Branched metal and alloy nanoparticles for plasmonic and electrochemistry applications

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NANYANG
TECHNOLOGICAL
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**BRANCHED METAL AND ALLOY NANOPARTICLES FOR
PLASMONIC AND ELECTROCHEMISTRY APPLICATIONS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2017

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A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2017

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

7 May 2017

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Date

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Tran Thi Nhung

Abstract

Noble metal nanoparticles are fundamental to modern science and technology and have been utilized in many applications such as sensing, energy, biology, and medicine. Manipulation of the morphology and composition of noble metal nanoparticles enables the control over their optical/electrochemical properties and also to improve their performance in targeted applications. Among different classes of morphology-engineered nanoparticles, branched nanoparticles have attracted tremendous research attention recently due to their unique optical and electrochemical properties. The high charge density and charge polarization at tip extremities of branched nanoparticles generate a huge enhancement of the local electromagnetic (EM) field and a tunable localized surface plasmon resonance (LSPR) response over a wide spectral range. In addition, branched nanoparticles also exhibit pronounced electrocatalytic efficiency attributed to their large surface area, the exposure of certain high-index facets at tip edges/corners, and the synergetic effect arisen from the alloying character. However, the anisotropic growth of highly branched nanoparticles is not energetically favored in solution because of their large surface energy and the high crystalline symmetry of face centered cubic (fcc) metal nanocrystals. The growth of highly branched nanoparticles often required multi-steps, high pressure/temperature treatment, or the addition of capping agents which led to tedious and time-consuming purification steps. Besides, the synthesis of alloy nanoparticles composing of multi-metals is also challenging because of the mismatches in the reduction potential, solubility, and lattice of all metal precursors. Therefore, my aim is to develop new and facile routes for the synthesis of complex branched metallic particles and further explore their applications in plasmonics and electrocatalysis.

Herein, I developed a one-step, aqueous-based, and surfactant-free method to synthesize highly branched gold mesoflowers (AuMFs) with multilevel long and sharp tips. The method enables me to control the size, morphology, and the optical properties of the AuMFs by manipulating the reaction condition. I also demonstrated that chlorite ions Cl^- played a critical role in the formation of long and sharp tips and the tip branching by regulating the formation of multiple twin defects in the crystal structure of growing

particles. The branched AuMFs exhibit a LSPR peak maximum in the NIR to MIR region (~1800-3000 nm), depending on the tip morphology. The simulation analysis based on finite-difference time domain (FDTD) model was also conducted to elucidate the effect of tip morphology on the optical property of the AuMFs. The simulation was done in collaboration with researchers in prof. Li Shuzou's group, MSE, NTU with the assistance on the simulation.

Besides, the galvanic replacement reaction was often used in the seed mediated growth approaches to form hollow alloy metallic nanoparticles. I also established a new way to synthesize highly branched trimetallic hollow PdAgCu nanoparticles by coupling galvanic replacement with co-reduction reaction. The particles exhibited a high density of multiple tips on the surface, hollow interiors, and a tunable LSPR response in the NIR region. I also investigated the refractive index (RI) sensitivity and electrocatalytic activity of branched trimetallic PdAgCu nanoparticles towards ethanol oxidation reaction (EOR). The results showed that highly branched trimetallic PdAgCu nanoparticles exhibited a higher RI sensitivity and pronounced electrocatalytic improvement compared to that of branched bimetallic PdAg and PdCu nanoparticles. This work was done in collaboration with researchers in Prof. Jason's group, MSE, NTU with the assistance on electrocatalytic measurement and discussion.

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Abbreviations

AuMFs	Gold mesoflowers
AuNSs	Gold nanostars
BSE	Backscattered Electron
CVs	Cyclic Voltammetry Scanning
EDS	Energy Dispersive X-ray Spectroscopy
EOR	Ethanol Oxidation Reaction
EM	Electromagnetic Field
FDTD	Finite-Difference Time-Domain
FFT	Fast Fourier Transform
GO	Graphene Oxide
HRTEM	High Resolution Transmission Electron Microscopy
LSPR	Localized Surface Plasmon Resonance
MIR	Mid-Infrared
NIR	Near-Infrared
NPs	Nanoparticles
RI	Refractive index
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
SEI	Secondary Electron Images
TEM	Transmission Electron Microscopy
UPD	Under-Potential Deposition
XRD	X-ray Diffraction

Chapter 1

Introduction

The past few decades have witnessed increasing demand for biosensors and diagnostic technologies in healthcare, environment, food safety, sports, and etc. The aim of this thesis is to develop novel sensing plasmonic transducers by synthesizing complex metal and alloy nanoparticles with the focus on branched nanoparticles. Such nanoparticles might find applications in next generation of diagnostic and therapeutic tools. Thus, this chapter provides a general overview of the whole thesis concerning the motivation and inspiration for conducting the research, the hypotheses proposed, the objective and the scope of the study undertaken. A brief summary of following chapters, and lastly the contributions of the thesis regarding the original outcomes and findings are also presented.

1.1 Hypothesis/ Problem Statement

Branched metal and alloy nanoparticles have attracted a great number of research attentions recently due to their interesting optical and electrochemical properties arising from the high charge density and charge polarization at small-radii sharp tips.¹⁻³ It turns them into promising candidates for field enhanced spectroscopy, electrocatalysis, and sensing/therapeutic applications.³⁻⁵ However, the anisotropic growth of highly branched metal and alloy nanoparticles is challenging because the high surface energy and the high symmetry in the crystal structure of face centered cubic (fcc) metal nanoparticles would hinder such progress.^{6, 7} My PhD thesis focuses on the synthesis of such nanoparticles and their applications in optics and catalysis. Its scientific foundation can be summarized in the following hypotheses.

Hypothesis 1: Multiple twin defects can be used to control the morphology and branching of sharp tip metal particles – importance of halide ions.

The anisotropic growth of metallic nanoparticles can be controlled by manipulating the type and the number of defects in the crystal structures during the growth process.^{8, 9} The high strain energy at the defect areas induces a driving force to facilitate the anisotropic growth of metallic nanoparticles with complex morphologies.⁶ The role of twin defects in the growth of branched metallic nanoparticles has been acknowledged since twin planes were observed along the tip growth directions.^{10, 11} Therefore, one way to target the synthesis of branched particles with high density of branches on the surface is to incorporate multiple twin defects in the crystal structures of the growing nanoparticles. To obtain multiple twin defects, one may need to induce a disturbance in the atomic arrangement during the growth process. It was reported that adding a trace amount of silver ions can induce the growth of branched gold nanoparticles based on the under-potential deposition mechanism.¹² Besides, halide ions Cl^- was reported to form weak and movable adsorptions on the surface of gold nanoparticles and thus affecting the silver under-potential deposition.¹³ Hence, we hypothesized that halide ions Cl^- can be used to direct the tip growth and tip branching to obtain highly complex branched gold particles

by generating multiple twin defects in the crystals of growing nanoparticles.

Hypothesis 2: The combination of the galvanic replacement and co-reduction reactions produces highly branched trimetallic PdAgCu alloy nanoparticles.

Branched palladium (Pd) based nanoparticles are capturing tremendous research interest as a third plasmonic material and non-platinum based catalyst in fuel cell applications.^{5, 14} However, the growth of highly branched Pd-based nanoparticles often requires high pressure, high temperature treatment, or addition of capping agents which lead to tedious and time-consuming purification steps.^{15, 16} Recently, highly branched hollow AuAg nanoparticles and hollow bimetallic PdCu nanoboxs were prepared via controlling the galvanic replacement and co-reduction reaction pathway and demonstrated great potentials in plasmonic and electrocatalytic applications.^{3, 17} The galvanic replacement reaction was often used in the seed mediated growth approach to form hollow alloy metallic nanoparticles.^{3, 17, 18} The basic principle is based on the deviation in the reduction potentials between the seed particles and metal precursor ions. In general, the seed particles with lower reduction potentials are oxidized and dissolved into the solution by metal precursor ions with higher reduction potential. The co-reduction reaction is generated by simultaneously adding a reducing agent into the growth solution as the galvanic replacement reaction is proceeding. The resulting hollow alloy nanoparticles are of great research interest attributed to their large surface area and complex optical and electronic properties.⁶ Herein, I hypothesized that highly branched hollow trimetallic Pd-based nanoparticles can be prepared by exploiting the galvanic replacement and co-reduction reaction controlled pathway. In brief, silver nanoparticles were employed as seed particles for the galvanic replacement reaction with the mixture of H_2PdCl_4 and CuCl_2 solutions whereas ascorbic acid served as reducing agent to promote the co-reduction reaction.

Hypothesis 3: Highly branched trimetallic nanoparticles provide better LSPR sensitivity and electrocatalytic activity compared with branched bimetallic nanoparticles.

Alloy and intermetallic nanoparticles of transition metals have attracted a lot of research attention as promising materials in catalytic, optical, and electrical applications.^{14, 19-21} The synergetic effect and lattice mismatch of different metallic components can alter the crystal structure, the electronic and optical properties of alloy nanoparticles.²² For example, the incorporation of Cu, Ag, Au, or Sn in the composition of Pd nanoparticles exhibited a profound electrocatalytic improvement compared to pure Pd nanoparticles.^{4, 5, 21, 23} In addition, a recent report showed that spherical Pd nanoparticles provided a better refractive index sensitivity compared to that of spherical Au and Ag nanoparticles with similar size.²⁴ Therefore, I hypothesized that branched trimetallic alloy PdAgCu nanoparticles can improve the refractive index sensitivity and electrocatalytic activity compared to other branched bimetallic PdAg and PdCu nanoparticles.

1.2 Objectives and Scope

At the Centre for Biomimetic Sensor Science, School of Materials Science and Engineering, Nanyang Technological University, we work mainly on developing novel concept, theory, and methodology relevant to bio-sensing. A biosensor is a device composing of two main parts: a specific biological recognition element (receptor) and a transducer. The transducer plays the key role to convert the analyte-receptor interaction into a measurable and readable signal. Based on the nature of transducer, biosensor can be divided into different types such as optical, electrical, colorimetric sensor and so forth. My interest is to focus on developing novel sensing plasmonic transducers by synthesizing complex metal and alloy nanoparticles. The sensitivity and the reliability are key requirements to build up a sensing platform. Normally, spherical gold and silver nanoparticles have been used as plasmonic transducers primarily because of their sharp resonances and sensitivity. Moreover, the synthetic protocols of such nanoparticles are firmly established. However, conventional spherical nanoparticles often exhibit low sensitivity compared to metallic nanoparticles with other shapes. That encouraged me to

design new structures of metal and alloy nanoparticles to meet the requirements in biosensing via tailoring morphology and composition. Among different morphology-engineered nanoparticles, branched metal and alloy nanoparticles have attracted a great number of research attentions arising from their attractive optical and electrochemical properties. Besides, I am also interested in exploring the applications of such nanoparticles in other field such as electrocatalysis. Therefore, the objectives of my thesis can be listed as below:

- Develop a facile method (ex. green, one-pot and surfactant-free) to synthesize new branched sharp tip metal and metal alloy nanostructures
- Elucidate the growth mechanisms, the optical and electrochemical properties of the obtained branched particles
- Explore the applications of branched nanoparticles in sensing and electrocatalysis

1.3 Dissertation Overview

The thesis addresses the morphological and composition-controlled synthesis of novel branched metal and alloy nanoparticles, elucidating their growth process, their optical and electrochemical properties, exploring the potential applications, and lastly building novel sensing platforms based on hybrid nanoparticles for plasmonic sensing.

Chapter 1 provides a rationale for the research and outlines the goals and scope of the thesis. It also presents research challenges and proposed hypotheses for the works afterwards. The overview of the whole thesis is previewed through the brief summaries of the contents in each chapter. The outcomes of this thesis are also elaborated on at the end of the chapter.

Chapter 2 reviews the literature concerning strategies, pioneering works, and recent progresses in the synthesis of various types of metal and alloy nanoparticles with the emphasis on branched metallic nanoparticles. The optical and catalytic properties and potential applications of branched metal and alloy nanoparticles in plasmonics and electrocatalysis are elaborated on. Lastly, research gaps and the relevance of my thesis in

the context of literature are also stated.

Chapter 3 discusses the underlying theories, principles, and techniques concerning the synthesis, characterization, and applications of the branched metal and alloy nanoparticles. This chapter also provides the basic working principles, the instrumental setups, the data analysis, and the experimental handling conditions of all the concerned equipment.

Chapter 4 elaborates the synthesis of highly branched gold mesoflowers with high density of long sharp tips on the surface and a tunable red shift of the localized surface plasmon resonance (LSPR) peak to the range of 2000 ~ 3000nm. The growth mechanism of the obtained particles is revealed by the systematical investigation of different reaction parameters. The simulation based on finite-difference time-domain (FDTD) model was conducted to elucidate the optical properties and the electromagnetic field enhancement of the obtained gold mesoflowers with different branch morphologies.

Chapter 5 demonstrates the synthesis of trimetallic branched PdAgCu nanoparticles with high density of tips on the surface by coupling galvanic replacement and co-reduction reaction pathway. The growth mechanism and optical properties of the resulted nanoparticles are elucidated by controlling different reaction parameters. The effect of morphology and composition of different Pd-based nanoparticles on the refractive index sensitivity and the electrocatalytic activity towards ethanol oxidation reaction is also investigated.

Chapter 6 provides some preliminary results on the synthesis of hybrid nanoparticles of branched gold nanoparticles and graphene oxide for surface enhanced Raman scattering (SERS) sensing applications. The opportunities and strategies for future studies are also listed.

Chapter 7 summarizes of the dissertation. All the results, findings, and limitations are restated here and put in context of the proposed hypotheses.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Establishing a facile, one pot, surfactant-free and aqueous-based synthesis of branched gold mesoflowers with high density of long sharp tip on the surface. A tunable red shift of the LSPR peak to the range of 2000~3000 nm was observed, depending on the morphology of the tips. Halide ions Cl^- played a decisive role in the growth of long sharp tips and tip branching by controlling the formation of multiple twin defects. The quick aggregation and multiple twin defects were accounted for the growth of highly branched nanoparticles. The morphology of branched AuMFs was also facilely tuned by controlling other reaction parameters such as the amounts of AgNO_3 , ascorbic acid, and reaction temperature. The simulation results based on FDTD model revealed a significant electromagnetic field enhancement of E^2 up to $\sim 10^4 - 10^5$ at the resonance wavelengths. The synthesis approach in this study offered a great opportunity to facilely design novel complex supra-structures of gold particles with interesting optical and structural properties.
2. Establishing the new way of controlled synthesis of branched trimetallic alloy PdAgCu nanoparticles based on combining the galvanic replacement and co-reduction reactions. The obtained particles exhibited a high density of multiple tips on the surface, hollow interiors, and tunable LSPR peaks in the NIR region. The obtained branched trimetallic PdAgCu nanoparticles exhibited a higher refractive index sensitivity (653 nm/RIU) compared to bimetallic PdAg (509 nm/RIU) and PdCu (380 nm/RIU) nanoparticles. The electrocatalytic activity of highly branched trimetallic PdAgCu nanoparticles towards ethanol oxidation reaction was also 1.8, 6.2, and 4.6 times higher than that of the bimetallic PdCu and PdAg nanoparticles and pure Pd nanoparticles, respectively. The reasons are attributed to the exposure of certain high index crystal facets at tip edges/corners and the synergetic effect arising from the trimetallic alloy nature.

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Chapter 2

Literature Review

The aim of this thesis is to address challenges in both synthesis and applications of metallic nanoparticles. This chapter presents an overview of pioneering works on the synthesis of various noble metal and alloy nanoparticles with the emphasis on branched metallic structures because of their unique optical and electrochemical properties. The potential applications of branched metal and alloy nanoparticles in label-free localized surface plasmon resonance sensing, plasmonic field enhanced spectroscopy, and electrocatalysis are also discussed. Finally, the research gaps and opportunities are identified and set as the overarching aim of the thesis. Thus, this thesis focuses on developing novel and facile routes for the synthesis of branched metal and alloy nanoparticles based on engineering their morphology and composition; and further exploring their potential applications in plasmonics and electrocatalysis.

2.1 Synthesis of metal and alloy nanoparticles

2.1.1 Introduction

Noble metal and alloy nanoparticles have attracted intensive research interest in many fields such as sensing, energy, biology, and medicine due to their attractive optical and electrochemical properties.¹⁻³ To date, various kinds of noble metal and alloy nanoparticles with different morphologies and chemical compositions have been produced, Table 2.1. The optical and electrochemical properties of metal and alloy nanoparticles can be controlled by engineering their size, shape, and chemical composition.⁴⁻⁷ Therefore, it is appealing to develop new routes for the synthesis of complex metal and alloy nanoparticles with tunable optical and electrochemical properties. Recent progresses on the synthesis of metal and alloy nanoparticles were summarized in numerous books and review papers.^{1, 8, 9}

The preparation of metal and alloy nanoparticles through either the top-down or bottom-up approaches has been the focus for decades of research.⁸ The top-down methods such as lithography technique or mechanical method can facilely produce nanoparticles in large scale and has been used widely in industry. However, this method is time-consuming and costly, and it is also difficult to precisely control the morphology and composition of the obtained nanoparticles.⁹ In the bottom-up approach, nanoparticles are typically formed from building blocks (zero-valence atoms) generated by the decomposition or reduction of metal precursors.¹ By this method, nanoparticles with a designed morphology and composition can be produced by regulating reaction condition. Hence, this thesis will discuss about the bottom-up approach with the focus on wet chemical-based synthesis of metal and alloy nanoparticles.

In the typical wet chemical-based synthesis, metal and alloy nanoparticles are formed via three stages: atom generation, self-nucleation, and subsequent growth, as shown in Figure 2.1.¹⁰ In the first stage, zero-valence metal atoms are generated by chemical decomposition or reduction of metal precursors in the reaction solution. The concentration of metal atoms in the solution will rapidly increase during this stage as

the reaction proceeds. The second stage, so-called self-nucleation, starts when the number of generated metal atoms reaches the supersaturated concentration. The supersaturated solution is not stable due to the high free surface energy of initial atoms. It leads to the formation of nuclei in the reaction solution upon the self-aggregation of small and isolated metal atoms. To reduce surface energy, these small nuclei keep increasing in size by attracting more free atoms from solution to deposit on the pre-existing nuclei to form stable nucleuses. In the third stage, so-called growth stage, stable nuclei act as seed particles and subsequently grow into the final nanoparticles. This stage is governed by the continuous supply of free atoms from solution and the atomic arrangement on the surface of seed particles. The concentration of free atoms in the growth stage is kept lower than the supersaturated concentration to avoid the co-occurrence of the self-nucleation step. The uniformity in size, shape, and composition of resulted nanoparticles depend strongly on the separation between the nucleation and growth stages. To achieve the synthesis with high yield and purity of designed morphology and composition, one requires that the nucleation step proceeds rapidly and instantaneously whereas the growth step is well-controlled.

Figure 2.1 Schematic illustration of different stages in the formation of metal and alloy nanoparticles based on wet chemical synthesis. Copy from ref.¹⁰

Table 2.1 Summary of nanostructures of various metals have been synthesized. Reprinted with permission from ref.¹

Structures	Shapes	Schematic drawings	Metals
single-crystal	perfect/truncated cube ^[a]		Pd, Ag, Au, Pt, Cu, Rh, Bi, Fe
	perfect/truncated octahedron ^[a]		Pd, Ag, Au, Pt
	perfect/truncated tetrahedron ^[a]		Ag, Au, Pt, Rh
	rectangular bar		Pd, Ag, Pt
	octagonal rod		Pd, Au, Fe, Co, Ni
	rectangular or octagonal wire		Pb, In, Sn, Sb, Fe, Co
singly twinned	right bipyramid		Pd, Ag
	beam		Ag
multiply twin-ned	decahedron ^[a]		Pd, Ag, Au
	icosahedron ^[a]		Pd, Au
	five-fold twinned pentagonal rod		Pd, Ag, Au, Cu
	five-fold twinned pentagonal wire		Ag, Au, Cu
	triangular/hexagonal plate		Pd, Ag, Au, Cu, Pb, Bi, Co, Ni
	disc		Sn, Co

2.1.2 Strategies for the synthesis of metal and alloy nanoparticles

In general, metal and alloy nanoparticles with specific morphology and composition can be prepared by controlling their anisotropic growth kinetically or thermodynamically.⁸ One way to accomplish it is to control the reaction rate by adjusting a number of experimental parameters including metal precursors, reducing agents, solvent, temperature, additives, absorbents, surfactants, and so forth.¹¹ Each of these parameters can influence the nucleation or the growth stage and then control the reaction rate and/or atomic diffusion.¹² Besides, capping agents such as surfactants, polymers, or additives can bind to different crystal facets with different binding strengths via physical or chemical adsorption. As the result, they change the relative surface energies of different crystal facets and thus direct the further growth of the nanoparticles. Normally, nanoparticles which are bound by high index facets are not thermodynamically stable. However, they can be prepared in solution by the assistance of capping agents.^{8, 11} The final morphologies of nanoparticles are also affected by the number of defects in the crystal structure such as single twin, planar twin, stacking faults, multiple twins, etc.⁸ The incorporation of defects breaks the symmetry of the crystal structure and provides a driving force for the subsequent anisotropic growth.¹ Controlling the crystal structure and the morphology of the seed particles also provides an effective way to tailor the morphology and composition of the final nanoparticles.² The presence of etchants causes significant change on morphology and composition of nanoparticles.¹² Every single factor can cause a progressive change in the growth behavior of the nanoparticles. Therefore, it is important to understand and distinguish the role of each factor as well as their interplay to design a proper protocol for the synthesis of metal and alloy nanoparticles with desired morphology and composition. In later parts, I will discuss about general strategies developed recently for the synthesis of metal and alloy nanoparticles.

(a) Kinetic and surface passivation controlled growth

The common ways to direct the growth of metal and alloy nanoparticles involve manipulation of reaction kinetics and/or surface passivation.¹¹ In term of kinetic controlled pathways, the morphology of nanoparticles is governed by the reaction rate of the atomic generation and diffusion processes. At first, generated atoms deposit on the surface of pre-existing nanoparticles to form adsorbed atoms. The adsorbed atoms will move on the surface to the positions which possess a lowest energy to form crystals.⁸ At slow reaction rate, the atoms have time to rearrange themselves onto low index facets which are energetically stable such as triangular {111} and {110}, octahedral {111}, or nanocube {100}.¹ However, at high reaction rate, the atomic diffusion is prevented by the rapid growth, resulting in the formation of nanocrystals that are exposed to high index facets such as trisoctahedra {221}, Figure 2.2. In addition, the strength of reducing agents and the presence of impurities, additives, adsorbents, or gaseous species (O_2 or CO) can also alter the reduction potentials of precursors; eventually controlling the reaction rate.¹ In practice, the capping agents such as polymers, surfactants, or absorbents are introduced to adjust the relative surface energy of different crystal facets and thereby controlling the growth of nanoparticles in different directions, so-called surface passivation pathway.¹¹ The capping agents can adsorb on the surface of crystal facets by the electronic interaction between electrons in the capping agents and the surface atoms of the nanocrystals. Since different crystal facets have different electronic states, thus capping agents will adsorb on the surface of different crystal facets with different binding strengths.⁸ By strongly adsorbing on certain crystal facet, the capping agents can lower the surface energy and thus promote the growth of the crystals in other facets until the final nanoparticles are covered entirely by the passivated crystal facets. For instance, polyvinyl pyridine (PVP) was exploited in the synthesis of Ag, Pd nanocubes or nanobars because it binds strongly on the {100} facets rather than the {111} facets of Ag and Pd.¹ ¹³ However, in contrast to the Ag and Pd systems, the binding of PVP on the Au {100} is not sufficiently strong to promote the formation of gold nanocubes. As a result, Au nanocrystals which are enclosed by {111} facets such as octahedrons, truncated tetrahedrons, and icosahedrons were obtained in the presence of PVP.¹ Gold

nanoparticles with different morphologies were obtained by varying the concentration of Ag atoms in the reaction solution as shown in Figure 2.2 B.¹¹ Besides, halides ions such as Γ^- , Br^- , and Cl^- ions were reported to adsorb on the surface of Au nanocrystals with different binding strengths and consequently govern the morphology of the final nanoparticles.^{8, 11}

Figure 2.2 Schematic illustration displays the effect of kinetics and surface passivation controlled pathways on the morphology of metal nanoparticles. Copy from ref.¹¹

(b) Defects induced growth

Shape controlled synthesis of metal and alloy nanoparticles can be achieved upon manipulating the type and the number of defects in the crystal structures of growing nanoparticles during the growth process.^{14, 15} Since, most of metals have highly symmetric face centered cubic (fcc) crystal, there is no intrinsic force for them to grow into anisotropic nanoparticles such as nanorod (1D), plate or triangular (2D), and branched nanoparticles (3D).¹ The incorporation of defects into the crystal structures of metal nanoparticles may break the fcc crystalline symmetry and thus trigger the anisotropic growth of metal nanoparticles.¹ Stacking faults commonly occur in the cubic close packed lattices, which consist of hexagonally packed atomic planes with six fold symmetry.¹¹ The stacking sequence of these layers should be ABCABC. However, when

the stacking faults are introduced, there is a disruption in the sequence for one or two layers such as ABCABABC. A twin defect is a special case of stacking faults in which the stacking faults create a mirror plane in the atomic arrangement such as ABCACBA, Figure 2.3.^{1, 11} This defect is common in fcc crystal because the coordination number of atoms in each layer is the same as in the perfect crystal when the twin defect is present.¹¹ The reaction rate, the presence of absorbents, additives, and surfactants etc. can also cause disturbances in the atomic arrangement and thereby supporting the defect formation. The lattice strain at the defect acts as active sites promoting the anisotropic growth of metal and alloy nanoparticles. Various kinds of metal nanoparticles with different morphologies were prepared based on manipulating the types and numbers of defects in the growth process as shown in Figure 2.4.^{1, 2, 11, 14-16}

Figure 2.3 Illustration of a twin plane in a face-centered cubic (fcc) metal: (A) fcc lattice; (B) fcc lattice with the repeating ABCABCABC stacking layers; (C) annotated fcc lattice from (B) viewed down from the [110] zone axis; (D) annotated fcc lattice which contains a twin plane, as viewed down the [110] zone axis. Here, the insertion of a C layer in place of A B layer (ABCACBA) in the repeating pattern creates a structure which is mirrored around the central A layer (mirror plane). Copy from ref.¹¹

(c) Seed mediated growth

The seed mediated growth approach is exploited tremendously in the controlled synthesis of metal and alloy nanoparticles.^{2, 15} In the typical approach, pre-synthesized nanoparticles are added into the growth solution and serve as nucleation sites for the subsequent growth of nanoparticles. It is also referred as heterogeneous nucleation process. Compared with the seedless approach (homogeneous nucleation), the seed

mediated growth approach offers the synthesis of high yield and mono-dispersity due to the well separation between the nucleation and the growth stages. The shape and crystal structure of seed particles also play crucial roles in the formation of metal and alloy nanoparticles, Figure 2.4.¹⁵ Single-crystalline seed particles are likely to grow into nanoparticles which are enclosed by {111} crystal facets (octahedron), {100} crystal planes (cube), or both (cubooctahedron).¹¹ In addition, the type and the number of defects such as single, planar, and multiple twinned defects influence strongly the final morphologies of resulting nanoparticles.^{1, 8, 15} For instance, the highly symmetric gold nanostars with the distributed arms in I_h symmetry manner were obtained by using gold octahedron as seed particles.¹⁷ Palladium tripod nanoparticles were formed from the triangular Pd seed nanoparticles which contain planar twinned defects in their crystal structures.¹⁸ The seed particles can have the same or different chemical composition of the metal precursor solution, resulting in the formation of pure or alloy/core-shell nanoparticles, respectively.¹⁹⁻²¹ The lattice mismatch between initial seed particles and deposited atoms also affects the final morphology and crystallography of the obtained nanoparticles.²² The lower lattice mismatch (less than 5 %) is reported to favor the formation of nanoparticles which share similar shape and crystallography to that of seed particles.¹ An unanticipated morphological growth is expected when the lattice mismatch is larger than 10%.^{8, 22} In addition, the galvanic replacement reaction facilitated the formation of hollow alloy nanoparticles such as nanoshell, nanobox, and triangular frames, etc. based on the deviation in their reduction potentials.^{23, 24} Hence, controlling the size, shape, crystal structure, and composition of the seed particles offers an effective way to direct the growth of metal and alloy nanoparticles.²⁵

Figure 2.4 Schematic illustration displays the effect of the crystal structure of seed particles in the obtained morphology of nanoparticles. Copy from ref.¹¹

(d) Etching induced growth

Chemical etching can be exploited to generate complex structures of metal and alloy nanoparticles by manipulating the type of etchants and the reaction condition.⁸ The etchants can attack nanoparticles at susceptible sites such as edges, corners, high index facets, or defects because of the high surface energy at these areas. It results in a profound morphological transformation.^{1, 12} For instance, the pair chloride ions and oxygen Cl^-/O_2 promoted the formation of single-crystalline truncated silver nanocubes by selectively etching the corner sites of nanocubes in the shape-evolution process.²⁶ This pair of etchants was also capable of oxidizing and dissolving twin-containing seeds and thus allow the synthesis of single-crystalline nanoparticles with high yield and purity.²⁷ Branched Pd tripods were formed from Pd triangular nanoparticles owing to the edge etching effect triggered by bromide ions Br^- .¹⁸ Jin and coworkers reported that H_2O_2

served as a mild etchant to dissolve Ag atoms from the AgAu bimetallic hollow nanoshell to produce porous hollow nanostructures.⁸ By using mixture of NH_4OH and H_2O_2 , the morphology of Ag nanoparticles was progressively transformed from octahedron to octapods.²⁸ Therefore, controlling the etching strength and the reaction condition offers a powerful approach for the morphological controlled synthesis of metal and alloy nanoparticles, Figure 2.5.

Figure 2.5 Effect of oxidative etching in the morphological controlled growth of metal nanoparticles. Copy from the ref.¹²

2.1.3 Formation of alloy metallic nanoparticles

Alloy and intermetallic nanoparticles of transition metals have attracted a lot of research attention as promising materials in catalytic, optical, and electrical applications.^{23, 29-31} The synergetic effect and lattice mismatch of different metallic components can alter the crystal structure, the electrical, and optical properties of alloy nanoparticles.⁸ Moreover, it can overcome high cost issue of using pure rare earth materials by incorporating with other popular metals. Various kinds of alloy nanoparticles such as AuAg, PdCu, PdAg, and AuAgPd have been prepared and demonstrated great potentials in catalysis and electromagnetic field enhanced spectroscopy applications.^{18, 20, 24} In principle, alloy nanoparticles can be formed by the above mentioned approaches including controlling

the reaction rate, defects, seeds, etchant, capping agents, etc. The decrease of the free Gibbs energy in the system is the driving force for the formation of a stable alloy phase between immiscible metals. For instance, metal B nanoparticles tend to aggregate on the surface of metal A to reduce the surface energy, step I and II in Figure 2.6. After that, the atomic diffusion facilitates the formation of A-B alloy nanoparticles.⁸ The strain energy due to the lattice mismatch at the interface and the interfacial energy can be tuned by the assistance of surfactants; resulting in the heterogenous deposition and formation of core/shell or alloy nanoparticles, Figure 2.7 a.⁸ In addition, alloy and intermetallic nanoparticles have also been obtained by the under-potential deposition, electrochemical alloying (galvanic replacement reaction), or chemical reaction-driven reconstruction methods as described in Figure 2.7 b-d.⁸ In the typical under-potential deposition, metal ions are reduced at the potential which is higher than its Nernst reduction potential, Figure 2.7 b. Silver ions, for example were reduced by ascorbic acid and formed a monolayer on the surface of gold seeds and subsequently directed the growth of bimetallic AuAg nanostars.³² The electrochemical alloying or the galvanic replacement reaction occurs due to the deviation in the reduction potentials of the seeds and metal precursors, Figure 2.7 c. The metal with lower reduction potential is oxidized and dissolved by metal ions with higher reduction potentials. The chemical composition of nanoparticles can be tuned by the alloying and de-alloying processes. For example, hollow branched bimetallic alloy AuAg nanoparticles were obtained by using Ag nanoparticles as seeds in the galvanic reaction with gold salt solution.²⁰ Besides, the surface composition of alloy nanoparticles can be altered by exposing them to reacting gases such as CO, NO, H₂, Figure 2.7 d.⁸ For instance, Pd/Rh alloy nanoparticles were enriched with Rh atoms on the surface when the particles was exposed to an oxidizing gas atmosphere of NO whereas Rh atoms were “pushed” back to the core, if the particles were exposed to a reducing gas of CO.⁸

Figure 2.6 Formation of intermetallic nanoparticles through atomic diffusion: step I, mixing the suspensions of colloid A and B; step II, heating or sonicating the samples to form core-shell nanoparticles; step III, forming alloy nanoparticles via atomic diffusion. Copy from ref.⁸

Figure 2.7 Schematic illustration of (a) synthesis of bimetallic core-shell or core-shell-like NPs from metal precursors and (b–d) methods for the synthesis and structural control of core-shell multimetallic NPs: (b) Underpotential deposition (UPD) and replacement, (c) electrochemical de-alloying, and (d) reaction-driven process. Copy from ref.⁸

2.2 Branched metal and metal alloy nanoparticle background

2.2.1 Introduction

Among different classes of morphology-engineered nanoparticles, branched metal and alloy nanoparticles have attracted a lot of research attention recently due to their advanced optical and electrochemical properties.^{19, 20, 33, 34} Branched nanoparticles including tripod, tetrapods, star, and sea urchin compose of a number of tips radiating from the central core particles.³⁵ The high charge density and charge polarization at small radii sharp tips and their large surface area turn them into promising candidates in label-free localized surface plasmon resonance sensing, plasmonic field enhanced vibrational spectroscopy, catalysis, and therapeutic applications.^{20, 36, 37} However, it is challenging to develop a synthesis with high yield and purity of branched metal nanoparticles.^{17, 20} So in the later parts, I will summarize and discuss about recent progresses concerning the synthesis and characterization of branched metal and alloy nanoparticles as well as their potential applications.

2.2.2 Synthesis and Characterization

Branched metal and alloy nanoparticles with tunable morphologies and optical properties were synthesized by either seed-mediated growth or one-step approach.^{2, 35, 38} In the seed mediated growth approach, seeds may compose of the same or different chemical composition to the metal precursors. For example, small palladium Pd, platinum Pt nanoparticles were employed as seeds in the growth of branched gold nanoparticles.^{19, 20} Hollow branched bimetallic AuAg nanoparticles were obtained when Ag nanoparticles were used as seeds in the galvanic replacement reaction with gold salt solution.²⁰ The morphology and crystallography of the seeds were found to significantly affect the morphology of the final nanoparticles. For instance, symmetrically branched AuPd nanocrystals including five-branched pentapods, 24-branched nanocrystals, 12-branched nanocrystals, and 8-branched octopods were prepared by using Pd nanoparticles with different morphologies as seeds.² Twin defects were reported to induce the growth of

branched Pd and Pt nanoparticles by promoting the anisotropic growth of metal nanoparticles.¹⁴ Besides, the under-potential deposition mechanism was arguably responsible for the growth of branched metal and alloy nanoparticles.^{11, 39} For instance, the under-potential deposition of copper Cu atoms facilitated the growth of Pd tripods.¹⁸ In addition, defects and impurities as well as seed concentration, pH, and temperature were also found to significantly influence the morphology of the branched metal and alloy nanoparticles.^{11, 15, 40, 41} It was reported that branched gold nanoparticles were unstable and reshaped to form spherical nanoparticles when stored at high pH condition or temperature.^{19, 41} By the assistance of CTAB, stable branched gold nanoparticles was produced at high reaction temperature.¹⁹ All these opportunities and challenges inspired us to systematically investigate the shape controlled synthesis of complex branched metal and alloy nanoparticles.

2.2.3 Properties and applications

This part will discuss about optical and catalytic properties of branched metal and alloy nanoparticles arising from their large surface area, complex optical and electronic properties. The potential applications of branched metal and alloy nanoparticles in plasmonics and electrocatalysis are also elaborated on.

2.2.3.1 Optical properties and plasmonic applications

(a) Localized surface plasmon resonance and optical properties

Localized surface plasmon resonance (LSPR) is the collective oscillation of conductive electrons near the surface of metal nanoparticles in response to the external light excitation and restoring forces from nucleus, Figure 2.8.⁴² It induces charge polarizations over the surface of nanoparticles, which can be assigned to dipolar or multipolar modes (quadrupole, octapole, etc), depending on the geometry of metal nanoparticles. The plasmon resonance frequency of metal nanoparticles can be controlled by engineering their size, shape, composition, and the inter-particle distance.⁴⁻⁷ To explore the LSPR

phenomenon and its effect on the optical properties of metal nanoparticles, one needs to consider the Mie scattering theory which is the solution of the Maxell's equation for small spherical metal nanoparticles.

According to the Mie theory, the extinction cross-section (σ_{ext}), absorbance cross-section (σ_{abs}), and scattering cross-section (σ_{scat}) of spherical nanoparticles are calculated by the below equations:

$$\sigma_{scat} = \frac{8\pi k^4 a^6}{3} \left| \frac{\epsilon_{sphe} - \epsilon_{med}}{\epsilon_{sphe} + 2\epsilon_{med}} \right|^2 = \frac{k^4}{6\pi} |\alpha_{sphe}|^2 \rightarrow C_{scat} \propto \frac{a^6}{\lambda^4} \quad (2.1),$$

$$\sigma_{abs} = 4\pi k a^3 \text{Im} \left\{ \frac{\epsilon_{sphe} - \epsilon_{med}}{\epsilon_{sphe} + 2\epsilon_{med}} \right\} = k \text{Im} \{ \alpha_{sphe} \} \rightarrow C_{abst} \propto \frac{a^3}{\lambda} \quad (2.2),$$

$$\sigma_{ext} = \sigma_{abs} + \sigma_{scat} \quad (2.3),$$

In which $k = 2\pi/\lambda$; α_{sphe} is the dipolar polarizability of spherical metal nanoparticles with radius (a); ϵ_1 and ϵ_2 are the real and imaginary parts of the complex dielectric constant (ϵ_{sphe}) of metal nanoparticles, respectively; and ϵ_{med} is the dielectric constant of surrounding medium.

$$\epsilon_{sphe} = \epsilon_1 + i\epsilon_2 \quad (2.4),$$

And the dipolar polarizability (α_{sphe}) of the spherical nanoparticles is expressed as:

$$\alpha_{sphe} = 4\pi a^3 \frac{\epsilon_{sphe} - \epsilon_{med}}{\epsilon_{sphe} + 2\epsilon_{med}} \quad (2.5),$$

The electric dipole moment (p) can be described through the particle polarizability (α_{sphe}) and the incident electric field (E_0) by the equation:

$$p = \alpha_{sphe} \times E_0 \quad (2.6),$$

The localized electric field E is proportional to the electric momentum (p). When metal nanoparticles are characterized by a plasmon frequency (ω_P), the dielectric constant is described based on the Drude model as below:

$$\epsilon_1 = 1 - \frac{\omega_P^2}{\omega^2 + \omega i \gamma} \quad (2.7),$$

In which ω and λ are the frequency and wavelength of the excitation light, respectively, and γ represents the damping of the oscillating electrons caused by the electron-phonon scattering in metal nanoparticles. For small spherical metal nanoparticles, the damping effect can be ignored and thus, the real part of the dielectric constant can be rewritten as:

$$\epsilon_1 = 1 - \frac{\omega_P^2}{\omega^2} \quad (2.8),$$

This equation describes that the dielectric constant of metal nanoparticles is a frequency-dependent constant. The resonance occurs when it meets the requirement: $\epsilon_1 + 2\epsilon_{med} = 0$. At the resonance condition, the extinction cross-section of metal nanoparticles is maximized according to the equation (2.3). It results in squeezing down of the external electromagnetic field to the sub-wavelength regions on the surface of metal nanoparticles and thus enhances the local electromagnetic field.^{1, 13, 43, 44} In addition, the equation below also shows the relation between the dielectric constant of metal nanoparticles (ϵ_{spha}) and their refractive index (n).

$$n = n_R + in_I = \sqrt{\epsilon_{spha}} \quad (2.9),$$

Where n_R and n_I are the real part and imaginary part of the refractive index constant. Any change in the refractive index induces a change in the dielectric constant of metal nanoparticle and consequently the corresponding plasmon resonance frequency (ω_p). This is also the basic working principle of label-free LSPR sensing in which any change in the refractive index is monitored by the shift of the LSPR peak position of the LSPR substrates.

Figure 2.8 Illustration of localized surface plasmon resonance in silver nanoparticles.

Copy from ref.⁴⁵

In case of branched nanoparticles, numerous experiments and simulations have been performed to elucidate their LSPR properties including the huge electromagnetic enhancement.^{4, 21, 32, 46} Different models such as discrete dipole approximation (DDA) and finite-difference time-domain (FDTD) have been used to explore the optical properties of branched metal nanoparticles.⁵ According to the literature, the LSPR of branched nanoparticle relied on the plasmon hybridization of different plasmon modes corresponding to the core and the individual tips, respectively, Figure 2.9.^{46, 47} Feng Hao and co-workers proposed that the core of the branched gold nanoparticles serves as nanoscale antenna for the tips, which consequently enhances the excitation cross section

and the local electromagnetic field.^{38, 46} In addition, the length, sharpness and the tip density of branched nanoparticles are also found to affect significantly on the LSPR properties of branched nanoparticles.^{20, 47} For instance, a red shift in the LSPR peak positions was observed upon increasing the tip length and/or tip sharpness.⁴⁷⁻⁴⁹ Moreover, branched nanoparticles also exhibit a pronounced LSPR sensitivity and local electromagnetic field enhancement as compared to nanoparticles with other morphologies. It is attributed to the high charge density and charge polarization at small radii sharp tips which serve as hot-spot area in plasmon field enhanced spectroscopy applications.

Figure 2.9 Model illustrates the plasmon hybridization in branched nanoparticles. Copy from ref.⁴⁶

(b) Label-free localized surface plasmon resonance sensing

Label-free LSPR sensing is an analytical method used to detect the refractive index (RI) change by monitoring the shift of the LSPR peak position of the sensing substrates..³⁷ It can be used to detect the RI change in the bulk surrounding medium or on the surface of the sensing substrates caused by the attachment of analytes. The sensitivity of the sensing substrates is defined by dividing the LSPR peak shift to the RI change and has the unit of nm/RIU. However, it is challenging to precisely define the LSPR peak positions of sensing substrates which possess broad LSPR spectral bandwidths. It results in a high level of noise which affects the sensitivity of the detections. An alternative way to

evaluate the RI sensitivity of the sensing substrates is to estimate the figure of merit (FOM) value.³⁷ The FOM value is determined by the ratio of the RI sensitivity (nm/RIU) divided to the spectral bandwidth (nm). Metal nanoparticles with higher FOM value are preferred as an ideal substrate in LSPR sensing since they can achieve a lower limit of detection. Among different classes of shape-engineered nanoparticles, branched metal and alloy nanoparticles exhibit better LSPR sensitivities due to their high charge polarization and charge confinement at small radii sharp tips. For example, branched gold nanoparticles demonstrated an improved bulk RI sensitivity (703 nm/RIU) compared to that of gold nanoparticles with different morphologies such as gold spheres (~50 nm/RIU), gold nanorods (~288 nm/RIU), and gold pyramids (~540 nm/RIU).⁶ An extremely low limit of detection down to 0.1 pM for biotin-streptavidin interaction was achieved upon using gold nanostars as the LSPR sensing substrates.⁵⁰ By using an enzyme to direct the deposition of silver atoms on the surface of gold nanostars, the prostate specific antigen PSA, a cancer biomarker, was detected at the level of 10^{-18} g/mL in whole serum by a so-called inverse sensitive LSPR mechanism.³⁴ As mentioned before, the LSPR of branched nanoparticles relies on the plasmon hybridization of different plasmon modes corresponding to the core and the individual tips, respectively.^{46, 47} Due to the narrow spectral bandwidth of each single tip, the FOM value of gold nanostars reached the value of 5 which was much higher than what was reported for other gold nanostructures such as spheres (0.6), nanocubes (1.5), and nanorods (2.6).⁵¹ This allowed the use of single gold nanostar as a highly sensitive substrate in LSPR sensing. In addition, measuring the spectral curvature may offer an alternative way to overcome the broad spectral bandwidths of the sensing substrates and thus increasing the sensitivity of the LSPR detection.⁵²

(c) Surface enhanced Raman scattering

Raman scattering (discovered by Sir C. V. Raman in 1928) is one kind of inelastic scattering in which part of the absorbed energy from the incident photons is transferred to the vibrations of molecules.⁵³ Most of molecules display a small Raman cross section of $\sim 10^{-30}$ cm². Therefore, without enhancement, it is nearly impossible to detect their Raman

scattering signals. Surface enhanced Raman scattering (SERS) was first discovery in 1974 by Fleischmann.⁵⁴ They observed an intense Raman scattering signal from pyridine adsorbed onto a roughened silver electrode. SERS nowadays has been applied in many fields including environment, food toxins, explosives, and biology detection as a powerful analytical method.^{33, 36, 55, 56} Compared to other techniques (LSPR, SPR, and fluorescence), the fingerprint spectral bandwidth (~ 1 nm) in SERS can provide richer spectral information of the molecules and also limit the interference from background signal.⁵⁷ There are two mechanisms which are responsible for the SERS enhancement including the charge transfer effect and electromagnetic field enhancement.⁹ The charge transfer effect only occurs when the analyzed molecule is in closed contact with the surface of the sensing substrates and contributes of ~ 10 -1000 times to the signal enhancement.⁹ The electromagnetic field enhancement mechanism is attributed to the LSPR effect and contributes dominantly in the SERS enhancement up to $\sim 10^7$ - 10^{10} times.²⁰ To date, numerous metal nanoparticles with complex roughened morphologies, for examples, meatball, hierarchical, nanostar, multipod, sea urchin nanotextures have been synthesized and demonstrated as effective SERS substrates.^{1, 58-61} Among different classes of shape-engineered nanoparticles, branched nanoparticles have captured a lot of research interest recently as promising SERS substrates.^{9, 33, 35, 36, 55, 56} The high charge confinement at small sharp tip can generate a huge local electromagnetic field enhancement and consequently increases the SERS sensitivity, so called “sharp tip effect”.⁶² Besides, the huge electromagnetic field enhancement was also observed at the nano-gaps between adjacent tips in highly branched nanoparticles.⁶³ The electromagnetic field was also further enhanced by the conjugation of branched gold nanoparticles with metal films or satellite nanoparticles such as small gold, silver nanoparticles.^{33, 64, 65} Hybrid of branched nanoparticles and 2D material such as grapheme, (reduced) grapheme oxide was reported to profoundly increase the SERS sensitivity.^{55, 66, 67} The dye embedded in nano-graphene oxide wrapped gold nanostars showed an enhancement up to 5.2 folds higher than if the dye molecules just absorbed directly on the surface of gold nanostars.⁶⁶ Gold nanostars loaded on nano-graphene oxide substrates was also developed as a multifunctional materials for SERS imaging, drug loading, and

photothermal therapy applications.^{68, 69} The high SERS sensitivity of gold nanostars has opened a golden age in biomedical applications as SERS nanosensors or nanoreporters.⁷⁰

2.2.3.2 Catalytic properties and electrocatalytic applications

Metal nanoparticles have been used widely as catalysts in many reactions such as oxidation, cross-coupling, electron transfer, and hydrogenation reactions.⁷¹ It is well known that the catalytic reactions are sensitive to the electronic state and surface atomic arrangement/coordination of the catalysts; which can be tailored by manipulating size, shape, and composition of the catalysts.⁵⁹⁻⁶¹ In general, nanocrystals which are bounded by high index crystal facets display greater catalytic activities compared to that of nanocrystals with low index crystal facets owing to their coordinative unsaturation.^{72, 73} Branched metal and alloy nanoparticles displayed a profound electrocatalytic improvement compared to other shape-engineered nanoparticles due to their large surface area and complex electronic structure.^{18, 74-76} For examples, branched Pd nanodendrites showed 4.8 times higher catalytic activity (normalized to equivalent noble metal mass) to the oxygen reduction reaction than that of the commercial Pd/C catalysts.⁷³ The alloying of different metals in the composition was reported to further increase the catalytic activity of branched metallic nanoparticles, attributed to the synergetic effect.^{18, 23, 30} For instance, the catalytic performance of branched Pd₈₇Cu₁₃ tripods to the formic acid oxidation showed 8.7 times higher catalytic activity than commercial Pd black with the same Pd mass.¹⁸ In addition, high index facets found at tip edges and corners served as active sites to significantly improve the catalytic activity. For example, the superior electrocatalytic activity of high branched concave bimetallic AuPd nanoparticles towards ethanol oxidation which was 9 times better than that of commercial Pt black was attributed to their high index facets {411} located at tip edges.⁷⁴

2.3 Research gaps and research opportunities

Complex anisotropic metal nanoparticles have attracted intensive research interest in many applications such as sensing, medicine, and energy due to their large surface area

and advanced optical and electronic properties.^{58, 77, 78} The properties of metal and alloy nanoparticles depend strongly on their size, shape, and composition.⁴⁻⁷ Therefore, it is appealing to develop elaborate nanostructures with advanced optical/electrical properties by engineering their morphology and composition. However, the anisotropic growth of complex nanoparticles is not energy favored and one needs to induce driving forces to overcome the energy barrier and the high crystalline symmetry of face centered cubic (fcc) metals.^{1, 5} Current synthetic methods often required multi-steps or the addition of surfactants/polymers as structure directing agents which lead to tedious and time consuming purification process.⁷⁹ Thus, developing facile ways to the synthesis of nanoparticles with complex morphologies is of great demand. Moreover, alloy nanoparticles exhibit unique electrochemical properties due to the synergetic effect, making them attractive in catalytic applications.^{30, 80} Importantly, it also overcomes the high cost issue of using pure rare earth materials by alloying with other popular metals in the composition. In addition, hybrid nanoparticles of metal nanoparticles and carbon materials (CNT, graphene oxide) displayed interesting optical and electrochemical properties and have captured a lot of research attention in plasmonic and electrochemistry applications.^{55, 55, 65} Therefore, engineering the chemical composition of nanoparticles or preparing hybrid nanoparticles offer an effective way to improve their performance in desired applications.

2.4 PhD in context of literature

From the above discussed research gaps and research opportunities, the ambition of this thesis is to address challenges in both synthesis and applications of metallic nanoparticles. Herein, I have developed novel and facile routes for the synthesis of complex metallic nanoparticles which can overcome the drawbacks of current existing synthetic approaches. The growth mechanism and the properties of the obtained particles were elucidated based on both experimental and simulation methods and in reflection to previously reported works. It may contribute more insights to understand the growth process and the effects of morphology on the optical properties of complex metallic nanoparticles. After that, potential applications of the resulted particles were

demonstrated with the focuses on plasmonic and electrocatalytic applications. I also worked on building a new platform based on hybrid nanoparticles of branched metal nanoparticles and graphene oxide GO to target the highly sensitive SERS substrate for the detection of small molecules.

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Chapter 3

Experimental Methodology

This chapter fundamentally discusses the underlying theories, principles, and techniques involved in the synthesis, characterization, and applications of metal and metal alloy particles. In the synthesis part, the under-potential deposition, the galvanic replacement reaction, and the twin-induced growth mechanisms are exploited to synthesize highly branched particles. The as-prepared particles are characterized by different techniques to elucidate their morphology (field emission scanning electron microscopy and transmission electron microscopy), crystal structure (high resolution transmission microscopy and X-ray diffraction spectroscopy), composition (energy diffraction X-ray and element mapping), and optical properties (UV–Vis –NIR spectroscopy). The theories for the simulation of the optical properties of gold mesoflowers based on of the finite-difference time-domain (FDTD) method are also briefly introduced. The working principles of surface enhanced Raman spectroscopy and cyclic voltammetry were included. It also provides the instrumental setups, the data analysis, and the experimental handling conditions of all the concerned equipment.

3.1 Wet chemical synthesis of branched metal and alloy nanoparticles

In this work, branched gold mesoflowers, branched trimetallic PdAgCu nanoparticles, and hybrid nanoparticles based on gold nanostars and graphene oxide were facilely synthesized at room temperature based on one-step, aqueous and surfactant-free method. The morphology, composition, and corresponding optical properties of the synthesized nanoparticles were easily tuned by simply manipulating of different reaction parameters such as the precursor, halide concentration, and the seed amount.

3.1.1 Synthetic strategies

This part discussed synthetic strategies used in my approaches for the synthesis of branched metal and alloy nanoparticles. These synthetic mechanisms are also mentioned in the literature review chapter, including: under potential deposition mechanism (UDP), galvanic replacement reaction, and twin-induced growth mechanism.

According to the Nernst's equation, the reduction potential of an element is expressed as in this equation:

$$E = E_0 + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}} \quad (3.1)$$

Where: E_0 is the standard reduction potential at the equilibrium state, E is the reduction potential in the solution, a_{ox} and a_{red} are denoted as the chemical activity of oxidant and reductant reagents; R and F are the universal gas and Faraday constants; T is the temperature measured in Kelvin scale; and n is the number of exchanged electrons in the reaction.

The under potential deposition (UPD) mechanism is defined when metal ions are reduced and deposit on the surface of other existing metal nanoparticles at the reduction potential positive to its Nernst's potential.¹ Ascorbic acid, for example, is a mild reducing agent and unable to reduce silver ions under acidic conditions (pH ~ 1-2) which was used in my experimental condition. However, silver ions were still reduced and deposited on growing gold nanoparticles and then directing the growth of nanoparticles. This process is catalyzed by the surface of nanoparticles in the growth solution despite the mismatch between the reduction strengths of ascorbic acid and reduction potential of silver ions.¹

Copper ions was also reported to govern the growth of branched palladium nanoparticles and sharp edges-containing palladium concave cubes by the UPD mechanism.^{2, 3} Hence, in this work the pairs Au/Ag and Pd/Cu were exploited in the synthesis of branched gold mesoflowers and hollow branched trimetallic PdAgCu nanoparticles, respectively. Other reaction factors such as halide amount, temperature, precursor concentration etc. could influence the UPD process and were investigated accordingly.

The galvanic replacement reaction is often employed in the seed mediated growth approach as an elegant way to synthesize hollow alloy nanoparticles.⁴ The basic principle is based on the deviation in the reduction potentials between the seed particles and metal precursor. Generally, the seed particles with lower reaction potential will be oxidized and dissolved to the solution by metal precursors with higher reduction potential. The resulting hollow alloy nanoparticles are of great research interest attributed to their large surface area and unique optical and electronic properties.⁵ In this thesis, the alloy trimetallic PdAgCu nanoparticles were synthesized by exploiting the galvanic replacement reaction between the pre-synthesized silver seed nanoparticles and the H_2PdCl_4 and CuCl_2 mixture. Halide chloride ions were added to the reaction solution to tune the relative reduction potentials of the silver seed nanoparticles and the H_2PdCl_4 and CuCl_2 mixture, facilitating the galvanic replacement reaction to form the hollow alloy nanoparticles.

Twin-induced growth mechanism The high strain energy at the defect areas induces a driving force to facilitate the anisotropic growth of metal and alloy nanoparticles of different morphologies.⁵ The role of twin defects in the growth of branched nanoparticles has been acknowledged in the literature since twin planes were observed along the tip growth directions.^{6, 7} Therefore, one way to target the synthesis of highly branched nanoparticles is to incorporate multiple twin defects in the crystal structure of growing nanoparticles during the growth process. This can be done by controlling the reaction rate, the aggregation process, and crucially the amount of halide chloride ions in the reaction solution.

3.1.2 Synthetic protocols

Branched gold mesoflowers with high density of sharp tips were synthesized at room temperature based on the aqueous, seedless, and surfactant-free method. The effect of different reaction parameters (precursors, halides, temperature) on the morphology of gold mesoflowers was investigated by altering on parameter while fixing other experimental conditions. The branching level of the tip was facilely controlled by simply altering the amounts of chloride ions added to the reaction solution. Compared to previously presented approaches, this method offers the advantages of being simple, rapid, and surfactant-free. The details of the method will be presented in chapter 4.

Branched alloy trimetallic PdAgCu nanoparticles were synthesized based on combining the galvanic replacement and co-reduction reactions in the growth process. The pre-synthesized silver nanoparticles prepared by the citrate method were used as the seed particles and underwent the galvanic replacement reaction with the mixture of H_2PdCl_4 and CuCl_2 solution. In the subsequent step, ascorbic acid was introduced as reducing agent to trigger the growth of sharp tips on the surface of hollow alloy nanoparticles. The effect of different reaction parameters (precursors, seed amount, and halide) on the morphology and corresponding optical properties of the obtained nanoparticles were investigated by altering its value and fixing other experimental conditions. This method provides a new and facile way of controlled synthesis of trimetallic alloy branched nanoparticles. The details on the synthesis protocol will be presented in chapter 5.

Hybrid nanoparticles of branched metal nanoparticles and carbon materials are prepared by wrapping graphene oxide around pre-synthesized gold nanostars based on the electrostatic interaction. At first, gold nanostars were prepared by seed growth method and modified with cysteamine or 4-aminothiophenol molecules to make the surface positive charged. After that, the graphene oxide wrapped around the particles by simply mixing modified gold nanostars and the graphene oxide solution. The particles were later used as the substrate for further applications.

3.2 Characterization

After the synthesis and purification processes, the as-prepared particles were characterized by different techniques to elucidate their morphology, crystal structure, composition, and optical properties. The morphology was examined by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The crystallography was studied by high resolution transmission microscopy (HRTEM) and X-ray diffraction spectroscopy (XRD). The composition was analyzed by energy diffraction X-rays (EDX) and element mapping STEM mode equipped in the TEM machine. The optical properties were studied by experiment (UV–Vis –NIR spectroscopy) and theoretical calculation based on the finite-difference time-domain (FDTD) model. The following part discussed about the fundamental working principles and instrumental setups of each technique used in characterization.

3.2.1 The interaction of specimen with electromagnetic field: principles for characterization techniques

Electromagnetic field is composed of two perpendicular electric field and magnetic field component and has a wave-particle duality.⁸ In terms of a wave model, the electromagnetic field is broadly divided into different types including Gamma rays, X-rays, ultraviolet, visible, infrared, and radio waves depending on their wavelength/frequency, as shown in Figure 3.1. Light is one kind of electromagnetic wave. When it passed through the specimen, part of the energy is absorbed and transferred into heat, part is scattered in different directions, and the remaining is transmitted in the same direction to the detector. By comparing intensity of the incident light and the transmitted light, one can identify the extinction spectrum of the sample. This is also the basic working principle of the UV-Vis-NIR spectroscopy for studies of the optical properties of particular materials.

Electron beam is one type of ionizing radiation (electromagnetic field) which carries high energy due to the high acceleration voltage.⁹ Unlike photons in light, electrons are charged particles and thus they are scattered by both electron cloud and nucleus when

entering the specimen. Due to high energy, electrons are capable of removing inner shell electrons of the specimen and leading to varieties of secondary signals such as secondary electrons, backscattering electrons, characteristic X-rays, visible light (cathodoluminescence), and heat (phonon vibration), Figure 3.2. Each of the signals can be used in imaging or quantitative analysis of the specimen. For example, backscattering electrons, secondary electrons, and Auger electrons are generated near the surface of the sample and can be used to study the morphology as in SEM technique. The bremsstrahlung electrons or continuous radiation is generated by rapidly slowing down the fast electron beam as it passes through the electric field of the specimen, forming the background signal in the XRD spectra. Characteristic X-rays is generated when electrons located in high energy orbitals move back to empty orbitals at lower energies in the electron configuration of atoms. They can be used in quantitative or semi-quantitative analysis, for examples, EDX or XRD techniques. Transmitted electron and diffracted electron beams carry information about the crystallography and atomic arrangement of samples and are utilized in the TEM technique. Details of each analysis technique and equipment are presented in the following parts.

Figure 3.1 Category and spectrum of electromagnetic field. Copy from ref.⁸

Figure 3.2 Scheme of different types of interaction between electrons and sample.
Copy from ref.^{10, 11}

3.2.2 Instruments

3.2.2.1 UV-Vis-NIR spectroscopy

The UV-Vis-NIR (Cary 5000) with the scanning range of 175~3300 nm and UV-Vis (Perkin Elmer) with the scanning range of 175~1100 nm were used to measure the extinction spectra of the obtained particles. Figure 3.3 shows the schematic setup of a standard spectroscopy. It composes of a light source with different lamps to generate light, filters to filter out unwanted wavelengths, and a grating system (monochromator) to select specific wavelengths during the measurement. For particles which the extinction spectrum located in the wavelength range of 400~1100 nm, water was used as the solvent during the measurement. However, gold mesoflowlers in my experiments showed the extinction spectra in the range of 1500~3000 nm in which water shows strong absorption.¹² Therefore, to avoid the strong background signal from water, gold mesoflowlers were spread on the glass substrate, dried under ambient condition and the measurement was done in the air atmosphere.

Figure 3.3 Schematic illustration of UV-Vis-NIR spectrophotometer.

3.2.2.2 Field Emission Scanning Electron Microscopy

Scanning electron microscopy (SEM) is an instrument using a focused electron beam to scan or raster over the surface of the sample to reveal levels of details and complexity of the topography of the investigated samples. Different detectors are used to re-construct an image from the signals generated within the sample. Figure 3.4 shows the basic schematic setup of a typical SEM instrument. The electron gun is the source of electron beam and is divided into different types such as thermionic electron gun (W, LaB₆) or field emission electron gun. I used a field emission electron gun, so-called field emission scanning electron microscopy (FESEM). A variety of lenses are placed in the column in order to accelerate and focus the electron beam before it reaches the specimen. The backscattered electrons are produced by the elastic scatterings in which the incident electrons are being re-emitted from the sample. Since the number of backscattering electrons is proportional to the atomic numbers of different components in the specimen, they can provide compositional information of the sample based on the contrast of the image. The secondary electrons are generated by the inelastic scatterings in which loosely bound electrons in the outer orbitals of the specimen are ejected by the incident electrons.

They are detected when they escape from the surface. The escape probability of secondary electrons depends strongly on the topography and the geometric configuration of the sample, thus they carry information about the surface morphology of the scanned samples. The resolution of the image is dependent on the acceleration voltage, probe current and working distance. In my work, to maximize the secondary electron generation and consequently acquire the highest image resolution, the secondary electron images (SEI) mode was operated at the accelerate voltage at 5 KV and the probe current at 12 μ A. The samples were spread on the conductive substrate like silicon, dried under ambient condition prior to the measurement. A coating with Au or Pt is necessary to avoid the charging effects on non-conductive samples and to improve the image resolution. However, for taking the EDX, element mapping, or BSE images the samples need to be polished and no coatings can be accepted. A lot of good review papers and handbooks provide comprehensive guides to this subject.^{13, 14}

Figure 3.4 Schematic illustration of scanning electron microscopy. Copy from ref.¹³

3.2.2.3 Transmission Electron Microscopy

Transmission electron microscope (TEM) is an analytical instrument to visualize and analyze the specimen at micrometer to nanometer scale.⁹ It uses a high energy electron beam accelerated at high voltage (~100/200 KV) with the wavelength (λ) in the range of 0.01~0.1 nm. Therefore the resolution of the image can be achieved down to atomic scale which is inaccessible by optical microscopes. The crystal structure, atomic arrangement, sample orientation, and chemical composition of the samples can be revealed by selected area electron diffraction pattern (SAED), energy diffraction X-ray spectra (EDX), scanning transmission electron microscope with element mapping (STEM) techniques equipped in TEM instrument. Figure 3.5 shows the typical construction of a TEM instrument. Similar to the SEM instrument, an electron gun placed at the top of the machine is used to generate the electron beam. A set of lenses (condenser, objective, and intermediate) and stigmators (objective and condenser) are used to accelerate, align and focus the electron beam in adapt with the crystal orientation of the specimen in order to achieve the highest image resolution and avoid errors. Diverse apertures (condenser or objective) are inserted into the column to select proper beams (transmitted beam or scattered beam) for building up the image. The diffracted electron beams are used to produce diffraction pattern of the sample whereas the transmitted beams and part of the diffracted beams are used to produce the dark field or bright field images. The X-rays are utilized to analyze the composition of the samples. A lot of good review papers and handbooks providing comprehensive guides to this subject can be found elsewhere.^{9, 11} In my experimental setup, the investigated particles were dropped cast on the copper grid, dried at room temperature prior to measurements. For those samples containing copper in the composition like PdAgCu nanoparticles, the silicon TEM grid was used instead. The TEM JOEL 2010F was used to investigate the morphology of the sample whereas the crystallography (high resolution TEM, HRTEM) and composition (EDX, element mapping) of the samples were analyzed using TEM JOEL 2100F.

Figure 3.5 Schematic illustration of transmitted electron microscopy. Copy from ref.¹⁵

3.2.2.4 X-Ray Diffraction Spectroscopy

X-ray diffraction spectroscopy is an analytical tool to characterize the crystal structure and the preferred orientation of the matters. It is used widely today in analyzing varieties of materials in chemistry, pharmacy, and construction since the discoveries of the X-Rays (1895) and the interaction of X-rays with the electrons of solid materials (1912).¹⁶ The wavelength of X-rays is in the order of $1 \text{ \AA}$ (molecule level), thus it allows the beam to penetrate and be scattered by the internal lattices of the solid objects. The fundamental physics explained for the X-ray diffraction is based on the Bragg's law, Figure 3.6a. The Bragg's law correlates the relationship among the wavelength of the radiation, the angle

of the incident X-rays, and the internal spacing of the atom arrangement in the crystal structure and followed the equation:

$$2 d \sin \theta = \lambda \quad (3.3),$$

In which λ is the wavelength of the X-rays, d is the planar spacing of the crystal structure, θ is the incident angle. In my experiment λ is of 1.54 Å ($K\alpha$ of copper). The conditions for the constructive diffraction which later appear as peaks in XRD spectra are: (i) the scattered beam must radiate at the same angle with the incident beam to maintain the same path length and remain in-phase; (ii) the deviation in length between the incident beam and the scattered beam is by a whole number of the ray wavelength (λ). The XRD spectra are the set of different d -planar spacing recorded at different angles. It can be operated in the powder or thin film modes depending on the type of samples and the experimental purpose. Figure 3.6b shows the typical schematic setup of the XRD instrument operating under the powder mode in which both sample and detector move accordingly in the angles of θ - 2θ . For the thin film measurement, the incident angle is fixed at about $\sim 0.5^\circ$ - 3° and the detector moves by the angle of 2θ in order to avoid background signals from the substrates. The samples were prepared by well spreading the analyzed particles on the substrates with randomly angular distribution in order to avoid the preferred orientated effect. The X-rays are produced in the X-ray tube by using copper as anode material. Copper can generate the K_α X-rays which is 90 times higher than the intensity of the bremsstrahlung rays and thereby the background signals are sufficiently reduced. Many good review papers and handbooks offering comprehensive guides to this subject can be found elsewhere.^{14, 16, 17} In my experimental setting, the thin film mode was used since the amount of samples was small. All the samples were dispersed in water, spread on the silicon substrate, and dried completely at ambient condition prior to the measurements. The XRD spectra was recorded by X-ray (Rigaku) equipped with a rotation anode operating at 40 kV and 30 mA. The raw data was analyzed using ICSD software. For alloy metal nanoparticles, the XRD peaks of pure elements were collected from the JCPDS database and used as references.

Figure 3.6 Schematic illustration of (a) electron diffraction, (b) X-ray diffraction spectroscopy. Copy from ref.¹⁶

3.2.3 Simulation

The finite-difference time-domain (FDTD) is a computational method used to solve problems related to electromagnetic field and is arguably the simplest method both in concept and in term of implementation.¹⁸ The FDTD method can accurately solve a wide range of complex problems categorized in resonance region. However, it requires a large memory and extensive computation time. In principle, the FDTD method uses the finite difference as an approximation to both the spatial and temporal derivatives related to the electric field and magnetic field in Maxwell's equations, specifically Ampere's and Faraday's law.

The Maxwell-Ampere's law states that: for a time varying field, the divergence of the magnetic field (H) is the sum of the current density (j) and the temporal derivative of the electric flux density (D) to the time-varying (t).

$$\nabla \times H = j + \frac{\partial D}{\partial t} \quad (3.4),$$

The Faraday's law states that: the divergence of the electric field (E) is conversely

proportional to the derivative of the magnetic flux density for the time-varying field (B).

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (3.5),$$

In which $\mathbf{H}$ is the magnetic field, $\mathbf{j}$ is the current density through the closed surface or conduction current, $\mathbf{D}$ is the electric flux density, and $\mathbf{B}$ is the magnetic flux density.

$$\mathbf{B} = \mu \times \mathbf{H} \quad (3.6), \text{ and}$$

$$\mathbf{D} = \varepsilon \times \mathbf{E} \quad (3.7),$$

In which μ and ε are permeability and permittivity constants, respectively.

The central difference approximation of the field $f(x)$ at the point x_0 with the offset of $\pm\sigma/2$ is defined as the below equation calculated by Taylor series expansions:

$$\frac{f(x_0 + \frac{\sigma}{2}) - f(x_0 - \frac{\sigma}{2})}{\sigma} = f'(x_0) + \frac{1}{3!} \frac{\sigma^2}{2^2} f'''(x_0) + \dots \quad (3.8),$$

The term on the left is equal to the derivative of the function $f(x_0)$. If the σ is sufficiently small we can ignore all the terms after $f'(x_0)$ to get a reasonable approximation. So the central difference approximation is given by:

$$\frac{df(x)}{dx} \{x = x_0\} \approx \frac{f(x_0 + \frac{\sigma}{2}) - f(x_0 - \frac{\sigma}{2})}{\sigma} \quad (3.9),$$

The FDTD algorithm can be summarized as below^{18, 19}:

- i. Replace all the derivatives in Ampere's and Faraday's laws with finite differences. Discretize space and time so that the electric and magnetic fields are staggered in both space and time.
- ii. Solve the resulting difference equations to obtain "update equations" that express the (unknown) future fields in terms of (known) past fields.
- iii. Evaluate the magnetic fields one time-step into the future so they are now known (effectively they become past fields).
- iv. Evaluate the electric fields one time-step into the future so they are now known (effectively they become past fields)
- v. Repeat the previous two steps until the fields have been obtained over the desired duration.

We can find a lot of good review papers and handbooks providing comprehensive information to this subject.^{18, 19} Finite-difference time-domain (FDTD) simulations were performed to study the optical properties and electromagnetic field distributions using a

commercial packages offered by Lumerical Solutions (FDTD solutions 8.6, Lumerical solutions, Inc., Vancouver, Canada). In all the calculations, the incident light used was a TFSF plane wave propagating along the z-axis and polarized along the x-axis. Air was chosen as the surrounding medium for the optical property and electromagnetic field calculation. The mesh size used was of 4 nm for spherical core and ($x = 2.5$ nm, $y = z = 1$ nm) for the tip. The dielectric function of bulk gold was obtained from CRC* database.²⁰ The local electromagnetic field distributions were plotted in the log scale.

3.3 Applications

The as-synthesized particles were employed in different applications such as label-free surface plasmon resonance (LSPR), surface enhanced Raman scattering (SERS), and electrocatalysis depending on their optical and electrochemical properties. The following part introduces the fundamental working principles and the experimental conditions of each instrument employed.

3.3.1 Cyclic voltammetry and electrocatalytic measurement

The cyclic voltammetry scanning was used to examine the catalytic activity of as-prepared nanoparticles toward ethanol oxidation reaction, one of the most basic reactions in fuel cell applications.²¹ Figure 3.8 shows the typical setup of the electrocatalytic measurement which consists of three electrodes known as working electrode, reference electrode, and counter electrode. The as-prepared nanoparticles were attached onto the surface of working electrode as electro-catalyst to facilitate the ethanol oxidation reaction. The reference electrode composes of an Ag wire coated with a layer of AgCl and dipped in a saturated Cl^- ion solution. The potential of reference electrode was kept constant during the operation life time. The applied voltage on the working electrode was scanned in a certain range with respect to the reference electrode. A Pt wire was used as counter electrode. The current flows between the working and counter electrode as the ethanol oxidation reaction proceeds was read out during the measurement by an operating computer with equipped software. The current response is plotted as a function of applied

voltage and takes the shape as indicated in Figure 3.9. The reduction potential equilibrium established at the surface of working electrode is described as in the Nernst equation:

$$E = E_0 + \frac{RT}{nF} \ln \frac{a_{oxd}}{a_{red}} \quad (3.10),$$

where E_0 is the reduction potential at the equilibrium state when no bias is applied; E is the potential difference at the surface of working electrode associated with the applied voltage; a_{oxd} and a_{red} are defined as the chemical activity of oxidant and reductant reagents; R and F are the universal gas and Faraday constants, respectively; T is the temperature measured in Kelvin scale; and n is the number of exchanged electrons in the reaction.

In the forward scan (from left to right), the current response increases steadily until peaks up at certain voltage and starts to decline along with the further increase in the applied voltage. The current is measured as the electric flux density transferred at the interface of the electrode surface and electrolyte solution, Figure 3.9. The equilibrium state at the surface of the working electrode is broken down as increasing the applied voltage. It causes the ethanol oxidation reaction to proceed and thus, the current response increases. The peak intensity and the peak position of the current in the forward scan are the key factors to estimate the catalytic activity of the catalyst. Since the reaction is mainly kinetically controlled, the fast electron transfer at the interface of working electrode and electrolyte solution causes the peak current to shift to more negative voltage. However, the adsorption of intermediate species blocks the electrode surface and thus causing the current to level off as further increasing the applied voltage. In the backward sweep, the behavior is reverse to the forward sweep but otherwise the mechanism is explained in the identical manner.

In this experiment, ethanol oxidation reaction was chosen to examine the catalytic efficiency of different types of Pd-based nanoparticles in alkaline medium. The reaction mechanism is explained as following equations:²²

In the forward scan, ethanol at first adsorbs on the surface of Pd electrode and undergoes the oxidation reaction to form the intermediate species $\text{Pd}-(\text{CH}_3\text{CO})_{\text{ads}}$ (equation 1, 2) and the final product acetic acid CH_3COO^- (equation 6, 7). It leads to the increase in the current. When further increase the voltage, Pd is oxidized to form PdO (equation 3, 4, 5), blocks the surface of catalyst and thus results in the decline of the current. The activity of the catalyst will be recovered in the backward scan as described in this equation:

Figure 3.7 Schematic illustration of the setup for electro-catalytic measurement. Copy from ref.²³

Figure 3.8 Diagram of the cyclic voltammetry scanning. Copy from ref.²⁴

3.3.2 Confocal Raman spectroscopy and surface enhanced Raman scattering (SERS) measurement

Confocal Raman spectroscopy is an analytical instrument used to detect a wide variety of analytes based on the Raman scattering effect of molecules under laser radiation.²⁵ Figure 3.10 indicates the typical confocal Raman spectroscopy setup. It composes of four main components including power source, necessary apparatus (lenses, filter, notch, CCD), the temperature controller, and the controlling computer equipped with specific operating software to read the signal. The whole system is maintained at very low temperature (-60°C) to avoid damages caused by the heating effect of high power laser. The Raman instrument (Witec) used in my experiments is equipped with three different excitation wavelengths at 532 nm, 633 nm, and 785 nm. The excitation wavelength was chosen depending on the nature of the analytes and the SERS substrate. To avoid the burning of bio-samples, longer laser wavelength is considered as proper choices. A better SERS enhancement is achieved when the excitation wavelength matches the LSPR peak of the SERS substrate. In addition, other operating parameters such as the accumulation time, integration time, and grating also affect the intensity and resolution of the signals. The Raman shift peak of Si substrate at $\sim 522\text{ cm}^{-1}$ was used to calibrate the instrument before starting measurements. To avoid deviation, all the instrumental setups and adjustments were kept constant for all the measurements.

Figure 3.9 Schematic illustration of Raman spectroscopy.

3.4 Overview of Methodology

Noble metal nanoparticles have attracted a lot of research attention since the past few decades due to their unique optical and electrochemical properties. Among different classes of morphology-engineered nanoparticles, I have chosen to focus on branched nanoparticles because of their large surface area and interesting optical and electrochemical properties, attributed to the sharp-tip effect. The overarching aim was to develop facile synthetic protocols for the synthesis of new branched metal and alloy nanoparticles that can offer improved optical and electrochemical properties compared to conventional reported nanoparticles. The synthetic approaches presented in this study relied on combining different synthetic strategies employed for the synthesis of metal nanoparticles of different morphologies and compositions. Herein, the synthetic methods provide the advantages of room temperature, aqueous-based, and surfactant-free synthesis. After that, different analytical techniques including experiments and simulations were used to characterize the morphology, composition, crystallography, and optical/electrocatalytic properties of the as-prepared particles. Each type of synthesized nanoparticles was used for various applications including LSPR and electrocatalysis, depending on their properties. Lastly, hybrid nanoparticles composing of branched metal nanoparticles and graphene oxide were prepared and investigated in SERS sensing. Conclusively, the methodology employed in this dissertation aimed at obtaining a deeper insight into the nano-world from different angles including synthesis, characterization, and applications of noble metallic nanoparticles.

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Chapter 4

Gold Mesoflowers (AuMFs) with High Density of Multilevel Long Sharp Tips: Synthesis and Characterization

A one-step, aqueous-based, and surfactant-free method to synthesize gold mesoflowers (AuMFs) with multilevel long sharp tips is reported. The method enables control of the size, morphology, and optical properties of the AuMFs by tuning the reaction parameters such as concentration of precursor, halide, and reducing agent. The nanoparticle growth process is studied in detail and my findings suggest that chloride ions play a decisive role in formation of long sharp tips and tip branching. The synthesized particles exhibit a tunable localized surface plasmon resonance (LSPR) response in the NIR and MIR regions (~1800-3000 nm). These experimental observations are in agreement with simulations based on the finite-difference time-domain (FDTD) method. Moreover, the simulations also point towards a highly morphology-dependent field enhancement that opens up for future applications of the AuMFs in surface-enhanced vibrational spectroscopy and sensing/therapeutic.

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4.1 Introduction

Complex anisotropic metal nanoparticles have attracted intensive research interest due to their unique optical properties arising from the localized surface plasmon resonance (LSPR) phenomenon.¹⁻³ Particularly, the ability to concentrate light at the nanometer length scale, fine tune the LSPR peak across a wide spectral range, and enhance the local electromagnetic (EM) field turn such particles into promising candidates for surface enhanced vibrational spectroscopy (surface enhanced Raman scattering SERS and surface enhanced IR absorbance SEIRA) as well as for sensing/therapeutic applications.^{1, 4-10} To date, various types of metal nanoparticles with complex morphologies have been prepared such as meatball, hierarchical, nanostar, multipod, sea urchin, nanotextures, etc.^{2, 9, 11-15} Most of these metal nanoparticles exhibit LSPR peaks in the visible to NIR regions, ranging up to ~2000 nm. However, for molecular spectroscopy using SEIRA, one requires that plasmon excitation is further pushed into the MIR region.^{1, 4-10} Therefore, it is appealing to fabricate novel and complex metal nanoparticles with tunable optical properties.

The extinction spectrum of noble metal nanoparticles can be tuned by engineering their size, shape, composition and inter-particle distance.¹⁶⁻¹⁹ Among the different classes of shape-engineered nanoparticles, branched gold nanoparticles, including nanostars, nanourchins, spiky balls, etc. have recently attracted tremendous attention.^{6, 20, 21} Due to the high charge density and charge polarization at small-radii tip extremities, branched gold nanoparticles provide a huge enhancement of the local EM field and a tunable LSPR peak over a wide spectral range.²¹⁻²³ Numerous experiments and simulations have been performed to elucidate the LSPR properties including the huge electromagnetic enhancement of branched gold nanoparticles at the nanoscale. However, mesoscale branched gold particles have not been studied in detail.^{10, 16, 24} According to Feng Hao and co-workers, the core of the branched gold nanoparticles serves as nanoscale antenna for the tips, which enhances the excitation cross-section as well as the local EM field.^{24, 25} In addition, the length, sharpness, and the density of tips also influence the LSPR properties.^{21, 26} For example, a red-shift of the LSPR peak position is expected when the tip length and/or tip sharpness increases.²⁶⁻²⁸ However, the anisotropic growth of long

sharp tips is not energetically favored in solution because of the high surface energy and the high symmetry in face centered cubic (fcc) metal crystals.¹⁷ The atoms at the tip tend to dissolve and rearrange to form roughened protrusions (truncations) upon formation or during storage because of the Ostwald ripening effect.²⁷ Noteworthy, controlled synthesis of multilevel branched particles is challenging and only a few examples have been reported.^{8, 29} For example, Yuan et al. exploited a multistep protocol of seed-mediated growth approach to grow multilevel 3D gold particles with long thorns.⁸ They proposed that AgNO₃ contributed decisively to the growth of multilevel gold particles.³⁰ However, it is still challenging to control the tip branching-level as a trace amount of AgNO₃ can cause drastic change in the morphology of the thorny gold particles.^{8, 27} In addition, defects and impurities as well as seed concentration, pH, and temperature also were found to significantly influence the morphology of the branched gold particles.³⁰⁻³³

Despite tremendous ongoing research on the shape-controlled synthesis, the actual mechanism for the formation of branched gold structures is still under debate.³⁰⁻³³ All these opportunities and challenges inspired us to systematically investigate the shape-controlled synthesis of complex multi-level branched mesoscale gold particles with optical excitations in the NIR/MIR spectral regions.

Herein, I report on a facile, aqueous based, one-step, and surfactant-free route for the synthesis of highly branched AuMFs. I found that halide ions Cl⁻ played a crucial role during the growth of long and sharp tips by regulating the formation of multiple twin defects in the crystal structure of the growing particles. The lattice strain at the twin defects provides a driving force that facilitates the tip elongation. Noteworthy, the branching level of each tip was facilely tuned by adjusting the amount of halide ions Cl⁻ added into the growth solution. Moreover, the effect of AgNO₃ and ascorbic acid on the morphology of branched AuMFs was also investigated. A tunable and extreme red shift of the LSPR peak position to ~1800-3000 nm was observed, depending on the morphology of the tips. The finite-difference time-domain (FDTD) method was conducted by the assistance of the researchers in Prof. Li Shuzhou group to provide an in depth understanding of the morphology-dependent optical properties and the EM field enhancement of highly branched AuMFs.

4.2 Experimental section

4.2.1 Materials

All chemicals were of reagent grades and used without purification. Tetrachloroauric acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), silver nitrate (AgNO_3), ascorbic acid ($\text{C}_6\text{H}_6\text{O}_6$), sodium chloride (NaCl), sodium iodide (NaI), sodium bromide (NaBr), acetic acid, and chitosan (low molecular weight) were purchased from Sigma Aldrich

4.2.2 Methods

Synthesis of branched gold mesoflowers (AuMFs) All the glassware was washed intensively with freshly prepared aqua regia solution ($\text{HCl}:\text{HNO}_3 = 3:1$ v/v) and rinsed thoroughly with milli-Q water before using. Briefly, 180 μL of HAuCl_4 (10 mM), 20 μL of AgNO_3 (10 mM), and 30 μL of HCl (1.0 M) were added into 3 mL of milli-Q water in a 20 mL glass vial. The mixture was magnetically stirred for 5 min at 700 rpm. Subsequently, 150 μL of ascorbic acid (10 mg/mL) was rapidly added to the solution under vigorous stirring. The solution was kept stirring for further 4 min. To suspend the as-prepared particles, 1.4 mL of chitosan 1.0 wt% in 10 v/v% acetic acid solution was added drop-wisely to the above solution and followed by sonication for 1 min. The particles were then left undisturbed overnight. The purification step was carried by three times of centrifugation at 3000 rpm in 10 min and washing with milli-Q water to remove all excess amounts of unbound chitosan and reagents prior to further characterization. The reaction was conducted at room temperature, air exposure, and in a curtain-covered place. A lower yield synthesis of branched AuMFs was observed when the reaction was conducted in an extremely bright or dark place. To examine the effect of each reaction parameter on the morphology of resulted particles we altered the investigated parameter while fixing other reaction parameters.

Characterization and simulation The morphology and composition of AuMFs were characterized by field emission secondary electron microscope (FESEM-6340F), transmission electron microscope (TEM-JEOL 2010), electron dispersive

X-rays spectrometer (EDX-TEM-JOEL 2100), dark-field scanning transmission microscope image (STEM), and electron energy loss spectroscopy (EELS) equipped in TEM-JOEL 2100. The crystallography information was studied by high resolution transmission microscopy (HRTEM) with TEM-JOEL-2100 and X-ray diffraction spectroscopy (XRD). The XRD spectrum was recorded with a Shimadzu X-ray spectrometer equipped with a rotation anode. The Cu K α source was used with a fixed power source 2.0 kW at 40 kV and 30 mA. In a typical measurement, the sample was scanned at a rate of (1.5 deg/min) over a range from 30° to 80°. The extinction spectra of AuMFs were taken using UV-Vis-NIR spectrophotometer (Cary 5000). The finite-difference time-domain (FDTD) method³⁴ was performed to study the optical properties and EM field distributions using a commercial package offered by Lumerical Solutions (FDTD solutions 8.6, Lumerical solutions, Inc., Vancouver, Canada). In all the calculations, the incident light used was a TFSF plane wave propagating along the z-axis and was polarized along the x-axis. Air was chosen as the surrounding medium for the calculation of optical property and EM. The mesh size used was of 4 nm for spherical core and (x = 2.5 nm, y = z = 1 nm) for the tip. The dielectric function of bulk gold was obtained from CRC* database.³⁵ The local EM field distributions were plotted using the log scale.

4.3 Results and Discussion

Characterization of AuMFs

Branched AuMFs with a high density of long and sharp tips on the surface were synthesized in high yield at room temperature by a one-pot, aqueous-based, and surfactant-free approach. Briefly, an acidic solution (pH~1-2) was used as the growth solution for the reduction of HAuCl₄ and AgNO₃ precursors by ascorbic acid. The reaction solution turned transparent immediately after adding ascorbic acid, indicating the reduction of Au³⁺ ions to Au⁺ ions.³⁰ After that, the suspension gradually changed into grey color (4 min of stirring) that was taken as a sign of formation of AuMFs. The SEM

and TEM images of the as-synthesized particles are shown in Figure 4.1a and 4.1b, respectively. The dark contrast at the body center in the TEM image suggests that the branched AuMFs are composed of a solid core from which the tips grow.^{36, 37} A high density of ~ 200 - 300 nm long and sharp tips are extending from the ~ 400 nm core particles. Noteworthy, the branched AuMFs in this study exhibit a higher density of long and sharp tips compared to those found in other reports on branched gold structures.^{1, 7, 9, 38} Moreover, a twin plane is observed along the tip growth direction with the d-spacing of ~ 0.23 nm which is assigned to the $\{111\}$ reflections of fcc Au, Figure 1c.^{25, 27} The FFT pattern (Inset in Figure 4.1c) indicates that the tip is of single crystalline character. However, the XRD spectrum, Figure 4.1d, and the selected area electron diffraction (SAED) pattern, Figure 4.1e, indicate that the resulting AuMFs (core plus tip) are polycrystalline and dominated by $\{111\}$ crystal facets.

Figure 4.1 (a) SEM, (b) TEM, and (c) HRTEM image and the inset FFT pattern of the tip, (d) XRD spectrum, (e) SAED pattern of branched AuMFs synthesized at typical conditions: 30 μ L HCl (1.0 M), 180 μ L HAuCl₄ (10 mM), 20 μ L AgNO₃ (10 mM), and 150 μ L ascorbic acid (10 mg/mL $\approx$ 56 mM).

Moreover, the overlapping STEM-elemental mapping, Figure 4.2a, and the EDX spectrum, Figure 4.2b, demonstrate that branched AuMFs are primarily composed of Au with trace amount of Ag randomly distributed throughout the particles.

Figure 4.2 (a) STEM image, (b) over lapping elements, (c) gold element, (d) silver element, and (e) EDX–spectrum of branched AuMFs synthesized at typical condition: 30 μL HCl (1.0 M), 180 μL HAuCl₄ (10 mM), 20 μL AgNO₃ (10 mM), and 150 μL ascorbic acid (10 mg/mL $\approx$ 56 mM).

Roles of halide

The synthetic protocol used for the branched AuMFs was modified from the seedless synthetic approach of gold nanostars earlier reported in the literature.²⁷ Importantly, the concentrations of HCl and HAuCl₄ in the growth solution were higher than normally used in the reported synthetic protocols for gold nanostars.^{25, 28, 39} It is anticipated that the presence of a high concentration of halide ions (Cl[−]) in the growth solution is responsible for the formation of highly branched AuMFs.

To verify this hypothesis, a set of experiments was conducted where I systematically replaced HCl with approximate amounts of either H₂SO₄ or a mixture of H₂SO₄ and NaCl at fixed pH. When 15 μ L H₂SO₄ (1.0 M) was used instead of 30 μ L HCl (1.0 M), gold nanostars with few tips on the surface were obtained, Figure 4.3a. The obtained tips exhibit twin defects along the growth direction as observed in previously reported work on gold nanostars,²⁵ and in Figure S4.1. Interestingly, addition of 15 μ L H₂SO₄ (1.0 M) with 30 μ L NaCl (1.0 M), Figure 4.3b, led to the formation of extensively branched mesoscale particles that possess a similar morphology as the branched AuMFs prepared in the presence of 30 μ L HCl (1.0 M), Figure 4.1. I further studied the effect of other halides by replacing NaCl with the same amount of either NaBr or NaI. Figure 4.3c and 4.3d show the SEM images of the particles prepared by adding 15 μ L H₂SO₄ (1.0 M) with either 30 μ L NaBr (1.0 M) or 30 μ L NaI (1.0 M), respectively. Neither Br⁻ nor I⁻ ions were able to produce particles with long and sharp tips. For instance, Br⁻ ions produced roughened gold mesoscale particles with a small number of long and sharp tips, whereas I⁻ ions produced irregularly shaped gold nanoparticle aggregates/clusters without sharp tips. These results clearly indicate that the nature of the halide ion is crucial for the formation of mesoscale gold particles with a high density of long and sharp tips. The morphology and growth of AuMF is influenced by the type of halide ions mainly for three reasons. Firstly, the reduction potential of Au⁺ to Au⁰ is reduced with halides in the order of Cl⁻ > Br⁻ > I⁻. Secondly, the solubility of Au-halide complexes is reduced in the same order. Thus, the presence of Br⁻ and I⁻ ions can slower the reaction rate compared to that of Cl⁻ ions. Thirdly, the binding strength of halide ion with Au is in the order of I⁻ > Br⁻ > Cl⁻. Thus Br⁻ and I⁻ ions can block the exposed Au surface which may inhibit the growth of gold nanoparticles into flower shape.

Figure 4.3 SEM images of branched AuMFs synthesized at different conditions upon replacing 30 μL of HCl (1.0 M) by: (a) 15 μL H_2SO_4 (1.0 M), (b) 15 μL H_2SO_4 (1.0 M) + 30 μL NaCl (1.0 M), (c) 15 μL H_2SO_4 (1.0 M) + 30 μL NaBr (1.0 M), (d) 15 μL H_2SO_4 (1.0 M) + 30 μL NaI (1.0 M). The inset scale bar is 100 nm and all other scale bars are 500 nm.

To further explore the effect of the amount of Cl^- ions on the morphology of branched AuMFs, a series of experiments were undertaken where the amount of NaCl added into the growth solution was varied while other reaction parameters were kept unchanged (30 μL HCl 1.0 M, 180 μL HAuCl_4 10 mM, 20 μL AgNO_3 10 mM, and 150 μL ascorbic acid 10 mg/mL). Figure 4.4 shows the corresponding SEM and TEM images of branched particles obtained by varying the volume of Cl^- ions added from a NaCl stock solution (1.0 M). Interestingly, adding 30 μL of NaCl led to the formation of branched AuMFs that exhibited a high density of sharp tips extending from the 400 nm core particles (about 400 tips/particle),

Figure 4.4a-c. The tips were sharp and the average length of each tip reached ~ 300 nm. Small protrusions or secondary tips also appeared at the extremities of the long tips. Increasing the volume of Cl^- ions to $60\ \mu\text{L}$ prompted the elongation of the secondary tips on the primary tips, leading to the formation of multilevel branched AuMFs, Figure 4.4d-f. The initiation and elongation of new tips on the previously formed tips induced by Cl^- ions did not stop at this stage. With a further increase in the added volume of Cl^- ions to $120\ \mu\text{L}$, the hierarchy of branched AuMFs was further extended, with tertiary tips growing on the secondary tips and so on, Figure S4.2 and S4.3.

Figure 4.4 SEM and TEM images of branched AuMFs synthesized at various concentrations of NaCl by adding different volumes of NaCl from an 1.0 M stock solution: (a, b, c) $30\ \mu\text{L}$ and (d, e, f) $60\ \mu\text{L}$.

The crystal structure of the tips with different branching levels obtained by varying the volume of NaCl in the growth solution is shown in Figure 4.5. A 5-fold twinned defect at the tip extremity is observed in the primary long tip prepared without NaCl, Figure 4.5a. The HRTEM images reveal that both primary tip and higher level tips grew parallel to the twin boundary along the $\langle 11\bar{2} \rangle$ direction with a d-spacing of 0.23 nm which again is attributed to the $\{111\}$ reflections of

fcc gold, Figure 4.5a-c.^{25, 40} Such a growth/tip elongation process has been observed before for related particles.^{8, 25} In the absence of twin defects, short tips are formed which often exhibit a single crystalline character.^{8, 41} The twin defects break the high symmetry of fcc crystals thus providing a driving force for the anisotropic growth of metal nanoparticles.⁴² Therefore, incorporation of multiple twin defects in the crystal structures of growing particles results in the formation of highly branched tips. It is also worthwhile emphasizing that Cl^- ions are known to be mobile on the gold surface due to weak interaction with gold.³⁰ This mobile character of Cl^- ions may regulate the formation of multiple twin defects in the crystal structure of growing particles either by inducing disturbances in the atomic arrangement or by reducing the lattice strain in the twinned regions.^{12, 43} Moreover, the presence of halide counter ions such as H^+ and Na^+ ions and the high concentrations of metal precursors might cause a dramatic aggregation of small nuclei during the growth process, thus promoting the formation of mesoscale particles of different shape and morphology.

Furthermore, time-dependent SEM images of the particles at different growth stages were also recorded to reveal the morphological evolution of branched AuMFs, Figure S4.4. From this set of data and the observations in Figure 4.1 to 4.5, I propose that nanoscale crystals formed in the growth solution aggregate into twin defect-rich solid cores from which the tips can grow into multilevel, highly branched mesoscale particles as schematically outlined in Figure 4.6.

Figure 4.5 HRTEM image of the tip with different branching level prepared by varying the volume of NaCl added to the growth solution from a NaCl (1.0 M) stock

solution: (a) 0 μL , (b) 30 μL , (c) 60 μL . The white dash-lines indicate the twin defect planes. The inset FFT patterns are along the $\langle 1-10 \rangle$ zone axis.

Figure 4.6 Proposed growth mechanism of branched AuMFs: the sharp tips grow from the twin defect and the concentration of Cl^- ions in the growth solution influence the tip morphology. The black dash lines indicate the twin defect planes from which the sharp tips extend from the solid core.

Effect of AgNO_3

The role of silver ions Ag^+ in the synthesis of branched gold nanoparticles are arguably reported since gold nanostars were obtained both in the presence^{8, 27} and absence of Ag^+ ions.⁴⁴ The under potential deposition (UPD) of Ag^0 on the surface of growing gold nanoparticles is supposed to alter the surface energy of different crystal facets and thereby dictate the morphology of the formed nanoparticles.³⁰ Besides, the presence of halide ions may affect the Ag UPD process by forming insoluble Ag-halide complexes or by competitively adsorbing on the gold surface and thereby stabilize/destabilize the Ag_{UPD} layer.³⁰ However, during the synthesis of branched gold nanoparticles, silver can adsorb on the gold surface in the form of Ag^0 or AgCl .^{27, 45} To explore the role of AgNO_3 on the morphology of branched AuMFs, I conducted a series of experiments by adding different volumes of AgNO_3 from a stock solution (10 mM) while keeping other reaction parameters unchanged (30 μL HCl 1.0 M, 180 μL HAuCl_4 10 mM, and 150 μL ascorbic acid 10 mg/mL), Figure 4.7. In the absence of AgNO_3 , gold sticky balls were obtained because of aggregation of small gold nanoparticles, Figure 4.7a. Adding 10 μL of AgNO_3 resulted in the formation of branched AuMFs with long tips on the surface,

Figure 4.7b. Moreover, branched AuMFs with a high density of long and sharp tips on the surface were observed upon increasing the added volume of AgNO_3 to 20 μL , Figure 4.7c. Upon further increasing the volume of AgNO_3 to 30 μL , the tips appeared to be shorter and less branched as compared to those obtained using 20 μL of AgNO_3 , Figure 4.7d. In some parts of the image the particles appear roughened. These findings indicate that a trace amount of AgNO_3 can cause a progressive change in the morphology of the obtained particles. However, due to the huge morphological sensitivity observed upon addition of trace amount of AgNO_3 it is advisable to utilize Cl^- ions to effectively and reproducibly control the morphology in the shape-controlled synthesis of multilevel branched AuMFs.

Figure 4.7 SEM images of branched AuMFs synthesized at different added volumes of AgNO_3 from an AgNO_3 (10 mM) stock solution: (a) 0 μL , (b) 10 μL , (c) 20 μL , (d) 30 μL . The inset scale bar is 200 nm and all other scale bars are 500 nm.

Effect of ascorbic acid

Ascorbic acid is commonly used in the synthesis of anisotropic metal nanoparticles as the mild reducing agent.³⁶ To investigate the effect of ascorbic acid on the morphology of branched AuMFs, I conducted a series of experiments by adding different volumes of ascorbic acid from a stock solution (10 mM) into the growth solution while keeping other reaction parameters unchanged (30 μ L HCl 1.0 M, 180 μ L HAuCl₄ 10 mM, and 20 μ L AgNO₃ 10 mM), Figure 4.8. Addition of a small volume of ascorbic acid (50 μ L) yielded AuMFs with multiple leaf-like sheets extending from the core of the particles, Figure 4.8a. Increasing the volume of ascorbic acid to 100 and 200 μ L, respectively, led to the formation of branched AuMFs with multiple long and sharp tips on the surface, which attributed to a faster reaction rate, Figure 4.8b and c. The tip size (width and length) and the synthesis yield also increased with increasing volumes of ascorbic acid. However, excessive amounts of ascorbic acid (450 μ L) generated AuMFs with roughened morphology lacking sharp tips, Figure 4.8d. The rapid reaction rate caused by excess amount of ascorbic acid most likely resulted in the formation of a large number of nuclei in the growth solution. I anticipate therefore that, the amount of Au⁰ atoms available in the growth solution is no longer enough to feed the elongation of the tips. The excessive amount of ascorbic acid also may induce a negative charge effect on the surface of growing particles by adsorbing on the particle surface.^{33,39} For instance, it might block the adsorption of Cl⁻ ions on the gold surface which is essential for the growth of multiple long and highly branched tips.

Figure 4.8 SEM images of branched AuMFs synthesized at different added volumes from an ascorbic acid (10 mg/ml) stock solution: (a) 50 μL , (b) 100 μL , (c) 150 μL , (d) 450 μL . All the scale bars are 500 nm.

Optical properties of AuMFs

To gain insight into the optical properties including the EM field distribution of the branched AuMFs numerical simulation using FDTD method was conducted. Three geometrical models of branched AuMFs numbered as 1, 2, and 3, respectively, were considered to examine the effect of the tip morphology (sharpness and branching level) on their optical properties, Figure 4.9. The 400 nm core particle was kept at the same for the three models. In brief, the tip in model 2 shows a higher aspect ratio (length/width) compared with the features in model 1 (250/25

vs. 250/45). The tip in model 3 contains secondary small tips extending from the primary tip found in model 2 (so-called hyper-branched tip). The tip in model 1 can be found in the branched AuMFs in Figure 4.1 (so-called AuMFs 1) and the tips in model 2 and 3 can be found in the branched AuMFs in Figure 4.4a-c (so-called AuMFs 2+3). The simulated optical properties including the EM field enhancement for the three investigated models are shown in Figure 4.10 and table S4.1.

The extinction spectra are characterized by one pronounced red shifted peak in the NIR-MIR region (~1500-3000 nm), one distinct asymmetric peak in the NIR region (~1100-1500 nm), and several weak features located in the visible/NIR region (~540, 635, and 860 nm), Figure 4.10a. According to the literature, the extinction spectra of branched gold particles rely on the results of the hybridization of different plasmon modes corresponding to the core and individual tips.^{24, 26} High-order LSPR modes can be excited along with the dipolar LSPR mode located at the far-most wavelength upon increasing the size of particles or the length of tips.² Therefore, weak features in the extinction spectra located at ~540, 635 and 860 nm could be assigned to the plasmon excitations of hexadecapolar, octopolar, and quadrupolar LSPR modes of the 400 nm core particle. This is consistent with the findings for mesoscopic gold meatball particles reported by Wang et al.² Interestingly, an asymmetric peak located in the NIR region after a broad-continuum is observed in the extinction spectra for all three models. The overlapping of the broad dipolar plasmon mode (so-called superradiant) of the core particle and the narrow quadrupole plasmon mode (so-called subradiant) of the tip is accounted for the appearance of this Fano-type profile.⁴⁶ The Fano-resonance peak is of great interest in label-free LSPR sensing because of its unique shape.^{47, 48} Model 2 exhibits a significant red shift of the LSPR peak position in MIR region compared to that of model 1, attributed to the higher aspect ratio tip. Notably, the longitudinal plasmon peak of gold nanorods was found to shift in a similar manner (towards longer wavelengths) upon increasing the aspect ratio (length/width) of the particles.⁴⁹ Model 3 causes a further red shift of the LSPR peak position compared to that of model 2, attributed to the hyper-branched tip. The corresponding

experimental extinction spectra of branched AuMFs 1 and branched AuMFs 2+3 are shown in Figure 4.10b. To avoid the strong absorbance of H₂O in the NIR region, branched AuMFs were spread on a clean glass surface, dried completely under ambient condition, and the measurement was conducted in the air. Both particles exhibit a significantly broadened LSPR peak in the NIR~MIR region. The extinction spectrum of the branched AuMFs 1 is found at ~1800 nm, whereas the extinction spectrum of the branched AuMFs 2+3 appears to reach its peak value in the 2500~3000 nm region. The results are in agreement with the far-most red shifted peaks in the simulated spectra. The inhomogeneity in the experimental sample and the high density of multiple tips in branched AuMFs may account for the broadening seen in the experimental spectra as compared to the much sharper peaks seen in the simulated spectra. However, I did not observe the high-order LSPR peaks locating in the visible and NIR region (~1100-1500 nm) as displayed in the simulated spectra. The reason for the damping of high-order LSPR peaks is attributed to the surface roughness of the real samples whereas the perfect smooth-surface core particle was used for simulation. The damping of high-order LSPR peaks caused by surface roughness was also reported for gold meatball and nanoshell particles.^{2, 50}

The simulated EM field distributions for the three models in the MIR and NIR regions are shown in Figure 4.10c. All three models exhibit a huge enhancement of the local EM field $|E|^2$ of $\sim 10^5$ and $\sim 10^3$ - 10^5 at the MIR and NIR resonance wavelengths, respectively.⁵¹ The strongest EM field enhancement is found at the tip extremities, attributed to the sharp-tip effect.²⁴ Note that, model 2 exhibits the greatest EM field enhancement and the largest hot-spot volume compared to model 1 and model 3. It is also worth pointing out that the hyper-branched tip in model 3 shifts the LSPR peak position to longer wavelength at the expense of a slight reduction in the EM field enhancement and the hot-spot volume compared to those of model 2. This result is important to consider upon designing complex metallic particles with the desired LSPR peak position and EM field enhancement. The EM field enhancements of branched AuMFs in this study are comparable to those of current high-performance SERS and SEIRA substrates fabricated by

nanolithography technique such as nano-gaps,^{52, 53} plasmonic nanoantennas,⁵⁴ bowtie antennas,⁵⁵ and recently fan-shape antennas⁴. Importantly, the abundant and open hot-spot areas of branched AuMFs that provide easy access for analytes offer a great potential in applications such as surface enhanced vibrational spectroscopy and sensing/therapeutics.

Figure 4.9 Depiction of three models used for the simulation and corresponding TEM images of branched AuMFs 1 contained the tips in model 1 and branched AuMFs 2+3 contained the tips in model 2 and model 3. AuMFs 1 (Figure 4.1) was synthesized by the typical synthetic condition and AuMFs 2+3 (Figure 4.4 a-c) was obtained by adding 60 μL of NaCl from a 1.0 M stock solution to the typical synthetic condition. The typical synthetic condition: 30 μL HCl (1.0 M), 180 μL HAuCl₄ (10 mM), 20 μL AgNO₃ (10 mM), and 150 μL ascorbic acid (10 mg/mL $\approx$ 56 mM).

Figure 4.10 (a) Calculated extinction spectra of model 1, 2, and 3, (b) experimental extinction spectra of the branched AuMFs 1 and branched AuMFs 2+3, referred to TEM images in Figure 4.9, (c) Calculated EM field enhancement in log scale of three models at two resonance peaks in NIR and MIR regions. Polarization direction is indicated by the arrow.

4.4 Conclusion

A facile, aqueous-based, seedless, and surfactant-free approach to synthesize highly branched AuMFs with high density of multilevel long and sharp tips on the surface is reported. The concentration of Cl^- ions played a decisive role in the formation of long and sharp tips by regulating the formation of multiple twin defects in the growing particles. Noteworthy, the branching level of each tip was

facilely tuned by adjusting the amount of Cl^- ions added into the growth solution. Other reaction parameters such as the amounts of AgNO_3 and ascorbic acid were also found to influence the morphology of the particles primarily through manipulation of reaction kinetics and blocking of adsorption sites for the Cl^- ions. A tunable red shift of the LSPR peak position to the $\sim 1800\text{-}3000$ nm region was observed, depending on the morphology of the tips. Simulations based on FDTD method also revealed a significant EM field enhancement E^2 of up to $\sim 10^4\text{-}10^5$ at MIR resonance wavelength as well as large hot-spot volumes. The clean synthesis and massively red shifted LSPR peak position toward NIR-MIR region as well the huge EM field enhancement turn the AuMFs into promising candidates for surface enhanced vibrational spectroscopy as well as for bio- and chemical sensing/photothermal applications. Thus, the proposed synthesis route offers great opportunities to facilely produce novel complex mesoscale particles with advanced optical and structural properties.

4.5 Supporting information

The supporting information provide the TEM images of gold nanostars synthesized by replacing HCl with H_2SO_4 , TEM images of different tip branching levels, SEM and TEM images of AuMFs synthesized by adding 120 μL NaCl (1M) stock solution, SEM images of AuMFs at different growth stages, the summary of all the simulated results.

Figure S4.1 (a) TEM image of gold nanostars in Figure 2a synthesized upon replacing 30 μL of HCl (1.0 M) by 15 μL H_2SO_4 (1.0 M) and (b) HRTEM image of single tip.

Figure S4.2 Additional TEM images of multilevel tips with different branching levels corresponding to the branched AuMFs shown in Figure 4.4: (a) tip heads, (b) 2nd tip, (c) 3rd tip, and (d) schematic illustration of tip branching levels.

Figure S4.3 SEM and TEM images at different magnifications of supra-structure of AuMFs containing of hyper-branched tips synthesized by adding 120 μL from a NaCl stock solution (1.0 M). The white dash-lines indicate the twin planes.

Figure S4.4 Time-dependent SEM images of typical branched AuMFs at different growth stages: (a) 15 s, (b) 30s, (c) 90s, (d) 240s. The interval particles were taken at different reaction time, diluted by 20 times in the aqueous solution containing 1.0 mM 4-aminothiophenol to block the further growth of the particles. The obtained particles were followed by centrifugation at 5000 rpm in 2 minutes to remove all excess amount of 4-aminothiophenol before taking SEM. Small protrudes were observed in the early stage of branched AuMFs and followed by further elongation to form long and sharp tip when the reaction proceeded.

The electromagnetic field enhancement plays a dominant role in surface-enhanced spectroscopy. To demonstrate the great potential applications of the AuMFs in surface-enhanced spectroscopies, the maximum electromagnetic field enhancement and hot spots volume in AuMFs in the MIR and NIR regions are further calculated. For comprehensive comparison, three criterions are used to define the hot spot, i.e., regions with electric field enhancement larger than 1×10^3 , 1×10^4 , and 1×10^5 . And “hot spots volume” is defined as the whole volumes of all the regions with electric field enhancement larger than the defined criterion. The simulated EM field distributions for the three models in the MIR

and NIR regions are shown in Figure 4.8c, and the calculated maximum electric field enhancement and hot spots volume are summarized in Table S4.1.

Table S4.1 Summary of the simulation results for three models of branched gold mesoflowers. The hot-spots volume is defined as the regions where the EM field enhancement (E^2) larger than 10^3 , 10^4 , and 10^5 accordingly.

Models			1 (Low aspect ratio tip)	2 (High aspect ratio tip)	3 (Hyper-Branched tip)	
					Main tip	Small tip
Core size diameter (nm)			400	400	400	
Tip length (nm)			250	250	250	25
Tip bottom diameter (nm)			45	25	25	10
Tip head diameter (nm)			10	7	7	7
First SPR peak 1000~1500 nm	Maximum EM enhancement		5.9×10^3	7×10^4	2.1×10^4	
	Hot- spot volume (nm ³)	$ E ^2 > 10^3$	4680	57788	58658	
		$ E ^2 > 10^4$	0	2106	884	
		$ E ^2 > 10^5$	0	0	0	
Second SPR peak 1500~3000 nm	Maximum EM enhancement		1.45×10^5	3.82×10^5	2.62×10^5	
	Hot-spot volume (nm ³)	$ E ^2 > 10^3$	268482	751062	597622	
		$ E ^2 > 10^4$	13902	73766	56174	
		$ E ^2 > 10^5$	128	2626	1268	

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Chapter 5

Controlled Synthesis of Highly Branched Hollow Trimetallic PdAgCu Nanoparticles and its Applications

A room temperature, aqueous-based, and surfactant-free method to synthesize highly branched trimetallic hollow PdAgCu nanoparticles by coupling galvanic replacement with co-reduction reactions was reported. The particles exhibited a high density of multiple tips on the surface and a tunable localized surface plasmon resonance (LSPR) response in the NIR region. The method enables control over the size, morphology, and optical properties of the branched PdAgCu nanoparticles by tuning the experimental parameters such as the concentration of CuCl₂, seeds, and chloride ions. The branched trimetallic PdAgCu nanoparticles exhibited pronounced refractive index (RI) sensitivity and electrocatalytic activity towards ethanol oxidation reaction compared to the bimetallic PdAg and PdCu nanoparticles. It highlights future applications of the branched trimetallic PdAgCu nanoparticles as a multifaceted and multifunctional nanomaterial in combined plasmonic and electrocatalysis applications.

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5.1 Introduction

Palladium-based nanoparticles (NPs) have captured intensive research interest recently as a third-plasmonic material and a promising electro-catalyst in fuel cell applications.¹⁻⁴ Base on experiments and simulations, Sugawa and co-workers revealed that spherical Pd NPs exhibited a higher RI sensitivity than spherical Au and Ag NPs with similar size.⁵ It is attributed to the small dispersion in the real part of the dielectric constant of Pd.⁵ Besides, Pd has been also demonstrated as an effective alternative to Platinum (Pt) electro-catalyst in fuel cell applications, attributed to its lower cost and competitive electrocatalytic activity.⁶ In addition, the incorporation of multi-metals in the composition of Pd-based NPs can improve their efficiency in plasmonics and electrocatalysis, arising from the synergetic effect of multi-metallic components.⁷⁻¹² For instance, the alloy PdCu, PdAg, and AuAgPd NPs have been prepared and demonstrated excellent surface enhanced Raman scattering activity and electrocatalytic efficiency.^{10, 13, 14} Therefore, it is appealing to study the optical and electrocatalytic properties of Pd-based NPs with different morphologies and compositions.

The size-, shape-, and composition-dependent properties of noble metal NPs have stimulated research into exploring the synthesis of various types of anisotropic NPs with different morphologies and compositions.^{6, 15-17} Among different classes of morphology-engineered NPs, my interest was focused on branched metallic NPs including nanostars, nanourchins, spiky balls, etc.¹⁸ Due to the high charge confinement and charge polarization at tip extremities and tip edges, branched NPs provide a huge electromagnetic field enchantment and high RI sensitivity which are ultimately useful in field enhanced vibrational spectroscopy and label-free LSPR sensing applications.^{14, 19, 20} In addition, branched NPs also exhibit a pronounced electrocatalytic efficiency attributed to their large surface area and the exposure of certain high-index facets at tip edges/corners that are intrinsically more-active towards many specific reactions.⁶ For example, the Pd tripods, tetrapods, and multipods NPs have been prepared and demonstrated excellent electrocatalytic activities towards various reactions.^{3, 6, 10, 21} In addition, the strain energy at twin defects which were usually found along the tip growth directions in branched NPs also contributed to the electrocatalytic improvement.^{17, 22}

However, to synthesize highly branched Pd-based NPs, one often requires high pressure/temperature treatment or the addition of capping agents which leads to tedious and time-consuming purification steps.^{21, 23} Recently, copper ions have been exploited to facilitate the synthesis of complex branched Pd-based NPs based on the under-potential deposition mechanism.^{3, 10, 24} For instance, Pd concave nanocubes with sub-10-nm edges and corners were prepared by adding Cu^{2+} ions in the growth solution.³ Besides, forming alloyed multi-metallic NPs is challenging because of the mismatches in the reduction potential, solubility, and lattices of all metal precursors in growth solution.¹³ Jing and co-workers have recently developed a wet chemical-based approach for the geometry-controlled synthesis of hollow bimetallic alloy PdAg NPs based on combining the galvanic reaction with the addition of an appropriate mild reducing agent.¹³ Noteworthy, Weiner et al. has reported for the first time the synthesis of hollow trimetallic Ag-Au-Pd nanocubes by coupling of seed mediated co-reduction and galvanic replacement approach.²⁵ All these opportunities and challenges have inspired me to systematically investigate the synthesis of novel branched multi-metallic Pd-based NPs for plasmonic and electrocatalytic applications.

Herein, I report on a room temperature, aqueous-based, and surfactant-free synthesis of highly branched trimetallic PdAgCu NPs with hollow interiors by coupling galvanic replacement and co-reduction reaction. The galvanic replacement reaction between the pre-synthesized silver NPs (Ag NPs) as seeds and the mixture of H_2PdCl_4 and CuCl_2 solution ($\text{H}_2\text{PdCl}_4/\text{CuCl}_2$ mixture) was performed spontaneously at room temperature by the assistance of a high concentration of chloride Cl^- ions in the growth solution. The morphology and optical properties of the branched PdAgCu NPs were tuned by simply manipulating the reaction parameters such as the concentration of CuCl_2 , Cl^- ions, and Ag NPs seeds. The RI sensitivity and electrocatalytic activity towards ethanol oxidation reaction (EOR) of the PdAgCu NPs were also examined. The results showed that the branched trimetallic PdAgCu NPs exhibited a superior RI sensitivity and electrocatalytic activity than that of bimetallic PdCu and PdAg NPs. The electrocatalysis measurement and discussion was conducted in collaboration with researchers in Prof. Jason Xu Zhichuan group.

5.2 Experimental section

5.2.1 Materials

Palladium (II) chloride (99%), commercial Pd black (99.95%), silver nitrate, copper (II) chloride, sodium chloride, sodium bromide, sodium iodide, ascorbic acid, chitosan (low molecular weight), and acetic acid were purchased from sigma Aldrich, hydrochloride acid fuming 37% was purchased from EMSURE®. All chemicals were of reagent grades and used without further purification.

5.2.2 Method

All glassware was washed intensively with freshly prepared aqua regia solution ($\text{HCl}:\text{HNO}_3 = 3:1$ v/v) and rinsed thoroughly with mili-Q water before using.

Synthesis of silver nanoparticle Ag NPs of ~50 nm in diameter were synthesized based on the citrate method. Briefly, 5.3 mL of silver nitrate AgNO_3 (10 mM) was added into 44.7 mL water in an erlenmayer flask. The solution was vigorously stirred and quickly heated to boiling in an oil bath. Subsequently 1.1 mL of sodium citrate (1.0 wt%) was added into the solution under vigorous stirring. The color of the solution changed from colorless to light yellow, brown, and permanent greenish brown in about 20 minute that was taken as sign of the formation of Ag NPs. After that, the heater was removed and the solution was kept under gentle stirring until it cooled down to room temperature. Milli-Q water was added to the solution to adjust the concentration of Ag NPs in the solution at 2.4 mM related to Ag^+ ions concentration. The particles were kept in refrigerator at 4 °C for further use.

Synthesis of highly branched trimetallic PdAgCu nanoparticle the synthesis process was conducted in air exposure. Briefly, 200 μL of as-prepared Ag NPs, 50 μL of NaCl (1.0 M), and 50 μL of HCl (1.0 M) were added into 5.3 mL of milli-Q water in 20 mL vial and stirred for 5 minutes. After that, a mixture of 300 μL H_2PdCl_4 (10 mM) and 100

μL of CuCl_2 (15 mM) solutions ($\text{H}_2\text{PdCl}_4/\text{CuCl}_2$ mixture) was added into the above solution under vigorous stirring for another 60 s. The color of the solution changed immediately from brown to dark green upon adding the $\text{H}_2\text{PdCl}_4/\text{CuCl}_2$ mixture. The aqueous solution of H_2PdCl_4 (10 mM) was prepared by dissolving 71.65 mg of PdCl_2 (99%) powder in 40 mL HCl (20 mM) solution and gently shaking overnight. After that, 150 μL of ascorbic acid (100 mM) was added rapidly to the reaction solution. The color of solution slowly turned from dark green to permanent deep black after a few minutes of stirring. To disperse the as-prepared PdAgCu NPs, 2 mL of chitosan solution (10 mg/mL) in (10 v/v%) acetic acid solution was added drop-wise to the above solution under gently stirring for another 15 minutes and kept untouched for few hours. The purification step was conducted by three times of centrifugation at 8000 rpm for 10 minutes and washing with milli-Q water to remove all excess amounts of unbound chitosan and reagents prior to characterizations. To study the structural evolution, the time-dependent TEM images were recorded at different growth stages. Briefly, the interval particles were taken at different reaction time and immediately dropped on TEM grids. After that, the TEM grids were quickly washed by water to remove all excess reagents and dried in the air completely prior to the TEM analysis. For the EDX mapping measurement of the PdAgCu NPs, silicon TEM grids were used instead of copper TEM grids to avoid the overlapping of copper element contained in both TEM grid and the sample.

Characterizations the morphology and composition of the branched PdAgCu NPs were characterized by field emission scanning electron microscopy (FESEM-6340F), transmission electron microscopy (TEM-JEOL 2100), electron dispersive X-rays (EDX) equipped in FESEM, dark field scanning transmission microscopy image (STEM) and electron energy loss spectroscopy (EELS) equipped in TEM-JOEL 2100. The crystal structures were studied by HRTEM (TEM-JEOL 2100) and X-ray diffraction spectroscopy (XRD). The XRD spectra were recorded by XRD Shimadzu equipped with a rotation anode. A $\text{Cu K}\alpha$ was used with a fixed power source of 2.0 kW at 40 kV and 30 mA. The samples were scanned at the rate of (2 deg/min) over a range from 30° to 90° . The XRD peaks of pure Pd, Cu and Ag crystals were collected from the JCPDS database

as references. The extinction spectra of as-synthesized NPs were recorded by UV-Vis spectrophotometer (Perkin Elmer).

Electrochemical measurement: the electrochemical measurements were carried out in a standard three-electrode cell on an Autolab potentiostat/galvanostat electrochemical voltammeter with the scan range from -0.8 V to 0.2 V and the scan speed at 50 mV/s. A Pt wire and Ag/AgCl electrode filled in saturated KCl solution were used as the counter and reference electrode, respectively. The working electrodes were prepared by casting an aliquot amount of different catalysts solution including the PdAgCu, PdAg, PdCu, and Pd NPs (5 μ L, 0.125 mg/mL in milli-Q water with respect to Pd-mass loading) on the cleaned glassy carbon electrodes (3 mm in diameter) and dried under ambient condition. The Pd NPs were prepared by the same typical synthetic procedure of the branched PdAgCu NPs without adding CuCl₂ and Ag NPs seed solution. To prevent erosion of the catalysts during the measurement, 5 μ L of Nafion 0.5 wt% in ethanol solution was dropped cast on the surface of the electrode and dried under the ambient condition. The measurement for ethanol oxidation reaction was performed in an aqueous solution containing KOH (1.0 M) and C₂H₅OH (1.0 M). All data were recorded after 35 cycle scans for each sample.

5.3 Results and Discussion

The galvanic replacement is often used in the seed mediated growth approach to form hollow alloy metallic NPs.^{13, 14, 25, 26} The basic principle relies on the deviation in the reduction potentials between the seeds and metal precursor ions. In typical, the seeds with lower reduction potential are oxidized and dissolved into the solution by metal precursor ions with higher reduction potentials. Herein, highly branched trimetallic PdAgCu NPs with hollow interiors were synthesized based on coupling galvanic replacement with co-reduction reaction. Figure 5.1a and b show the SEM image and extinction spectrum of the pre-synthesized Ag NPs which were used as seeds in the galvanic replacement reaction. The morphology evolution of the branched PAgCu NPs at different growth stages was indicated in the time-dependent TEM images, Figure 5.1c. The galvanic replacement

reaction between Ag NPs seeds and the $\text{H}_2\text{PdCl}_4/\text{CuCl}_2$ mixture to form hollow NPs was clearly observed at the initial growth stage, Figure 5.1ci. In principle, the galvanic replacement of the pre-synthesized Ag NPs with the $\text{H}_2\text{PdCl}_4/\text{CuCl}_2$ mixture is not thermodynamic favored since the reduction potential of Ag^+/Ag^0 (0.8 V vs SHE) is higher than that of $\text{PdCl}_4^{2-}/\text{Pd}^0$ (0.59 V vs. SHE) and $\text{Cu}^{2+}/\text{Cu}^0$ (0.34 V vs. SHE) ions. A high reaction temperature was required to decompose PdCl_4^{2-} complexes into Pd^{2+} ions which possess a more-positive reduction potential ($\text{Pd}^{2+}/\text{Pd}^0$, 0.951 V vs. SHE) and thereby facilitated the galvanic replacement thermodynamic favored.¹³ However, in my experimental settings, the high concentration of Cl^- ions in the growth solution assisted the spontaneous galvanic replacement reaction between Ag NPs seeds and the $\text{H}_2\text{PdCl}_4/\text{CuCl}_2$ mixture at room temperature to form hollow NPs with lots of interstices. The complexes of Ag^+ and Cl^- ions reduced the reduction potential of Ag seeds (AgCl/Ag^0 , 0.22 V vs. SHE) and thus favored the galvanic replacement reaction with $\text{PdCl}_4^{2-}/\text{Pd}^0$ (0.59 V vs. SHE) and $\text{Cu}^{2+}/\text{Cu}^0$ (0.34 V vs. SHE) ions.²⁵ I also investigated if the galvanic replacement still occurred in case of adding solely H_2PdCl_4 or CuCl_2 solution into the Ag NPs seed solution, Figure S5.1. When solely adding H_2PdCl_4 into Ag NPs seeds, the initial brownish color of the solution immediately changed to dark green, indicative for the formation of hollow shell NPs, Figure S5.1b. However, no noticeable change was observed when adding solely CuCl_2 to the Ag NPs seeds after 1 minute recording, Figure S5.1a. The reaction solution slowly turned to light pink color upon extending the reaction time to few hours, attributed to the small deviation in the reduction potentials between AgCl/Ag^0 and $\text{Cu}^{2+}/\text{Cu}^0$ (0.22 V vs. 0.34 V). In addition, I should not ignore the oxidative etching effect of the pair O_2/Cl^- in the reaction solution which expedited the dissolution of Ag NPs into the solution to form hollow interiors.^{10, 16} All these facts together contributed to the spontaneous galvanic replacement reaction at room temperature between Ag NPs seeds and the $\text{H}_2\text{PdCl}_4/\text{CuCl}_2$ mixture at the early reaction stage. The subsequent addition of ascorbic acid caused a fast reduction of all metal ions (Pd^{2+} , Ag^+ , Cu^{2+}) presented in the reaction solution and consequently facilitating the tip elongation to form multiple branched NPs, Figure 5.1cii-iv. Highly branched NPs (~250 nm) with hollow interiors and uniform size distribution were obtained as shown in the TEM image in Figure 5.1d. Notably, the tip density reduced upon conducting the reaction

in an opposite way like adding ascorbic acid to the Ag NPs solution prior to adding the $\text{H}_2\text{PdCl}_4/\text{CuCl}_2$ mixture, Figure S5.2. This result indicated the important role of the reaction sequence on the tip density of the branched NPs. The inset SAED pattern in Figure 5.1d was composed of homocentric rings indicating the polycrystalline nature of the branched PdAgCu NPs. A twin plane with the d-spacing of 0.22-0.23 nm, assigned to the (111) facets of fcc Pd nanocrystals was observed along the tip growth direction, Figure 5.1e.^{13, 17} The inset FFT pattern confirmed that the tip was of single crystalline character. Interestingly, no twin defects were observed in the crystal structure of short tips although some dislocations may be found, Figure S5.3. The strain energy at twin defects break the high symmetry of fcc crystal structures and thus triggered the tip elongation.^{27, 28} The huge lattice mismatches among different metals e.g. Pd (3.89 Å), Ag (4.09 Å), and Cu (3.61 Å) might promote the formation of twin defects and dislocations in the crystal structures of the tips.²⁹ High-step atoms were observed along the tip edges/corners, Figure 5.1f and S5.3. The high-step atoms are intrinsically catalytic active to many reactions due to their unsaturated electronic state.⁷ The elemental mapping images and EELS line scanning confirmed the multi-metallic nature of the branched PdAgCu NPs, composing of Pd, Ag, and Cu components in the composition, Figure 5.1g and h. The overlapping in the intensity profiles revealed that all the metal components were evenly distributed throughout the alloy PdAgCu NPs.¹² In addition, the dip of the intensity in the line scanning profile revealed the hollow interiors of the branched PdAgCu NPs.

Highly branched PdAgCu NPs displayed a broadened extinction peak in the NIR region, Figure 5.1b. Theoretically, the extinction spectra of branched NPs relies on the plasmon hybridization of different plasmon modes corresponding to the core and individual tips.^{19, 30} For hollow NPs, there is an additional hybridization arising from the interior core and the outer shell.³¹ Besides, Pd was reported to possess a large imaginary part in the dielectric constant compared to conventional plasmonic materials such as Au and Ag.⁵ It can cause a large damping effect and consequently a broadening in the extinction spectral appearance under plasmon excitation. All these facts explained for the broadness of the extinction peak of the branched PdAgCu NPs.

Figure 5.1 (a) SEM image of Ag NPs. The inset shows the TEM image, (b) the extinction spectra of Ag NPs (left) and branched PdAgCu NPs (right), (c) time dependent-TEM images of the branched PdAgCu NPs at different growth stages, (d) TEM image of the branched PdAgCu NPs. The inset shows the FFT pattern of concentric rings, (e, f) HRTEM image of a single long tip. The inset shows the FFT pattern of well-defined spots, (g) STEM image and elemental mapping, (h) line-scanning profile of the

branched PdAgCu NPs synthesized at the typical condition: 300 μL H_2PdCl_4 (10 mM), 100 μL CuCl_2 (15 mM), 200 μL of Ag NPs seed solution, and 50 μL NaCl (1.0 M).

To explore the effect of the amount of CuCl_2 on the morphology and optical properties of branched PdAgCu NPs, a series of experiments was undertaken by varying the volume of CuCl_2 added into the growth solution from a CuCl_2 (15 mM) stock solution while fixing other experimental parameters (300 μL H_2PdCl_4 (10 mM), 200 μL of Ag NPs seed solution, and 50 μL NaCl (1.0 M)), Figure 5.2a1-3 and 5.2d. In the absence of CuCl_2 , branched NPs containing sharp edges or protrudes on the surface were observed, Figure 5.2a1. The increasing addition of CuCl_2 (~100-200 μL) led to the formation of highly branched NPs, followed by an increase in the tip density and a decrease in the tip length, Figure 5.2a2 and a3. The increase in the tip density also caused a red shift of the corresponding extinction peak upon increasing the added amount of CuCl_2 , Figure 5.2d.^{30, 32} These results indicated that Cu^{2+} ions played a decisive role to obtain branched NPs with high tip density. Copper ions improved the reducing strength of ascorbic acid by facilitating the formation of ascorbic acid radicals.³ Ascorbic acid radical is a stronger reducing agent than ascorbic acid and thereby it caused a fast co-reduction of all metal precursors ions in the growth solution. In addition, the energy required to form crystalline defects in Cu crystals is lower compared to that of Pd crystals (41 vs. 220 mJ/m^2).¹⁰ The huge lattice mismatch between Cu and Ag (11.74 %) may also cause a disturbance and the atomic arrangement and thus favored the twin defect formation. All these facts together can facilitate the formation of multiple twin defects in the crystal structures of growing NPs which subsequently developed to multiple tips in the branched PdAgCu NPs.²⁹

To investigate the effect of Cl^- ions on the morphology and optical properties of branched trimetallic PdAgCu NPs, a series of experiments was conducted by adding different volumes of NaCl from a NaCl (1.0 M) stock solution while keeping other reaction parameters at the fixed values (300 μL H_2PdCl_4 (10 mM), 100 μL CuCl_2 (15 mM), and 200 μL of Ag NPs seed solution), Figure 5.2b1-3 and 5.2e. Notably, there was always a small amount of Cl^- ions presented in the growth solution supplied from the CuCl_2 and H_2PdCl_4 precursors. An increase in the tip density followed by a red-shift in the corresponding extinction peak was observed upon increasing the added volume of Cl^-

ions (~ 0 -100 μL), Figure 5.2b1-2 and 5.2e. However, excessive addition of Cl^- ions (150 μL) produced roughened NPs with less pronounced tips and bigger features that were likely due to severe aggregations, Figure 5.2b3. As a result, the extinction peak broadened and shifted back to shorter wavelengths, Figure 5.2e. This result indicated that Cl^- ions played an important role in controlling both tip density and colloidal stability of the nanoparticle suspension.^{2, 10, 33}

To investigate the effect of the Ag NPs seeds on the morphology and optical properties of branched PdAgCu NPs, I conducted a set of experiments by varying the volumes of Ag NPs seeds added into the reaction solution from a stock solution while keeping other reaction parameters unchanged (300 μL H_2PdCl_4 (10 mM), 100 μL CuCl_2 (15 mM), and 50 μL NaCl (1.0 M)), Figure 5.2c1-3 and 5.2f. In the absence of AgNP seeds, branched NPs with smaller size (~ 100 nm in diameter) and containing solid core and multiple tips/sharp edges on the surface were obtained, Figure 5.2c1 and S5.5a. Increasing the addition of Ag NPs seeds (~ 100 -400 μL) resulted in formation of branched hollow NPs composed of multiple small tips, Figure 5.2c2-3. The hollow interiors were a result of the galvanic replacement reaction between the Ag NPs seeds and the $\text{H}_2\text{PdCl}_4/\text{CuCl}_2$ mixture. The overall size and the length of the tips reduced upon increasing the added volumes of the Ag NPs seeds. As a result, the corresponding extinction spectral peaks shifted to shorter wavelength, attributed to the reduction in the tip lengths, Figure 5.2f.^{27, 34} Hence, manipulating the amount of Ag NPs seeds in the growth solution provided an effective way to tune the morphology as well as the optical properties of the resulting branched NPs.

Figure 5.2 (a1, a2, a3) SEM images of branched PdAgCu NPs prepared by adding different volumes of 0, 100, and 200 μL from a CuCl_2 (15 mM) stock solution, respectively; (b1, b2, b3) SEM images of branched PdAgCu NPs prepared by adding different volumes of 0, 100, and 150 μL from a NaCl (1.0 M) stock solution, respectively; (c1, c2, c3) SEM images of branched PdAgCu NPs prepared by adding different volumes of 0, 100, and 400 μL from a Ag NPs seed stock solution, respectively; (d, e, f) extinction

spectra of branched PdAgCu NPs corresponding to the SEM images in (a1, a2, a3), (b1, b2, b3), and (c1, c2, c3), respectively. All the scale bars are 200 nm.

To further study the composition and crystallography of the branched PdAgCu NPs synthesized at typical condition (Figure 5.1), their EDX and XRD spectra were collected and shown in Figure 5.3a and b, respectively. The EDX and XRD spectra of the PdAg (Figure 5.2a1, synthesized in the absence of CuCl_2) and the PdCu NPs (Figure 5.2c1, synthesized in the absence of Ag NPs seeds) were also examined and shown in the same figure. The corresponding TEM images of all the investigated NPs were shown in Figure S5.5a-c. The EDX spectra revealed the multi-metallic composition of all the investigated NPs, Figure 5.3a. While the atomic percentage of Ag element in the three investigated NPs obtained by the EDX analysis agreed well with the predicted value from the designed synthetic protocol, however, the atomic percentage of Cu element was lower than what was expected. The mild reducing strength of ascorbic acid and the low reduction potentials of Cu^{2+} ions may result in the remaining of a small amount of unreduced Cu^{2+} ions in the growth solution. In addition, EDX is known as a semi-quantitative analysis method; thereby the slight reduction in the atomic percentage of Cu element in the composition of the obtained NPs was anticipated. All the investigated NPs displayed the XRD patterns of typical fcc Pd crystals, Figure 5.3b. In details, the branched PdAgCu NPs showed five distinct peaks at 2θ of 40.25, 46.6, 68.4, 82.5, and 87.1 degrees, respectively, which were assigned to {111}, {200}, {220}, {311}, and {222} crystal planes of typical fcc Pd crystals.^{10, 35} These peaks were found to shift to smaller angles for the PdAg NPs and larger angles for the PdCu NPs, respectively. The XRD spectra of pure Pd, Ag, and Cu fcc crystals collected from JCPDS database were used as references. Noted that, the XRD peaks of pure Cu fcc crystals locate at the far-most angles and the XRD peaks of pure Ag fcc crystals lie at the smallest angles compared to the XRD peaks of pure Pd fcc crystals, Figure 5.3b. Therefore, the incorporation of Cu in Pd-based NPs was expected to shift the XRD peaks of fcc Pd-based crystals to larger angles whereas the opposite manner was expected upon alloying with Ag. These observations were consistent with the formation of statistically mixed

alloy NPs which confirmed the well-alloyed composition of the PdAgCu, PdAg, and PdCu NPs.¹²

Figure 5.3 (a) EDX spectra and (b) XRD spectra of the PdCu, PdAg, and PdAgCu NPs, respectively. The PdAgCu NPs (Figure 5.1) were obtained by the typical synthetic condition (300 μ L H_2PdCl_4 (10 mM), 100 μ L $CuCl_2$ (15 mM), 200 μ L of Ag NPs seed solution, and 50 μ L NaCl (1.0 M)) whereas the PdAg (Figure 5.2a1) and PdCu NPs (Figure 5.2c1) were obtained in the absence of $CuCl_2$ and Ag NPs seeds, respectively.

To get an insight to the effect of morphology and composition on the RI sensitivity of all the investigated NPs including the trimetallic PdAgCu and the bimetallic PdAg and PdCu NPs, I recorded their LSPR peak positions in different RI mediums prepared upon mixing different volume ratios of glycerol to H_2O (0, 18, 36, 54, 72 v/v%), Figure 5.4a and S5.4. The branched PdAgCu NPs exhibited a better RI sensitivity of 653 nm/RIU compared to the PdAg (509 nm/RIU) and PdCu NPs (380 nm/RIU), respectively. Noted that the RI sensitivity of the branched PdAgCu NPs in this study was comparable to conventional highly sensitive LSPR substrates such as gold nanostars (703 nm/RIU), gold nanobipyramids (540 nm/RIU), gold nanorods (288 nm/RIU), and Pd nanospheres (351 nm/RIU).^{5, 20, 36} However, the branched PdAgCu NPs displayed a broad extinction spectral peak in the NIR region due to the nature of Pd element, therefore the FOM value was expected to be low. It is well-known that the RI sensitivity of NPs depends strongly on their size, shape, and compositions.²⁰ Nanoparticles containing sharp features on the surface provided better RI sensitivities, attributed to their high charge density and charge polarization at sharp regions.²⁰ Moreover, the hollow interiors are also expected to

increase the RI sensitivity compared to solid-core NPs.²⁰ Besides, the trimetallic nature of the branched PdAgCu NPs may alter the density of electronic states in the Fermi level and thus affected their dielectric properties compared to the bimetallic PdAg and PdCu NPs.⁴

Figure 5.4 (a) RI sensitivity of the PdCu, PdAg and PdAgCu NPs and (b) the electrocatalytic activity towards EOR of the PdCu, PdAg, PdAgCu, and Pd NPs. The Pd NPs were prepared by the typical synthetic condition without adding both Ag NPs seeds and CuCl₂ solution. The typical synthetic condition: 300 μ L H₂PdCl₄ (10 mM), 100 μ L CuCl₂ (15 mM), 200 μ L of Ag NPs seed solution, and 50 μ L NaCl (1.0 M).

The catalytic activity of all the three as-made NPs including PdAgCu, PdAg, and PdCu NPs toward ethanol oxidation reaction (EOR) in alkaline medium was examined and shown in Figure 5.4b. The catalytic activity of spherical Pd NPs (~50-150 nm in diameter) prepared by the typical synthetic condition of the branched PdAgCu NPs without adding Ag NPs seeds and CuCl₂ was also recorded for reference, Figure S5.5d. All the peak currents were normalized to the electrochemically active surface area (ECSA) which were calculated based on the electric charges required to the reduction of PdO during the negative scan, Figure S5.6.¹¹ A well separation of the oxidation peaks in the forward scans and reduction peaks in the backward scans towards EOR was observed for all the investigated NPs. Notably, the anodic peak current of the branched trimetallic PdAgCu NPs (2.16 mA/cm² in the forward scan) was 1.8, 6.2, and 4.6 times higher than the PdCu, PdAg, and Pd NPs, respectively. The superior electrocatalytic activity of the branched PdAgCu NPs was attributed to the large number of high-step atoms that located on

certain high-index crystal facets at the tip edges/corners, Figure S5.3. The high-step atoms served as hot-spot sites to improve the electrocatalytic performance of the branched PdAgCu NPs. In addition, the synergetic interaction among Pd, Ag, and Cu multi-metallic elements in the branched trimetallic PdAgCu NPs might generate extra catalytic activity compared to that of the bimetallic PdAg, PdCu and pure Pd NPs.⁸⁻¹¹ The high degree of alloying and the lattice mismatches of the Pd, Ag, and Cu metal components in the branched PdAgCu NPs might alter the electronic state on the surface of the nanocatalyst and thus led to a pronounced catalytic improvement.¹²

5.4 Conclusion

Highly branched hollow trimetallic PdAgCu NPs have been synthesized for the first time by coupling galvanic replacement with co-reduction reaction. In brief, Ag NPs were used as the seeds for the galvanic replacement reaction with the $\text{H}_2\text{PdCl}_4/\text{CuCl}_2$ mixture whereas ascorbic acid served as reducing agent to promote the simultaneously reduction reaction. The obtained PdAgCu NPs displayed a high density of multiple tips on the surface, hollow interiors, and alloyed composition. The facile, one-step, and surfactant-free synthetic route in this study enabled the facile tune of the morphology and optical properties in the NIR region of the PdAgCu NPs by manipulating different reaction conditions such as the concentration of CuCl_2 , Ag NPs seeds, and Cl^- ions in the reaction solution. The branched hollow trimetallic PdAgCu NPs exhibited a better RI sensitivity and a pronounced electrocatalytic activity towards EOR compared to those of the bimetallic PdAg and PdCu NPs, and spherical pure Pd NPs, attributed to the highly branched morphology and trimetallic alloyed composition. The coupling galvanic replacement and co-reduction reaction offers a facile way to synthesize complex branched multi-metallic NPs with advanced structural and optical properties. The pronounced RI sensitivity and electrocatalytic activity turned the branched trimetallic PdAgCu NPs into a promising multifunctional nanomaterial in combined plasmonic and electrochemistry applications such as hydrogen LSPR sensing or in-situ monitoring catalytic reactions by surface enhanced Raman scattering.

5.5 Supporting information

The supporting information provides the SEM images of NPs prepared by adding solely CuCl_2 or H_2PdCl_4 into Ag NPs seed solution, the TEM images of branched PdCuAg NPs prepared by different reaction sequence, the HRTEM images of different tips in the branched PdAgCu NPs, the extinction spectra of the branched PdAgCu, PdAg, and PdCu NPs in different RI solutions, the TEM images of PdCu, PdAg, PdAgCu, and spherical Pd NPs, the CVs scans of the PdAgCu, PdAg, PdCu, and Pd-modified electrodes in in KOH (1.0 M) solution.

Figure S5.1 TEM images of the as-synthesized NPs prepared by adding solely (a) 100 μL CuCl_2 (15 mM) and (b) 300 μL H_2PdCl_4 (10 mM) into the Ag NPs seed solution. The obvious sign of the galvanic replacement reaction between H_2PdCl_4 solution and AgNPs was observed as the formation of hollow NPs (b) whereas it was unclear in case of CuCl_2 solution (a).

Figure S5.2 SEM images of the branched trimetallic PdAgCu NPs obtained when conducting the reaction in different sequences: (a) adding ascorbic acid before adding mixture of H_2PdCl_4 and CuCl_2 solutions and (b) adding mixture of H_2PdCl_4 and CuCl_2 solutions before adding ascorbic acid (identical synthetic condition). All the scale bars are 200 nm. The tip density of the branched NPs (b) prepared by the identical synthetic condition (galvanic replacement – reduction reaction) was higher compared to the branched NPs (a) prepared in the reverse way (reduction – galvanic replacement reaction).

Figure S5.3 HRTEM images of different tips of the branched trimetallic PdAgCu NPs synthesized at typical synthetic condition (300 μL H_2PdCl_4 (10 mM), 100 μL CuCl_2 (15 mM), 200 μL of Ag NPs seed solution, and 50 μL NaCl (1.0 M)). The tips contained twin defects, dislocation, or were perfect single crystalline structures. The black-dash lines indicate twin defect planes. All the scale bars are 5 nm.

Figure S5.4 The extinction spectra of the three branched NPs including (a) PdCu, (b) PdAg, and (c) PdAgCu NPs in different refractive index solutions prepared by mixing different volume ratios of glycerol and water. The PdAgCu NPs were obtained at the typical synthetic condition. The PdCu and PdAg NPs were prepared by the typical synthetic condition without adding Ag NPs seeds and CuCl_2 solution, respectively. The typical synthetic condition: 300 μL H_2PdCl_4 (10 mM), 100 μL CuCl_2 (15 mM), 200 μL of Ag NPs seed solution, and 50 μL NaCl (1.0 M).

Figure S5.5 TEM images of (a) the branched PdCu NPs, (b) the branched PdAg NPs, (c) the branched PdAgCu NPs, and (d) the irregular Pd nanoparticles. The branched PdCu and PdAg NPs were prepared by the typical synthetic condition without adding Ag NPs seeds and CuCl_2 solution, respectively. The Pd NPs were obtained by the typical synthetic condition without adding both Ag NPs seeds and CuCl_2 solution. The typical

synthetic condition: 300 μL H_2PdCl_4 (10 mM), 100 μL CuCl_2 (15 mM), 200 μL of Ag NPs seed solution, and 50 μL NaCl (1.0 M).

Figure S5.6 CVs scan of the nanocatalyst-modified electrodes including the PdCu, PdAg, PdAgCu and Pd NPs (TEM images in Figure S5.5) in KOH (1.0 M) solution at the scan rate of 50 mV/s. The nominal electrochemically active surface areas (ECSA) were calculated by quantification of the electric charges associated with the reduction of PdO and were of 52.34, 69.76, 83.84, and 65.88 cm^2/mg for the PdCu, PdAg, PdAgCu, and Pd NPs normalized to the same Pd-mass loading, respectively.

The electrochemically active surface area is calculated by the equation:

$$ECSA = \frac{Q}{m \times C \times \vartheta}$$

Where: Q is the charge for PdO reduction on the surface which can be obtained from the area integral of the backward current peaks in Figure S6, m is the mass loading of Pd (2 μg), C is the charge required to reduce the layer of PdO (420 $\mu\text{C}/\text{cm}^2$), and ϑ is the scan rate which is 50 mV/s at my experimental setting.¹¹

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Chapter 6

Preliminary Results on the Preparation of Hybrid Nanoparticles of Gold Nanostars and Graphene Oxide

This chapter presents preliminary results and highlights opportunities for future work concerning the preparation of hybrid nanoparticles of gold nanostars and graphene oxide by the assistance of linker molecules, 4-aminothiophenol molecules. Upon binding to the surface of gold nanostars via $-SH$ groups, 4-aminothiophenol molecules can modify the gold nanostars with positively charged groups via NH_2^+ groups and thus facilitate the self-assembly of negatively charged graphene oxide to wrap around the surface of gold nanostars. The hybrid nanoparticle can serve as a multifunctional platform for further applications in surface enhanced Raman scattering sensing, imaging, and thermal/chemo-therapy.

6.1 Introduction

Graphene and its derivatives (graphene oxide and reduced graphene oxide) are 2D materials composed of single-atom thick sheets of sp^2 bonded carbon atoms that arrange in perfect honeycomb lattice.¹ Due to this unique structure, graphene exhibits advanced optical and electronic properties which turn them into a promising candidate in energy, electronics, and biological applications.² In addition, graphene and its derivatives have been widely used for anticancer-drug loading in chemo-therapy applications attributed to their large surface area and the ability to form π - π interactions with aromatic compounds.³ Recent reports show that the combination of graphene and plasmonic nanoparticles in hybrid structures not only possess advantages from each material, but also obtained exceptional structural and electrochemical properties which are not observed in the individual material alone.^{2,4} For example, Lim and co-workers found that reduced graphene coated gold nanoshell/nanorods produced an enhanced photothermal effect and killed cancer cells more rapidly than that of the non-coated nanoparticles.⁴ Hybrid structures of graphene and its derivatives with metal nanoparticles can be prepared by depositing small nanoparticles on large graphene sheets or coating small graphene sheets around large-size nanoparticles.^{1,5} Among various types of plasmonic nanoparticles, gold nanostars (branched, urchin, or spiky nanoparticles) have attracted tremendous research attention due to their advanced localized surface plasmon resonance properties.^{6,7} The high charge density and charge confinement at sharp tips enable branched gold nanoparticles to generate a huge enhancement of the local electromagnetic field under laser excitation.⁸ The local electromagnetic field was further enhanced by the conjugation of branched gold nanoparticles with metal films or satellite nanoparticles such as small gold/silver nanoparticles.⁹⁻¹¹ Therefore, this work aims at exploring hybrid nanoparticles of gold nanostars and graphene oxide for potential application in SERS sensing, imaging, and photothermal/chemo-therapy.

6.2 Experimental section

6.2.1 Materials

All chemicals were of reagent grades and used without purification. Tetrachloroauric acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), silver nitrate (AgNO_3), ascorbic acid ($\text{C}_6\text{H}_6\text{O}_6$), 4-aminothiophenol, and graphene oxide colloid solution (2mg/mL) were purchased from Sigma Aldrich.

6.2.2 Methods

All the glassware was washed intensively with freshly prepared aqua regia solution ($\text{HCl}:\text{HNO}_3 = 3:1$ v/v) and rinsed thoroughly with milli-Q water before using.

Synthesis of 13 nm gold nanoparticles (AuNPs) as seeds AuNPs of ~13 nm in diameter were synthesized based on the citrate method. Briefly, 1.524 mL of HAuCl_4 (10 mM) was added to 55.476 mL water in an erlenmayer flask. The solution was vigorously stirred and quickly heated to boiling. Subsequently 3 mL of sodium citrate (10 mg/mL) was added into the solution under vigorous stirring. The color of the solution changed from colorless to deep red in about 30 minute as a sign of the formation of AuNPs. After that, the heater was removed and the solution was kept under gentle stirring until it cooled down to room temperature. Milli-Q water was added to the suspension to adjust the concentration of AuNPs in the solution at 0.125 mM related to Au^{3+} ions. The particles were kept in refrigerator at 4 °C for further use.

Synthesis of gold nanostars coated 4-aminothiophenol (AuNS-ATP) Briefly, 2700 μL of HAuCl_4 (10 mM), 750 μL of AgNO_3 (10 mM), 450 μL of HCl (1.0 M), and 1500 μL of AuNPs seeds were added into 45 mL of milli-Q water in a 100 mL beaker. The mixture was magnetically stirred for 5 min at 700 rpm. Subsequently, 2250 μL of ascorbic acid (10 mg/mL) was rapidly added to the solution under vigorous stirring. The solution was kept stirring for further 1 min. To stabilize the as-prepared particles, 700 μL

of 4-aminothiophenol 4-ATP (0.1 M) was added drop-wisely to the above suspension and followed by stirring for other 5 min. The 4-ATP modified gold nanostars were then kept in the fridge for further use.

Wrapping of graphene oxide colloids around 4-ATP modified gold nanostars (AuNS-ATP-GO) Graphene oxide colloids in water (2 mg/mL) was fully dispersed by sonication for 3h in a sonication bath prior to use. Briefly, 2 mL of 4-ATP modified gold nanostars were purified by two times of centrifugation at 5000 rpm in 5 min and washing with milli-Q water to remove all excess amounts of unbound 4-ATP before the wrapping step. After that, 20 μ L of well dispersed graphene oxide colloid solution (2 mg/mL) was added to the above nanoparticles suspension. The nanoparticles suspension was vortexed rapidly for few seconds and then gently shaken for 2h to allow graphene oxide sheets to wrap around the nanoparticles. The purification step was conducted by 2 times of centrifugation at 5000 rpm in 3 min and washing with milli-Q water to remove all excess amounts of free graphene oxide sheets in the suspension.

6.2.3 Characterization

The morphology of as-synthesized nanoparticles was characterized by field emission secondary electron microscope (FESEM-6340F) and transmission electron microscope (TEM-JEOL 2010). The extinction spectra of obtained nanoparticles were taken using UV-Vis-NIR spectrophotometer (Perkin).

6.3 Results and Discussion

Hybrid nanoparticles of gold nanostars and graphene oxide were prepared by the surface modification of gold nanostars with 4-aminothiophenol as a linker to facilitate the self-assembly of graphene oxide (GO) sheets around the nanoparticles. The 4-ATP molecules can rapidly bind onto the surface of the as-synthesized AuNS via –SH groups and render the nanoparticles positively charged via its –NH₂ groups. Therefore, negative charged graphene oxide self-assembled onto the surface of AuNS due to the electrostatic force.

Besides, the π - π interactions induced by the phenol rings in 4-ATP and graphene oxide can promote the adsorption of graphene oxide on the surface of gold nanostars. The strong interaction between the graphene oxide and 4-ATP modified gold nanostars allows the graphene oxide sheets to wrap around the nanoparticles, forming hybrid nanoparticles, (AuNS-ATP-GO). In this report, gold nanostars were synthesized by the seed mediated growth approach. Figure 6.1 shows the TEM image of 13 nm AuNPs serve as seeds in the growth process of gold nanostars. The SEM and TEM images of 4-ATP modified gold nanostars are shown in Figure 6.2. The obtained nanoparticle exhibits a solid core of ~ 50 nm in diameter and a number of tips extending from the core particle. After incubation with graphene oxide colloids for 2h, graphene oxide shells of ~ 1 -5 nm in thickness are observed around the 4-ATP modified gold nanostars, indicating the wrapping of graphene oxide sheets around the nanoparticles, Figure 6.3. The extinction spectra of 4-ATP modified gold nanostars before and after incubating with graphene oxide colloids are shown in Figure 6.4. Notably, the extinction spectrum of AuNS-ATP-GO nanoparticles exhibits a blue-shift of ~ 1 nm and a stronger background signal compared to that of 4-ATP modified gold nanostars. It is attributed to the presence of graphene oxide in the hybrid nanoparticles. Further characterizations such as X-ray photoelectron spectroscopy (XPS) and selective area electron diffraction (SAED) are required to confirm the coating of graphene oxide on the surface of AuNS. All these results indicate that I have successfully prepared the hybrid nanoparticles of gold nanostar and graphene oxide. The preliminary SERS spectrum of 4-ATP modified gold nanostars was also provided in Figure 6.5. The spectrum showed distinct peaks of 4-ATP molecules which demonstrated the potential applications of AuNS-ATP as highly sensitive SERS nanotags.

Figure 6.1 TEM image of as-synthesized AuNPs.

Figure 6.2 (a) SEM and (b) TEM image of 4-ATP modified gold nanostars.

Figure 6.3 TEM images of AuNS-ATP-GO nanoparticles. The black arrows show the graphene oxide shells wrapped around the nanoparticles. All scale bars are 20 nm.

Figure 6.4 Extinction spectra of graphene oxide, AuNS-ATP, and AuNS-ATP-GO nanoparticles.

Figure 6.5 Raman spectrum of 4-aminothiophenol modified gold nanostars (AuNS-ATP). The spectrum was recorded at the integration time 0.5s, the accumulation time 20, and the laser power 60 mW.

6.4 Conclusion and outlooks

In this work, hybrid nanoparticles of gold nanostars and graphene oxide were prepared by the assistance of linker molecules, 4-ATP. Upon binding to the surface of gold nanostars via –SH groups, 4-ATP can modify the gold nanostars with positively charged groups and thus facilitate the self-assembly of negatively charged graphene oxide on the surface of gold nanostars. Besides, the π - π interactions originating from the phenol rings in 4-ATP and graphene oxide can promote the adsorption of graphene oxide on the Au surface. Both factors led to the wrapping of graphene oxide sheet around the nanoparticles to form hybrid nanoparticles. In addition, 4-ATP has been reported as an active Raman reporter. Therefore, AuNS-ATP-GO nanoparticles can be used as SERS nano-tags in SERS immunoassay sensing and imaging applications. The further decoration of AuNS-ATP-GO nanoparticles with satellite nanoparticles such as small gold/silver nanoparticles is anticipated to improve the SERS sensitivity due to the plasmon hybridization in the AuNS-Graphene oxide-Au/Ag nanoparticles sandwich platform. Furthermore, the hybrid nanoparticles can be encapsulated in modified polymersomes or hydrogel to provide the bio-compatibility and specific targeting for bio-applications, e.g drug delivery. Future works can be conducted on exploring the applications of the as-prepared hybrid nanoparticles in sensing, imaging, drug loading, and therapeutics.

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Chapter 7

Research Summaries, Statements of Hypotheses, and Outlook

A summary of all the results are restated in this chapter. The statements in accounting for the original hypotheses are provided. The chapter ends with the outlooks. In this thesis, the facile, aqueous-based, and surfactant-free methods for the synthesis of highly branched gold mesoflowers and hollow trimetallic PdAgCu nanoparticle were established. The growth mechanisms and optical properties of the particles were elucidated based on experiment and simulation. Potential applications of the as-prepared particles in localized surface plasmon resonance, field enhanced spectroscopy, and electrocatalysis were also demonstrated.

7.1 Research Summary

In this thesis, I aimed at developing new routes for the synthesis of complex branched metal and alloy nanoparticles with advanced optical/electrochemical properties. The synthetic protocols were developed based on combining different synthetic strategies which were employed for the synthesis of metal nanoparticles of different morphologies and compositions. The methods presented in this thesis rely on room temperature, aqueous-based, and surfactant-free synthesis. The methods also enable me to control the morphology, composition, and corresponding optical properties of the resulting particles by simply manipulating different reaction parameters. To elucidate the growth mechanisms, the effect of different reaction parameters on the morphology of the obtained particles was investigated. The results show that multiple twin defects play a crucial role in the formation of highly branched particles since the twin planes were observed to be aligned with the tip growth directions. The strain field at the twin defects provides driving forces to prompt the elongation of the tips on the surface of branched metallic particles. Each type of the obtained particles was used for various application including LSPR and electrocatalysis, depending on their properties.

Highly branched AuMFs were prepared at room temperature by an aqueous-based, seedless, and surfactant-less approach. I found that halide ions, Cl^- in particular, played a decisive role in the formation of long and sharp tips by regulating the formation of multiple twin defects in the crystals of growing particles. Noteworthy, the branching level of each tip was facilely tuned by adjusting the concentration of Cl^- ions in the growth solution. Other reaction parameters such as the concentration of AgNO_3 and ascorbic acid were found to influence the reaction kinetics and surface blocking and thereby the morphology of the obtained particles. A tunable red shift of the LSPR peak position to the range of $\sim 1800\text{-}3000$ nm was observed, depending on the morphology of the tips. Simulations based on the FDTD method were also conducted to provide a better understanding of the morphology-dependent optical properties and the EM field enhancement of branched mesoscale gold particles. The simulation results revealed that branched AuMFs exhibit a significant EM field enhancement of E^2 up to $\sim 10^4\text{-}10^5$ at the resonance wavelengths, which suggests a great potential in applications such as surface

enhanced vibrational spectroscopy and sensing. The synthesis approach in this study offers a facile way to design novel complex supra-structures of gold particles with advanced optical and structural properties.

Highly branched hollow trimetallic PdAgCu nanoparticles were synthesized for the first time by coupling galvanic replacement with co-reduction reaction. In detail, pre-synthesized AgNPs were employed as seed particles for the galvanic replacement with the mixture of H_2PdCl_4 and CuCl_2 solutions while ascorbic acid served as the reducing agent to promote the co-reduction reaction. The obtained nanoparticles display a high density of multiple tips on the surface, hollow interiors, and tunable optical properties in the NIR region. The method enables us to facilely tune the morphology and optical properties of the resulted nanoparticles by manipulating reaction conditions such as the $\text{CuCl}_2/\text{H}_2\text{PdCl}_4$ molar ratio, the amount of seeds, and the content of halide Cl^- ions in the reaction solution. The highly branched trimetallic PdAgCu nanoparticles exhibited a higher refractive index sensitivity (653 nm/RIU) as compared to branched bimetallic PdAg (509 nm/RIU) and PdCu (380 nm/RIU) nanoparticles. The electrocatalytic activity of highly branched trimetallic PdAgCu nanoparticles toward ethanol oxidation reaction (EOR) was also 1.8 and 6.2 times higher than that of branched bimetallic PdCu and PdAg nanoparticles, respectively. I attribute the improvement to the exposure of certain high index crystal facets at tip edges/corners and the synergetic effect arising from the trimetallic alloy character of branched trimetallic particles. This work opens a new way for the controlled synthesis of branched multi-metallic nanoparticles and their applications in combined plasmonics and electrochemistry such as hydrogen LSPR sensing or in-situ monitoring catalytic reactions by SERS.

Lastly, I also worked on developing hybrid nanoparticles of gold nanostars and graphene oxide and further exploring their application in SERS. The preliminary results showed that I was successfully preparing graphene oxide-wrapped gold nanostars. Further studies on demonstrating their applications in SERS will be conducted.

7.2 Statements of Hypotheses

Statement 1: Multiple twin defects can be used to control the morphology and branching of sharp tip metal particles – importance of halide ions.

The morphology of metallic crystals can be governed by manipulating the type and the number of defects in the crystal structures of growing nanoparticles. The high strain energy at the defect regions provides a driving force to facilitate the growth of branched nanoparticles. Herein, branched AuMFs and branched trimetallic alloy PdAgCu nanoparticles were successfully prepared and shown in chapter 4 and 5, respectively. Both of the obtained particles display a high density of tips on the surface. Noteworthy, twin planes were observed along the tip growth directions in the single and multi-level tips, revealed by the HRTEM images in chapter 4. In addition, AuMFs with varying tip densities and branching levels were obtained upon adding different volumes of halide ions from a stock solution into the growth solution. These results indicated that Cl^- play an important role in the growth of highly branched metallic nanoparticles by regulating the formation of multiple twin defects in the crystal structures of growing particles. The results are in accounting for the first hypothesis.

Statement 2: The combination of the galvanic replacement and co-reduction reactions produces highly branched trimetallic PdAgCu alloy nanoparticles.

Highly branched trimetallic PdAgCu nanoparticles were successfully prepared by coupling galvanic replacement and co-reduction reaction. Pre-prepared AgNPs were employed as seed particles for the galvanic replacement with the mixture of H_2PdCl_4 and CuCl_2 solutions. The co-reduction process was triggered by the subsequent addition of ascorbic acid as the reducing agent. The obtained branched PdAgCu nanoparticles have hollow interiors with a high density of small-radii tips on the surface and display an even alloying of all metal components throughout the particles. The time-dependent TEM images of the growing nanoparticles at different growth stages were also recorded. The results demonstrated that the galvanic replacement between AgNPs and the mixture of

H_2PdCl_4 and CuCl_2 solutions occurred spontaneously. It resulted in the formation of hollow alloy nanoparticles without sharp tips. However, the subsequent addition of ascorbic acid causes the fast co-reduction of all metal ions presented in the reaction solution and then the elongation of the tips. The density of tips on the surface of the obtained nanoparticles reduces upon conducting the reaction in the reverse manner like adding ascorbic acid into the Ag NPs seed solution prior to adding the mixture of H_2PdCl_4 and CuCl_2 solutions. It indicated the importance of the reaction sequence on the growth of highly branched particles. The results successfully proved the second hypothesis and were shown in chapter 5.

Statement 3: Highly branched trimetallic nanoparticles provide better LSPR sensitivity and electrocatalytic activity compared to branched bimetallic nanoparticles.

The optical and electrochemical properties of metallic alloy nanoparticles depend strongly on their morphology and chemical composition. The synergetic effect and lattice mismatch of different metal components can alter the crystal structure, the electronic state, and the optical properties of multi-metallic alloy nanoparticles. Consequently, the LSPR sensitivity and the electrocatalytic activity are also influenced. To test for the hypothesis, three types of as-synthesized branched nanoparticles with different compositions including PdAgCu, PdAg, and PdCu nanoparticles were chosen. All the investigated nanoparticles were exposed to series of solution with different RI values and monitored the shift of the LSPR peak positions. My finding showed that the highly branched trimetallic PdAgCu nanoparticles exhibited a higher RI sensitivity (653 nm/RIU) compared to branched bimetallic PdAg (509 nm/RIU) and PdCu (380 nm/RIU) nanoparticles. The electrocatalytic activity toward EOR of branched trimetallic PdAgCu nanoparticles was also 1.8 and 6.2 times higher than that of branched bimetallic PdCu and PdAg nanoparticles normalized to the same ECSA, respectively. The results greatly supported the third hypothesis and were showed in chapter 5.

7.3 Outlooks

Some of the future directions related to my works are outlined below:

1. Branched gold mesoflowers AuMFs can find a great potential in SEIRA for sensing and molecular characterization due to: (1) the location of the LSPR peak in the NIR~MIR region, (2) the huge enhancement of the local electromagnetic field under laser excitation, and (3) the abundance of open hot-spot areas of branched AuMFs that can provide easy access for analytes.
2. Control the morphology of the seeds in the galvanic replacement reaction, for examples, nanocubes, nanotriangles, nanooctaherons, etc. instead of spheres may generate metallic alloy nanoparticles with interesting and useful structural and optical properties.
3. The coupling of galvanic replacement and co-reduction reaction can be also applied in the synthesis of multi-metallic nanoparticles with different compositions such as PtAg, PtAgAu, PdAgAu, etc.
4. The pronounced RI sensitivity and electrocatalytic activity of the branched trimetallic PdAgCu nanoparticles open up future applications of these nanomaterials in biosensors and combined plasmonics and electrochemistry.
5. Hybrid of branched metallic nanoparticles and carbon materials can find a great potential in surface enhanced vibrational spectroscopy (SERS), drug delivery, and therapeutic applications.

Publications

1. Nhung Thi Tran, Anran Li, Peng Chen, Wang Yi, Shuzhou Li, Bo Liedberg; Gold Mesoflowers with High Density of Multilevel Long Sharp Tips: Synthesis and Characterization; *J Mater. Chem. C.*, 2017, DOI: 10.1039/C7TC00968B.
2. Nhung Thi Tran, Hanbin Liao, Xueling Feng, Zhichuan J. Xu, Bo Liedberg; Controlled Synthesis of Highly Branched Hollow Trimetallic PdAgCu Nanoparticles and its Applications; *Manuscript in hand*.

3. Peng Chen, Nhung Thi Tran, Xinglin Wen, Qihua Xiong, Bo Liedberg; Inflection Point of the Localized Surface Plasmon Resonance (LSPR) Peak: a General Method to Improve the Sensitivity; *ACS Sens.*, 2017, **2**, 235.
4. Yi Wang, Xiaohu Liu, Peng Chen, Nhung Thi Tran, Jinling Zhang, Wei Sheng Chia, Souhir Boujday, Bo Liedberg; Smartphone Spectrometer for Colorimetric Biosensing; *Analyst*, 2016, **141**, 3233.
5. Chih-Tsung Yang, Lin Wu, Xiaohu Liu, Nhung Thi Tran, Ping Bai, Bo Liedberg, Yi Wang and Benjamin Thierry; Exploiting Surface Plasmon-enhanced Light Scattering for the Design of Ultrasensitive Immunoassays; *Anal. Chem.*, 2016, **88**, 11924.
6. Peng Chen, Xiaohu Liu, Nhung Thi Tran, Daniel Aili, Bo Liedberg; Enzyme Free Colorimetric Detection of Hydrogen Peroxide by Oxidation-Triggered Polypeptide Bridging Aggregation of Gold Nanoparticles; *Submitted*.
7. Peng Chen, Xiaohu Liu, Nhung Thi Tran, James Chin Shing Ho, Yi Wang, Daniel Aili, Bo Liedberg; Optimization of Plasmonic Nanoparticle-based Colorimetric Assays: from the Human Vision Perspective; *Manuscript in hand*.