (8 by 1.5 mm).

• During the light exposure, dispense the previously prepared solution from a syringe into the vial containing AgDeNP seeds. This can be done by utilizing a syringe pump with the dispensing speed of 6.0 mL/hour for 30 minutes. (200 % of new silver relative to the silver present in seed AgDeNPs per hour).

• Leave the prepared reaction mixture under the light exposure for 3 hours. (The described procedure is for the preparation of large AgDeNPs with the largest dimension across the pentagonal rim of 51±4 nm and maximum wavelength of 488 nm). See Figure 2.6d-g for the description of the synthesis setup and Table 2.2 for the reagent amounts and dispensing speeds used for different LEDs.
Synthesis of pentagonal silver nanorods (AgPRNPs).

- Concentrate previously prepared AgDeNP five times by volume through centrifugation of a 5.00 mL of the prepared solution at the speed of 5500 rpm (4000 g) for 30 minutes. Remove the supernatant and disperse particles in high-purity deionized water to one fifth of the original size (1.00 mL). (This concentrated solution needs to be prepared immediately prior to the rod preparation rather than being stored for longer periods of time). During the centrifugation process, up to ca. 15% of the original AgDeNP seeds can remain in the supernatant. The percentage of the lost AgDeNPs can be estimated precisely through the comparison of the UV-vis spectra for the original AgDeNP solution with that of the supernatant. Quantifying AgDeNP concentration is important for the precise synthetic control in the length of AgPRNPs (see Figure 2.27).

- Set the reaction temperature near boiling (most commonly 98 °C).

- To a 20-mL vial containing 6.00 mL of high-purity deionized water, add 0.720 mL of 0.050 M sodium citrate and 0.135 mL of 0.050 M PVP solutions. Place the capped vial in the preheated aluminum heating block for 10 minutes. (The actual solution temperature will reach ~98 °C).

- Continue heating, add 1.00 mL of freshly concentrated AgDeNP solution followed by 0.400 ml of 0.005 M silver nitrate then continue heating for additional 10 minutes.

- Add another 0.400 ml of 0.005 M silver nitrate and continue heating for 10 minutes.
• Take off the vial and allow it to cool to room temperature.

The color progression of the solution during the synthesis is displayed in Figure 2.6c. (The amount of silver nitrate used in this procedure is for rods with an average length of 115±5 nm and width of 42±2 nm (the aspect ratio of 2.7); for other lengths see Figure 2.9 and Table 2.3).
2.6.2 Supplementary Tables

Table 2.1 Optimal amounts of the reagents used in the synthesis of AgDeNPs*

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Sodium Citrate (0.05 M)</th>
<th>PVP (0.05 M)</th>
<th>L-arginine (0.005 M)</th>
<th>Silver nitrate (0.005 M)</th>
<th>Sodium borohydride (0.1 M)</th>
<th>Hydrogen peroxide (10.4 M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume (mL)</td>
<td>0.520</td>
<td>0.015</td>
<td>0.050</td>
<td>0.400</td>
<td>0.200</td>
<td>0.300</td>
</tr>
<tr>
<td>Final total concentration in the reaction (mM)</td>
<td>1.679</td>
<td>0.0484</td>
<td>0.0161</td>
<td>0.129</td>
<td>1.292</td>
<td>201.4</td>
</tr>
</tbody>
</table>

* All reagents were added to 14.0 mL of deionized water.

Table 2.2 Maximum SPR wavelength of larger AgDeNPs synthesised by the regrowth of AgDeNP precursor upon LED exposure*

<table>
<thead>
<tr>
<th>LED maxima</th>
<th>Volume (mL) of 0.005 M AgNO₃ added</th>
<th>Molar ratio Ag_{\text{added}}/Ag_{\text{original}}</th>
<th>λ_{\text{max}} (nm)</th>
<th>Rate of dispensing mL/hour</th>
<th>Rate of dispensing as % of added silver relative to that present in the seed solution per hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue (472 nm)</td>
<td>0.070</td>
<td>0.9</td>
<td>486</td>
<td>6.0</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>0.077</td>
<td>1.0</td>
<td>488</td>
<td>6.0</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>0.092</td>
<td>1.2</td>
<td>489</td>
<td>6.0</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>0.108</td>
<td>1.4</td>
<td>491</td>
<td>6.0</td>
<td>280</td>
</tr>
<tr>
<td></td>
<td>0.139</td>
<td>1.8</td>
<td>497</td>
<td>6.0</td>
<td>360</td>
</tr>
<tr>
<td>Cyan (505 nm)</td>
<td>0.154</td>
<td>2.0</td>
<td>511</td>
<td>1.0</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>0.193</td>
<td>2.5</td>
<td>513</td>
<td>1.0</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>0.270</td>
<td>3.5</td>
<td>521</td>
<td>0.5</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>0.539</td>
<td>7.0</td>
<td>544</td>
<td>0.5</td>
<td>116</td>
</tr>
</tbody>
</table>

* Total volume of the dispensed solution, including the volume of AgNO₃ and 0.300 mL of 0.05 M sodium citrate, is 3.0 mL.
Table 2.3 Optimal mounts of silver nitrate used in the growth of AgPRNPs with different length and SPR peaks.*

<table>
<thead>
<tr>
<th>Volume (mL) of silver nitrate** (0.005 M)</th>
<th>150</th>
<th>300</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>800</th>
<th>1000</th>
<th>1200</th>
<th>1400</th>
<th>3000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average AgNPR length (nm)</td>
<td>49±2</td>
<td>70±4</td>
<td>85±5</td>
<td>83±10</td>
<td>97±4</td>
<td>115±5</td>
<td>147±6</td>
<td>175±7</td>
<td>196±13</td>
<td>354±30</td>
</tr>
<tr>
<td>Average SPR λ_{max} (nm)***</td>
<td>417</td>
<td>493</td>
<td>541</td>
<td>600</td>
<td>620</td>
<td>690</td>
<td>790</td>
<td>900</td>
<td>975</td>
<td>--</td>
</tr>
</tbody>
</table>

* The amounts used with 1.0 mL of five-time concentrated AgDeNP seeds.

** Silver nitrate was added in two equal increments.

*** Two-SPR peaks become well defined with a SPR wavelength larger than 600 nm, for which longitudinal (primary) SPR peak maxima are tabulated.
2.6.3 Supplementary Figures

**Figure 2.6 (a)** Optical photographs of the LED setup used in AgDeNP synthesis (1) High-power 1 Watt, 350 mA royal blue LED ($\lambda_{\text{max}} = 449\pm2$ nm) with 100-degree light emitting angle and equipped with a 30 degree clear lens (Cree XR series XLamp); (2) TDC power LED power supply operating at 350 mA constant current, used to simultaneously drive typically three 1-Watt LEDs simultaneously; (3-4) sets of vials on LEDs; **(b)** A setup for AgNPR synthesis with heating at controlled temperatures using an aluminum heating block. **(c)** Optical photographs of the vials demonstrating the progression in colour development during the synthesis of AgPRNPs. **(d)** Optical photographs of the syringe pump and LED setup used in AgDeNP regrowth. Optical photographs of the synthesized AgNPs: **(e)** precursor AgDeNPs and larger AgDeNPs regrown using **(f)** blue LED ($\lambda_{\text{max}} = 472\pm2$ nm) and **(g)** cyan LED ($\lambda_{\text{max}} = 505\pm2$ nm).
Figure 2.7 Illustration of the major steps in the optimized AgDeNP synthesis: (a) UV-vis spectra, measured using a 0.5-cm path length cell, and (b) optical photographs of AgNP solutions.
Figure 2.8 UV-vis spectra, measured using a 0.5-cm cell, of prepared (a) optimized AgDeNPs with the prominently narrow HWHM of the SPR peak of 15 nm (0.082 eV HWHM at 2.62±0.01 eV peak) (b) AgPRNPs with length of 115±5 nm and width of 41±2 nm. The dashed ovals in both graphs highlight transverse SPR peaks.
Figure 2.9 (a) UV-vis spectra of large AgDeNPs (normalized to the same absorbance of the main SPR peaks) synthesized using blue LED ($\lambda_{\text{max}} = 472 \pm 2$ nm) and cyan LED ($\lambda_{\text{max}} = 505 \pm 2$ nm). (b) SPR maxima for AgDeNPs with various largest dimensions across the pentagonal rim (represented by their width). The dashed red spectrum in (a) represents precursor AgDeNPs with the largest dimensions across the pentagonal rim of ca. 41 nm prior to the regrowth.
Figure 2.10 UV-vis spectra of AgPRNPs prepared with different amounts of added silver ions (expressed as the percentage relative to the amount of silver ions present in the original AgDeNP solution before centrifugation): (1) 77%; (2) 200%; (3) 300% and (4) 600%. The dashed spectrum corresponds to the seed AgDeNPs used for the thermal transformation to AgPRNPs.
Figure 2.11 The effect of the amount of added silver ions (expressed as a percentage relative to the amount of silver ions present in the original AgDeNP solution before centrifugation) on the (a) average length and (b) $\lambda_{\text{max}}$ of the longitudinal SPR peak of the synthesized AgPRNPs.
Figure 2.12 Emission spectra of different LEDs plotted with UV-vis spectra of AgNP solutions synthesized using these LEDs. Optical photograph insets in each figure illustrate the actual color of each AgNP solutions produced.
Figure 2.13 (a) Emission spectra of LEDs with the maximum wavelengths of ① 417; ② 435; ③ 449; ④ 474; ⑤ 499; ⑥ 505 and ⑦ 520 nm. (b) UV-vis spectra of AgNP solutions synthesized using LEDs described in (a) as the light exposure sources. (c-h) TEM images of synthesized AgNPs using LEDs with various \(\lambda_{\text{max}}\). The scale bar is 100 nm for all images.
Figure 2.14 UV-vis spectra of AgDeNP photochemical development using different light exposure sources: (a) royal blue LED ($\lambda_{\text{max}} = 449 \pm 2$ nm); (b) normal blue LED ($\lambda_{\text{max}} = 472 \pm 2$ nm) and (c) metal halide lamp with the blue filter cut off ca. 450 nm. The thin arrows depict the growth pathway, whereas the bolded orange arrow in graph (a) shows the wavelength of the exposure source.

Figure 2.15 Modeling of the spectral component analysis, using SIMPLISMA syntax. (a-c) Time development pathways for the two pure major components using (a) royal blue LED ($\lambda_{\text{max}} = 449 \pm 2$ nm), (b) normal blue LED ($\lambda_{\text{max}} = 472 \pm 2$ nm) and (c) high intensity metal halide lamp with the blue filter cut off at ca. 450 nm as sources of light exposure. (d-f) Purity spectrum that estimates a concentration profile of platelets as a component in
AgDeNP solution using (d) royal blue LED ($\lambda_{\text{max}} = 449\pm2$ nm), (e) normal blue LED ($\lambda_{\text{max}} = 472\pm2$ nm) and (f) high intensity metal halide lamp with the blue filter cut off at ca. 450 nm as the sources of light exposure. The lowest platelet concentration was estimated for the royal blue LED ($\lambda_{\text{max}} = 449\pm2$ nm).

Figure 2.16 UV-vis spectra (top panel) and TEM images (bottom panels) of AgDeNPs synthesized using ① low (9 to 1) and ② high (36 to 1) molar ratio of citrate relative to that of silver ions. The dashed spectrum represents the optimized AgDeNPs with the citrate to silver molar ratio of 13 to 1 (1.67 mM total citrate concentration in the AgDeNP preparation). The scale bar is 100 nm for all TEM images.
Figure 2.17 UV-vis spectra (top panel) and TEM images (bottom panels) of AgDeNPs synthesized using \( \textcircled{1} \) low (0.13 M) and \( \textcircled{2} \) high (0.26 M) total concentration of hydrogen peroxide in AgDeNP solution. The dashed spectrum represents the optimized AgDeNPs synthesized using 0.20 M of hydrogen peroxide as the optimal total concentration in the final AgDeNP solution. The scale bar is 100 nm for all TEM images.
Figure 2.18 UV-vis spectra (top panel) and TEM images (bottom panels) of AgDeNPs synthesized using \( \textcircled{1} \) low (5 to 1) and \( \textcircled{2} \) high (16 to 1) molar ratio of borohydride relative to that of silver ions. The dashed spectrum represents the optimized AgDeNPs with the borohydride to silver molar ratio of 10 to 1 (1.28 mM total borohydride concentration). The scale bar is 100 nm for all TEM images.
Figure 2.19 UV-vis spectra (top panel) and TEM images (four bottom panels) of AgDeNPs synthesized \( \textcircled{1} \) without arginine and using \( \textcircled{2} 0.004, \textcircled{3} 0.016 \) (optimal concentration) and \( \textcircled{4} 0.032 \) mM total arginine concentration in the AgDeNP preparation. The scale bar is 100 nm for all TEM images.
Figure 2.20 UV-vis spectra and TEM images of AgNPs synthesized using (1) no PVP, (2) 5 times, and (3) 125 times the optimal total PVP concentration (0.048 mM total concentration in solution of monomer units) in the AgDeNP preparation. The dashed spectrum represents the optimized AgDeNPs with optimal PVP concentration. The scale bar is 100 nm for all TEM images.
Figure 2.21 UV-vis spectra (a) and TEM image (b) of AgDeNPs synthesized using poly(sodium 4-styrene sulfonate) (PSS) as a steric stabilizer. The dashed spectrum represents the optimized AgDeNPs prepared using PVP as a steric stabilizer for comparison. The scale bar in a TEM image is 100 nm.

Figure 2.22 UV-vis spectra (a) and TEM image (b) of AgDeNPs synthesized using chloride with the molar ratio of 1 to 2 relative to silver ions. The dashed spectrum represents the optimized AgDeNPs synthesized without chloride. The scale bar in a TEM image is 100 nm.
Figure 2.23 UV-vis spectra (top panel) and TEM images (bottom panels) of AgDeNPs synthesized using different percentages of gold as a doping metal. Dashed spectrum represents the optimized AgDeNPs prepared without the gold. The scale bar is 100 nm for all TEM images.
Figure 2.24 Effect of the reaction pH on the AgDeNP synthesis. (a, b) UV-vis spectra at pH of (a1) 11.5; (a2) 10.5; (a3) 9.5; (a4) 8.5; (b1) 5.5 and (b2) 4.5. (c-g) TEM images of AgDeNPs prepared at different pH. The dashed spectra and TEM image (f) correspond to the optimized AgDeNPs prepared at pH of 7.5. The scale bar is 100 nm for all images.
Figure 2.25 TEM images of (a) optimized AgDeNPs with the longest dimension across the pentagonal rim of 41±2 nm and (b-f) larger AgDeNPs regrown from the seeds described in (a) upon exposure to (b) blue (λ\text{max} =472 nm); (c) cyan (λ\text{max}=505 nm); (d) violet (λ\text{max}=409 nm); (e) royal blue (λ\text{max}=449 nm) and (f) green (λ\text{max}=520 nm) LEDs, respectively with the addition of silver ions at the molar ratio relative to that present in the precursor AgDeNP solution of 1 to 1 for (b) and 4 to 1 for (c-f). The scale bar is 100 nm for all images.
Figure 2.26 Dependence of wavelength maxima of SPR peaks on AgPRNP dimensions: 
(a) length and (b) width, which affect longitudinal (primary) and transverse SPR 
resonances, respectively.
Figure 2.27 The length of AgNPR as a function of the amount of added silver ions (expressed as a percentage relative to the amount of silver ions present in the original AgDeNP solution prior to centrifugation), for experimentally prepared and theoretically expected average length of synthesized AgPRNPs from pure geometric considerations. Error bars represent the standard deviation from the average length for prepared AgPRNPs. The theoretically expected average length is calculated based on geometric considerations and assuming typical experimental values of 15% AgDeNP seeds lost during centrifugation (ca. 15%).
Figure 2.28 UV-vis spectra (top panel), normalized by the absorbance of the longitudinal peak) and TEM images (four bottom panels) of AgPRNPs synthesized at different reaction temperatures of (1) 98 °C; (2) 90 °C; (3) 80 °C and (4) 70 °C. All scale bars are 100 nm.
**Figure 2.29** Effect of temperature on the time of the development of AgNPRs.

**Figure 2.30** Effect of citrate concentration on AgPRNP synthesis. (a) UV-vis spectra of AgNPR synthesized using total citrate concentration in the reaction of (1) 0 mM; (2) 2.2 mM (low); and (3) 6.5 mM (high). (b) TEM image of truncated AgDeNPs produced in absence of citrate. (c) SEM image of rounded (with undefined {111} cap facets) AgPRNPs synthesized using low concentration (2.2 mM) of citrate. (d) SEM image of AgPRNPs with relatively large proportion of ill-shaped particles synthesized using high concentration (6.5 mM) of citrate. The scale bar is 100 nm for all images.
Figure 2.31 TEM images demonstrating the high yield and shape selectivity of synthesized AgDeNPs, using the reported optimized protocol, with the longest AgDeNP dimension across the pentagonal rim of $41\pm2$ nm. The scale bar is 300 nm in (a) and 100 nm in (b).
2.7 References


Chapter 3
Gold-Plated Silver Nanoparticles with Superior Stability and Plasmon Resonance
Chapter 3

Gold-Plated Silver Nanoparticles with Superior Stability and Plasmon Resonance

3.1 Introduction

Silver nanoparticles (AgNPs) and gold nanoparticles (AuNPs), as primary chemically stable plasmonic metal nanoparticles (PNPs), have diverse applications in catalysis,\textsuperscript{3.1} sensing,\textsuperscript{3.2,3.3} and biomedicine.\textsuperscript{3.4} Among the coinage metals, silver features the highest energy of d-sp transitions with much sharper and stronger SPR that can span throughout the entire visible range and into NIR (ca. 395 nm to 1300+ nm).\textsuperscript{3.5,3.6,3.7} At the same time, many applications of AgNPs, especially in biological systems, are hindered by low AgNP stability in various aggressive environments, e.g. in presence of chloride ions that are common in physiological fluids.

In this chapter we introduce a feasible synthetic protocol to stabilize silver nanoparticles by controlled uniform deposition of thin surface coating of gold. It was found that the prepared gold-plated AgNPs (Au@AgNPs, shell@core) have superior stability in most of aggressive media, such as: 150 mM NaCl, 1.5 M NH\textsubscript{3}, and 0.5 M H\textsubscript{2}O\textsubscript{2}. Strong and sharp SPR of AgNPs has been preserved after the uniform gold plating. We introduce an optimal protocol to accomplish uniform gold plating of both silver decahedral nanoparticles (AgDeNPs) and silver pentagonal rod nanoparticles (AgPRNPs). The key factor in controlling the uniformity deposition of gold and minimizing the galvanic replacement effect is in reducing the reduction potential of the gold ions.
3.2 Results and Discussion

**Figure 3.1 (a)** Schematic illustration showing preparation of Au@AgDeNPs by slow addition of gold ions to AgDeNPs. TEM images of (b) Au@AgDeNPs and (c) Au@AgPRNPs treated with hydrogen peroxide solution (0.5 M total concentration). UV-vis spectra of (d) precursor AgDeNPs and the 10% Au@AgDeNPs (shell@core) (e) the precursor AgPRNPs and 2% Au@AgPRNPs. The scale bars are 100 nm in all TEM images.

3.2.1 Optimized gold plating protocol

As shown in Figure 3.1a, low rate of gold addition (3.21 nmol/h) to the negatively charged AgNPs (AgDeNPs have zeta potential of -41±10 mV) stabilized with citrate and PVP resulted in reduced Au-Ag galvanic replacement and in uniformly deposition of thin layer of gold at the surface of AgNPs. The TEM images (Figure 3.1b and 3.6 in SI†) show the fully covered surface of AgDeNPs with uniform thin layer of gold (ca. 1.5 nm).
without altering the characteristics of the original decahedral morphology and without noticeable galvanic replacement. The same can be judged from TEM image (Figure 3.1c) for the gold coated pentagonal rods.

Figure 1d shows the UV-vis spectra for AgDeNPs before coating and after deposition of 10 Au% (molar percentage of deposited gold relative to silver present in gold coated AgNPs). Upon gold deposition, SPR maximum was red-shifted from ca. 472 to ca. 485 nm due to d-d transition of gold. Plasmonic properties of AgDeNPs were retained with low reduction in intensity by ca. 15%. Preservation of the strong plasmon properties is indicative of minimization of galvanic replacement and the uniform deposition of thin layer of gold. The deposited gold layer at the AgDeNP was quantitatively and qualitatively detected using EDX (Figure 3.7 in SI†). Strong SPR of AgPRNPs was also preserved after gold coating. This can be concluded from UV-vis spectra for AgPRNPs before and after uniformly deposition of 2 Au% (Figure 3.1e).

AgDeNPs and AgPRNPs were synthesized in high yield with shape and size-selectivity using new-generation synthetic protocols developed based upon our previous work (see Experimental Section in Chapter 2).\textsuperscript{3.8,3.9} Uniform deposition of gold at the surface of AgNP has been accomplished by controlled slow addition of HAuCl\textsubscript{4} solution into the as prepared AgNP solution. Detailed procedures for the synthesis of AgDeNPs, AgPRNPs, and Au@AgDeNPs are provided in the Experimental Section in SI†.
3.2.2 Chemical stability

Figure 3.2 Stability of the Au@AgDeNPs (shell@core) monitored by UV-vis spectrophotometry in aqueous solutions of (a) 0.150 M NaCl (with 1.5 mM PVP), (b) 0.5 M NH₃ and (c) 0.5 M hydrogen peroxide. (d) Stability of the AgDeNPs in 0.5 M hydrogen peroxide. The insets in (a-c) are TEM images of Au@AgDeNPs after treatment for ten days in the corresponding conditions. The scale bars are 100 nm for all TEM images.

Successful deposition of a uniform thin protective layer of gold at the surface of AgDeNPs yielded nanostructures with superior stability in most etching environments with preservation of advantageous SPR properties of AgNPs. Figure 3.2a-c shows the stability of the prepared Au@AgDeNPs in the NaCl (150 mM), NH₃ (0.5 M), and H₂O₂ (0.5 M) solutions, respectively. By monitoring the change of the plasmon intensity using UV-
vis spectroscopy, the long-term stability (at least several weeks) of Au@AgDeNPs in etching media compared with pure silver can be confirmed. As shown in Figure 3.2d and Figure 3.8 in SI†, the etching reagents used are able to dissolve uncoated AgDeNPs completely in several minutes. The stability of the prepared Au@AgDeNPs is corroborated by their TEM images that shown in the inset of each graph. TEM images illustrate the stability of Au@AgDeNPs in high concentration of NaCl (0.30 M) and NH₃ (1.5 M) solutions are given in Figure 3.9 in SI†. UV-vis spectra and TEM image illustrate the stability of Au@AgDeNPs in L-arginine solution are provided in Figure 3.10 in SI†. Stability of Au@AgPRNPs in hydrogen peroxide solution monitored by UV-vis spectra is illustrated in Figure 3.11 in SI†.

3.2.3 Effect of gold percentage (Au%)

Figure 3.3a shows the change of the plasmonic band of the Au@AgDeNPs, prepared using different Au%, monitored by UV-vis spectroscopy. The intensity of the plasmonic band of the AgDeNPs decreased as the added Au% increased. It is clearly observed that the red shift of the SPR maximum progressed slowly (from ca. 472 to 500 nm) upon increasing Au% up to ca. 40%, whereas after ca. 50% the SPR shift increased dramatically to ca. 700 nm (Figure 3.12 in SI†). Below the Au% boundary of ca. 40%, there is almost none of galvanic replacement of silver. In absence of galvanic replacement, the plasmonic properties of AgNPs are not drastically changed with the expected red shift due to the higher SPR maximum of gold nanostructures.
Figure 3.3  (a) UV-vis spectra of the precursor AgDeNPs and the Au@AgDeNPs (shell@core) prepared by the addition of various Au mol. % relative to silver to AgDeNP precursor solution.  (b-g) TEM images of the Au@AgDeNPs prepared using different Au%. The scale bars are 100 nm for all TEM images.
Figure 3.3b-g shows representative TEM images of the prepared Au@AgDeNPs using different percentages of gold. For Au% less than 10% (optimal percentage), there is not sufficient amount of gold for uniform deposition to protect the entire surface of AgDeNPs which resulted in dissolving of uncovered parts after the treatment with hydrogen peroxide. Increasing of Au% more than 10% increases the formation of hollow Au-Ag nanoparticles due to increasing in the galvanic replacement. The hollow nanoparticles become the predominant particles after the boundary (>50%). The initially added gold ions during slow addition are deposited uniformly at the surface of negatively charged AgDeNPs. As concentration of gold increased in the solution the reduction potential of gold ions increased. As a result, subsequently added gold ions were reduced and deposited unevenly at the surface by oxidizing the silver atoms that found in the core. During the galvanic replacement, the first gold layer worked as an electron carrier between Ag (core) and the new deposited Au (shell). Silver atoms subsequently dissolved in the solution leaving a hollow Au-Ag decahedral nanoparticle, which resulted in drastically red shifted SPR maxima with the decreased peak intensity.

3.2.4 Effect of reducing and complexing agents

To avoid the galvanic replacement of silver atoms of the core AgDeNPs when using high percentage of gold, several routes have been explored. The main efforts were concerned in using a mild reducing agents such as ascorbate, formate and KOH and/or complexing agents such as, KI and citrate. Introducing KOH using different addition conditions resulted in the reduction of the excess gold ions (after formation of the first layer) in solution as a new nucleation forming a worm ill-defined shape (Figure
When ascorbate used as reducing agent, reduction of added gold ions occurred at the edges of the decahedral particles and in the solution instead of their reduction at the \{111\} triangular facets. As a result, ill-defined gold frames were produced after etching the core AgNPs using hydrogen peroxide solution (Figure 3.13b in SI\textsuperscript{†}). At the same time, formate could not prevent the galvanic replacement from producing hollow nanoparticles (Figure 3.13c in SI\textsuperscript{†}). In order to reduce the reduction potential of the gold ions, KI was introduced to form complexes with the gold ions during dispensing into the AgDeNP solution. Destroyed ill-defined shape was observed after treatment with hydrogen peroxide which resulted from the incomplete covering of the AgDeNPs (Figure 3.13d in SI\textsuperscript{†}).

**Figure 3.4** UV-vis spectra and TEM images of 60\%Au@AgDeNPs (shell@core) (1) with addition of citrate and (2) without addition of citrate. Optical photograph insets in each TEM image illustrate the actual colour of Au@AgDeNP solutions. The scale bars are 100 nm for all TEM images.

It was noticeable, as shown in Figure 3.4, that the slow addition of the Au-citrate solution (with Au\% of ca. 60\%) to the AgDeNPs reduced the red shifting of the SPR maximum (from ca. 700 to 510 nm) and enhanced the uniformity of gold deposition.
Using Au% more than 60% resulted in reduced of excess gold ions in the solution as a new nucleation (Figure 3.14 in SI†). Unfortunately, these attempts could not achieve the perfect uniform deposition of high Au% and still need more investigations.

3.3 Conclusion

In summary, an affordable room temperature synthetic protocol in aqueous medium to produce Au@AgDeNPs (shell@core) has been developed and described. Besides their sharp and strong SPR, produced Au@AgDeNPs show superior stability against most of the chemical etching environments. Therefore gold-plated AgNPs should be promising for versatile biological and optical applications. Optimization of the uniform gold plating for AgDeNPs using high Au% (>50%), AgPRNPs, and other morphologies with different dimensions and tunable SPR will be explored and reported in our future work.
3.4 Supporting Information (SI†):

3.4.1 Experimental Section

3.4.1.1 Reagents

Silver nitrate (99.9%), tetrachloroauric acid (99.5%), hydrogen peroxide (30-32 wt.% solution in water (ca. 10.4 M), semiconductor grade, 99.99, L-arginine (TLC, 98%), sodium citrate tribasic dihydrate (99+%), and sodium borohydride (99%), were supplied by Aldrich and used as received, polyvinylpyrrolidone (PVP, M_w = 40K) was supplied by Caledon. High-purity deionized water (> 18.4 MΩcm) was produced using Millipore A10 Milli-Q.

3.4.1.2 Synthesis of silver decahedral nanoparticles (AgDeNPs)

AgDeNPs were synthesized using a new-generation photochemical synthetic protocol developed by our group (see Experimental Section in Chapter 2). To a 20-mL vial containing 14.00 mL of high-purity deionized water, the following solutions were added in the listed order: 0.520 mL of 0.050 M sodium citrate, 0.0150 mL of 0.050 M PVP (total concentration of monomer units), 0.050 mL of 0.005 M L-arginine, 0.400 mL of 0.050 M silver, and freshly prepared 0.200 mL of 0.100 M sodium borohydride. A pale yellow solution is first formed, which then turned to bright yellow upon continuing medium stirring (600 rpm). Subsequently, 0.300 mL of ca. 10.4 M hydrogen peroxide was added. The solution then has been kept stirring for ca. 20 min. Subsequently, the produced solution was exposed to royal blue 449 nm LED for 14 hrs (see Experimental Section in Chapter 2).
3.4.1.3 Synthesis of silver pentagonal rod nanoparticles (AgPRNPs)

Silver pentagonal rods nanoparticles with average length of ca. 120 nm are typically produced thermally using an adapted synthetic protocol that reported by our group (see Experimental Section in Chapter 2). An aqueous solution containing 6.00 mL of high-purity deionized water, 0.720 mL of 0.05 M citrate and 0.135 mL of 0.05 M PVP was heated at controlled temperature near boiling (ca. 98 °C) for 10 minutes. Subsequently, 1.00 ml of five-time concentrated AgDeNP dispersion followed by a 0.800 mL of 0.005 M silver nitrate were added. Finally, the reaction mixture was heated for additional 15 minutes (see Experimental Section in Chapter 2).

3.4.1.4 Synthesis of gold plated AgDeNPs

In a typical synthetic procedure to prepare gold plated silver decahedral nanoparticles (Au@AgDeNPs), (shell@core), a 3.00 mL of freshly prepared aqueous solution (in a 5.0 ml plastic syringe) containing 0.077 mL of 0.0005 M tetrachloroauric acid (10% molar relative to silver present in plated AgDeNPs) and 2.92 ml of high-purity deionized water was dispensed at constant rate during 12 hours (3.21 nmol/hr) into a 20-mL vial containing 3.00 mL of as prepared AgDeNP solution during uniform stirring at 200 rpm.

3.4.1.5 Characterization

AgNPs and Au@AgNPs were cleaned and concentrated using a Clinical 100 Centrifuge (VWR). For slow controlled addition, a KDS100 syringe pump (KDS Scientific)
has been used. UV-vis spectra were acquired with either Ocean Optics QE65000 fibre-optic UV-Vis spectrometer or Cary 50Bio UV-vis spectrophotometer. EM imaging was performed with a Hitachi S-5200 using a copper grid with a formvar/carbon film (FCF-200, Electron Microscopy Science). EDX was carried out using an Oxford Inca system for quantitation, line scans, and mapping. Zeta potentials of AgNPs were measured using Zetasizer S (Malvern Instruments).

3.4.2 Supplementary Figures

Figure 3.5 UV-vis spectra of the 10% Au@AgDeNPs (10 mol. Au% relative to Ag present in gold coated AgDeNPs) produced using different addition rate of gold precursor solution (volume of the gold precursor solution is 3.00 mL).
Figure 3.6 Transmission electron microscopy (TEM) images of (a) silver decahedral nanoparticles (AgDeNPs) before gold coating and (b) Au@AgDeNPs (shell@core). Preservation of the decahedral shape uniformity and sharp edges after coating is indicative of the uniformity of the gold coating layer. The scale bars are 100 nm for all TEM images.
Figure 3.7 (a) Energy-dispersive X-ray (EDX) spectra and (b) EDX analysis of the gold coated decahedra nanoparticles prepared by deposition of 5 mol. % of gold relative to silver present in precursor AgDeNPs.
Figure 3.8 Stability of the uncoated silver decahedral nanoparticles (AgDeNPs) in aqueous solution of (a) 0.5 M hydrogen peroxide and (b) 0.5 M NH$_3$ monitored by UV-vis spectroscopy.
Figure 3.9 Transmission electron microscopy (TEM) images of Au@AgDeNPs (shell@core) after treatment for five days in (a) 1.5 M NH₃ and (b) 0.30 M of NaCl solutions. The scale bars are 100 nm for all TEM images.
Figure 3.10 UV-vis spectra (a) and TEM image (b) of Au@AgDeNPs (shell@core) after treatment in L-arginine solution (1.5 M total concentration) for 2 days. The intensity of SPR peak is decreased over time with the formation of a new red-shifted peak at 650-750 nm that is indicative of the aggregation of the particles, which is also confirmed by TEM. At the same time, the stability of the gold coated particles is fully preserved, as can be seen in the TEM image. The scale bar is 100 nm for TEM image.
Figure 3.11 UV-vis spectra of gold coated silver pentagonal rod nanoparticles (Au@AgPRNPs) before (blue) and after (red) the treatment for five days with 0.5 M (total concentration) hydrogen peroxide solution.
Figure 3.12 (a) The effect of the amount of added gold (expressed as a percentage of gold relative to silver present in AgDeNPs) on the $\lambda_{\text{max}}$ of the SPR peak of the produced Au@AgDeNPs. (b) Optical photographs of the prepared AgDeNPs and Au@AgDeNP (shell@core) dispersions prepared with various percentages of gold.
Figure 3.13 TEM images of Au@AgNPs prepared by slow addition of [AuCl$_4$]$^-$ to AgDeNPs in the presence of (a) KOH, (b) ascorbate, (c) formate and (d) KI. Produced Au@AgNPs were treated with 0.2 M (total concentration) hydrogen peroxide solution. The scale bars are 100 nm for all TEM images.
Figure 3.14 Transmission electron microscopy (TEM) images of 80% Au@AgDeNPs (shell@core) produced (a) without using additional citrate and (b) with addition of Au-citrate solution. The scale bars are 100 nm for all TEM images.
3.5 References


Chapter 4
Conclusions and Other Projects
Performed for Future Work
Chapter 4

Conclusions and Other Projects Performed for Future Work

4.1 Conclusion

Mastering preparation of silver nanoparticles (AgNPs) with controllable shape and dimensions enabled us to attain AgNPs with tunable SPR covering the visible-NIR range. A new-generation photochemical synthetic protocol to produce silver decahedral nanoparticles (AgDeNPs) with a 99.7% yield of decahedral particles and excellent size-dispersity (ca. 4.5% standard deviation from average) was described with the detailed discussion of synthetic parameters.

Photochemical regrowth of large AgDeNPs was tailored by controlling the amount of added silver ions and the \( \lambda_{\text{max}} \) of used LED. The SPR maximum wavelength was increased with the increase in the size of AgDeNPs. One-dimensional elongation of AgDeNPs into silver pentagonal rod nanoparticles (AgPRNPs) produced AgNPs with two plasmonic bands: longitudinal, which was tailored by increasing the length of AgPRNPs; and transverse, which was tuned by controlling the width of AgDeNP seeds. As shown in Figure 4.1, synthetic protocol for preparation of plasmonic platform based on silver nanoparticles with pentagonal symmetry was optimized.
Figure 4.1 Representative UV-vis spectra of silver decahedral and pentagonal rod nanoparticles with tunable SPR bands.

The stability of AgNPs has been greatly improved by the uniform deposition of thin layer of gold at the surface of AgNPs. Produced gold-plated silver nanoparticles (Au@AgNPs, shell@core) retained strong SPR similar to that of AgNP seeds. Advantageously, compared to AgNPs, which have low stability in many aggressive media including 150 mM NaCl, 1.5 M NH₃, and 0.5 M H₂O₂ solutions, Au@AgNPs have been found to have superior stability in these environments. Figure 4.2 shows representative transmission electron microscopy (TEM) images of AgDeNPs prior to coating, gold-plated silver decahedral nanoparticles (Au@AgDeNPs, shell@core), and gold-coated silver pentagonal rod nanoparticles (Au@AgPRNPs, shell@core).
Figure 4.2 Representative TEM images of (a) AgDeNPs, (b) Au@AgDeNPs, and (c) Au@AgPRNPs. The scale bars are 100 nm for all TEM images.

The key factor in controlling the uniform deposition of gold and minimizing the galvanic replacement side reaction was found in reducing the reduction potential of the gold ions. The reduction potential was lowered using slower rates of gold deposition onto AgNPs in present of citrate ions (Figure 4.3). Optimal gold-plating of AgDeNPs was attained at 10 mol. % of gold relative to silver present in coated AgDeNPs.

Figure 4.3 Schematic illustration showing preparation of Au@AgDeNPs by slow addition of gold ions to AgDeNPs.

Further development of the gold project will deal with optimization of the uniform gold plating for AgDeNPs using high Au% (>50 mol. %) as well as using other AgNP morphologies to attain variable SPR of gold-coated NPs.
4.2 Other projects

This section summarizes other research projects in addition to the main two projects that have been described in the second and third chapter of this thesis.

4.2.1 Synthesis and Characterization of Polystyrene Latex at Room Temperature Using Green Initiator System (Third-Year Teaching Lab)

The introduction of latex polymerization in undergraduate labs is valuable for students to acquire strong applied knowledge in addition to theoretical background in polymerization. It is an appreciable challenge to introduce emulsion polymerization in the teaching lab due to its running time, reagents, and equipment involved. Another difficulty is the glassware used, especially its cleaning. In Appendix A of this thesis we include an adapted procedure of polystyrene (PS) emulsion polymerization, where we overcome these challenges by scaling down the reaction; using a 20 mL-vial at room temperature with a green initiator system consisting of ascorbic acid and hydrogen peroxide. This educational project was developed as a continuation of the scientific project initiated as a part of the direct study course (CH685, Polymer Theory and Synthesis). The adapted experiment should serve as a valuable tool for teaching emulsion polymerization to students: they will be able to observe nucleation and early growth intervals during the lab time. During nucleation, students will be able to characterize previously prepared latex samples. As seen in Figure 4.4 in the successfully performed adapted experiment, the different groups of students have synthesized and characterized monodisperse PS lattices with different particles sizes.
Figure 4.4 Representative EM images of the prepared PS latex with average diameter of (a-b) 185 nm, (c-d) 240 nm, and (e-f) 300 nm.

Further scientific studies in the lab include investigation of latex film colors, particle sizes, and the influence of the amount of steric stabilizer used (polyvinylpyrrolidone, PVP). From their results, students are expected to analyze the effect of the amount of the stabilizer on the average particle size (Figure 4.5) and to compare the average particle size with the color of the prepared films (Figure 4.6).

Figure 4.5 Effect of the total PVP concentration on the average size (expressed as the diameter) of the produced PS latexes.

101
Figure 4.6 Optical microscopy images of the prepared PS lattices films with average diameter of the particles (a) 185 nm, (b) 240 nm, and (c) 300 nm. The insets illustrate the optical photographs of the prepared films.

4.2.2 Is PVP a Miracle Reagent for Stabilization and Formation of Nanoparticles with \{100\} Facets?

Several studies report a crucial role of polyvinylpyrrolidone (PVP) in preparation and stabilization of metal nanoparticles (MNPs) enclosed with \{100\} facets, such as cubes and pentagonal rods. In this work we proved that PVP role is limited to steric stabilization of prepared MNPs. Using PVP in our optimized AgDeNP synthetic protocol enhanced formation of stable AgDeNPs enclosed with \{111\} facets and no particles with \{100\} facets were produced (Figure 2.21). Furthermore, other steric stabilizing agents (e.g. Polystyrene sulfonate (PSS), polyacrylic acid (PAA), and polystyrene sulfonic acid (PSSA)) gave essentially the same results as that of PVP.

Several experimental series have been performed to prepare AgPRNPs enclosed with ten triangular \{111\} and five side rectangular \{100\} facets. As shown in Figure 4.7, AgPRNPs were successfully obtained with defined \{100\} facets using several different
steric stabilizing agents other than PVP. AgPRNPs could be also prepared with defined {100} facets even without using any of these stabilizing agents, although such particles have been aggregated easily, e.g. during multiple cleaning.

![Figure 4.7](image)

**Figure 4.7** (a) UV-vis spectra of AgPRNPs prepared using PVP and PSS. EM images of AgPRNPs prepared using (b) PAA and (c) PSS. The scale bars are 100 nm for all EM images.

Unlike other reported studies, in this project we have judiciously concluded that the role of PVP and other steric stabilizing agents is limited in steric stabilization of the prepared MNPs without selective preference for formation of particular facets, such as {100}.

### 4.2.3 Silica Encapsulation of MNPs for the Formation of Metallodielectric Arrays

Silica has a stable charged surface that together with the availability of precursors (e.g. tetraethyl orthosilicate, TEOS) makes it a good choice to form protective stabilizing coating. Furthermore, the silica coating can be further functionalized for
versatile potential applications. Silica encapsulation of Au@AgNPs enables tuning of the plasmonic properties of the metal cores with the tunable shell thickness, which is beneficial for applications of metallodielectric arrays.

Figure 4.8 (a) TEM image of silica encapsulation of Au@gDeNPs and (b) schematic illustration of the target metallodielectric arrays. The scale bar for TEM image is 100 nm.

Achieving Au@AgNPs with superior stability in aggressive environments such as arginine and NH$_3$, allowed us to develop a simple reproducible procedure of silica encapsulations for these stable particles. In the developed synthetic protocol, we hydrolyzed TEOS in basic medium using 1.0 M of NH$_3$ solution in presence of Au@AgNPs. Rate of TEOS hydrolysis has been reduced and controlled using isopropanol as a medium. Our initial results with the newly developed Au@AgNPs were promising (Figure 4.8a) to achieve our target metallodielectric arrays (Figure 4.8b). This project will be further actively developed by the group.
4.3 Manuscripts summary

In summary, a new-generation synthetic protocol for the preparation of a versatile plasmon platform based on silver nanoparticles with pentagonal symmetries has been achieved by optimization of the synthetic protocol of AgDeNPs and their transformation with tunable SPR. The manuscript based on this work has been accepted for publication in *Particle & Particle Systems Characterization* without change on August 1st, 2013.

Gold-plating of silver nanoparticles for superior stability and preserved plasmonic and sensing properties has been accomplished and optimized to attain AgDeNPs and AgPRNPs with uniform deposition of a thin layer of gold with Au% of 10% and 2%, respectively. The manuscript has been submitted to *Chemical Communications in August 2013*.

Synthesis and characterization of polystyrene latex at room temperature using hydrogen peroxide and ascorbic acid as a green initiator system have been developed as a third-year teaching lab. Monodisperse polystyrene latex has been synthesized and characterized in a pilot run by third-year students in *Polymers and Soft Matter* course at WLU (CH340), during 3-hour laboratory work. The manuscript is in preparation and will be submitted to a chemical education journal in September 2013.

The role of PVP in formation of MNPs enclosed with {100} facets has been elucidated and proved to be limited only to steric stabilization of MNPs without the selective preference for the formation of particular facets, such as {100}. The manuscript is in preparation to be submitted to *Chemical Communications* in September 2013.
Appendix A
Emulsion Polymerization: Synthesis of Monodisperse Polystyrene Latex at Room Temperature Using Green Redox Initiator System (Third-Year Teaching Lab)
Appendix A  (Student Lab Material)

Emulsion Polymerization: Synthesis of monodisperse polystyrene latex at room temperature using green redox initiator system

A.1 Overview

Latex polymers have a versatile environmentally friendly application as emulsion paints, water-born adhesive, paper coating and in preparation of synthetic rubbers. Polymerization of polystyrene (PS) latex is an example of emulsion polymerization which involves the propagation reactions of free radicals with monomer particles in a heterogeneous radical polymerization. In emulsion polymerization, the initiator must not be soluble in monomer but soluble only in the aqueous dispersion medium. The product of emulsion polymerization in aqueous medium is a colloidally-stable polymer dispersion in water which is known as latex. A.1,A.2

Free-radical polymerization reactions, as depicted schematically in Figure A.1, can be divided into three basic stages: initiation, propagation and termination. An initiation stage involves production of an active center (free-radical), which is commonly created by homolytic scission involving thermolysis (by application of heat) or photolysis (by light exposure) or by a red-ox reaction. Using red-ox reaction, as it is the case in our experiment, enables performing the reaction at low temperature in a simple experimental setup. In a propagation stage, polymer chains grow rapidly by rapid consecutive addition of monomer molecules to free-radical active centers. Specifics of

the propagation process are determined by a specific method (technique) of radical polymerization (see Figure A.2). In a final termination stage of a radical polymerization process, the active center is destroyed by either combination (combining of two chains forming a single polymer molecule) or disproportionation (transfer of hydrogen atom from one chain to another). Another important process that occurs in most of chain polymerization is a chain transfer (not included in Figure A.1), in which an active center is transferred from an active chain end to another component of the polymerization system (solvent, monomer, a special chain-transfer agent added, etc.)

![Radical polymerization diagram](image)

**Figure A.1** Schematic representation of the three basic stages of free-radical polymerization.

Emulsion polymerization is one of the most commonly used methods of free-radical polymerization among the four principal methods illustrated in Figure A.2.
Aqueous emulsion polymerization involves heterogeneous dispersion of water-insoluble monomer droplets (micelles) which often stabilized by surfactants or sterically-stabilizing polymers. By means of its hydrophobic tails that are compatible with the monomer and anionic hydrophilic heads stable in an aqueous phase, surfactants stabilize monomer or polymer particles in water (~micelles). Commonly, surfactant is not added to the polymerization system, but amphiphilic species are generated during polymerization process. As a result, three phases are established; aqueous phase, monomer-swollen micelle, and large monomer droplets. Then a propagation step takes place in three main intervals: particle nucleation and two intervals of particle growth. Figure A.3 illustrates schematic stages of the emulsion polymerization process.
A.2 Synthesis and characterization of polystyrene latex

Synthesis of polystyrene latex, as emulsion polymerization, uses monomer of very low solubility in water (styrene) polymerized in an aqueous solution containing initiators (hydrogen peroxide and ascorbic acid), a charge stabilizer (4-vinylbenzenesulphonic acid sodium salt, St(-)), and a steric stabilizer (PVP). As a result, three reaction phases are established.

- **Aqueous phase**: contains initiator, surfactant and small quantity of monomer.
- **Monomer-swollen micelle**: small droplet containing a relatively small amount of monomer stabilized with surfactant.
- **Large droplets**: contains a larger amount of monomer with small amount of adsorbed surfactant.

![Figure A.3 Schematic representation of the emulsion polymerization stages.](image)

Initiator activator (L-ascorbic acid as reducing agent) is added to the reaction mixture after thorough degassing with nitrogen to remove traces of oxygen.
In a red-ox reaction between ascorbic acid and hydrogen peroxide (1), free-radical active centers are created.

\[
\begin{array}{c}
\text{HO-CH}\_2\text{-CH} \\
\text{H-}\_2\text{O} + \text{CH}_2=\text{CH} \\
\end{array}
\]  
\[
\text{H-O-CH}_2\text{-CH} 
\]

After creation of an active radical center in the initiation step, subsequent latex formation can be divided into three intervals: nucleation (interval I), and particle growth (interval II and III).

**A.2.1 Interval I (Nucleation)**

In this stage, the free radicals that formed in an aqueous phase react with styrene to produce oligomeric radicals that continue to propagate in an aqueous phase until they reach just some critical degree of polymerization (> z-mer and < j-mer) to become insoluble. Then the reaction proceeds to a micellar nucleation step (Figure A.4).

The following steps summarize the nucleation stage.

- Initiation of the polymer chain growth by transferring an active center to a styrene monomer found in the aqueous phase.
• Propagation of the chain (chain growth) by continuous formation of oligomeric radicals in an aqueous phase until their degree of polymerization reaches the critical degree of polymerization ($z$), where oligomeric radicals are just at their solubility equilibrium (saturation concentration).

\[
\begin{align*}
\text{H-O-CH}_2\text{-CH} + \text{CH}_2\text{-CH}_2 & \rightarrow \text{H-O-CH}_2\text{-CH} - \text{CH}_2\text{-CH} - \text{CH}_2\text{-CH} \\
\text{H}_n & \rightarrow \text{H}_{n-1} \\
\end{align*}
\]

(3)

• Micellar nucleation: the (z-mer) oligomeric radicals aggregate into the monomer phase creating monomer-swollen micelles, where further polymerization process is continued. Each monomer-swollen micelle that captures an oligomeric radical becomes a particle nucleus within which the propagation is supported.

A.2.2 Interval II (Particle growth)

Polymerization continues supported by monomer diffusion from the monomer droplets to the micelles through the aqueous phase. In this interval, particle number, $N_p$, as well as the rate of polymerization remains constant.
A.2.3 Interval III (Particle growth)

In this interval both concentration of monomers and rate of polymerization decreases continuously as the remaining monomers present in the particles are polymerized.

A.3 Characterization methods

Properties of polymers are strongly dependent on chain-size and molar mass distribution. Therefore, measuring of number average molar mass and mass average molar mass is very important for polymers characterization.

Number average mass ($M_n$) can be measured using several methods, such as end-group analysis, which can be used for those polymers with end functional group that can be characterized (e.g. spectroscopically) or chemically (e.g. by elemental analysis). Second method is membrane osmometry, where osmotic pressure is proportional to polymer concentration (and thus $M_n$).

Mass average molar mass ($M_w$) can be characterized by several versatile techniques, such as light scattering. Light scattering can be also used to characterize latex particle size in dispersions. For determination of $M_w$, latex needs to be dissolved in appropriate solvent (such as toluene or cyclohexane for PS). Viscosimetry is another technique to characterize polymer molar mass that is based on flow of (or through) polymer solutions. Ultracentrifugation (most capable but laborious method) is based upon molecule separation in density gradients upon action of centrifugal forces. High performance gel permeation chromatography (GPC) is the most convenient method to estimate both $M_n$ and $M_w$; this method is based on injection of polymer solution into a highly porous column that separates the polymer molecules propagating by its size.
Electron microscopy (both scanning (SEM) and transmission (TEM)) is a convenient method to directly visualize latex particles and characterizing their size distribution, shape anomaly, and also self-assembly of monodisperse particles into close-packed lattices.

To determine thermal stability and phase transition temperatures of polymer samples, differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) are used. DSC is a thermo-analytical technique that is used to measure the heat flow and temperatures associated with transitions in which the difference in the amount of heat required to increase the temperature of a sample and reference. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. TGA is used to measure weight changes in materials to determine composition, thermal stability, and related phenomena. Charge stability of synthesized latex particles can be determined by measuring zeta potential.

In a summary of characterization, GPC is one of the most effective methods to evaluate molar mass characteristics of latex polymer samples. Electron microscopy, Zeta sizer, and light scattering allow evaluating size distribution of latex particles. TGA and DSC can be used to determine glass transition temperature (Tg) and thermal stability of the samples.
A.4 Experimental Section

In this lab, you will synthesize a monodisperse polystyrene latex using 4-vinylbenzenesulphonic acid sodium salt (St(-)) as charge stabilizer, polyvinylpyrrolidone (PVP) as steric stabilizer and redox initiation system consists of hydrogen peroxide and ascorbic acid. During the lab time you will be able to observe nucleation process as well as early stage of particles growth. Observations and characterization of the final product will be performed for previously prepared polystyrene latex. So you can gain the knowledge about entire process.

Safety: All of the stages of synthesis process of polystyrene latex should be performed in a fume hood.
1. Give a brief definition of the emulsion polymerization.
2. What is the purpose of the initiator in the emulsion polymerization and what type of an initiator system will be used in this experiment?
3. Hydrogen peroxide can function both as a reducing and oxidizing agent, write chemical equations to demonstrate it. Does hydrogen peroxide work in our experiment as an oxidizing or reducing agent?
4. Styrene monomer has density of 0.909 g/mL; calculate the mass of 560 µL of styrene that used in this experiment?
5. In characterization of conversion percentage, why should we wait till the aluminum weighing pan is cooled to room temperature before recording the mass?
6. Define the glass transition temperature, $T_g$, and describe how it can be measured?
7. Use the SEM image below to measure an average diameter ($d_{av}$ in nm) of polystyrene latex particles.
Experiment

EMULSION POLYMERIZATION: Synthesis of monodisperse polystyrene latex

OBJECTIVE

The objective of this experiment is to synthesize and characterize monodisperse polystyrene latex.

REAGENTS

Table A.1 CHEMICAL INFORMATION TABLE

<table>
<thead>
<tr>
<th>Chemical name/role</th>
<th>Structural formula</th>
<th>Properties</th>
<th>Hazards</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene (monomer)</td>
<td><img src="image" alt="styrrene" /></td>
<td>- molar mass: 104.15 g/mol&lt;br&gt;- density: 0.909 g/cm³&lt;br&gt;- melting point: -30 °C&lt;br&gt;- boiling point: 145 °C</td>
<td>Flammable liquid&lt;br&gt;- Carcinogen, moderate skin and eye irritant, mutagen</td>
</tr>
<tr>
<td>4-vinylbenzenesulphonic acid sodium salt (St(-)) (charge stabilizer)</td>
<td><img src="image" alt="4-vinylbenzenesulphonic acid sodium salt" /></td>
<td>- molar mass: 206.19 g/mol&lt;br&gt;- melting point: 300 °C&lt;br&gt;- powder</td>
<td>Harmful&lt;br&gt;- Moderate skin, respiratory and eye irritant</td>
</tr>
<tr>
<td>Poly(vinylpyrrolidone) (PVP) (steric stabilizer)</td>
<td><img src="image" alt="Poly(vinylpyrrolidone) (PVP)" /></td>
<td>- unit molar mass: 111 g/mol&lt;br&gt;- melting point: 150 °C&lt;br&gt;- water soluble powder</td>
<td>Not WHMIS controlled&lt;br&gt;- Not a dangerous substance according to GHS</td>
</tr>
<tr>
<td>Hydrogen peroxide (initiator)</td>
<td><img src="image" alt="Hydrogen peroxide" /></td>
<td>- concentration: 30% w/w&lt;br&gt;- vapor pressure(at 30 °C): 23.3 mmHg</td>
<td>Oxidizer, toxic by ingestion, severe eye irritant, corrosive</td>
</tr>
<tr>
<td>L- ascorbic acid (initiation activator)</td>
<td><img src="image" alt="L- ascorbic acid" /></td>
<td>- molar mass: 176.12 g/mol&lt;br&gt;- melting point: 190 °C&lt;br&gt;- powder soluble in water</td>
<td>Not WHMIS controlled&lt;br&gt;- Not a dangerous substance according to GHS</td>
</tr>
</tbody>
</table>
PROCEDURE

I. Synthesis.

1. In the fume hood, assemble a retort stand and a magnetic stirrer plate.

2. Clamp a 20 mL-vial containing a 32 by 2 mm Teflon-coated magnetic stir bar and place it on the magnetic stirrer plate. LAB TIP: record the mass of an empty 20-mL vial with provided a silicone rubber stopper and stir bar.

3. Add 10 ml of deionized water to the 20-mL vial and set the stirrer at 1200 rpm. LAB TIP: position the vial on the stirrer plate so that you can observe a good vortex that is indicative of uniform stirring.

4. Using a micro pipette, add 150 µL of 0.025 M St(-) followed by 200 µL of 0.05 M PVP and 370 µL of 0.2 M hydrogen peroxide.

5. During steady fast stirring, add 560 µL of styrene.

6. Add 370 µL of 0.2 M ascorbic acid to the mixture.

7. Using setup shown in Figure A.4, start degasing with uniform flow (~30 bubbles per minute) of inert nitrogen gas. LAB TIP: during degasing, start with the characterization section.

8. After complete development, record the mass of the 20-mL vial with the product, stir bar and stopper. This mass will be used later to calculate the conversion percentage.
II. Characterization.

Previously prepared latex with different particle sizes will be provided by your instructor.

II-1. Latex film

1. Using a disposable pipette, place one drop (~10 µL) of the previously synthesized latex on a glass slide and leave it in a fume hood to dry.

2. Record your observations in the data sheet.

3. Using optical spectroscopy or photograph, document the properties of the latex film and write down your observations.
II-2. Measurement of the average size of latex particles (using SEM images)

1. Take SEM image of the latex samples from your instructor.
2. Determine the size of different particles using the scale bar.
3. Calculate the average particle size ($d_{av}$) and standard deviation (STD) and record your results in a data sheet.

II-3. Conversion percentage

1. Using an analytical balance, mass empty aluminum weighting pan then transfer 100 µL of polystyrene latex and record the new mass.
2. In an oven, dry the latex sample at ~100 °C for 10 minutes.
3. Remove your sample from the oven and leave it to cool at room temperature and then record the mass.
4. Return the sample to the oven for more 2 minutes, cool it and record the mass.
5. Repeat step 4 until you get constant mass measurements.
DATA SHEET

- Particles Size (sample #______)

\[
\text{Particle size (nm)} = \text{diameter in cm} \times \frac{\text{scale bar in nm}}{\text{scale bar in cm}}
\]

<table>
<thead>
<tr>
<th>#</th>
<th>Particle diameter (cm)</th>
<th>Scale bar (nm)</th>
<th>Scale bar (cm)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[d_{av} = \text{nm}\]

- Latex Film (sample #______)

Observations:

- Conversion percentage

\[
\text{conversion percent} = \frac{\text{mass of solid} \times \text{mass of total latex}}{\text{mass of sample} \times \text{mass of styrene}} \times 100\%
\]

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Volume of Styrene</th>
<th>Mass of styrene (g) (density: 0.909 g/cm³)</th>
<th>Mass of total latex (g)</th>
<th>Mass of empty aluminum weighing pan</th>
<th>Mass of 100 µl of latex with aluminum pan</th>
<th>Mass of 100 µl of latex</th>
<th>Mass of dried sample with aluminum pan</th>
<th>Mass of solid</th>
<th>Conversion percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>