Design and syntheses of anisotropic metal nanostructures with tailored morphology for applications in electro-catalysis and surface enhanced raman scattering

Srikanth Pedireddy

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**DESIGN AND SYNTHESIS OF ANISOTROPIC METAL
NANOSTRUCTURES WITH TAILORED MORPHOLOGY FOR
APPLICATIONS IN ELECTRO-CATALYSIS AND SURFACE
ENHANCED RAMAN SCATTERING**

SRIKANTH PEDIREDDY

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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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

2015

This dissertation is dedicate to my loving Wife

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Abstract

The main goal of this thesis is to design and develop synthesis methods which enable the preparation of more efficient noble metal nanoparticles with tailored morphologies for optical, catalytic and SERS applications. In chapter 2, we demonstrate a two-step seed-mediated growth method to synthesize a new class of spiky Ag-Au octahedral nanoparticles with tunable spike length from 10 – 130 nm with sharp tips. Spatially resolved EELS study on individual spiky Ag-Au nanoparticles illustrates multipolar plasmonic responses. In chapter 3, we develop a one-step solution phase synthesis of tunable nanoporous gold (np-Au) nanoparticles and demonstrated their superior catalytic activity towards methanol electro-oxidation. Furthermore, we demonstrate a seed mediated route to synthesize morphology controlled np-Au nanoparticles (chapter 4) with reduced symmetry and ligament size control down to <6 nm. In the last chapter 5, we demonstrate np-Au nanoparticles with reduced symmetry, will hold intense electromagnetic fields exploitable for location dependent SERS on single np-Au nanoparticles under near-infrared excitation.

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LIST OF SYMBOLS

<u>Symbol</u>	<u>Definition</u>
μm	Micrometer
μg	Microgram
μL	Microliter
μA	Microampere
μC	Microcoulomb
$^{\circ}\text{C}$	Degree Celsius
cm	Centimeter
m	Meter
g	Gram
M_w	Molecular weight
mL	Milliliter
s	Seconds
min	Minutes
eV	Electron volt
keV	Kilo electron volts

mM	Millimolar
mW	Milliwatt
M	Molar
nm	Nanometer
ppb	Parts per billion
mV	Millivolts
V	Volt
kV	Kilovolts

LIST OF ACRONYMS

0D/2D	Zero dimensional/ Two dimensional
AA	Ascorbic acid
Au NPs	Gold nanoparticles
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CPC	Cetylpyridinium chloride
CTAC	Cetyl trimethylammonium chloride
CTAB	Cetyltrimethylammonium bromide
CV	Cyclic voltammetry
EDS	Energy-dispersive X-ray spectroscopy
EELS	Electron energy loss spectroscopy
EM	Electromagnetic enhancement
FIB	Focused ion beam
HRTEM	High Resolution Transmission Electron Microscopy
LSPR	Localized surface plasmon resonance
Np-Au	Nanoporous gold

NRS	Normal Raman spectroscopy
PDDA	Poly (diallyldimethylammonium) chloride
PVP	Poly (vinyl pyrrolidone)
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscopy
SERS	Surface enhanced Raman spectroscopy
SERRS	Surface enhanced resonance Raman scattering
SPR	Surface-plasmon resonance
UV-Vis-NIR	Ultra Violet/Visible/ Near-infrared
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
4-MBT	4-Methylbenzenethiol

Chapter 1

ABSTRACT

This chapter provides an introduction to the syntheses of noble metal nanoparticles, focusing on the wet chemical syntheses approach in particular. Following which, we systematically discuss the effect of several critical factors that includes type of adsorbates, kinetic factors and effect of ions in controlling the final morphology of the nanoparticles. Next, we discuss the optical properties of Ag/Au nanoparticles and use a number of examples to demonstrate the effect of size and shape on their optical properties. In the later section, SERS is introduced and the importance of employing morphology controlled noble metal nanoparticles for the detection of environmental pollutants is discussed. Finally, we introduce electrocatalysis and summarize the importance of size, shape and surface structure of the gold nanoparticles to their electrocatalytic performance. The thesis outline is also presented.

1.1 INTRODUCTION

In general, metal nanoparticles are fabricated using two approaches: top-down and bottom-up approach. The former approach uses traditional lithographic techniques to pattern nanostructures onto a substrate. Though this technique has good control over structures such as clean surfaces, control of composition and to achieve periodic arrays, it involves complex and multistep procedures which may also result in undesirable polycrystalline nanostructures. The cost and time invested increases with the decrease in size of the nanoparticles. These disadvantages are overcome by the latter approach which uses chemical synthesis routes to directly synthesize the metal nanostructures in large scale with tailored morphologies. Here we focus on only noble metal nanoparticles because of their enhanced optical and catalytic properties, and discuss the various synthetic strategies used for morphology control with high uniformity.

1.1.1 CITRATE REDUCTION METHOD

This method is discovered by J. Turkevich et al.¹ in 1951 and developed by G. Frens in 1970s.² It is considered one of the oldest and most popular methods for preparing spherical gold nanoparticles. A typical synthesis involves the reduction of HAuCl_4 in a boiling aqueous sodium citrate solution sometimes in the presence of surface passivating agents such as thiols. Addition of sodium citrate into the reaction will reduce the Au^{3+} ions to gold atoms (Figure 1). As the time proceeds the concentration of gold atoms rises rapidly until it exceeds saturation, resulting in the formation of nuclei.³ The free gold ions in the solution will then bind to the nuclei surface and growth continues.

In this method, citrate ions function as both surface stabilizer and reducing agent. The nanoparticles size can be tuned by varying the ratios of HAuCl_4 and sodium citrate. This method is simple and quick to produce gold nanoparticles where surface

functionality can be modified due to weak charge stabilization between citrate and nanoparticles.

Figure 1. Schematic illustrating the various stages during the growth of gold nanoparticles with time.

The main disadvantage of the citrate reduction method is the production of nanoparticles from dilute solution of metal precursor (0.25 mM). Simply increasing the concentrations of precursors will have influence on the size dispersity and stability of the nanoparticles. Hence, this method will have limitation in the large-scale production.

1.1.2 POLYOL METHOD

The method was implemented by Fievet et al. and others which involve the reduction of a metal precursor using polyols such as ethylene glycol to generate spherical nanoparticles.^{4, 5} Subsequently, Xia et al. modified the polyol process to obtain nanoparticles with tailored morphologies.⁶ The synthesis typically involves the use of 1, 5-pentanediol or ethylene glycol, as both solvent and reducing agent, and the polymer, PVP, as the shape directing agent (Figure 2).^{6, 7}

A variety of anisotropic noble metal nanoparticles such as nanocubes, nanowires, nanobars, nanoplates, octahedron and so forth^{8, 9, 10} can be prepared using this modified

method. It was proposed that the selective binding of PVP molecules to specific facet results in anisotropic growth to produce variety of morphologies with high precision.

Figure 2. Schematic for polyol method for synthesizing Ag nanostructures.

This method is successful in obtaining silver nanostructures of various shapes and sizes. The growth mechanism begins with the formation of a small cluster of Ag, and as the reaction proceeds the cluster grows into larger nuclei which will emerge in one of the three forms: single crystalline, single and multiply twinned. These large clusters are known as seeds and they eventually grow into nanoparticles with different shapes.¹⁰ This is well depicted in the figure 3.

Figure 3. Polyol method for synthesizing silver nanoparticles with different morphologies. Adapted with permission from ref 9.

Despite its versatility, polyol method is limited by the use of high temperatures during reaction, restriction in reducing power of the polyol and poor stabilization of non-polar metal surfaces by the polar polyol.

1.1.3 SEED MEDIATED METHOD

The synthesis of larger nanoparticles from smaller seeds is hindered by the formation of wide distribution of sizes without uniformity. This problem could be overcome by seed mediated synthesis approach where control over the size of the nanoparticles is achieved by selective growth on seeds and secondary nucleation is hence prevented. In this method growth and nucleation steps are separated to get a better control over the morphology of the nanoparticles (Figure 4A).¹¹ Typically the synthesis involves the injection of seed (small cluster of metal) solution, prepared by the reduction of metal precursor, to the growth solution. Control over the size and morphology could be achieved by controlling the parameters such as concentration of seed solution, morphology of seed, temperature, etc. There are two main strategies employed in the seed-mediated syntheses: epitaxial and non-epitaxial growth. In epitaxial growth, metal atoms are deposited on to seeds in a layer-by-layer fashion such that both seed and deposited metal atoms are of the same lattice structure. If both the seed and deposited atoms are of the same metal, it is termed a homo-epitaxial process, such as the growth of gold nanostars using Au seeds. If the seed and deposited atoms are of different metals, the process is termed a hetero-epitaxial process (Figure 4C).¹² In this process, core shell, alloys and complex nanostructures can be obtained. Murphy et.al demonstrated the synthesis of gold nanorods where small spherical nanoparticles, prepared by reduction of HAuCl_4 using sodium borohydride, are added as seeds to a growth solution containing CTAB, HAuCl_4 and a weak reducing agent like AA (Figure 4B).^{13, 14} On the other hand, non-epitaxial growth occurs if there is huge lattice mismatch between the seed and the metal deposited, hence

morphology of deposited metal do not conform to the seed particles.¹⁵ For example, Au nanorods (Figure 4D) are grown using Pt cube seeds (Pt and Au with lattice mismatch of 3.9%).¹⁶

Figure 4. (A) Schematics for seed mediated approach for the synthesis of Au nanorods and (B) TEM images of (B) Homo-epitaxial growth of Au nanorods, (C) hetero-epitaxial growth of Au@Ag core-shell nanoparticles, (D) non-epitaxial growth of Au nanorods on Pt nanocubes. Adapted with permission from (A) ref 10, (B) ref 13, (C) ref 11, (D) ref 15.

The major disadvantage of seed mediated method is complex multi-step route, which involves preparation of seed and its growth with necessary time duration between the steps. Homogeneity of the seed will dictate the formation of final shapes of the nanoparticles and its size dispersity.

1.2 FACTORS AFFECTING MORPHOLOGY OF NANOPARTICLES

In this section, we will summarize the common strategies employed during the synthesis of noble metal nanoparticles. Several examples are used to demonstrate (i) how adsorbates control the surface structure of nanoparticles, (ii) how kinetic factors affect the shape control and (iii) how ions present control the final morphology of the metal nanoparticles.

1.2.1 EFFECT OF ADSORBATES

To date a large number of surfactants, polymers and small chemical and bio-molecules adsorbates have demonstrated the ability to direct the shape of noble metal nanoparticles. In this section we will summarize the various polymers and small molecules reported for the growth of anisotropic metal nanoparticles. For example, cationic surfactants, such as CTAB, have been demonstrated to facilitate the controlled synthesis of Au nanorods (Figure 5A).¹⁴ Furthermore, Mirkin et al. showed that halide ions present act as counterions along side CTAC to exert a strong influence on the final morphology of the gold nanoparticles (Figure 5B-C).¹⁷ In addition to cationic surfactants, Tian et al. reported the synthesis of tadpole shaped gold nanoparticles using SDS, an anionic surfactant (Figure 5D).¹⁸ It is shown that mixing anionic and cationic surfactants also allowed for precise shape control of nanoparticles. For example, gold nanobelts and nanocombs are readily synthesized using mixed surfactants solution containing CTAB and SDS (Figure 5E-F).¹⁹

PVP has been established as an efficient capping agent to tailor the morphology of the nanoparticles in the polyol synthesis approach. Yang et al. demonstrated that silver cubes, truncated cubes, octahedra, cuboctahedra and truncated octahedra can be synthesized in single reaction system (Figure 5G-K).⁷ Although it has been proposed that shape control is achieved through selective binding of PVP to certain facets during crystal

growth, the reason for selectivity is still unclear. In addition to shape directing ability, Xia et al. demonstrated that PVP can also serve as a reducing agent to metal ions due to presence of multiple hydroxyl end groups. As a result, hexagonal or thin triangular nanoplates of noble metals including Au, Pd, Ag and Pt have been synthesized by using PVP (Figure 5L-M).²⁰ In another report, Tang et al. synthesized Pd nanochains with the aid of arginine molecules while using PVP as both reductant and stabilizing agent (Figure 5S).²¹

Using CPC as a surfactant Tang et al. reported a method for the selective synthesis of octahedral, rhombic dodecahedral, and cubic gold nanocrystals from CPC-capped single-crystalline gold nanocrystal seeds (Figure 5N).²² Cho et al. synthesized gold octahedral nanoparticles with tunable sizes through a polyol approach using PDDA as a polymer.²³ PDDA was found to play a key function in the formation of octahedral shaped gold nanoparticles (Figure 5O). Xia et al. Synthesized ultrathin gold nanowires by using oleylamine molecules, to form [(oleylamine)AuCl] complex chains through aurophilic interactions (Figure 5P).²⁴ Small molecules such as methylamine are also known to play a critical role in the solvothermal synthesis of concave Pt nanocrystals covered by (411) high-index facets by acting as structure directing agents (Figure 5Q).²⁵ Wang et al. demonstrated the crucial role of glycine in directing the shape of Pt concave nanocubes bound by high-index facets (Figure 5R).²⁶ Zheng et al. reported the synthesis of hexagonal palladium nanosheets by using carbon monoxide (CO) as shape directing agent due to strong and selective adsorption of CO on (111) surface Pd nanosheets (Figure 5T).²⁷

One of the major disadvantages involved with the use of capping agents is the existence of organic species on the surface of the nanoparticles. It is challenging to completely remove the adsorbed capping molecules/polymers from the nanoparticles surface and often results in surface oxidation. The presence of the capping agents will

hinder their applications in the catalysis and biological applications. For example, CTAB coated gold nanoparticles are illustrated to be toxic to the cell lines.

Figure 5. SEM images of (A) Au nanorods, (B) Au trisoctahedra, (C) Au truncated bitetrahedra, (D) Au tadpoles, (E) Au nanobelts, (F) Au nanocombs, (G) Ag cubes, (H) Ag truncated cubesNPs, (I) Ag cuboctahedra, (J) Ag truncated octahedra, (K) Ag octahedra, (L) Ag nanoplates, (M) Pd nanoplates, (N) Au rhombic dodecahedral, (O) Au octahedra, (P) Au nanowires, (Q) Pt concave polyhedral, (R) Pt concave nanocubes, (S) Pd nanochains and (T) Pd nanosheets. Adapted with permission from (A) ref 13, (B and C) ref 16, (D) ref 17, (E and F) ref 18, (G-K) ref 6, (L-M) ref 19, (N) ref 21, (O) ref 22, (P) ref 23, (Q) ref 24, (R) ref 25, (S) ref 20, (T) ref 26.

1.2.2 KINETIC FACTORS

Kinetic factors such as concentration of reactant, diffusion, reaction rate etc., also play an important role in determining nanocrystal morphology. Factors such as concentration of reactants and additives, temperature, pH, type of reducing agent used, type of solvent used during the synthesis and sometimes even the order in which reactants are added, can all act as local driving forces in controlling the final morphology of the nanoparticles. This is well illustrated, using the polyol synthesis method, where various polyhedral shapes can be obtained in high yield by varying the time interval for addition of precursor.⁷ In another report, Mirkin et al. systematically controlled the final morphology of the gold nanoparticles to obtain octahedra, cubes and trisoctahedra by increasing the concentration of AA from 0.5 – 10 mM in the reaction (Figure 6A-C).¹⁷ Similarly, Sau et al. used the synthesis of gold nanostars to demonstrate that size and density of spikes decreases with the increase in AA concentration (Figure 6D-E).²⁸

Figure 6. SEM images of (A) Au octahedra, (B) Au cubes, (C) Au trisoctahedra, (D) Au nanostars, and (E) Au nanostars with low number of spikes. Adapted with permission from (A-C) ref 16, (D and E) ref 27.

1.2.3 EFFECT OF IONS

External agents such as inorganic metal or halide ions can also modify growth of nanoparticles by selectively binding to certain crystal facets to promote the growth in other facets that will eventually result in the formation of anisotropic metal nanoparticles. For instance, trace amount of chloride ions (Cl^-) in the polyol synthesis of silver nanowires can afford higher nanowire yields (Figure 7A).²⁹ In this reaction, chloride serves to stabilize silver seeds electrostatically stabilize silver seeds and to reduce the availability of free Ag^+ ions by forming AgCl nanocrystals. Xia et al demonstrated the selective etching of twinned seeds using chloride ions and oxygen for the formation of silver nanocubes (Figure 7B).³⁰

In another report, the role of bromide ions (Br^-) in the synthesis of silver bipyramids is illustrated.³¹ Xia et al. found that the concentration of NaBr played a crucial role in the control of final structure (Figure 7D-E). On doubling the concentration of NaBr in the reaction a totally different shape was obtained in the form of silver nanobars.³² Mirkin et al. demonstrated that presence of iodide ions (I^-) play a crucial role in the growth of gold nanoprisms in higher yields. The iodide ions act as shape directing agents by selectively binding to (111) planes of gold, resulting in the formation of Au nanoprisms. Tuning the concentration of I^- ions allowed for the shape of nanostructures to be changed from spheres to rods and prisms (Figure 7F-G).³³ In another paper Zheng et al. reported the high yield hydrothermal synthesis of 5-fold twinned Pd nanowires and nanorods in the presence of iodide ions by using PVP as reducing agent (Figure 7I).³⁴ In a recent work, Zhang et al. illustrated the role of tri-iodide ions (I_3^-) in the one-pot seedless growth of monodispersed triangular gold nanoplates. The I_3^- ions forms planar nuclei by selectively binding to Au (111) facet via oxidative etching, to eventually produce such

monodispersed triangular nanoplates with tunable edge lengths in high yield (Figure 7H).³⁵

Figure 7. SEM images of (A) Ag nanowires, (B) Ag nanocubes, (C) figure illustrating the role of Fe(III) ions in synthesis of silver nanoparticles, (D) Ag bipyramids, (E) Ag nanobars, (F) Au rods, (G) Au nanospheres, (H) triangular Au nanoplates, (I) Pd nanowires, (J) Au octahedra, (K) Au rhombic dodecahedra, (L) Au truncated ditetragonal prisms, (M) Au concave cubes, (N) Nanoporous gold. Adapted with permission from (A)

ref 28, (B) ref 29, (C) ref 35, (D) ref 30, (E) ref 31, (F and G) ref 32, (H) ref 34, (I) ref 33, (J-M) ref 36, (N) ref 37.

In addition to halide ions, metal ions are also proven to exert control over the morphology of metal nanoparticles. For example, inclusion of Fe (III) ions in polyol synthesis of silver nanowires resulted in high yields.³⁶ Wiley et al. demonstrated the synthesis of silver nanoparticles with different shapes by controlling the concentration of Fe (III) ions, where high concentrations yielded silver nanowires while low concentrations resulted in nanocubes. Figure 7C explains the role of Fe (III) ion in removing atomic oxygen from the surface during the growth of silver nanoparticles. The introduction of silver ions (Ag^+) into growth solutions also greatly affects the final morphology of nanoparticles synthesized. Mirkin et al. reported the syntheses of Au nanoparticles of various morphologies such as octahedra, truncated ditetragonal prisms, rhombic dodecahedra, and concave cubes by tuning concentration of Ag^+ ions in the growth solutions (Figure 7J-M).³⁷ Besides this, Ag^+ is also demonstrated to stabilize the low coordinated atoms in np-Au (Figure 7N).³⁸

The disadvantage of using secondary ions in the synthesis of anisotropic nanoparticles will result in deposition of secondary ions on the growing nanoparticles, which will later affect the catalytic performance of the nanoparticles. For example, trace amount of silver on the gold nanoparticles will greatly enhance its catalytic performance.

1.3 SURFACE PLASMONS

The interest in optical properties of metal nanoparticles dates back to ancient Rome when the famous Lycurgus cup was created. The presence of gold and silver nanoparticles in the stained glass caused the cup to appear as two different colours depending on whether light is reflected or transmitted through it. The chemistry behind these properties was only understood when Michael Faraday studied colloidal gold

dispersions in 1850s. Subsequently, Mie solved Maxwell's equations in 1908 to explain the extinction spectra (scattering and absorption) of spherical nanoparticles of random size, and also calculated the spectra of gold nanoparticles of different sizes for the first time. To date, Mie's solution still remains of great interest.

The optical properties of metal nanoparticles can be classified as linear or non-linear. Linear optical properties include absorption, fluorescence, Rayleigh scattering, etc., whereas non-linear optical properties include hyper-Rayleigh scattering, second and higher order harmonic generations, etc.

Figure 8. (A) Pictorial representation of localized surface plasmon resonance, (B) figure illustrating the effect of aspect ratio of gold nanorods on its optical properties. Adapted with permission from (B) ref 38.

The optical properties of metal nanoparticles arise from a response generated by the interaction with light, a phenomenon that is widely known as SPR. The term “surface plasmon” is defined as a collective oscillation of free electrons in the conduction band of a metal upon interaction with incident light. When the size of the particle (reaches nano

size) becomes smaller than the photons' mean free path, these coherent oscillations are confined to the particle's surface and frequency of oscillation is then referred to as localised LSPR. This principle is demonstrated in figure 8A.

Metal nanoparticles possess different optical properties as function of size due to size dependent polarizability. An example of such an ability is shown in figure 8B.³⁹ Shape is another factor, which also shows a significant effect on optical properties of metal nanoparticles. There has been growing interest in the synthesis of anisotropic metal nanoparticles and in understanding their structure property relations due to the promising shape and size dependent applications. Mie theory predicted the optical extinction of very small spherical particles where $2R \ll \lambda$, using the equation

$$\sigma_{ext} = \frac{9 \cdot V \cdot \epsilon_m^{3/2}}{c} \left(\frac{\omega \cdot \epsilon_2(\omega)}{[\epsilon_1(\omega) + 2\epsilon_m]^2 + \epsilon_2(\omega)^2} \right)$$

Where V represents volume of the particle, ω is the angular frequency incident light, and c is speed of light in vacuum. ϵ_m and $\epsilon(\omega)$ denote the dielectric functions of the surrounding medium and the metal, respectively. It is clear from the above equation that the optical properties of metal nanoparticles are strongly dependent on size, shape and surrounding media.

The LSPR of metal nanoparticles is very sensitive to surrounding dielectric medium, which is useful to tailor the optical properties. Generally, a red shift in LSPR position is observed with the increase in refractive index of the surround medium. Whitney et al. systematically studied the LSPR dependence of triangular silver nanoparticles to the change in refractive index using atomic layer deposition of Al_2O_3 .⁴⁰ In this study, they demonstrated the detection of single atomic layer of Al_2O_3 . VanDuyne et al. studied the effect of solvents with increased refractive index on LSPR scattering spectra of single silver nanoparticles on a glass cover slip.⁴¹ A linear fit between peak

position and refractive index of a surrounding solvent was demonstrated. They observed a LSPR shift of ~ 40 nm with adsorption of $\sim 60,000$ 1-hexadecanethiol molecules on a silver nanoparticle.

Figure 9. Experimental (red curve) and calculated (black curve) UV-Vis extinction spectra of Au nanosphere with different diameters. Adapted with permission from ref 39.

To date, several studies have demonstrated the effect of these structural parameters on the LSPR of metal nanoparticles. The wavelength of the LSPR can be tailored through tuning the size of the nanoparticles. For example, figure 9 shows the experimentally measured and calculated (using Mie's theory) extinction spectra of spherical gold nanoparticles with sizes from 5 to 80 nm, where LSPR peak is observed to red shift with the increase in size of the gold nanoparticles.⁴²

Figure 10. (A-D) SEM images and (E-H) Extinction spectra of Ag spheres, cubes, cuboctahedron and octahedron respectively. Insets of (E-H) show the real scattering color of respective nanoparticles as indicated in the figure. Adapted with permission from (A and E) ref 40, (B-D and F-H) ref 41.

In contrast to spherical metal nanoparticles, particles with asymmetric morphology can result in more complex surface plasmon resonances because of larger polarizabilities. For example, Ag spheres have only one SPR peak⁴³ whereas Ag cubes, cuboctahedra and octahedra have multiple resonance peaks (Figure 10).⁴⁴ The insets of extinction spectra show the real scattering colors measured using dark field microscope. Particles showed noticeable color change in scattered light with increase in particle size as seen in the color images from single isolated particles.

In addition to extinction and scattering, the interaction of light with metal nanoparticles produce enhanced local electromagnetic field particularly at gaps between the particles,⁴⁵ sharp corners and edges.⁴⁶ In the case of inter-particle junctions, enhanced local electromagnetic field is only confined to a small fraction of volume compared to total available surface area. It has been demonstrated that the enhanced local

electromagnetic field (hot spot) on nanoparticle surfaces can be achieved by the introduction of nanoscale features such as spikes to the surface of nanoparticles.⁴⁷ Hence, there is a surge in research for the syntheses of metal nanoparticles with sharp tips, corners and edges (Figure 11). With the increase in complexity of metal nanostructures as in case of Au nanocups the enhanced local electromagnetic field is localized at the brim of the structure.⁴⁸ In contrast, the enhanced local electromagnetic field are distributed over the whole surface of the nanoparticles, as in case of np-Au disks and spiky nanoparticle.⁴⁹

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Figure 11. (A-B) HRTEM image of Ag@SiO₂ nanoparticle dimer with interparticle separation of 3 and 15 nm and their respective electric field distributions, (C-D) SEM images of Au nanoprism and np-Au disk and their respective electric field distribution, (E-H) TEM images of Au nanocups, nanorods, spike and spiky nanoparticles with their respective electric field distributions. Adapted with permission from (A and B) ref 42, (D) ref 46, (E) ref 45, (F) ref 43, (G) ref 44, (H) ref 47.

1.4 SURFACE ENHANCED RAMAN SPECTROSCOPY

The Raman effect originates from the elastic scattering of a photon upon interaction with a molecule where the incident photon loses some of its energy to the molecule in the form of molecular vibrations, resulting in a shift of energy.⁵¹ This shift of energy can be high or low depending on whether the photon is interacting with the ground or excited states of the molecule. The use of Raman scattering is limited by very low cross-sections of the molecules (10^{-29} - 10^{-32} cm²) since only one in every 10^6 - 10^8 photons gets inelastically scattered.

1.4.1 ORIGIN: WHAT IS SERS?

Surface plasmons are electromagnetic waves originating from the collective oscillations of free electrons of metal nanostructures and bound to the surface. These waves can propagate parallel along metal interfaces. Surface plasmons that are excited by light produce surface plasmon resonance (SPR) for planar metal surfaces ($\lambda \ll \text{diameter}$) or localized surface plasmon resonance (LSPR) for nanoscale metallic structures ($\lambda \gg \text{diameter}$). Metals such as gold, silver and copper are commonly used because their absorption maxima fall within the visible region range of the electromagnetic spectrum. The interaction of light with these metal nanostructures produces an enhanced local electromagnetic field near the surface of nanostructures. An analyte molecule adsorbed on these metal nanostructures will interact with this enhanced electromagnetic field causing an increase in magnitude of induced dipole resulting in an enhancement of inelastic scattering intensity. This process of magnifying Raman scattering intensities by using metal nanostructures is known as SERS. Currently there are two mechanisms, (i) electromagnetic enhancement and (ii) chemical enhancement, which contribute to this enhancement at varying degrees of intensity.

1.4.2 ELECTROMAGNETIC MECHANISM

The EM comes from the special optical properties of metal nanostructures to confine surface plasmons. Surface plasmons are collective oscillations of free electrons of metal nanostructures resulting in an enhanced local electromagnetic field at the surface. The interaction of this field with molecules located close to the metal surface comprises the electromagnetic mechanism. This mechanism is more pronounced when the molecule is only physisorbed or in close proximity to surface of the metal nanostructure, typically within 10 nm from the surface, at most and doesn't have a direct contact with the surface. Thus the effectiveness of this mechanism is strongly dependent on distance of molecule from the surface of metal. This mechanism can be observed as enhancement in signal intensity with no shift in the band position. Surface roughness is a necessary prerequisite of SERS. In the case of a smooth metal surface, surface plasmons exist as waves of electrons bound to the metal surface and can move only in direction parallel to the surface. In the case of a roughened surface, the plasmons are not constrained and the electric field can radiate in both parallel and perpendicular directions to the surface. The photon excitation of plasmon resonance of the metal permits scattering. In addition to change in dielectric constants of the surrounding media and roughened surface, electric field is concentrated at the sharp features on the metal surface. This is found to be a major contribution and give rise to greater than 10^6 - 10^8 times enhancement in signal strength over normal Raman scattering.

The size and morphology of the metal nanoparticles are two key parameters that affect the EM enhancement factor. Anis et al. demonstrated the dependence of EM enhancement on the size of spherical silver nanoparticles ranging from 20 to 70 nm.⁵² They found that the optimal particle size is ~50 nm for maximizing the SERS intensity. Morphology of the nanoparticles is another important factor that influences the EM

enhancement since anisotropic nanoparticles hold wide tunable LSPR and strong localized EM fields compared to spherical nanoparticles. It is demonstrated that enhancement factors as high as $\sim 10^{10}$ could be achieved from sharp vertices and edges of the nanoparticles.^{53, 54}

1.4.3 THE CHEMICAL ENHANCEMENT

This mechanism is not clearly understood because decoupling it from the electromagnetic mechanism is a practical problem as both operate simultaneously. The three major processes that contribute to the chemical enhancement are (i) nanoparticle to molecule charge transfer resonance, (ii) increase in molecular polarizability with the adsorption of molecule on nanoparticles, and (iii) enhancement due to resonance scattering.⁵⁵ In the former case, it is proposed that the analyte forms a bond with the metal surface which facilitates charge transfer between the metal and analyte. Chemical enhancement is characterised through the shift of SERS signal rather than enhancement alone. This may be due to charge transfer from metal to analyte and vice versa. Here, the enhancement decreases with the number of layers on the surface of the metal. The chemical enhancement is of the order 10^2 whereas the electromagnetic enhancement is of order 10^6 - 10^8 . This difference in the magnitudes of the two enhancements mechanism clearly highlights the EM mechanism as more pronounced.

1.4.4 SURFACE-ENHANCED RESONANCE RAMAN SPECTROSCOPY

SERRS is a combination of the above mentioned electromagnetic and chemical enhancement mechanisms in addition to fulfilment of resonance condition. The resonance condition is fulfilled when an incoming photon activate an electric dipole transition of the molecule into an excited state, instead of an intermediate state. In SERRS experiment, analyte molecules first are adsorbed on a metal surface and the extinction spectrum is measured. Following this, an excitation wavelength close to analyte molecule adsorption

is chosen for the SERRS measurement, which enhances the normal Raman scattering signal by 10^9 – 10^{11} times. This enhancement corresponds to the collective efforts of SERS enhancement ($>10^8$ times) and the resonance Raman enhancement (10^3 – 10^5 times).

1.4.5 CALCULATING SERS ENHANCEMENT FACTORS

The method gives only the overall SERS enhancement factor (EF) by measuring both the SERS and NRS signals of a given analyte. Individual enhancements can be obtained only theoretically. The calculation of Raman intensity can be written as,

$$I_{\text{NRS}} = K(\nu) \times N_{\text{NRS}} \times \delta\sigma/\delta\Omega \times I_{0,\text{NRS}} \times \nu^4 \times t_{\text{NRS}}$$

where $K(\nu)$ is the instrument response function, N_{NRS} is number of analyte molecules within the probe volume, $\delta\sigma/\delta\Omega$ is the differential Raman cross section of molecules, $I_{0,\text{NRS}}$ is the incident laser intensity, ν^4 is the dependence of frequency in the scattering process and t_{NRS} is the acquisition time. Scattering intensity SER is analogous to that of NRS but is multiplied by a factor EF_{SERS} due to enhancement.

$$I_{\text{SERS}} = K(\nu) \times N_{\text{SERS}} \times \delta\sigma/\delta\Omega \times I_{0,\text{SERS}} \times \nu^4 \times t_{\text{SERS}} \times EF_{\text{SERS}}$$

The relationship of I_{SERS} and I_{NRS} is simplified if the collection geometry is similar and the excitation frequency used is same such that $K(\nu)$ and ν^4 are constant. When the laser power intensities are normalised the enhancement can be calculated by the ratio of these two intensities.

$$\text{Enhancement factor } EF = \left(\frac{I_{\text{SERS}} / N_{\text{SERS}}}{I_{\text{NRS}} / N_{\text{NRS}}} \right)$$

1.4.6 SERS SUBSTRATES

SERS enhancement is strongly dependent on scattering properties of metal nanoparticles, type of metal and excitation laser wavelength that are crucial in controlling the observed Raman intensities. The metal substrate should support the excitation of

surface plasmons at the selected laser wavelength. Conductive metals such as Ag, Cu, and Au give strong SERS enhancements. Since Cu and Au have inter-band transitions, substrate of Ag exhibit strongest SERS enhancements.

Figure 12. Schematic diagram showing how molecules are detected by SERS from an isolated nanoparticle substrate.

To date scientists have utilized SERS for the identification and ultra sensitive detection of exogenous molecules at the surface of metal nanoparticles, since the first observation of SERS by Fleischmann et al. in the 1970s where strong Raman bands were observed for pyridine absorbed on to rough silver electrode.⁵⁶ Most of the early works on SERS were only performed on roughened metal electrodes that consist of irregular and non-uniform sizes features, as SERS is very sensitive to the small change in structure and size of particles through localization of enhanced local electromagnetic field. Since then, there have been tremendous interests in the syntheses of morphology controlled anisotropic metal nanoparticles to obtain more reproducible and strong enhancements. A wide variety of metal nanostructures were previously studied by correlating the structure of the metal nanoparticles with the SERS signal intensity to understand the SERS (Figure 12).⁵⁷ Localization of enhanced electromagnetic field at inter-particle junctions and sharp vertices was demonstrated experimentally in conjunction with theoretical methods.⁵⁸ For

example, intense signals were observed from sharp tips of nanoplates,⁵⁹ nanorods,⁶⁰ cubes,⁶¹ nanostars,⁶² octahedral nanoparticles,⁶³ and so forth.

Figure 13. SEM images showing close packed films of (A) cubes, (B) cuboctahedra, and (C) octahedra; (D) SERS spectra collected on LB films of each of the nanocrystal shapes 1×10^{-6} M arsenate solution. Peaks at 800 and 425 cm^{-1} can be assigned to Na_2HAsO_4 . (E) SERS response of octahedra LB arrays coated with various organic species. Benzenethiol (BT), hexadecanethiol (HDT), and mercaptodecanoic acid (MDA). Adapted with permission from (A-E) ref 49.

Yang et al. demonstrated that Langmuir Blodgett assemblies of various shaped silver nanoparticles synthesized by polyol method can detect arsenite and arsenate with ultra low detection limit of 1 ppb (Figure 13).⁶⁴ Luis et al. reported higher single particle

SERS activity on spiked gold beads due to enhanced local electromagnetic field at the sharp tips.⁶⁵ Recently, Guo et al fabricated dye-free NIR SERS nanoprobe by coupling conducting polymer and NIR reporter molecule directly on to gold nanorods.⁶⁶ These probes are used for bio-imaging and photothermal cancer therapy.

1.5 ELECTROCATALYTIC OXIDATION OF METHANOL

Electrocatalysis facilitates the change of reaction rates of an electrochemical reaction on the surface of electrode. The key process in electro catalysis reaction is interfacial electron transfer. Three main processes usually occur during electrocatalysis. First, electroactive species diffuse to electrode surface from the bulk solution. Second, electron exchange occurs between the electrode and active species. Third, products are detached from the surface of electrode through desorption.

Direct methanol fuel cells (DMFC) are a class of proton-exchange fuel cells where methanol is used as fuel. The use of methanol is appealing due to the ease of storage, handling and transport besides its high energy density. Noble metal nanoparticles are widely used as an electrocatalyst for methanol oxidation reactions. In comparison to other metals, pure gold is found to be chemically inert. However, Au NPs are found to exhibit significant catalytic properties as compared to inert bulk gold. Owing to their excellent catalytic properties they are utilized in various electrochemical reactions including those in fuel cells.

In research labs, the performance of the catalyst towards electro-oxidation of methanol is typically carried out in a three-electrode system, as shown in Figure 14. In a methanol free solution (Figure 14B), chemisorption of OH⁻ ions occur at potential <0.25 which can be formally written as⁶⁷

The anodic peak during the positive scan at potential ≥ 0.25 result from the formation of gold oxide Eq. [2]

Figure 14. (A) Schematic of the three electrode electrochemical cell. (B) CV of spherical Au NPs of size 30 nm in deoxygenated solutions containing 0.5 M KOH with and without 2 M CH₃OH.

In the presence of methanol (Figure 14B), the molecules of methanol are mostly oxidized to form formate by a four electron mechanism Eq. [3].⁶⁸ This process occurs at the low potential region prior to formation of gold oxide layer. This reaction occurs in few steps as depicted in Eqs. [4, 5 and 6] and overall net reactions in shown in Eq. [7]

In the high-potential region, methanol is mainly oxidized to carbonates through a six electron transfer mechanism as shown in Eq. [8].

Methanol oxidation reaction (MOR) has been studied on different Au NPs including polycrystalline and single crystalline gold electrodes,⁶⁹ dendritic nanostructures,⁷⁰ nanowires,⁷¹ spheres,⁷² nanotubes,⁷³ nanoporous gold,⁷⁴ trisoctahedral,⁷⁵ concave cubes,⁷⁶ cubes,⁷⁷ nanorods,⁷⁶ octahedral⁷⁷ and nanoflowers.⁷⁸ Size and shape of the particles are two main factors that dictate the physio-chemical and electrocatalytic performance of the prepared gold nanoparticles. Cheng et al. systematically investigated the size and shape dependent electro-oxidation of methanol on gold nanoparticles using spherical Au NPs of 20 nm (Au20), 40 nm (Au40) and gold nanorods (AuNR).⁷² The measured catalytic activity towards MOR is in the order Au20 > Au 40 > AuNR.

Surface structure of the Au NPs also plays a critical role in the performance towards MOR. Xia et al. systematically demonstrate the catalytic performance of different shaped Au NPs such as trisoctahedral (331), concave cubic (720), nanorods (111 and 100), cubic (100) and spherical (111 and 100), towards MOR.⁷⁶ Trisoctahedral and concave cubic Au NPs show higher electrocatalytic activity for MOR due to the presence of high-index facets on the surface.

1.6 THESIS OUTLINE

The main goal of this thesis is to design and develop synthesis methods which enables the preparation of more efficient noble metal nanoparticles with tailored morphologies for optical, catalytic and SERS applications.

First part of the thesis presents a new approach to synthesize spiky nanoparticles with tunable spike length and to study their fundamental optical properties. Spiky nanoparticles exhibit higher overall plasmonic excitation cross sections than their non-spiky peers. In this work, we demonstrate a two-step seed-mediated growth method to synthesize a new class of spiky Ag–Au octahedral nanoparticles with the aid of a high molecular weight PVP polymer. The length of the nanospikes can be controlled from 10 to 130 nm with sharp tips by varying the amount of gold precursor added as well as the injection rates. Spatially resolved EELS study on individual spiky Ag–Au nanoparticles illustrates multipolar plasmonic responses. While the octahedral core retains its intrinsic plasmon response, the spike exhibits a hybridized dipolar surface plasmon resonance at lower energy. With increasing spike length from 50 to 130 nm, the surface plasmon of the spike can be tuned from 1.16 to 0.78 eV. The electric field at the spike region increases rapidly with increasing spike length, with a 10^4 field enhancement achieved at the tips of 130-nm spike. The results highlight that it is important to synthesize long spikes (>50 nm) on nanoparticles to achieve strong electric field enhancement. A mechanism for the formation of sharp spikes is proposed based on our studies using XPS, SEM, and HRTEM.

The second part of this thesis focuses on the design and wet-chemical synthesis of np-Au nanoparticles and their application in catalysis. Np-Au with networks of interconnected ligaments and highly porous structure holds stimulating technological implications in fuel cell catalysis. Current syntheses of np-Au mainly revolve around dealloying approaches that are generally limited by stringent and harsh multistep protocols. Here we develop a one-step solution phase synthesis of 0D hollow np-Au nanoparticles with tunable particle size (150–1,000 nm) and ligament thickness (21–54 nm). With faster mass diffusivity, excellent specific electroactive surface area and large density of highly active surface sites, our 0D np-Au nanoparticles exhibit 1.4 times enhanced catalytic

activity and improved tolerance towards carbonaceous species, demonstrating their superiority over conventional np-Au sheets. Detailed mechanistic study also reveals the crucial hetero-epitaxial growth of gold on the surface of silver chloride templates, implying that our synthetic protocol is generic and may be extended to the synthesis of other nanoporous metals via different templates.

The third part of this thesis focuses on tailored synthesis of morphology controlled np-Au nanoparticles with tunable ligament sizes. Precise control of ligament size and porosity in np-Au nanoparticles allows for enhanced catalytic activities as well as utilization efficiencies. Currently, np-Au is synthesized using the dealloying approach; however, the fast diffusion of gold atoms at the alloy-electrolyte interface limits formation of small ligaments and pores. Hence, high yield syntheses of np-Au nanoparticles with tunable ligament size, porosity and morphology are yet to be realized. Here, we report a simple wet-chemical approach to synthesize np-Au nanoparticles with tailored morphology. We use a two step seed-mediated method, with silver templates as sacrificial seeds, hydroquinone and PVP as reducing agent and shape directing agent respectively. Our synthetic protocol is robust, rapid, and reliable. This method is effective in achieving large scale synthesis of np-Au particles (~ 0.4 g) with well-defined morphology in a cost-effective and time-saving manner (< 30 min). We systematically tailor the size of the ligament 21 to 6 nm by varying the final concentration of hydroquinone in the solution. Furthermore, we study the detailed mechanism for the formation of np-Au nanoparticles by evaluating the role of individual reactants, such as reducing agent, PVP, seed particles their shape and composition, on the formation of np-Au nanoparticles. We evaluate the electrochemical properties of these np-Au nanoparticles as a function of morphology and ligament size. Np-Au nanoparticles with a ligament size of 8 nm exhibits 2 times increase in electro active surface area ($20.3 \text{ m}^2.\text{g}^{-1}$) compared to that of 21 nm ($10 \text{ m}^2.\text{g}^{-1}$). These

results highlight the importance of having sub 10 nm ligament sizes to improve the catalytic activity of np-Au nanoparticles.

Finally, we demonstrate that np-Au nanoparticles with reduced symmetry possess enhanced local electromagnetic field that can be exploited for location dependent, single particle SERS. We study the plasmonic properties of individual np-Au nanoparticles of four geometries – nanocups, nanotubes with open and closed ends and plates – particularly focusing on their SERS performance as substrates for single particle sensing under near-infrared excitation. Np-Au particles demonstrated at least 5-fold increase in SERS enhancements compared to that of smooth Au nanoparticles of similar dimensions. In general, we obtain similar SERS intensity on the surface of the np-Au nanoparticles, with np-Au cups displaying higher SERS enhancement, 6×10^3 , compared to that of other structures. Furthermore, we demonstrate an additional 5-fold increase in SERS enhancement resulting from the open cavities when np-Au cups are facing up and at the open ends of np-Au tubes.

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Chapter 2

Synthesis of Spiky Ag–Au Octahedral Nanoparticles and Their Tunable Optical Properties*

ABSTRACT. Spiky nanoparticles exhibit higher overall plasmonic excitation cross sections than their non-spiky peers. In this work, we demonstrate a two-step seed-mediated growth method to synthesize a new class of spiky Ag-Au octahedral nanoparticles with the aid of a high molecular weight polyvinylpyrrolidone polymer. The length of the nanospikes can be controlled from 10 – 130 nm with sharp tips by varying the amount of gold precursor added and the injection rates. Spatially resolved EELS study on individual spiky Ag-Au nanoparticles illustrates multipolar plasmonic responses. While the octahedral core retains its intrinsic plasmon response, the spike exhibits a hybridized dipolar surface plasmon resonance at lower energy. With increasing spike length from 50 – 130 nm, surface plasmon of the spike can be tuned from 1.16 eV - 0.78 eV. The results highlights that it is important to synthesize long spike (> 50 nm) on nanoparticles to achieve strong electric field enhancement. A hypothesis for the formation of sharp spikes has been proposed based on our studies using XPS, SEM and high resolution TEM studies.

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2.1 INTRODUCTION

Localized surface plasmon resonances (LSPRs) of metallic nanoparticles are coherent oscillations of conduction electrons in a nanostructured metal and can be excited by incident light.¹ The resonant frequency and amplitude of LSPRs are governed by the size,² shape^{3,4} and the dielectric function of the metal and its surrounding environment.⁵⁻⁹ Strong enhanced fields can be generated at sharp edges, corners and gap between nanoparticles. Among various metallic nanoparticle systems, anisotropic spiky nanoparticles, such as gold nanostars^{10,11} and nanoflowers,¹² are particularly interesting because of the intense electromagnetic field generated at their tips, an effect similar to the lightning rod effect.¹³ This local plasmonic feature allows the modulation of their LSPR modes by simply tuning the length, density and aspect ratio of the surface spikes. The highly tunable plasmonic response and strong localized fields of the anisotropic spiky nanostructures made them excellent materials for SERS and SPR platforms for tracing (bio) molecules detection,¹⁴ and/or non-linear optical applications.^{15,16} In addition, the relatively large extinction cross-section in the near-infrared (NIR) compared to non-spiky nanoparticles facilitates the enhanced photo thermal heating capacity of these spiky nanostructures, making them ideal for diagnosis and therapeutic medical applications.¹⁷⁻¹⁹

The wavelength-dependent plasmonic response of spiky nanoparticles enables the direct control of the light-matter interactions. This has triggered significant research interest in the syntheses of spiky metal nanoparticles with well-defined morphologies and tunable plasmon modes. Wet-chemistry synthetic strategies are commonly employed for the syntheses of spiky metallic nanoparticles. It can be broadly categorized into by two synthesis routes, i.e. (1) direct synthesis and (2) seed-mediated growth method. The direct synthesis method allows the direct formation of spiky nanoparticles by selecting suitable metal precursor, mild/strong reducing agents and surfactants.¹² On the other hand, the

seed-mediated growth method utilizes small metallic seed nanoparticles of < 10 nm in size as nuclei, where additional metal precursor and capping agent are added sequentially to promote anisotropic growth of protruding spikes on top of the seed nanoparticles.^{20,21} The advantage of the seed-mediated growth method is that different materials can be used as seed and growth materials to form bimetallic anisotropic nanostructures. For instance, silver plates have been used as seeds to form mono- and multi-pod gold nanocrystals with CTAB as capping agent.⁹ Other reported binary spiky nanoparticles, such as hollow silver–gold nanoparticles bearing nanospikes,²²⁻²⁴ and spiky gold nanoshells on polymer beads¹¹ were synthesized by using various reducing agents, such as hydroxylamine and sodium borohydride, respectively.

Yet, the current synthetic reports on spiky nanoparticles are limited to synthesis of short spikes in the range of 10 – 60 nm. Experiments and theoretical simulations have demonstrated that the plasmon resonance of these spiky nanoparticles is attributed to the hybridization of core and tips plasmon modes.^{21,25,26} In particular, the length of spikes and the shape of the core nanoparticles are the two major factors that dominate the plasmon response of the spiky nanoparticles. By manipulating the length of the spikes from tens to hundreds of nanometers, the LSPR band can be tuned from the visible to the near-infrared.²⁷ In addition, the core of nanoparticles can serve as an antenna²⁸ which can harvest light energy more readily than spikes and further increase the overall plasmon excitation cross section.²⁵ Most aforementioned methods are concentrated on using spherical nanoparticles as their core. However, shape-controlled metallic nanoparticles can also be used as alternative core materials due to their tunable extinction cross-section and unique plasmon resonant modes as compare to its spherical counterpart.²⁷ Thus, the ability of growing spikes with tunable length on any core nanoparticles presents great potential to tune the light-matter interactions at specific desired wavelength.

Here, we demonstrate the formation of a new class of anisotropic spiky Ag-Au nanoparticles, where the core is morphologically controlled (i.e. octahedral in shape) and the spikes' length is tunable to high aspect ratios. The optical responses of these anisotropic spiky Ag-Au bimetallic octahedral nanoparticles are examined experimentally and computationally. We aim to exploit the large extinction cross section of the core Ag octahedral nanoparticles, while controlling the LSPR and enhancing the electric field by manipulating spikes' lengths. The design of spiky nano-octahedra with tunable aspect ratio is based on our proposed reaction using high molecular weight PVP. To achieve this, we employ a two-step seed-mediated growth method. Firstly, a polyol method is used to synthesize Ag octahedral nanoparticles with diameters around 300 nm. Secondly, these nanoparticles subsequently serve as seeds for the anisotropic growth of nanometer-sized spikes of sharp tips, with the aid of high molecular weight PVP. We will address the experimental conditions to which the spike's length can be tuned from 10 to 130 nm while retaining the octahedral shape of its core particles. The crystallinity, the chemical and the near-field optical properties of the spiky nanoparticles are probed, and a proposition for the spike formation is discussed. The experimental EELS shows multipolar plasmonic responses, with the spikes exhibiting lower energy resonance than their core. We will also examine the effect of spike length the surface plasmon energy and electric field enhancement.

2.2 RESULTS AND DISCUSSION

The two-step seed-mediated growth synthesis of spiky Ag – Au nanoparticles is indicated in Figure 1A. In the first step, Ag octahedral nanoparticles are made using a reported polyol synthesis method.²⁹ In brief, silver nitrate and PVP ($M_w = 55,000$ g/mol) are dissolved in pentanediol separately. The solutions are added alternately into a pentanediol solution at 190 °C. The reaction is allowed for 60 minutes to produce octahedral nanoparticles. The SEM image of the as-synthesized nanoparticles (Figure 1B) indicates monodispersed octahedral nanoparticles with an average size of 267 ± 5 nm.

In the second step, Ag octahedral nanoparticles serve as seeds, where the growth of spikes is promoted by adding high molecular weight PVP (360,000 g/mol) and 5 mL of aqueous gold chloride respectively in a drop wise manner. The final suspension is brownish gray in color. SEM and TEM images (Figure 1 C) demonstrate that taper-like structures protrude from all facets of the octahedral nanoparticles. The hollow interior of spiky nanoparticles is similar to that of Ag-Au octahedral nanocages reported in literature³⁰ (Figure 2A).

The average spike length is of 50 ± 9 nm and will be shown to be tunable below. The spiky nanoparticles obtained are of high yield and uniformity, with an average core edge length of 286 ± 10 nm. We refer these particles as “SP50” hereafter throughout the text, where “SP” and the following number denote to “spiky nanoparticles” and their corresponding spike’s length, respectively. Although our growth process is based on the extensively reported galvanic replacement process, the conventional galvanic replacement process results in the epitaxial growth of Au layer on the top of Ag nanoparticle to form non-spiky hollow Ag-Au octahedral nanoparticles (such as in the case of Figure 2A).³⁰ The formation of spiky nanoparticles with the aid of high molecular weight PVP during the growth process has remained unexplored until now.

Figure 1. (A) Pictorial representation of the hypothesis for the formation Ag-Au spiky nanoparticles. SEM images, TEM images, camera pictures, and histogram of spikes' length of (B) Ag octahedral nanoparticles, and (C and D) Ag – Au spiky nanoparticles, SP50 and SP130, respectively. SP 50 and SP 130 correspond to spiky nanoparticles with an average spike length of 50 nm and 130 nm, respectively. The length of the spikes can be tuned from < 10 nm to 130 nm by varying the amount of gold chloride precursor and the precursor injection rate during the growth process.

Figure 2. (A – F) SEM images, TEM images, and the respective spike's length size distributions of Ag-Au octahedral nanocages, SP10, SP40, SP50, SP68, and SP130 Ag – Au spiky nanoparticles. Histograms of length of the spikes were calculated from high magnification SEM images by measuring at least 50 particles.

Following this, we vary the amount of gold chloride precursor and the precursor injection rate, respectively, to evaluate the morphology change in the spiky nanoparticles (Table 1). The length of the spikes is highly dependent on the amount of gold chloride precursor added (Figure 2). At the injection rate of 0.7 mL/min, the addition of 3 mL, 5 mL, and 8 mL of 0.3 mM gold chloride precursors result in average spike lengths of < 10 nm (Figure 2B), 50 ± 9 nm (Figure 2D) and 130 ± 27 nm (Figure 2E), respectively.

Table 1. The experimental conditions for the syntheses of spiky nanoparticles SP10 – SP130, and their corresponding spike’s lengths.

Sample	Volume of 0.3 mM gold chloride precursor (mL)	Injection speed (mL/min)	Spikes length (nm)
SP10	3	1.0	< 10
SP40	5	1.0	40 ± 11
SP50	5	0.7	50 ± 9
SP68	8	1.0	68 ± 13
SP130	8	0.7	130 ± 27

On the other hand, we observe that the injection rate of the gold precursor is inversely proportional to the spike’s length. With the same 8 mL of gold chloride precursor amount used in the reactions, the lengths of spikes are 68 ± 13 nm (Figure 2E) and 130 ± 27 nm (Figure 2F) when the injection rates are 1.0 mL/min and 0.7 mL/min, respectively. A similar trend is also observed for the addition of 5 mL gold chloride precursor (Figure 2C-D). In summary, the length of spikes can be tuned from < 10 nm to 130 nm by increasing the amount of gold precursor and decreasing the injection rate. As

observed in TEM images of all spiky nanoparticles, the cross-sectional diameter of nearly all vertices is 9 ± 3 nm. There are about 160 spikes per particle, as estimated from SEM images in Figure 2. The proposed method is a general protocol that can be applicable to other Ag nanoparticles. For example, we have synthesized spiky Ag-Au nanoparticles with Ag cubic core (Figure 3).

Figure 3. SEM image of Ag – Au spiky nanoparticles with cubic core. Inset shows the corresponding TEM image. The Au precursor added was 8 mL at 0.3 mM with injection rate of 0.7 mL/min.

The crystalline feature of the Ag – Au spiky nanoparticles is investigated by high resolution (HR)-TEM; an example is shown of a single spike from a SP130 spiky nanoparticle (Figure 4A). The spike exhibits high crystallinity, with distinctive lattice fringes observed over the entire longitudinal axis of the spike (Figure 4B). We measure several spikes, finding d -spacings at 2.4 Å, from Au (111) crystals.^{31,32} A detailed chemical analysis will be given in the section on the spike formation below.

The EELS spectra were obtained from inelastically scattered electrons due to electron-electron interactions. These spectra are useful to understand their physical, chemical and optical properties of the nanoparticles. Plasmonic modes of nanoparticles with nanometer spatial resolution are achieved using EELS. Recently, STEM EELS provided insights into the plasmonic properties of nanocross,³³ nanodumbbells,³⁴ prisms,³⁵ as well as fused colloidal networks.³⁶

Figure 4. (A) High resolution TEM images of single spike. (B) is the zoom in TEM image of dotted green box in (A).

The optical properties of the spiky nanoparticles are probed using monochromated EELS, one of the few tools available to probe and map the local electric field distribution near nanoparticles with nanometer resolution. EELS is done in scanning TEM (STEM) mode, where an electron probe is formed with a diameter of about 1 nm which is then scanned in a rectangular area of interest. The elastically scattered electrons are collected to

form high angle annular dark field (HAADF) STEM images, such as those in Figure 5A from a SP130 nanoparticle (edge length = 324 nm). Many of the inelastically scattered electrons on the other hand, are collected by the EELS detector, which measures the energy that they have lost during the local excitation of surface plasmons.³⁷⁻³⁹ Raster-scanning the probe in *x-y* direction over the entire nanoparticle yields a library of EELS spectra at nanometer spatial resolution. The loss intensities in three wide energy windows (each with 0.1 eV energy widths) are color-coded and presented in an EELS composite map in Figure 5B. Regions of high EELS intensity indicate the locations where these optical modes are most strongly active.

The plasmon oscillation frequency and amplitude are significantly modulated by the length of the spikes and the core of nanoparticles. Figure 5B shows that the plasmon energy strongly depends on the size of the spikes, with longer spikes absorbing at lower energies (longer wavelengths) and shorter spikes absorbing at higher energies (shorter wavelengths). Low energy modes also tend to be more delocalized; i.e. plasmon fields are distributed over longer distances for decreasing resonance energies. These localized and delocalized modes dominate the overall optical response from the spike nanoparticle. However, for the short spiky nanoparticle (SP10), the plasmon energy is localized at the core confirming earlier observations on star- and cross-shaped gold particles.^{40,41} For the EELS map at 0.75 eV (Figure 5C), the LSPRs of the long spikes are in resonance, where strong and intense field enhancements are localized at the tips of long spikes. From Figure 5D, we observe that shorter spikes are excited at slightly higher energy, i.e. ~ 1.05 eV. The general trend is that fast-oscillating, high energy modes are carried by short spikes and the core of the octahedral nanoparticle (Figure 5E), whereas lower-energy modes are distributed away from the core of the spiky nanoparticle and are localized at the tip of the long spikes.^{37,42}

Figure 5. (A) STEM HAADF image of a single spiky particle (SP130); (B) an EELS composite map from the same particle; monochromated EELS maps obtained from (C) 0.75 eV (blue), (D) 1.05 eV (red) and (E) 1.35 eV (green). (F) EELS spectra from whole particle, spikes of 50, 80, 120, and 137 nm in length, respectively, as indicated as locations (1 – 4) in the STEM image, showing the great variation in local optical response.

The averaged EELS spectrum of a single SP130 spiky nanoparticle is shown in Figure 5F – whole particle. A plasmon response from 0.5 – 1.8 eV (550 – 2700 nm) is observed, with a prominent low energy peak at 0.84 eV (1480 nm) and a less prominent shoulder peak at 1.1 eV (1127 nm), respectively. It should be noted that the EELS collection semi-angle is limited to about 7 mrad around the central, zero-degree diffraction spot. This means that all electrons that have scattered to high angles, such as the elastically scattered electrons that produce the HAADF STEM image, are lost for EELS analysis. Therefore, hardly any signal is obtained from the location of the particle core itself; plasmon information is gained only just off from the projected surfaces, in this case, the spikes. Absorption from the particle core itself is therefore very low. In this EELS analysis, we only focus on the effect of the spikes, and only indirectly on the effect that the (hollow) core has on the plasmon resonances.

The variation of plasmonic resonance with respect to spike length is studied using EELS. The spikes in Figure 5A (labeled 1, 2, 3, and 4) have lengths of 50, 80, 120, and 137 nm, respectively, and their respective EELS signals are revealed in Figure 5F. The EELS spectra collected from shorter spikes of 50 and 80 nm in lengths (location 1 and 2) exhibit energy loss of 1.16 eV and 1.08 eV, respectively. With increasing spike length, the surface plasmon resonances of spikes of 120 and 137 nm (location 3 and 4) shift to lower energy loss of 0.86 and 0.78 eV, respectively. In general, the EELS spectrum of individual spike exhibits a red-shift with increase of spike length. It is noted that the averaged spectrum has been broaden comparing with the individual spectrum obtained from specific spike's location, which can be attributable to the variation in spike's length within single spiky nanoparticle. Nevertheless, the prominent peak at 0.84 eV validates that the majority spikes' length in SP130 nanoparticle is in the range between 120 nm – 137 nm. In short, the EELS mapping and spectra have clearly demonstrated that the length of the spikes has significant influence over the oscillation frequency and amplitude of the

plasmons.⁴³ A small change in sub-wavelength dimensions can lead to local variations in light absorption.⁴⁴ Equipped with this knowledge and the ability to synthesize anisotropic spiky nanoparticles with morphologically controlled core and highly tunable spikes' length, we can design and fine-tune the plasmon resonance properties of the spiky nanoparticles with optimized light adsorption ranging from visible to NIR (550 – 2700 nm). This is an achievement that is otherwise not possible using Ag octahedral and Ag-Au cage nanoparticles.

The extinction properties of ensemble spiky nanoparticles are probed using UV-Vis-NIR spectroscopy (Figure 6). For Ag octahedral nanoparticles, a well-defined peak at 1200 nm, 823 nm and several other peaks in the region 400 – 600 nm have been identified as the dipolar, quadrupolar and higher order plasmon resonance modes, respectively.²⁹ Comparison of the UV-Vis-NIR extinction with simulated extinction will be discussed in the following simulation section. For Ag – Au spiky nanoparticles, the original quadrupolar mode peaks of the Ag octahedral nanoparticles are red-shifted to longer wavelength as the spikes' length increases. For example, short spiky nanoparticles (SP40) demonstrate a red shift in quadrupolar resonance mode at ~1015 nm (SP40 in Figure 6). The red-shift is resulted from the increase in the overall size of nanoparticles and the hybridization of gold spikes with the Ag-Au octahedral nanoparticles. As the growth of spikes continues to SP68 and SP130 nanoparticles, significant changes in extinction profile are observed. These particles exhibit a broad featureless plasmon mode, the extinction intensity onsets from 500 nm and gradually increases into the near infrared region. The individual features of spiky Ag octahedral nanoparticles are not observed. This is because UV-Vis spectroscopy is an ensemble measurement technique, where the local extinction spectrum obtained is averaged-out. Liz-Marzán et al. also reported the nature of the extinction broadening for their spiked gold beads.⁴⁵

Figure 6. (A) UV/Vis – NIR spectra of Ag octahedral nanoparticles, SP40, SP68 and SP130 of Ag-Au spiky nanoparticles.

Besides the extinction measurement, we used dark field microscope to observe the scattering color. Particles showed noticeable color change in scattered light as seen in the color images from single isolated particles, given in Figure 7. The color of the scattered light changes from yellow orange for Ag octahedral NPs to orange red for Ag – Au nanocages & shorter spikes (SP40) and finally red for longer (SP68) & longest spiked NPs

(SP130). The observed color changes, from yellow orange to red, of the scattered light were attributed to the surface plasmonic enhancement of oscillation. The strong scattering of red light from the spiky nanoparticles indicates presence of SPR with a frequency in the NIR region. This observation is in good agreement with observed extinction features from these particles, which showed a higher extinction in the NIR region.

Figure 7. SEM images on the top show particle shape and their corresponding real color darkfield images are shown at the bottom.

Hypothesis for the formation of spiky nanoparticles

XPS is used to determine the surface chemical composition of Ag-Au spiky nanoparticles. The high-resolution Ag 3d scan for the SP40 nanoparticles (Figure 8A) indicates two doublets from the spin-orbital splitting of Ag3d_{3/2} and Ag3d_{5/2} electron states.

Figure 8. XPS spectra of SP40 Ag-Au spiky nanoparticles in the region of (A) Ag 3d, (B) Au 4f, and (C) Cl 2p. (D) SEM, (E, F) Ag and Au EDS maps of spiky nanoparticle SP40. (G) Atomic percentages of samples SP40, SP50, SP68 and SP130 as obtained from EDS mapping analysis, respectively.

The main doublet at 373 eV and 367 eV, with intensity ratio of 2:3, corresponds to $\text{Ag}3d_{3/2}$ and $\text{Ag}3d_{5/2}$, respectively, confirming the presence of metallic Ag.^{47,48} The smaller doublet at 374 and 368 eV can be explained by the presence of small amounts of AgCl. The Au 4f scan (Figure 8B) reveals a doublet at 87.2 and 83.5 eV, with intensity ratio of 3:4, separated by ~ 3.7 eV, which is in good agreement with the characteristic of the metallic Au doublet spaced at 3.65 eV.⁵³ This observation confirms that spiky nanoparticles are bimetallic in nature.

In addition, we have performed a Cl 2p scan on SP40 spiky nanoparticles (Figure 8C) with bulk silver chloride crystals are used as a control experiment (Figure 9). Silver chloride crystals are made by the reaction of hydrogen chloride and silver nitrate in the presence of PVP as capping agent in ethylene glycol at 150 °C for 20 minutes.⁵⁴ In general, the observed Cl 2p feature from SP40 spiky nanoparticles can be deconvoluted into major peaks at 197, 198.6, and two minor peaks at 200.5, and 202 eV peaks. These four chloride peaks correspond to two types of Cl moieties. The peak at 197 eV and 198.7 eV are separated by ~ 1.60 eV, corresponding to Cl 2p₃ and Cl 2p₁ peaks respectively.⁵⁵ This is in good agreement with the Cl 2p spectrum of AgCl crystals (Figure 9A). The other minor peaks at 200.4 and 202 eV are attributed to NaCl's Cl 2p₃ and Cl 2p₁ peaks respectively, which could result from trace amount of NaCl in the nanoparticles solution after repeated washing with saturated NaCl solution to remove AgCl. The presence of NaCl is supported by the observation of Na 1s peak at 1070 eV in the survey scan (Figure 9B). The Na 1s peak can be greatly reduced by repeated washing with water.

To confirm the surface element and elemental distribution of our spiky nanoparticles, we performed EDS mapping on single SP40 nanoparticle (Figure 8D). The Au and Ag EDS maps (Figure 8E and F) are obtained from the peaks at 2.1 keV and 2.9 keV, which can be assigned to Au M α and Ag L α , respectively. In overview, the area of

Ag map is smaller compare to Au map. The majority of Ag mapping is confined to the octahedral core, and a small number of very short silver tips (Figure 8E, highlighted by arrows), suggesting the presence of protrusions in the form of silver compound on the surface of SP40. Whereas for gold EDS mapping (Figure 8F), in addition to the presence of gold on the octahedral core, large numbers of long gold spikes are found protruding from the core and expanding to the area unoccupied by Ag.

Figure 9. (A) XPS of AgCl at Cl 2p, (B) XPS survey scan of SP30 nanoparticles.

The EDS mapping analyses clearly indicates that the core of the spiky nanoparticles is composed of bimetallic Ag and Au, whereas the spikes are predominantly Au, with some very short silver tips at their base. The EDS elemental analysis using large area SEM indicates that the atomic percentage of gold on the surfaces of SP40 and SP50 nanoparticles is $13 \% \pm 1 \%$, whereas the surfaces of SP68 and SP130 contain $27 \% \pm 1 \%$ of gold (Figure 8G). The EDS analysis corresponds well to the amount of Au precursor added.

Based on the characterization results, we propose a hypothesis for the formation of these unique anisotropic spiky Ag–Au nanoparticles using a seed-mediated growth process aided by the use of high molecular weight PVP during the growth process (Scheme 1). We attribute the anisotropic growth process to the galvanic replacement

process because there is no additional reducing agent added during the growth process. In general, the reaction is initiated upon the addition of gold chloride precursor to the Ag nanoparticle solution. The differences in standard reduction potentials⁵⁶ of Ag and Au induce the diffusion of Ag atoms from their core and the oxidation of Ag^0 into Ag^+ ions, followed by the discharge of Ag^+ ions into the surrounding medium. Simultaneously, elemental gold is produced and deposited epitaxially onto Ag nanoparticles; free Cl^- ions are produced. The formation of Ag-Au nanocages with hollow interiors using galvanic replacement process has been extensively reported. To the best of our knowledge, the formation of spikes on Ag-Au nanocages via atypical galvanic replacement reactions has not yet been reported.

Scheme 1. Pictorial representation of hypothesized mechanism for the formation Ag-Au spiky nanoparticles.

We observe that the molecular weight of PVP used in the second step has a direct effect on the resulting morphology of the overgrown nanoparticles. When PVP of 55,000 g/mol is used for the overgrowth process, the color of the octahedral nanoparticle solution

changes from tan to brown. The Ag octahedral nanoparticles are transformed to Ag–Au nanocages (Figure 2A) via a typical galvanic replacement process. There is no spike or tip on the octahedral nanoparticles; the Ag–Au nanocages have average edge lengths of 292 ± 10 nm.

The uniqueness of our reaction is the use of high molecular weight PVP ($M_w = 360,000$ g/mol) to form spikes on Ag–Au octahedral nanocages. According to the Mark-Houwink equation, the viscosity of PVP with $M_w = 360,000$ g/mol reaction solution is about 3.6 times higher as compared to the typically used PVP of $M_w = 55,000$ g/mol.⁵⁷ We reason that this significantly reduces the mobility of free Ag^+ and Cl^- ions in the viscous PVP matrix. As a result, the probabilities of these free ions being trapped in close proximity to the surface of nanoparticles are higher. These ions subsequently react to form AgCl crystals, which are insoluble in aqueous medium and therefore likely to deposit on the surface through physical adsorption. The EDS mapping of single SP40 spiky nanoparticles (Figure 8 D – E) demonstrates the presence of short tips of Ag on the surfaces. Our hypothesis is further supported by XPS measurements. The detection of Cl moieties that are assigned to AgCl in the Cl 2p XPS spectrum (Figure 8C) can be explained by the deposition of AgCl crystals on the surfaces of growing gold.

As galvanic replacement continues, two sequential growths of Au occur on the surfaces of Ag nanoparticles simultaneously. Firstly, the typical epitaxial growth of Au onto surfaces of Ag nanoparticles. Secondly, AgCl crystals serve as foreign inclusions⁵⁸ and seeds that promote non-epitaxial growth of Au on AgCl sites. The epitaxial and non-epitaxial growth processes can be attributed to the lattice matching between Au and Ag ($d_{\text{Ag}} = 4.090$ Å and $d_{\text{Au}} = 4.080$ Å), and the huge lattice mismatch between Au and AgCl ($d_{\text{Au}} = 4.080$ Å and $d_{\text{AgCl}} = 5.5491$ Å), respectively. Note that the deposition of AgCl does not impede the diffusion of Ag from its core to the surface for galvanic replacement

reaction with the Au precursor. The observation of AgCl and/or AgBr deposition on growing gold nanoparticles has been previously reported by Murphy et al.⁵⁹ There have also been a few reports on the use of AgCl byproducts for the growth of Ag nanowires from AgCl nanocubes,⁶⁰ Au nanoneedles on Ag nanowires,⁶¹ and the synthesis of thorny gold nanoparticles.⁶²

Figure 10. SEM image of Ag – Au spiky nanoparticles after H_2O_2 etching. Inset shows the corresponding TEM image.

To further confirm the epitaxial and non-epitaxial growth Au, we selectively etched off Ag from SP40 nanoparticles (Figure 10) using H_2O_2 as Ag selective etchant. It is evident that after chemical etching, only a thin layer of Au in octahedral shape formed via epitaxial growth and spikes protruding on the surface from non-epitaxial deposition of Au are observed. With an increasing amount of gold precursor, the anisotropic growth of tapered gold spikes on AgCl continues, resulting in spiky nanoparticles of tunable spike length (Figure 2).

2.3 CONCLUSIONS

We developed a simple two-step seed-mediated growth method to synthesize spiky nanostructures from well-defined core nanoparticles with the help of a high molecular weight polymer. The length of the nanospikes can be controlled from 10 – 130 nm with sharp tips by varying the amount of Au added and by the injection rates, while the choice of the core material and size will retain the intrinsic plasmon response. Using monochromated EELS, the optical modes of these particles are spatially and spectroscopically resolved and shown to strongly modulate the plasmon absorption at low energies. With increasing spike length from 50 – 130 nm, surface plasmon of the spike can be tuned from 1.16 eV - 0.78 eV. The particles with long spike lengths showed notably higher intensities compared to that of short spikes; these particles will therefore be more efficient light absorbers in the NIR regime. The NIR absorbing characteristics of these particles can be used in the NIR band filters. From EELS, the electric field is delocalized on to the long spikes plasmon fields are distributed over longer distances. A red-shift in plasmon resonance is observed with increasing spike length. The ability of growing spikes with tunable length on any core nanoparticles presents great potential to tune the light-matter interactions at specific desired wavelength.

2.4 EXPERIMENTAL METHODS

Materials. Silver nitrate (99+ %), poly(vinyl pyrrolidone) (PVP, $M_w = 55,000$ and 360 K), anhydrous 1,5-pentanediol (≥ 97.0 %), gold (III) chloride trihydrate (≥ 99.9 %) were purchased from Sigma Aldrich; copper(II) chloride (≥ 98 %) was from Alfa Aesar; sodium chloride (99.5 %) was purchased from Goodrich Chemical Enterprise. All chemicals were used without further purification. Milli-Q water (> 18.0 M Ω .cm) was purified with a Sartorius arium 611 UV ultrapure water system.

Synthesis of silver octahedral nanoparticles. 0.20 – 0.40 g silver nitrate, 0.20 g PVP (Mw = 55 K) and 0.083 g of copper (II) chloride were dissolved in 10 mL pentanediol in a glass vial using an ultrasonic bath. In a temperature-controlled silicone oil bath, 20 mL of pentanediol was heated for 10 minutes at 190 °C. The two precursor solutions were then injected into the hot reaction flask at the following rates: 500 µL of the silver nitrate solution every minute and 250 µL of the PVP solution every 30 s. For cubes, this addition was continued for 16 min, while a duration of 60 minutes was required for octahedra. The nanoparticles were purified by vacuum filtration using different pore size filter membranes to exclude undesired particles.

Synthesis of spiky nanoparticles. In a typical synthesis, 1.5 mL of silver octahedral nanoparticles was dispersed in 12.5 mL of 9 mM aq. PVP (360K) solution under magnetic stirring and then heated at 95°C for 5 minutes. To this, a specific amount of 0.3 mM Gold precursor aqueous solution in the range of 1 – 8 mL was added using a syringe pump at a rate of 0.7 – 1 mL/minutes under magnetic stirring. The solution was heated for another 10 minutes and the cooled solution was centrifuged and washed with saturated NaCl solution to remove AgCl and with water to remove NaCl and PVP.

Measurement of particle size. The core size, length and width of the spikes of Ag - Au spiky nanoparticles were analyzed on the basis of SEM and TEM images using Nano Measurer analysis software (Department of Chemistry, Fudan University, China). The histograms are plotted by measuring at least 50 particles.

Characterizations. SEM images were obtained with a Jeol 7600F SEM operating at 5 kV in LBE mode. EDS was recorded on a Jeol 7600F at 20 kV. TEM images were obtained with a JEM-1400 (JEOL) transmission electron microscope operated at 100 kV while high-resolution (HR) TEM images were acquired using a JEOL-JEM-2100 electron microscope at an accelerating voltage of 200 kV. XPS spectra were measured using a

Phoibos 100 spectrometer with a monochromatic Mg X-ray radiation source. All XPS spectra were fit using XPS Peak 4.1 (freeware accessible at <http://www.phy.cuhk.edu.hk/~surface>). UV/Vis – NIR spectra were measured using SHIMADZU UV-3600 UV-VIS-NIR Spectrophotometer. EELS was performed in scanning TEM (STEM) mode using an FEI Titan TEM with Schottky electron source. The microscope was operated at 80 kV, and a STEM convergence semiangle of 13 mrad was used, forming a probe with a diameter around 1 nm. A Wien-type monochromator dispersed the electron beam in energy, and a narrow energy-selecting slit formed a monochrome electron beam with typical full-width at half-maximum values of 65 meV. A Gatan Tridiem ER EELS detector used for EELS mapping and spectroscopy, applying a 7 mrad collection semiangle. EELS was acquired with a modified binned gain averaging routine³⁷: individual spectra were acquired in 40 ms, using 16 times on-chip binning. The detector channel-to-channel gain variation was averaged out by constantly changing the readout location and correcting for these shifts after the EELS acquisition was finished. A high-quality dark reference was acquired separately, and used for post-acquisition dark signal correction. All spectra were acquired 1-2 nm off the metal surfaces. The quasi-elastic background signal was corrected for by fitting and subtracting a high-quality zero-loss peak spectrum without plasmon peaks. EELS mapping was done using the technique of Spectrum Imaging, where the small electron probe was scanned in a rectangular raster of pixels, while at each pixel an EELS spectrum is collected and stored. After data processing as described above, 0.1 eV energy windows around the plasmon peaks of interest were used to image the EELS intensity in each pixel in linear scale. The EELS intensity maps were color-coded and overlaid.

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Chapter 3

One-step Synthesis of Zero-dimensional Hollow Nanoporous Gold Nanoparticles with Enhanced Methanol Electro-oxidation Performance*

ABSTRACT. Np-Au with networks of interconnected ligaments and highly porous structure holds stimulating technological implications in fuel cell catalysis. Current syntheses of np-Au mainly revolve around de-alloying approaches which are generally limited by stringent and harsh multistep protocols. Here we develop a one-step solution phase synthesis of 0D hollow np-Au nanoparticles with tunable particle size (150 - 1000 nm) and ligament thickness (21 – 54 nm). With faster mass diffusivity, excellent specific electro-active surface area and large density of highly-active surface sites, our 0D np-Au nanoparticles exhibits ~1.4 times enhanced catalytic activity and improved tolerance towards carbonaceous species, demonstrating its superiority over conventional np-Au sheets. Detailed mechanistic study also reveals the crucial hetero-epitaxial growth of gold on the surface of silver chloride templates, implying that our synthetic protocol is generic and can be extended to the synthesis of other nanoporous metals via different metal-templates combinations.

* This chapter is based on the manuscript entitled “One-step synthesis of zero-dimensional hollow nanoporous gold nanoparticles with enhanced methanol electrooxidation performance.” By Srikanth Pedireddy, Hiang Kwee Lee, In Yee Phang, Weng Weei Tjiu, Hui Ru Tan, Shu Quan Chua, Cedric Troadec, and Xing Yi Ling, published in *Nature Communications*, **2014**, 5:4947.

3.1 INTRODUCTION

Np-Au structures are highly porous metallic structures characterized by their unique and comprehensive three-dimensional networks of nanoscale interconnected ligaments. These interconnected ligaments have curved surfaces dominated by highly active low-coordinated atoms, such as steps and kinks,^{1, 2, 3} that serve as excellent catalytic sites for chemical reactions.^{4, 5, 6, 7} Owing to the extensive porous networks, the diffusivity within np-Au is greatly enhanced which facilitates the mass transfer of reactants from exterior surface to the interior structure, significantly enhancing the catalytic reactions even at low temperatures.^{8, 9} Hence, np-Au structures have found potential applications in fuel cell, demonstrating remarkable catalytic activities towards various fuel cell reactions, such as oxidation of CO,^{10, 11, 12} methanol,¹³ ammonia borane,¹⁴ and hydrazine.¹⁵

Currently, most np-Au exists as 2D sheet-like structures fabricated using methods such as de-alloying,^{16, 17, 18, 19} self assembly,²⁰ template²¹ and electrochemical methods.²² In particular, the de-alloying approach is the most frequently used protocols, which can also be extended to other nanoporous metals/alloys such as copper,²³ silver,²⁴ palladium,²⁵ platinum,^{26, 27} Pt-Ru,²⁸ Pd-Pt^{29, 30} and Pt-Au.³¹ Erlebacher et al. pioneered in de-alloying Au_{32%}Ag_{68%} sheets into thin np-Au sheets, which exhibit characteristic 2D bicontinuous morphology and tunable pore size between 5 nm to 1 μ m.^{16, 17} However, such de-alloying approach is limited by its pre-requisite of >55 atomic% of silver to produce np-Au effectively and also restricted to the formation of 2D thin film np-Au with low surface area-to-volume ratio, which generally suffers from slow mass transfer of reactant and low density of catalytic sites.³²

Ideally, reducing the size of np-Au to 0D np-Au nanoparticle can further increases both its surface area-to-volume ratio and density of catalytic sites, boosting its catalytic performance over conventional 2D counterparts. Current synthesis of np-Au nanoparticles still mainly revolves around the de-alloying approach. For instance, Wang et al. reported

the synthesis of np-Au nanoparticles by de-alloying composite nanoparticles formed via thermal de-wetting of Au-Ag bilayer.³³ However, harsh reaction conditions, the need of at least 55 atomic% silver sacrificial template and the formation of poly-disperse nanoparticles that are strictly substrate-bounded greatly limit the practicality of such method for actual industrial application. While the reported catalytic activity of np-Au has been promising, we envisage that a simple and cost-effective strategy to synthesize mono-disperse free-standing nanoporous Au nanoparticle for superior catalytic performance is much needed to incorporate them to the existing membrane-based industrial fuel cell systems.

Here, we report the first solution-based, high-yield synthesis of free-standing hollow np-Au nanoparticles with tunable particle and ligament sizes. We will systematically characterize the morphology of our np-Au nanoparticles and provide a detailed mechanistic study on the formation of such nanoparticles. Methanol electro-oxidation activity, specific electro-active surface area and also tolerance towards carbonaceous species of various np-Au nanoparticles will be investigated thoroughly and their superiority over solid gold nanoparticles and conventional np-Au sheets will be demonstrated. The stability of our np-Au nanoparticles is also evaluated over > 400 catalytic cycles to demonstrate their suitability for future industrial applications.

3.2 RESULTS AND DISCUSSION

Synthesis of np-Au nanoparticles. We employ a one-step synthetic protocol to synthesize hollow np-Au nanoparticles using HAuCl₄ as precursor, hydroquinone as reducing agent, and PVP as surfactant in the presence of Ag⁺ ions. In a typical synthesis, 160 μ L of 28 mM hydroquinone solution, 60 μ L of 10 mM AgNO₃ solution and 100 μ L of 40 mM HAuCl₄ solution are added in sequence to a 4.5 mL of 90 mM PVP solution on gentle stirring at room temperature. The solution turns colorless immediately, changes to light green within the next 30 seconds, and eventually to reddish in 3 minutes. After that,

the solution is washed with concentrated NH_4OH to remove residual AgCl formed during the reaction, and purified by repeated centrifugations and re-dispersal in water.

Characterization of np-Au nanoparticles. SEM image indicates that the as-synthesized nanoparticles are spherical in shape but exhibit highly roughened surface with randomly interconnected curved ligaments, which resembles “gyri” ridges on human being’s brain (Figure 1A). Typically using the one-step synthesis, a yield of $> 90\%$ can be produced with monodisperse np-Au nanoparticle sizes of (150 ± 10) nm. A close inspection reveals a large number of nano-sized gaps in between the ligaments on the nanoparticles (Figure 1B). The surface texture of our nanoparticles is analogous to the 2D np-Au film made by de-alloying method.¹⁶ To the best of our knowledge, this is the first report on using solution-based approach to synthesize free-standing np-Au

Figure 1. Structural characterization of np-Au nanoparticles. SEM images of various sized np-Au nanoparticles (np-Au): (A, B) 150 nm, (C, D) 250 nm, (E, F) 350 nm, (G, H) 450 nm, (I, J) 550 nm, and (K, L) 650 nm in diameter. The size is tuned by varying the final concentration of hydroquinone from 0.4 mM to 1.3 mM while maintaining all other conditions during the synthesis. (A, C, E, G, I, K) Scale bars, 500 nm. (B, D, F, H, J, L) Scale bars, 100 nm.

nanoparticles. From here onwards, we will refer these particles as “np-Au 150”, where “np-Au” and the following number denote to “nanoporous gold nanoparticles” and their corresponding size in nanometer length scale, respectively. It is noteworthy that, comparing with conventional gold nanoparticles, our as-synthesized particles are highly porous in morphology. The reason for the formation of such porous structures will be discussed in details in the mechanism section. The np-Au with anisotropic morphology is expected to have a high surface area, which is particularly crucial for catalytic applications.

The size of the np-Au nanoparticles can be systematically controlled by varying the concentration of the reducing agent, hydroquinone. With increase in the final concentration of hydroquinone from 0.6 mM, 0.8 mM, 1 mM and 1.3 mM, np-Au particles with increasing average sizes of (246 ± 15) nm (Figure 1C - D), (350 ± 16) nm (Figure 1E - F), (448 ± 18) nm (Figure 1G - H) and (550 ± 14) nm (Figure 1I - J), respectively, are observed. We also notice the ligament thickness increases with the size of the nanoporous particles, i.e. from (21 ± 3) nm to (51 ± 8) nm for np-Au 150 and np-Au 550, respectively (Table 1).

Table 1. Summary of the structural properties of np-Au nanoparticles.

Sample	np-Au 150	np-Au 250	np-Au 350	np-Au 450	np-Au 550
Size (nm)	150	250	350	450	550
Ligament size (nm)	21 ± 3	23 ± 2	32 ± 4	41 ± 6	54 ± 8

Larger np-Au particle in the range of 650 - 1000 nm can be achieved by further increasing the concentration of hydroquinone and gold precursor used (Figure 2). For

instance, np-Au 650 (Figure 1K - L) with a ligament size of (54 ± 9) nm is synthesized by doubling the amount of hydroquinone and gold precursor during the synthesis.

Figure 2. Structural characterization of np-Au nanoparticles. SEM images of various sized np-Au nanoparticles (np-Au): (A, B) 720 nm, (C, D) 825 nm, (E, F) 950 nm, (G, H) 1000 nm in diameter. (A, C, E, G) Scale bars, 500 nm. (B, D, F, H) Scale bars, 100 nm.

We investigate the internal structure of np-Au nanoparticles by sectioning the np-Au using ultracut-microtome. Nanoparticles are casted in an epoxy, and sliced into a 100-nm thin section. Figure 3A shows a general morphology of microtome section of np-Au nanoparticles of size 550 nm, which clearly indicates the formation of a hollow nanoparticle. The periphery of the np-Au exhibits undulating curvatures and highly roughened surfaces, with occasional ligament protruding freely from the main body (see arrow in Figure 3A).

Figure 3. Internal structure of np-Au nanoparticles using electron microscopy characterization. (A) TEM image of a microtome-sectioned np-Au 550; the arrow indicates a free-standing ligament. (B) High resolution TEM image of a single ligament indicating the presence of step feature, dislocation, and atomic island. (C) Cross-sectional SEM image of a microtome-sectioned np-Au 550 nm. (D) Cross sectional SEM image of a FIB-sectioned np-Au 700 nm. Note that the hole at the centre, representing the hollow interior of our nanoparticle. (A, C, D) Scale bars, 100 nm. (B) Scale bar, 2 nm.

HRTEM image of a ligament offers insights into the atomic arrangement and morphology of the np-Au nanoparticles. In general, the ligaments possess concave

surfaces with high crystallinity. Characteristic lattice fringes are observed over the whole ligament. A d-spacing of 2.4 Å corresponding to face-centered cubic (fcc) Au (111) facet is measured (Figure 3B), indicating that (111) is the mostly exposed plane. Using the HRTEM images obtained (Figure 4); we determine an average crystallite size of (16.9 ± 4.2) nm for np-Au 550. A significant feature of ligament is that there are many zig-zag features on the exterior of the ligament demonstrating the presence of high density of atomic defects.

For example, we observe (111) terraces separated by atomic steps, which are probably stabilized by the trace amount of Ag along the edges of the ligaments.² In addition, we observe atomic layer islands (Figure 3B) even on the surface of the ligaments. It has been reported that the presence of high density atomic defects such as steps and kinks are the basis for the origin of high catalytic activity in gold catalyst.^{2, 34} Similarly, the presence of these features in our np-Au nanoparticles may aid the enhancement of the catalytic performance.

Figure 4. Internal structure of np-Au nanoparticles using electron microscopy characterization. (A,B,C,E) HRTEM image of np-Au nanoparticles showing grain size and grain boundaries, (D) HRTEM image of np-Au nanoparticles showing stepped and dislocation features on the single ligament. (F) Selected area electron diffraction pattern (SAED) of np-Au 550. (A, B, C, E) Scale bars, 5 nm. (D) Scale bar, 2 nm.

Furthermore, the high magnification SEM image of microtome-sectioned np-Au 550 demonstrates the entire body of our np-Au is formed entirely by interconnected ligaments (Figure 3C), with 3D porous network of pore size ranging from 3 to 30 nm. A

hole is visible at the centre of the particle, demonstrating its hollow interior. Similar hollow interior is also confirmed on FIB milled np-Au nanoparticle (Figure 3D).

Figure 5. Powder XRD of various np-Au nanoparticles and solid gold nanoparticle. Powder XRD patterns of np-Au 150 – 550 nanoparticles compared to that of solid gold nanoparticles of size 200 nm and the standard gold.

To resolve the crystallinity and structure of the bulk np-Au nanoparticles, powder XRD is employed. The XRD spectra for np-Au 150, 250, 350, 450, 550 are compared with the solid Au nanoparticles of size 200 nm (Figure 5). Five sharp diffraction peaks are observed for all the six samples at 38.3, 44.5, 64.7, 77.7, and 81.9 degree in the 2θ range of 20 – 85 degree, which are indexed to the {111}, {200}, {220}, {311}, and {222} reflections (Table 2) of fcc phase of metallic gold (JCPDS, card No. 04-0784). Among all,

the diffraction peak corresponding to the {111} plane at 38.3 degree is the most intense, which can be attributed to the large exposed area of the corresponding facets, whereas the remaining less intense peaks are associated to the less exposed facets. The relative intensities of diffraction peaks for all six samples differ with standard powder diffraction data. The intensity ratio of {200}:{111} diffraction is 0.34 for the as-prepared np-Au nanoparticles (Table 3), which is smaller than the 0.52 intensity ratio of the standard Au diffraction database. The result indicates our np-Au nanoparticles exhibit a preferred orientation along the {111} plane, whereas solid gold nanoparticles demonstrate random growth due to the differences in multiple relative intensities compared to standard Au data. In addition, the mean crystallite size is also calculated using the Scherrer equation owing to its influence on the properties of the metals, including strength and hardness. We would like to emphasize that although the Scherrer equation is largely based on cubic crystal model, the crystallite shape factor can be approximated to 0.9 in absence of shape information.^{36, 37} Using Scherrer equation and the full-width half maximum of the XRD peak at {111} plane,³⁸ the mean crystallite sizes are estimated at 13.1, 14.8, 14.8, 14.6 and 14.6 nm for np-Au 150 – 550, respectively (Table 4), consistent with the thickness of the ligaments measured from HR-TEM (Figure 3 and Figure 4).

Table 2. Calculation of lattice constants.

2 θ	$\sin^2\theta$	$1 \times \sin^2\theta / \sin^2\theta_{\min}$	$2 \times \sin^2\theta / \sin^2\theta_{\min}$	$3 \times \sin^2\theta / \sin^2\theta_{\min}$	$h^2+k^2+l^2$	hkl	a (Å)
38.3	0.107	1	2	3	3	111	4.067
44.5	0.142	1.327	2.654	3.981	4	200	4.075
64.7	0.286	2.673	5.346	8.019	8	220	4.072
77.7	0.393	3.673	7.346	11.019	11	311	4.074
81.8	0.429	4	8	12	12	222	4.073

$$a = (\lambda/2\sin\theta) \times \sqrt{(h^2 + k^2 + l^2)}$$

Copper source, $\lambda = 1.5406 \text{ \AA}$

Average $a = 4.0722 \text{ \AA}$

Table 3. Comparison of diffraction peaks. Relative intensities of diffraction peaks compared to standard powder diffraction data.

	Standard	np-Au 150	np-Au 250	np-Au 350	np-Au 450	np-Au 550	Solid Au 200
111							
200	0.52	0.34	0.36	0.35	0.34	0.33	0.34
220	0.61	0.51	0.55	0.53	0.58	0.52	0.34
311	1.12	1.02	1.02	0.98	0.98	0.94	1.17
222	0.33	0.33	0.31	0.32	0.34	0.37	0.48

Table 4. Calculations of crystallite size.

Sample	FWHM	Crystallite size (nm)
np-Au 150	0.672	13.08
np-Au 250	0.595	14.76
np-Au 350	0.593	14.82
np-Au 450	0.603	14.57
np-Au 550	0.603	14.56
Solid Au-200	0.499	17.59

Elemental composition and distribution of np-Au particles. XPS is used to determine the surface composition, both in terms of elements and oxidation states, of the as-synthesized np-Au nanoparticles. The high-resolution Au 4f scan (Figure 6a) for np-Au 150 reveals a doublet at 87.2 and 83.5 eV, with intensity ratio of 3:4, separated by ~ 3.7 eV, confirming the presence of zero-valent gold in np-Au nanoparticles. The high-resolution Ag 3d scan (Figure 6B) indicates two weak binding energy peaks at 373.5 eV and 367.5 eV, which can be attributed to the spin-orbital splitting of $\text{Ag}3d_{3/2}$ and $\text{Ag}3d_{5/2}$ electron states with intensity ratio of 2:3. This confirms the presence of silver in its elemental form. Based on the XPS results, an atomic ratio of 95:5 for Au:Ag is measured, affirming that np-Au nanoparticles are mostly made from gold with trace amount of silver. The atomic percentage of silver decreases from the initial stoichiometric of 13% to 5% may be due to the removal of silver entity from the final product, probably as silver chloride.

Figure 6. Elemental composition and distribution within the np-Au nanoparticles. XPS analysis of np-Au 150 at (A) Au 4f and (B) Ag 3d binding energy windows, respectively. (C) EDS elemental mapping of a microtome-sectioned np-Au nanoparticles indicating the Au and Ag elemental distribution, and (D) The corresponding EDS elemental spectrum of np-Au 550 (C) Scale bars for all, 100 nm.

We also perform EDS analyses to determine the distributions of gold and silver in the microtome section of np-Au 550 nm. The Au and Ag EDS maps are acquired from the peaks at 2.1 and 2.9 keV (Figure 6D), which can be assigned to Au M α and Ag L α , respectively. The EDS mapping (Figure 6C) clearly shows that gold is homogeneously distributed on the whole surface of np-Au 550, whereas only trace amount of silver is

present, which could be used to stabilize the curved surfaces.³⁹ EDS elemental spectra (Figure 6D) further confirms that the np-Au 550 is predominantly gold (99 atomic%) with residual silver (1 atomic%). From the higher silver percentage measured using XPS, we therefore suggest that silver is predominantly present on the nanoparticle surfaces to stabilize the low-coordinated gold atoms because XPS is a surface sensitive technique, whereas EDS of a cross-sectioned np-Au measures the overall silver percentage.

Mechanistic study on the formation np-Au. To better understand the formation process of np-Au nanoparticles, we monitor the evolution of the morphology of the nanocrystals over time (Figure 7 and Figure 8). In the absence of hydroquinone, the addition of AgNO₃ and HAuCl₄ to PVP solution results in a color change from yellowish to whitish yellow (inset of Figure 8A), indicating a reaction has taken place. From SEM, particles with cubic morphology of an approximate average size of 230 nm are observed (Figure 8A). These cubic particles are highly unstable and tend to decompose under electron beam. The reaction is hypothesized to be: $\text{AuCl}_4^- + 4 \text{Ag}^+ \rightarrow \text{Au}^{3+} + 4 \text{AgCl}$.

Figure 7. Mechanism of np-Au formation and electron microscopy characterization. (A, B, C) A schematic synthetic route for the formation of hollow np-Au nanoparticles using AgCl as sacrificial template. (D, E, F) The representative SEM images obtained at the

corresponding stages during the formation of np-Au nanoparticles. (D, E, F) Scale bars, 200 nm.

Our hypothesis is confirmed by the XPS elemental composition measurement of these particles which clearly indicates the presence of Ag^+ and Cl^- (Figure 8A). We also note a smaller doublet presents in the Ag scan, which is attributed to the presence of metallic silver due to the photoreduction of $\text{Ag}^+ \rightarrow \text{Ag}^0$ under electron beam.

Figure 8. Mechanism of np-Au nanoparticles formation and representative electron microscopy and XPS characterizations. The formation process of np-Au nanoparticles is monitored over time. SEM images, camera images, and XPS spectra (Ag 3d, Cl 2p and

Au 4f) of the particles obtained at (A) 0 μL of hydroquinone, (B) 20 μL of hydroquinone, (C) 160 μL of hydroquinone, (D) SEM image after removal of AgCl from sample C using NH_4OH , (E) table summarizing composition of samples A-C.

Upon the addition of 20 μL of hydroquinone into the above reaction mixture, nucleation of asymmetric (plate-like and spherical shape) particles onto the AgCl nanocrystals are observed (Figure 7D). These particles are identified as metallic Au nanoparticles with atomic ratio of $\text{Au}:\text{Ag}^+$ of 2:98 (as evident from XPS results in Figure 8B and 8E). We did not observe the formation of individual Au nanoparticles. This is probably because the heterogeneous growth of gold on the pre-formed AgCl seeds is energetically more favorable than the homogeneous nucleation of gold nanoparticle.

Further increasing the amount of hydroquinone leads to continual growth of gold on AgCl sacrificial template. In the meantime, the aqueous phase color gradually turns red (inset of Figure 8C). In addition, the originally asymmetric nanoparticles are transformed into ligament structures, indicating Ostwald ripening has occurred upon further addition of reducing agent (Figure 7E). Correspondingly, the atomic ratio of $\text{Au}:\text{Ag}^+$ also increases to 90:10 (Figure 8C and 8E). After treating the nanoparticle solution with NH_4OH solution, we observe a cavity of size about 200 nm at the centre of the particles (Figure 8D), which is consistent with the width of AgCl template (~ 200 nm). The result therefore clearly demonstrates that AgCl sacrificial template can be easily removed to form the hollow np-Au nanoparticles (Figure 7F). This observation is further confirmed by a decrease in Ag^0 to 5 atomic%, giving an overall Au:Ag ratio of 95:5 as quantified using XPS (Figure 6A, B).

Electrochemical performance of np-Au versus solid particles. The facets on the curved ligaments on our np-Au nanoparticles contain high density of low-coordinated atoms (Figure 3B), which are ideal catalytically active sites. In the following sections, we perform electro-oxidation of methanol as a model reaction to examine the catalytic

activity of our np-Au nanoparticles. We begin by comparing the CV of np-Au 250 nanoparticles with solid Au nanoparticles of ~ 250 nm and 30 nm, which are denoted as Au 250 and Au 30 from now onwards, in 2 M methanol and 0.5 M KOH solution (Figure 9A). The Au 250 resembles the macroscopic size of np-Au 250, whereas Au 30 resembles the ligament size of the np-Au 250.

In the presence of 2 M methanol in 0.5 M KOH solution, np-Au 250, solid Au-30 and solid Au-250 nanoparticles exhibit the characteristic methanol electro-oxidation behavior. For np-Au 250, an instant surge in current is observed from -0.15 V (versus Ag/AgCl) onwards in positive potential scan (Figure 9A). It peaks at 0.19 V, and reaches a maximum current of $16.8 \mu\text{A } \mu\text{g}^{-1}$, which corresponds to the oxidation peak of methanol.⁴¹ In the negative sweeping scan, the reduction peak is observed 0.14 V, indicating the reduction of Au-OH species to Au. A second oxidation peak observed at 0.01 V in the reverse scan is attributed to the removal of the incompletely oxidized carbonaceous species formed in the forward scan.⁴¹

Figure 9. Electrochemical performance of nanoporous versus solid gold nanoparticles. The catalytic methanol electro-oxidation measurements in the form of (A) cyclic voltammograms and (B) chronoamperograms of np-Au 200, solid Au-30, and solid Au-200 nanoparticles in deoxygenated solution of 0.5 M KOH and 2 M CH₃OH. The

chronoamperograms were collected at the peak methanol oxidation of the corresponding nanoparticles, i.e. 0.19 V, 0.22 V and 0.25 V for 120 min for np-Au 200, solid Au-30 and solid Au-200 modified electrodes, respectively. (C) Oxide stripping curves of the np-Au 200, solid Au-30 and solid Au-200 modified electrodes at a scan rate of 5 mV s⁻¹ in 0.5 M H₂SO₄ electrolyte.

On the other hand, solid Au 30 and Au 250 nanoparticles exhibit much reduced methanol oxidation peak with current of 8 $\mu\text{A } \mu\text{g}^{-1}$ and 0.6 $\mu\text{A } \mu\text{g}^{-1}$, at relatively higher oxidation potentials of 0.22 V and 0.25 V, respectively. The respective gold oxide reduction peaks of Au 30 and Au 250 are observed at 0.16 V and 0.20 V. This result indicates our np-Au nanoparticles exhibit a 2 and 28 times more superior catalytic activity towards methanol oxidation as compared to its solid counterparts. Such enhanced electrochemical activity of our np-Au nanoparticles is remarkable, especially when comparing with solid Au nanoparticles of 30 nm whose size is equivalent to the ligament's dimension. In addition, on the basis of electro-oxidation of methanol (1 M) under alkaline media (0.5 M KOH), our np-Au 250 exhibits 1.35 times higher catalytic activity (117 $\mu\text{A cm}^{-2}$) and improved tolerance towards carbonaceous species ($I_F/I_b = 2.5$) when compared to conventional np-Au sheets (88 $\mu\text{A cm}^{-2}$ and $I_F/I_b = 3$) (Figure 10B).⁴² We attribute the superior catalytic performance of our np-Au to the high density of highly-active low-coordinated atoms present on the interconnected network of ligaments which are densely distributed over the entire hollow spherical nanoparticles. Furthermore, the highly porous network of ligaments and large surface area-to-volume ratio of 0D nanoparticles facilitates the diffusion and mass transfer of electrolyte to the catalytically-active surface for reaction.

To affirm that the high electro-activity and characteristic oxidation peak are due to np-Au nanoparticles and oxidation of methanol respectively, we conduct similar CV studies in the absence of methanol and in blank glassy carbon electrode. In the absence of

methanol, the CV of np-Au 250 exhibits a single broad oxidation peak in the potential range between + 0.30 to 0.50 V, indicating the formation of surface Au oxide by the adsorption of OH⁻ ions (Figure 10A). In the negative sweeping scan, a reduction peak at 0.05 V, corresponding to Au oxide reduction is observed.⁴³ When using glass carbon only electrode, no characteristic oxidation peak is observed even in the presence of methanol (Figure 10A), indicating that the catalytic electro-oxidation effect is solely originating from the np-Au nanoparticles (Figure 10A).

One of the problems concerning the catalytic methanol electro-oxidation is the adsorption of poisoning intermediate carbonaceous species on catalysts' surfaces,^{44, 45} which will deactivate the catalysts' surface from further oxidation. The catalyst tolerance to the poisoning species in gold is often evaluated using the ratio of the forward anodic peak current (I_f) to the backward anodic peak current (I_b).⁴⁴ A high I_f/I_b value signifies poor capability of catalyst to remove incompletely oxidized carbon species from the surface. On the contrary, a lower I_f/I_b value indicates the improved performance to eliminate residual carbon species via oxidation in the reverse scan. Our np-Au 250 is observed to have the lowest I_f/I_b of 2.4, as compared to 6.7 and 9.4 of Au 30 and Au 250 (Figure 9A), respectively. Thus, np-Au 250 is expected to eliminate residual carbon species more readily and have prolonged electro-catalytic performance in comparison to Au 30 and Au 250.

Figure 10. CV at various electrochemical set-up. (A) Cyclic voltammograms of np-Au nanoparticles and blank glassy carbon in deoxygenated solutions containing 0.5 M KOH with and without 2 M CH₃OH. (B) CV of np-Au 250 in deoxygenated solutions containing 0.5 M KOH and 1 M CH₃OH. All scan rates are 20 mV s⁻¹.

To evaluate the long term electro-catalytic performance and tolerance of np-Au catalysts, we study the chronoamperograms of the np-Au 250, solid Au 250 and Au 30. The current – time response of the np-Au 250, Au-30 and Au-250 are recorded at a 0.19 V, 0.22 V and 0.25 V, which correspond to their respective peak oxidative currents (Figure 9B). np-Au 250 exhibits a gradual decrease in current, reaching steady state at 2.6 $\mu\text{A } \mu\text{g}^{-1}$ after 60 min, whereas the current of solid Au-30 and Au-250 nanoparticles decrease exponentially and diminish to 0.5 and 0 $\mu\text{A } \mu\text{g}^{-1}$ after 60 min. The rapid decreases of the current in Au-30 and Au-250 is mainly due to the higher tendency for the accumulation of carbonaceous intermediates that deactivates catalytic sites, as observed from their respective high I_f/I_b values of 6.7 and 9.4 determined previously. Hence, both

the comparison of chronoamperometry and I_f/I_b ratio collectively exemplify the superior stability and activity of our np-Au 250 nanoparticles as a catalyst over solid Au nanoparticles.

The electrochemical active surface area of np-Au 250, solid Au-30 and Au-250 nanoparticles are estimated by performing an electrochemical gold oxide stripping reaction in 0.5 M H_2SO_4 aqueous solution at a scan rate of 5 mV s^{-1} in room temperature (Figure 9C). The np-Au nanoparticles exhibit a lower oxidation peak around 1.1 V as compared to solid Au-30 and Au-250 nanoparticles (1.2 V), indicating that surface atoms on our np-Au nanoparticles are easier to oxidize. From these CVs, we estimate the electrochemically active surface areas by integrating the area of the gold oxide reduction curve near 0.9 V and assuming a specific charge of $450\text{ }\mu\text{C cm}^{-2}$ for the gold oxide reduction.⁴⁶ Electro-active surface areas of $8.91\text{ m}^2\text{ g}^{-1}$, $4.80\text{ m}^2\text{ g}^{-1}$ and $0.25\text{ m}^2\text{ g}^{-1}$ are obtained for np-Au 250, solid Au-30 and Au-250 catalysts, respectively (Table 5). That is, our np-Au nanoparticles are able to provide at least 2 and 36 times higher specific electro-active surface area for catalysis as compared to solid Au-30 and Au-250 nanoparticles, respectively. The superiority of our np-Au 250 is therefore a clear demonstration on the necessity of both nano-porosity and also large and extensive network of nanoscale ligaments, with high density of low-coordinated active surface Au atoms, to provide large electro-active surface area (Figure 3B).

Table 5. Summary of the structural and electrochemical properties of np-Au nanoparticles. The electrochemical active surface area of various np-Au nanoparticles as compared to their solid counterparts, as estimated by assuming a monolayer of O₂ is adsorbed on the gold surface, and the charge associated for oxide stripping is 450 $\mu\text{C cm}^{-2}$.

Sample	np-Au 150	np-Au 250	np-Au 350	np-Au 450	np-Au 550	Solid Au-30	Solid Au-250
Size (nm)	150	250	350	450	550	30	250
Ligament size (nm)	21 $\pm$ 3	23 $\pm$ 2	32 $\pm$ 4	41 $\pm$ 6	54 $\pm$ 8	-	-
Electro-active surface area (m^2g^{-1})	9.12	8.91	7.7	7.28	6.79	4.80	0.25

Size dependent electrochemical performance of np-Au. In the following section, the size-dependent methanol oxidation of np-Au nanoparticles of size ranges from 150 nm – 550 nm are performed (Figure 11A, Table 6). A clear size-dependency of maximum current and the onset potential are observed for np-Au nanoparticles of all sizes. In the oxidative scan, a negative shift in onset potential from -0.10 V to -0.13 V is observed with decreasing nanoporous Au nanoparticle size from 550 nm to 150 nm (Figure 11B). Earlier onset potential of 0.03 V observed in np-Au 150, when compared to np-Au 550, indicates that methanol is easier to be oxidized on nanoporous Au nanoparticles of smaller sizes which we attribute to the higher electro-active surface area available in np-Au 150. The greater ease of methanol oxidation on small nanoparticle sizes is again supported by the 1.2 times higher peak methanol oxidation current, a parameter indicative of reaction rate, using np-Au 150 (17 $\mu\text{A } \mu\text{g}^{-1}$) than that of np-Au 550 (15 $\mu\text{A } \mu\text{g}^{-1}$, Figure 11C). Furthermore, during a reduction scan, we observe a shift of the Au-OH reduction peak at 0.13 V to 0.17 V and also a decrease of current from -0.7 $\mu\text{A } \mu\text{g}^{-1}$ to -0.3 $\mu\text{A } \mu\text{g}^{-1}$ when particle sizes increase from np-Au 150 to np-Au 550. The reduced Au-OH reduction peak

current with particle sizes indicates a decrease in the extent of Au-OH to Au conversion, which can be explained by the higher coverage of hydroxide species on np-Au 150 as a consequence of larger electro-active surface area present when compared to np-Au 550. We would like to emphasize that mass-normalized current is discussed instead of surface area-normalized currents to clearly exemplify the importance of high specific electro-active surface area and large mass diffusivity associated with smaller 0D nanoporous Au nanoparticles (refer to Figure 11F for detailed illustration).

To investigate the size-dependent long-term electro-catalytic performance and tolerance of np-Au catalysts in methanol oxidation reaction, we monitor the chronoamperograms of the np-Au 150 to 550 nm at their oxidation potentials for 2 hr (Figure 11D, Table 6). In general, the current for methanol oxidation shows a gradual decay during first 25 min, attributed to the accumulation of poisonous intermediate species before reaching a steady state after 60 min.⁴⁷ Particularly, the np-Au 150 modified electrode exhibits the highest initial current and slowest current decay compared to electrodes using np-Au nanoparticles of larger size. In addition, the oxidation current of np-Au 150 is still noticeably higher ($2.52 \mu\text{A } \mu\text{g}^{-1}$) than other sizes even after extended reaction duration of 2 hours. Hence, the results indicate a better tolerance and stability of np-Au 150 towards methanol oxidation reaction compared to larger nanoparticle sizes. The superior stability of np-Au 150 is again supported by its I_f/I_b ratio of 2.4, which is the lowest among all the nanoparticle sizes analyzed (Table 6) and also an indication of improved tolerance towards residual carbon species compared to commercial Pt/C catalyst.⁴⁴

Figure 11. Size dependent electrochemical performance of np-Au nanoparticles. Comparison of (A) cyclic voltammograms, (B) onset potential and (C) peak methanol oxidation current activity of np-Au nanoparticles size from 150 nm to 550 nm. The methanol oxidation reactions were performed at a scan rate of 20 mV s^{-1} in deoxygenated solutions with 0.5 M KOH and 2 M CH_3OH . (D) Chronoamperograms of np-Au 150 – 550 modified electrodes at their corresponding peak oxidation potentials for 120 min. (E) Geometric current density normalized over geometric surface area (0.07 cm^2). (F) Specific current density normalized over electro-active surface area of np-Au nanoparticles size from 150 nm to 550 nm. (G) Oxide stripping curves of the np-Au 150 – 550 modified electrodes at a scan rate of 5 mV s^{-1} in 0.5 M H_2SO_4 electrolyte.

Table 6. Summary of onset potential, peak potential and mass activity for methanol oxidation as a function of np-Au nanoparticles' sizes.

Sample	Onset potential (V)	Potential (V)	Mass activity ($\mu\text{A } \mu\text{g}^{-1}$)	I_f/I_b
np-Au 150	-0.130	0.186	16.96	2.4
np-Au 250	-0.127	0.187	16.84	2.5
np-Au 350	-0.127	0.198	16.25	2.9
np-Au 450	-0.119	0.206	15.50	3.7
np-Au 550	-0.119	0.214	14.87	3.9
Solid Au-30	-0.090	0.222	7.96	6.7
Solid Au-250	-0.061	0.245	0.58	9.4

The electrochemical active surface areas of various sized np-Au nanoparticles are estimated by performing electrochemical gold oxide stripping reactions (Figure 11G). Our np-Au nanoparticles typically exhibit a constant oxidation peak around 1.1 V for all particle sizes and the corresponding electro-active surface areas for np-Au 150, 250, 350, 450 and 550 nm catalysts are calculated at $9.1 \text{ m}^2 \text{ g}^{-1}$, $8.9 \text{ m}^2 \text{ g}^{-1}$, $7.7 \text{ m}^2 \text{ g}^{-1}$, $7.3 \text{ m}^2 \text{ g}^{-1}$ and $6.8 \text{ m}^2 \text{ g}^{-1}$, respectively (Table 5). The oxidation peak potential using our np-Au nanoparticles is lower compared to reported concave gold nanocubes (1.2 V),⁴⁸ tetrahedral gold nanoparticles (1.18 V) and octahedral gold nanoparticles (1.35 V),⁴⁹ indicating that surface atoms on our np-Au nanoparticles are easier to oxidize and hence more catalytically active. It is also noted that all our np-Au nanoparticles exhibit higher electro-active surface compared to 2D np-Au sheets ($6.4 \text{ m}^2 \text{ g}^{-1}$),⁴⁶ with our best performing np-Au 150 demonstrating at least 1.4-fold higher catalytic surface area. That

is, our np-Au 150 can potentially provide at least 1.4-fold improved electro-catalytic performance compared to 2D np-Au sheets fabricated via de-alloying approach, emphasizing the importance of 0D particles, and the presence of hollow interiors and porous surfaces for enhanced catalytic activities.

Figure 12. Electrochemical performance of np-Au nanoparticles over 400 repetitive electro-catalytic cycles. Repetitive potential cycling in deoxygenated solutions containing 0.5 M KOH and 2 M CH₃OH at a scan rate of 50 mV s⁻¹ for 480 cycles.

In order to meet the requirements for actual fuel cell applications, we also evaluate the stability of our best-performing np-Au 150 through multiple electro-catalytic cycles of methanol oxidation. np-Au 150 exhibits highly stable current over 100 and 480 cycles, with the retention of at least 95 % and 64 % of electro-catalytic performance respectively (Figure 12).

Figure 13. Electron microscopy characterization of np-Au nanoparticles during repetitive electro-catalytic cycles. SEM images showing the morphological change over repetitive cycling in deoxygenated solutions containing 0.5 M KOH and 2 M CH₃OH after (A) 0, (B) 100 and (C) 480 cycles. (A, B, C) Scale bars, 200 nm.

It is noteworthy that no obvious change in morphology is observed for the first 100 cycles (Figure 13B and Figure 14). The ligaments on the surface only starts to appear coarsened and smoothened after an extended 480 electro-catalytic cycles which is potentially the cause of the observed decrease of electro-catalytic performance from 95 % to 64 % (Figure 13C). This smoothening of surface is attributed to the surface reconstruction experienced by np-Au nanoparticles during repeated CV scan.^{50, 51} Notably, particles possess hollow interiors with coarsened ligaments even after extended electrocatalytic cycles. Coarsening of ligaments is expected to increase the crystallinity in np-Au. Nevertheless, the highly reproducible and superior electro-catalytic performance of our np-Au nanoparticles, together with the ease of incorporation to existing membrane-based fuel cell systems, will enable it as an attractive candidate for actual fuel cell application.

Figure 14. Elemental composition of np-Au nanoparticles at various experimental stages. XPS spectra of (i) as-synthesized np-Au 150, (ii) after piranha washing and (iii) electro catalytic measurements in the regions of (A) Ag 3d and (B) Au 4f.

3.3 CONCLUSIONS

We have developed a synthetic approach to synthesize 0D hollow np-Au nanoparticles through a novel one-step solution phase method at room temperature. The mean size of our np-Au nanoparticles can be systematically controlled between 150 – 1000 nm by varying the concentration of hydroquinone. Using HRTEM, we identify the presence of high density of steps and kinks along the curved surface on the ligaments, whose width can be in turn tailored between (21 ± 3) nm and (54 ± 9) nm. The formation process for the np-Au is studied in detail using SEM and high resolution XPS, with the critical step for the formation of np-Au being the hetero-epitaxial growth of Au on the surface of AgCl. The importance of small 0D nanoporous nanoparticles is clearly demonstrated by the enhanced electro-catalytic performance and improved tolerance to carbonaceous species during methanol oxidation with the decrease of the size of np-Au nanoparticles. Our np-Au nanoparticles exhibit at least 1.4 times higher catalytic activity compared to

conventional solid Au nanoparticles and existing np-Au sheets. Our synthetic protocol is also generic and can be extended to different metal/templates to further tailor the thickness of ligament, porosity and ultimately, enhancing catalytic activities. With the ensemble of benefits, our np-Au nanoparticles and synthetic methodology are expected to have a strong impact in the area of fuel cell development, where scalable synthesis, high catalytic performance, and easy transition from lab-based system to industrial application are crucial.

3.4 EXPERIMENTAL METHODS

Materials. Silver nitrate (99+ %), poly(vinyl pyrrolidone) (PVP, $M_w = 10\text{ K}, 29\text{ K}, 40\text{ K}, 55\text{ K}, 360\text{ K}$ and 1300 K), hydroquinone($\geq 99\%$), sulfuric acid (95-97%) were purchased from Sigma Aldrich; ammonia solution (25%) was obtained from Goodrich Chemical Enterprise; ethanol (ACS, ISO, Reag.) and methanol were purchased from EMSURE®. All chemicals were used without further purification. Milli-Q water ($> 18.0\text{ M}\Omega\cdot\text{cm}$) was purified with a Sartorius arium611 UV ultrapure water system.

Synthesis of hollow np-Au nanoparticles. In sequence, $160\text{ }\mu\text{L}$ of 28 mM hydroquinone solution, $60\text{ }\mu\text{L}$ of 10 mM AgNO_3 solution and $100\text{ }\mu\text{L}$ of 40 mM HAuCl_4 solution were added to 4.5 mL of 90 mM PVP solution on gentle stirring at room temperature. Np-Au nanoparticles from 250 to 550 nm are synthesized by increasing the final concentration of hydroquinone from $0.6 - 1.3\text{ mM}$ respectively. The mixture was kept stirring for 3 min as the color of the solution changed from colorless to greenish to reddish brown. The solution was kept undisturbed for 30 min . After that, the solution is washed with concentrated NH_4OH to remove residual AgCl formed during the reaction, and purified by repeated centrifugations at 5000 rpm for 5 min and re-dispersal in water.

Synthesis of solid 30-nm gold nanoparticles. 0.5 mL of ascorbic acid (28 mM) was added to an aqueous solution containing 180 mM PVP and 0.5 mM HAuCl_4 on rigorous

stirring. The color of the solution turned from colorless to red immediately indicating the formation of nanoparticles.

Synthesis of solid 200-nm gold nanoparticles. 200 nm gold nanoparticles were prepared through the one-step seed mediated process using 30 nm gold seeds. Briefly, 100 μL of the as-synthesized 30 nm seed particles was added to a 10 mL growth solution containing 55 mM CTAB, 25 mM HAuCl_4 and 4 mM ascorbic acid. The solution was kept undisturbed for 1 hour at room temperature. The product was then collected by centrifugation at 6000 rpm for 5 min.

Measurement of particle size. The sizes of the np-Au nanoparticles were analyzed on the basis of SEM images using Nano Measurer analysis software (Department of Chemistry, Fudan University, China). The histograms were plotted by measuring at least 100 particles.

Piranha treatment of np-Au nanoparticles. Np-Au nanoparticles are treated with piranha solution (3:1 mixture of concentrated H_2SO_4 and 30% H_2O_2) to remove the PVP on the surface of the nanoparticles. Briefly, 5 mL of piranha solution was added to the aqueous solution containing np-Au nanoparticles and solution was undisturbed for 30 min prior to centrifugation at 6000 rpm for 5 min. The particles were further washed three times to remove trace amounts of acid and re-dispersed in ethanol followed by vacuum drying to collect the np-Au particles before conducting of the electrochemical measurements.

Np-Au modified electrode preparation. 1mg of np-Au sample was suspended in a solution containing 1mL ethanol by ultra-sonication. 1 μL of the suspension was drop-casted on glassy carbon electrode surface. The electrode was air dried for 1 hour at room temperature before use.

Electrochemical measurements. Electrochemical measurements were carried out using Metrohm Auto lab potentiostat instrument. Three electrodes configuration was employed.

The working electrode used was np-Au nanoparticles modified glassy carbon electrode, a leak-free saturated Ag/AgCl electrode as reference and the counter electrode was a Pt wire. 0.5 M KOH solution was used as an electrolyte.

Estimation of electrochemical surface area. The electrochemical active surface area of various sized np-Au nanoparticles and solid Au nanoparticles were estimated using CV. The surface redox behavior of the np-Au nanoparticles and solid Au nanoparticles were characterized using CV in 0.5 M H₂SO₄ aqueous solution at a scan rate of 5 mV s⁻¹ in room temperature. The electrochemical active surface area is estimated from the equation of $Q_o = 2eNA\Gamma_oA$, where Q_o is the charge passed during reduction of gold oxide was calculated by integration of the gold oxide reduction peak. The specific charge equivalent of 450 $\mu\text{C cm}^{-2}$ was used for converting the charge passed during the gold oxide reduction to a total surface area ($A = Q_o/450$), which was then divided by the mass of the np-Au electrode in order to obtain a specific surface area per unit mass.

Characterization. SEM images were obtained with a JEOL 7600F SEM operating at 5 kV in LBE mode. EDS was recorded on a JEOL 7600F at 30 kV. TEM images were obtained with a JEM-1400(JEOL) transmission electron microscope operated at 80 kV. For thin film sectioning, the nanoparticles were first embedded in epoxy resin then sectioned using a Leica Ultramicrotome with diamond knife under cryogenic condition. The 80-nm thin sections were collected and examined using HRTEM (JEOL-2100) at an accelerating voltage of 200 kV. The cross section of the np-Au nanoparticles was also obtained and imaged using FEI Helios Nanolab 600 Dual Beam FIB/SEM. The sample was pre-coated with silica as a protective layer against damage of the sample surface by the ion beam. XPS spectra were measured using a Phoibos 100 spectrometer with a monochromatic Mg X-ray radiation source. All XPS spectra were fit using XPS Peak 4.1 (freeware accessible at <http://www.phy.cuhk.edu.hk/~surface>). UV-Vis-NIR spectra were measured using Shimadzu UV-3600 UV-Vis-NIR spectrophotometer. XRD patterns were

recorded on a Bruker GADDS XRD diffractometer with Cu K α radiation. Electrochemical measurements were conducted using a Metrohm Auto lab potentiostat.

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Chapter 4

Design and Tailored Syntheses of Morphology Controlled Nanoporous Gold Nanoparticles

ABSTRACT. Precise control of ligament size and porosity in np-Au nanoparticles will enhance its catalytic activities and their utilization efficiencies. Fast diffusion of gold atoms at the alloy-electrolyte interface will limit the formation of smaller ligaments and pores in dealloying approach. However, high yield syntheses of np-Au nanoparticles with tunable ligament size, porosity and morphology by a simple wet-chemical approach are yet to be realized. Here, we report a two-step seed-mediated method to synthesize np-Au nanoparticles with tailored morphology using, silver templates as sacrificial seeds, hydroquinone and PVP as reducing agent and shape directing agent respectively. Our synthetic protocol is robust, rapid, and reliable. This method is effective in achieving large scale synthesis of np-Au nanoparticles (~0.4 g) with well-defined morphology in a cost-effective and time-saving manner (<30 min). We systematically tailor the size of the ligament 21 to 6 nm by varying the final concentration of hydroquinone in the solution. Furthermore, we study the detailed mechanism for the formation of np-Au nanoparticles by evaluating the role of individual reactants, such as reducing agent, PVP, seed particles their shape and composition, on the formation of np-Au nanoparticles. We evaluate the electrochemical properties of these np-Au nanoparticles as a function of morphology and ligament size. Np-Au nanoparticles with a ligament size of 8 nm exhibits 2 times increase in electro active surface area ($20.3 \text{ m}^2.\text{g}^{-1}$) compared to that of 21 nm ($10 \text{ m}^2.\text{g}^{-1}$). These results highlight the importance of having sub 10 nm ligament sizes to improve the catalytic activity of np-Au nanoparticles.

4.1 INTRODUCTION

Rational design and synthesis of np-Au nanoparticles offer a promising ability to enhance catalytic performance and utilization efficiency. In addition, controlling the multi-level porosity, macro (> 50 nm) and mesoporosity (2-50 nm), in the particles is also of great interest because bigger pores will increase the mass transport while smaller pores in the structure enhance the surface area.¹ In the past decade np-Au have been extensively studied, for example, exceptional catalytic behavior similar to oxide-supported gold nanoparticles,²⁻¹³ photothermal,¹⁴ drug delivery,^{15, 16} tunable plasmonics properties,^{17, 18} SERS,¹⁹ optical sensors,^{20, 21} for actuators,^{22, 23} and so forth.^{24, 25} Wet chemical synthesis of np-Au nanoparticles having structural complexity with multi-level porosity is still challenging.

Up to date, the most successful approach to fabricate np-Au is by dealloying method. For example, np-Au is fabricated by selectively leaching of silver from Au_{26%}Ag_{74%} alloy.²⁶ In this approach, fast diffusion of gold atoms at the alloy-electrolyte interface will limit the formation of smaller ligaments and pores in dealloying approach. Whereas the presence of smaller pores and ligament will greatly enhance the physiochemical properties of the np-Au. Chen et al. performed dealloying at low temperature (-20°C) to achieve pore size of ~ 5 nm. However, this process is limited by the requirement of >55 atomic% of silver to fabricate np-Au and also restricted to 2D thin films.⁷ Recent works avoided this disadvantage by fabricating np-Au disks by taking advantage of top-down (lithographic patterning) and bottom-up (dealloying),^{17, 27} wet chemical one-step synthesis of np-Au nanoparticles. Np-Au nanoparticles from the above approaches are robust and demonstrate tunable plasmon resonance and enhanced catalytic performance compared to the existing 2D np-Au thin films.³ However, this approaches have limited control over the structural parameters of the np-Au such as ligament size,

pore size (<10 nm) and morphology. To achieve this, we anticipate our previously reported protocol could be modified to include external silver templates of different sizes and shape.

In this work, we demonstrate a novel synthetic strategy to achieve morphology controlled np-Au nanoparticles. To achieve this, we employ a seed-mediated growth method. Firstly, AgX ($X=Cl^-$, Br^- , CO_3^{2-}) nanocrystals with different shapes are synthesized. In the second step, these AgX nanocrystals serve as sacrificial seeds for the heterogeneous growth of np-Au on surface with the aid of PVP and hydroquinone as shape director and reducing agent. A variety of np-Au morphologies, including semi shells, nanotubes, micro rods, and micro plates, are generated. Our synthetic protocol is robust, rapid, and reliable. This method is effective in achieving large-scale synthesis of np-Au particles (~0.4 g) with well-defined morphology in a cost-effective and time-saving manner (<30 min). The size of the ligament is tailored from 21 to <6 nm by varying the final concentration of hydroquinone in the solution. A detailed mechanism for the formation of our np-Au nanoparticles was studied and evaluated factors, such as reducing agent, PVP, seed particles their shape and composition, influencing the formation of np-Au nanoparticles. Np-Au nanoparticles produced by this method can be valuable in a wide range of applications, such as catalysis and SERS. In a proof-of-concept, we investigated the electrochemical properties of these nanostructures.

4.2 RESULTS AND DISCUSSION

The limited control over the morphology of AgCl seed and ligament size of np-Au nanoparticles in a one step protocol previously developed in our lab motivated us to make use of morphology controlled silver templates to achieve syntheses of morphology and ligament size controlled np-Au nanoparticles. In this report, we employed a two-step process to synthesize morphology controlled np-Au nanoparticles. In the first step, we

synthesized AgX (X=Cl, Br, CO₃²⁻) templates with shapes such as cubes, wires, rods and plates (Figure 1) through an ion exchange process (see experimental section) by following the previously reported procedures.²⁸⁻³¹ Thus, obtained particles are purified through repeated centrifugation in water at 3000 rpm for 5 min and redispersed in water.

In the second step, we hetero epitaxially grow np-Au on existing silver chloride seed using hydroquinone and PVP as reducing agent and shape directing agent respectively. Briefly, in sequence, 1 mL of AgCl (1.5 mg/mL), 2 mL of 28 mM hydroquinone solution and 1 mL of 40 mM HAuCl₄ solutions are added to 4.5 mL of 180 mM PVP solution on stirring at room temperature. The mixture was kept stirring for 1 min meanwhile the color of the solution changed to grayish green. The solution is kept undisturbed for 30 min and particles are reacted with NH₄OH solution and collected by centrifuging at 5000 rpm for 3 min. The morphology of these particles was investigated using SEM by drop casting reaction solution on to silicon substrate. The SEM image indicates that the as-synthesized nanoparticles are having bowl shape (Figure 2A, B) exhibiting roughened surface with high density of interconnected ligaments. Ligaments exhibit an average size of 21 ± 3 nm.

Figure 1. Structural characterization of silver templates. SEM images of morphology controlled np-Au nanoparticles grown on different silver templates (A, B) AgBr plates, (C, D) np-Au plates, (E, F) Ag₂CO₃ microrods, (G, H) hollow np-Au rods and (I, J).

Figure 2. Structural characterization of np-Au nanoparticles. Large area and corresponding high magnification single particle SEM images of np-Au nanoparticles (A, B) np-Au cups, (C, D) np-Au tubes, (E, F) np-Au rods, (G,H) np-Au plates and (I, J) np-Au rods synthesized using various silver templates as seed.

The growth of np-Au is found to be independent of morphology of the AgX seed used. Using AgCl wires as seed particles and while maintaining other conditions result in the formation of np-Au nanotubes (Figure 2C, D) with an average ligament size of 25 ± 4 nm. In case of AgCl rods as seed, we obtained hollow np-Au rods (Figure 2E, F) with an average ligament size of 21 ± 4 nm. Besides having micro- and mesopores on the surface, these structures additionally have macro porosity. To examine the applicability of our approach to other silver templates we investigate AgBr, Ag_2CO_3 as templates. We observe no effect of counter ions such as Br^- , CO_3^{2-} , on the formation of ligament size and porosity of the np-Au nanoparticles. We successfully synthesize np-Au plates (Figure 2G, H) and np-Au rods (Figure 2I, J) with an average ligament size of 24 ± 4 nm and 23 ± 5 nm respectively, by using AgBr plates and Ag_2CO_3 rods as sacrificial seeds.

Notably, our synthetic protocol for the preparation of morphology controlled np-Au nanoparticles can be readily scaled up. For example, to show the scale up synthesis, we carry out the reaction using 202 mM HAuCl_4 precursor and could be obtained up to 0.4 g of np-Au cups in a one-pot (Figure 3).

Figure 3. Large scale synthesis of np-Au cups (0.4 g)

Further insight in to structural details of the np-Au cups are obtained by using High resolution TEM. Figure 4A shows a HRTEM image of np-Au cup. We observe a

brightness contrast on closer examination confirms the presence of porous structure throughout the np-Au cup. This observation is further confirmed by high magnification SEM image of single np-Au cups, showing the interconnected ligaments forming mesoporous structure (Figure 4B). Furthermore, high magnification HRTEM image on single pore reveals the presence of cylindrical shape pore (Figure 4C). A d-spacing of 2.4 Å corresponding FCC Au (111) facet is measured (Figure 4D), indicating that (111) is the mostly exposed plane.

Figure 4. Internal structure of np-Au cups using electron microscopy characterization. (A) TEM image of np-Au cup, showing the presence of pores through the structure, (B) High magnification SEM image of np-Au cups, showing the interconnected ligaments forming mesoporosity, (C) High resolution TEM image of np-Au cups focused at single mesopore, and ligament indicating the presence of dislocation and stepped defects (D).

The N₂ sorption isotherms of np-Au cups are measured to acquire information on their specific surface area and pore size distribution. The hysteresis characteristic of np-Au cups can be classified into typical-IV isotherm with H₃ hysteresis, indicating the mesoporous structure of np-Au cups (Figure 5A). H₃ hysteresis is an indicative of disordered lamellar pore structures, wedge and slit shape pores. Pore-size distribution was calculated from the desorption data and BJH model showed that these structures have wide distribution of pore sizes ranging from 3 – 8 nm with an average pore size of 3 nm (Figure 5B). The specific surface area of np-Au cups was estimated to be 7 m²g⁻¹ using BET method.

Figure 5. BET isotherm and pore size distribution in np-Au cups. (A) N₂ isotherms of mesoporous np-Au cups with ligament size of 21 nm. (B) The pore-size distribution of np-Au cups determined by BJH analysis of the N₂ adsorption isotherm.

Table 1. Table summarizing elemental composition of samples.

Sample	Ligament size(nm)	At% of Au	At% of Ag
np-Au Cups	21	96.2	3.8
np-Au tubes	25	95.4	4.6
np-Au rods	21	95.7	4.3
np-Au plates	24	96.8	3.2

EDS analysis on the different shaped np-Au nanoparticles showed similar Au/Ag ratio (Table 1). We observed the presence trace amount of silver in all the samples. The trace amount of silver could be present as either Ag (0) or AgCl. It has to be noted that no traces of AgCl precipitate was observed on the particles from the SEM images. From EDS elemental maps, it is clear that nanoporous cups mostly made of Au with tiny amount of Ag distributed on the surface (Figure 6B-D). EDS elemental spectra on the nanoporous cups showed a composition of 96 wt % Au, and 4 wt % Ag (Figure 6D).

Figure 6. Elemental composition and distribution of np-Au cups. (A) SEM image of np-Au cups, (B) EDS elemental mapping overlay of np-Au cups, (C) Elemental map of Ag, (D) Elemental map of Au, and (E) the corresponding EDS elemental spectrum of np-Au cups; inset showing the atomic percentage of Au and Ag.

The catalytic activity of np-Au increases with the decrease in ligament size by increasing utilization efficiency of the particles; hence, in the following section we systematically tailor the ligament size of the np-Au cups from 21 nm to 6 nm (Figure 7)

by controlling final concentration of hydroquinone in the solution and maintaining the other experimental conditions.

Figure 7. Np-Au cups with tailored ligament sizes. SEM images of morphology controlled np-Au nanoparticles with varying ligament sizes (as indicated in the figure) synthesized by controlling the final volume of hydroquinone in the solution (A,B) 2000 μL , (C,D) 2060 μL , (E,F) 2100 μL , (G, H) 2140 μL , (I, J) 2200 μL .

It can be seen from Figure 7 that the average thickness of the ligaments decreased with the increase of the final volume of the hydroquinone from 2000 to 2200 μL in the reaction. The size of the ligament mainly depends on the nucleation and subsequent growth to form the np-Au cups. The density of nuclei on the seed particles has been dictated by the concentration of the hydroquinone. Additionally, we observe a decrease in pore size and porosity with the decrease in ligament size from 21 to 6 nm.

Mechanistic study

Here, by using ex-situ SEM, EDS and XPS we demonstrate the heterogeneous growth of gold on the surface of silver sacrificial templates (Figure 8C, 8F). Our mechanistic study indicated a heterogeneous growth of gold on the surface of AgX seed ($\text{X}=\text{Cl}, \text{Br}, \text{CO}_3$) particles (Figure 8B).^{30, 31} The heterogeneous growth of gold on to the existing AgCl seed is confirmed from the EDS elemental mapping (Figure 8F). Np-Au cups are eventually obtained by selective removal of silver template using NH_4OH (Figure 8D). Np-Au cups have an average surface elemental composition of $\text{Au}_{96} \text{Ag}_4$ in atomic percentage, as measured by EDS. Two plausible outcomes could be expected for such seeded mediated process. (i) Conformal growth of gold on the surface of AgCl seeds leading to a core/shell structure or (ii) Deposition of gold nuclei on specific sites on the surface of AgCl seed followed by the growth of gold nuclei, leading to Janus particles.

It has to be noted that, two factors obstruct the formation of gold shell on the surface of AgCl seed. Firstly, a huge lattice mismatch of $\sim 36\%$ between Au (4.08 Å) and AgCl (5.54 Å) and secondly the self-catalytic reduction and growth of gold on the preformed nuclei. Due to self-catalytic effect of gold, once some Au nuclei had been deposited someplace on the surface of a AgCl seed, the following reduction and growth of the gold would selectively occur at this sites instead of nucleating at other new sites.

Figure 8. Mechanistic study. (A) Schematic illustrating the formation of np-Au cups as model. Large area SEM images of (B) AgCl cubes, (C) AgCl/np-Au hybrid particles, (D) np-Au cups formed after removal of AgCl template with NH_4OH . EDS elemental mapping of (E) AgCl, (F) AgCl/np-Au hybrid particles and (G) np-Au cups.

Based on our mechanistic study of heterogeneous nucleation involved in the AgCl-Au system suggests the morphology of the seed particles will influence the nucleation and growth of gold on the surface. We observed that the sites with sharper features such as corners or edges will first act as the nucleation sites for the growth of Au due to more surface free energy and highest activity at these sites. Owing to this anisotropic heterogeneous nucleation we achieve the synthesis of Au nanoparticles with reduced symmetry such as nanocups. We have also demonstrated that similar growth approach could be extended to various other silver seed templates such as AgBr and Ag_2CO_3 .

Figure 9. Mechanistic study. XPS analysis of (i) AgCl in the binding energy regions of Ag (3d) and Cl (2p), (ii) AgCl/np-Au hybrid particles at Ag (3d) and Au (4f) regions, (iii) np-Au cups at Ag (3d) and Au (4f) binding energy windows.

Furthermore, XPS is used to determine the surface composition of the particles at three different stages of growth. The high-resolution Au 4f scan (Figure 9ii, iii) for AgCl-np-Au, np-Au reveals a doublet at 87.7 and 84 eV and 83.7 and 87.4 respectively separated by ~ 3.7 eV, confirms the appearance of Au in zero valent state in AgCl-np-Au and np-Au. The high-resolution Ag 3d scan indicated two weak binding energy peaks at 373.1 eV and 367.1 eV due to the spin-orbital splitting of $\text{Ag}3d_{3/2}$ and $\text{Ag}3d_{5/2}$ electron

states with intensity ratio of 2:3. This confirms the presence of Ag in its elemental form. After the etching AgCl using NH_4OH , XPS revealed that 96 at % of the sample was Au, with only trace amounts of Ag. SEM images confirmed that after removal of AgCl the sample were still have nanoporous structure. We observe a ratio of 9.6:0.4 of Au: Ag which confirms that np-Au nanoparticles are mostly made from gold with trace amount of silver. We observe a shift in binding energy for Au (4f) peak in AgCl-np-Au compared to np-Au due to the change in chemical environment and back donation of electrons from gold to AgCl because of Mulliken-Jaffe electronegativity difference. These data further support the heteroepitaxial growth of mesoporous gold on AgCl surface.

Effect of reaction parameters

The formation of np-Au is found to be very sensitive to the experimental conditions. Any deviation from experimental conditions resulted in remarkable morphological changes. We design control experiments to investigate the effect of individual reaction parameters especially influence of AgCl sacrificial template, reducing agent, PVP surfactant, concentration of PVP and molecular weight of PVP.

Effect of reducing agent

The use of hydroquinone is essential in obtaining the np-Au ligaments. When hydroquinone is replaced with alternative reducing agents, including ascorbic acid (Figure 10A, B) or hydroxylamine (Figure 10C, D), respectively. Reduction with ascorbic acid produced a mixture of plate like and pseudo spherical particles. While reduction with hydroxylamine led to plates with spikes on the surface. This observation is reasoned to the difference in reduction potentials of ascorbic acid (0.06 V) and hydroxylamine (-1.87 V) compared to that of hydroquinone (0.70 V). The milder reducing ability of hydroquinone results in slower and controlled growth of gold on AgCl.

Figure 10. Parametric study-morphology of gold nanoparticles. SEM images of particles obtained at various reaction conditions (A, B) Ascorbic acid as reducing agent, (C, D) Hydroxylamine as reducing agent, (E, F) Hydroquinone as reducing agent, (G, H) reaction in absence of AgCl, (I, J) reaction in absence of AgCl and PVP.

Effect of sacrificial template

Following this we study the effect of AgCl, in the absence of AgCl (Figure 10G, H) and maintaining other experimental conditions resulted in solid gold nanoparticles with pores on the surface and pseudo ligaments on the surface. This result indicates the importance of PVP in the formation of ligaments and pores on the surface. The key role of PVP is further demonstrated by a controlled experiment run in the absence of AgCl and PVP (Figure 10I, J) resulted in the formation of solid gold nanoparticles with smooth surface.

Effect of surfactant –PVP

A control experiment without the surfactant (PVP) added in the initial solutions was carried out to isolate the effect of the PVP surfactant on the formation of the np-Au. Absence of PVP in the reaction resulted in the formation of solid Au cups without any ligaments on the surface (Figure 11A), suggesting that the introduced PVP is critical for the formation of the nanoporous structure in porous gold.

Figure 11. Effect of PVP concentration and molecular weight on np-Au nanoparticles. SEM images of particles obtained at different PVP concentrations and PVP molecular weights (A) 0 mM, (B) 0.9 mM, (C) 1.8 mM, (D) 3 mM, (E) 10 K, (F) 40 K (G) 55 K, (H) 360 K.

To further investigate the role of PVP on the morphological evolution of np-Au nanoparticles, we study the effect of PVP concentration (0 to 27 mM) while maintaining other parameters as in typical process (Figure 11). Here the PVP concentration was calculated in terms of PVP repeating unit. As PVP concentration in reaction increased from 0 to 3 mM, an onset for the formation of ligaments on the surface of the nanoparticles is observed at 1.8mM (Figure 11C).

It has to note that PVP on the surface of AgCl is not eliminated. The morphology of the particles such as shape and ligament size remains unchanged on further increase in PVP concentration. Also noted that there is no noticeable influence on morphology by varying the molecular weight of the PVP from 10 K – 360 K (Figure 11E-H). These designed experiments prove that PVP plays an essential role in the formation of ligaments and porosity in np-Au nanoparticles.

Figure 12. Electrochemical properties of np-Au nanoparticles as a function of shape and ligament size. Oxide stripping curves of np-Au modified electrodes at a scan rate of

5 mV/s in 0.5 M H₂SO₄ electrolyte (A) np-Au cups, tubes, rods and plates and (B) np-Au cups with various ligament sizes as indicated in the figure.

Table 2. Table summarizing physical and electrochemical properties of the np-Au nanoparticles.

Sample	Ligament size (nm)	Peak area (μC)	Surface area ($\text{m}^2 \text{g}^{-1}$)
Np-Au tubes	25 ± 4	45.40	10.09
Np-Au rods	23 ± 5	44.50	9.89
Np-Au plates	24 ± 4	30.47	6.77
Np-Au cups	8 ± 1	91.1	20.24
Np-Au cups	10 ± 2	84.5	18.7
Np-Au cups	16 ± 2	56.2	12.48
Np-Au cups	21 ± 3	45.3	10.07

The electrochemical active surface area of morphology controlled np-Au are estimated by performing an electrochemical Au oxide stripping reaction in 0.5 M H₂SO₄ aqueous solution at a scan rate of 5 mV/s in room temperature (Figure 12A). The np-Au nanoparticles exhibit an oxidation peak around 1.1 V. From these CVs, we estimate the electrochemically active surface areas by integrating the area of the gold oxide reduction curve and assuming a specific charge of $450 \mu\text{C}.\text{cm}^{-2}$ for the gold oxide reduction. Electro-active surface areas of $10.08 \text{ m}^2.\text{g}^{-1}$, $10.09 \text{ m}^2.\text{g}^{-1}$, $9.89 \text{ m}^2.\text{g}^{-1}$ and $6.77 \text{ m}^2.\text{g}^{-1}$ are obtained for np-Au cups, np-Au tubes, np-Au rods and np-Au plates respectively (Table 2). The decrease in surface area in case of np-Au plates may be due to the very thick np-Au shell.

The electrochemical active surface area of np-Au cups with various ligament sizes are estimated by performing an electrochemical Au oxide stripping reaction in 0.5 M H₂SO₄ aqueous solution at a scan rate of 5 mV/s in room temperature (Figure 12B). From these CVs, we estimate the electrochemically active surface areas by integrating the area

of the gold oxide reduction curve and assuming a specific charge of $450 \mu\text{C}.\text{cm}^{-2}$ for the gold oxide reduction. Electro-active surface areas of $20.24 \text{ m}^2.\text{g}^{-1}$, $18.7 \text{ m}^2.\text{g}^{-1}$, $12.48 \text{ m}^2.\text{g}^{-1}$, and $10.07 \text{ m}^2.\text{g}^{-1}$ are obtained for ligament sizes 8, 10, 16, and 21 nm respectively (Table 2). We observe a two fold increase electroactive surface area when the ligament size reduced to 8 nm.

4.3 CONCLUSIONS

We have successfully demonstrate the syntheses of morphology controlled np-Au nanoparticles through a two step seed-mediated approach using silver templates as seeds, hydroquinone as reducing agent and PVP as shape directing agent. The growth of np-Au is found to be independent on the shape, size and composition of the silver template. Our synthetic protocol is robust, rapid, and reliable. We systematically tailor the size of the ligament 21 to 6 nm by varying the final concentration of hydroquinone in the solution. Furthermore, we study the detailed mechanism for the formation of np-Au nanoparticles by evaluating the role of individual reactants, such as reducing agent, PVP, seed particles their shape and composition, on the formation of np-Au nanoparticles. We evaluate the electrochemical properties of these np-Au nanoparticles as a function of morphology and ligament size. Np-Au nanoparticles with a ligament size of 8 nm exhibits 2 times increase in electro active surface area ($20.3 \text{ m}^2.\text{g}^{-1}$) compared to that of 21 nm ($10 \text{ m}^2.\text{g}^{-1}$). These results highlight the importance of having sub 10 nm ligament sizes to improve the catalytic activity of np-Au nanoparticles. Np-Au nanoparticles produced by this method can be valuable in a wide range of applications, such as catalysis and SERS.

4.4 EXPERIMENTAL METHODS

Materials

Silver nitrate (99+ %), poly(vinyl pyrrolidone) (PVP, $M_w = 1300$ K), hydroquinone (≥ 99 %), gold (III) chloride trihydrate (≥ 99.9 %), L-ascorbic acid (99%), hydroxylamine hydrochloride (99.99%), gold(III) chloride trihydrate (≥ 99.9 %), sulfuric acid (95-97%) were purchased from Sigma Aldrich; sodium bromide (99.5%), ammonia solution was obtained from Goodrich Chemical Enterprise; sodium carbonate was purchased from Alfa Aesar. Hydrochloric acid (37%) was purchased from VWR Chemicals. Ethanol (ACS, ISO, Reag.) was purchased from EMSURE[®]. All chemicals were used without further purification. Milli-Q water (> 18.0 M Ω .cm) was purified with a Sartorius arium 611 UV ultrapure water system.

Synthesis of Ag₂CO₃ microrods

In a typical procedure, 100 mg Na₂CO₃ was first dissolved into 25 ml water, and then 25 mL of solution containing 200 mg AgNO₃ was added upon stirring. The solution was magnetically stirred at room temperature for 1h, the resulting product was washed with water.

Synthesis of AgBr nanoplates

Typically, 270 mg of PVP and 123 mg of NaBr were added to Milli Q water (40 mL), and then the solution was kept at 90°C for 30 min under magnetic stirring. 6 mL of AgNO₃ containing 128 mL of NH₄OH solution is added dropwise to the above solution. After the solution was kept for another 1 h at 90°C and products were collected by centrifugation and washed several times with water.

Synthesis of AgCl nanocubes

Typically 425 mg of AgNO₃ and 415 mg of PVP were dissolved in 50 mL of ethylene glycol. To this solution 1.25 mL of HCl was added dropwise. The solution was then heated to 150°C for 20 min and products were collected by centrifugation and washed several times with water.

Synthesis of morphology controlled np-Au nanoparticles

In sequence, 1 mL of AgCl/AgBr/Ag₂CO₃ (1.5 mg/mL), 2 mL of 28 mM hydroquinone solution and 1 mL of 40.37 mM HAuCl₄ solution are added to 4.5 mL of 180 mM PVP solution on gentle stirring at room temperature. The mixture was kept stirring for 1 min meanwhile the color of the solution changed to grayish green. The solution is kept undisturbed for 30 min and particles are reacted with NH₄OH to remove AgCl template followed centrifugation at 5000 rpm for 3 min to collect the np-Au nanoparticles.

Synthesis of ligament size controlled np-Au cups

Ligament size of 22 nm

In sequence, 1 mL of AgCl cubes (1.5 mg/mL), 2000 µL of 28 mM hydroquinone solution and 1 mL of 40 mM HAuCl₄ solution are added to 4.5 mL of 180 mM PVP solution on gentle stirring at room temperature.

Ligament size of 16 nm

In sequence, 1 mL of AgCl cubes (1.5 mg/mL), 2060 µL of 28 mM hydroquinone solution and 1 mL of 40 mM HAuCl₄ solution are added to 4.5 mL of 180 mM PVP solution on gentle stirring at room temperature.

Ligament size of 10 nm

In sequence, 1 mL of AgCl cubes (1.5 mg/mL), 2100 μ L of 28 mM hydroquinone solution and 1 mL of 40 mM HAuCl₄ solution are added to 4.5 mL of 180 mM PVP solution on gentle stirring at room temperature.

Ligament size of 8 nm

In sequence, 1 mL of AgCl cubes (1.5 mg/mL), 2140 μ L of 28 mM hydroquinone solution and 1 mL of 40 mM HAuCl₄ solution are added to 4.5 mL of 180 mM PVP solution on gentle stirring at room temperature.

Ligament size of 6 nm

In sequence, 1 mL of AgCl cubes (1.5 mg/mL), 2200 μ L of 28 mM hydroquinone solution and 1 mL of 40 mM HAuCl₄ solution are added to 4.5 mL of 180 mM PVP solution on gentle stirring at room temperature.

Large-scale synthesis np-Au cups

In sequence, 5 mL of 281 mM hydroquinone solution and 5 mL of 201 mM HAuCl₄ solution are added to the 50 mL suspension containing 1 g of PVP and 25 mL of AgCl cubes (1.5 mg/mL) on vigorous stirring at room temperature. The mixture was kept stirring for 3 min meanwhile the color of the solution changed to brown. The solution is kept undisturbed for 30 min and particles are reacted with NH₄OH to remove AgCl template followed centrifugation at 5000 rpm for 3 min to collect the np-Au cups.

Np-Au modified electrode preparation. 1mg/mL suspension of np-Au nanoparticles sample in ethanol was prepared by ultra-sonication. 1 μ L of this suspension was drop-casted on glassy carbon electrode surface. The electrode was vacuum dried for 1 hour at room temperature before use.

Electrochemical measurements. Electrochemical measurements were carried out using Metrohm Auto lab potentiostat instrument. Three electrodes configuration was employed. The working electrode used was np-Au nanoparticles modified glassy carbon electrode, a leak-free saturated Ag/AgCl electrode as reference and the counter electrode was a Pt wire.

Estimation of electrochemical surface area. The electrochemical active surface area of different shaped and various ligament sized np-Au nanoparticles were estimated using CV. The surface redox behavior of the np-Au nanoparticles were characterized using CV in 0.5 M H₂SO₄ aqueous solution at a scan rate of 5 mV s⁻¹ in room temperature. The electrochemical active surface area is estimated from the equation of $Q_o = 2eNA\Gamma_oA$, where Q_o is the charge passed during reduction of gold oxide was calculated by integration of the gold oxide reduction peak. The specific charge equivalent of 450 $\mu\text{C cm}^{-2}$ was used for converting the charge passed during the gold oxide reduction to a total surface area ($A = Q_o/450$), which was then divided by the mass of the np-Au electrode in order to obtain a specific surface area per unit mass.

Characterization. SEM images were obtained with a JEOL 7600F SEM operating at 5 kV in LABE mode. EDS was recorded on a JEOL 7600F at 30 kV. TEM images were obtained with a HR-TEM (JEOL-2100) at an accelerating voltage of 200 kV. XPS spectra were measured using a Phoibos 100 spectrometer with a monochromatic Mg X-ray radiation source. Electrochemical measurements were conducted using a Metrohm Auto lab potentiostat. N₂ adsorption/desorption measurements for BET and BJH calculations were obtained using an autosorp-IQ instrument from Quantachrome Instruments Corporation.

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Chapter 5

Location Dependent SERS on Nanoporous Gold Nanoparticles

ABSTRACT

SERS is a powerful tool for the detection of molecules and to study chemical process on the surface of metal nanoparticles. Currently, research groups mainly focus to explore new SERS active substrates with reproducible and highly enhanced signal. Here, we demonstrate np-Au nanoparticles with reduced symmetry, will hold intense electromagnetic fields exploitable for location dependent SERS on single np-Au nanoparticles under near-infrared excitation. We systematically study the SERS performance of np-Au nanoparticles with four geometries – nanocups, nanotubes with open and closed ends and plates. In general, we obtain SERS signal with similar intensity from the surface of np-Au nanoparticles. Among the four different shapes of np-Au nanoparticles, cups with reduced symmetry show highest enhancement of the signal, 6×10^3 . In addition, we demonstrate a further 5-fold increase, 33×10^3 , in SERS enhancement resulting from open cavities when np-Au cups are facing up and at the open ends of np-Au tubes. These results put this substrate as a valuable and easy-to-fabricate tool for studying and detecting molecules on surfaces.

5.1 INTRODUCTION

SERS is a powerful tool for the detection of molecules and to study chemical process on the surface of metal nanoparticles.¹⁻⁶ The sensitivity of this technique relies on the localized intense electromagnetic fields, which is strongest at the sharp tips⁷⁻¹¹ and inter-particle gaps.¹²⁻¹⁴ Although SERS enhancements sufficient to detect single molecule could be achieved through inter-particle junctions^{15, 16} and particle aggregations,^{17, 18} these intense enhanced field account only for a small fraction of the total surface area accessed by the analyte. This results in a huge heterogeneity in the SERS signal over the whole substrate. Hence, the ability to control the hot spot over the entire surface of the nanoparticles is of paramount importance.

An ideal SERS substrate should possess significant enhancement in the signal, uniform and reproducible response, and easily synthesizable. Recently, np-Au films with uniform distribution of pores of diameters < 20 nm have been demonstrated as SERS substrate.¹⁹ Single particle SERS study on porous gold nanoparticles by Wang et al demonstrated an enhancement factor of 10^5 using 4-ATP as probe molecule.²⁰ Wi et al. demonstrate the fabrication of porous gold disks with a hybrid approach and reported a five-fold enhanced SERS signal compared to solid gold disks with a limit of detection of 1 μ M for R₆G.²¹ Shih et al. achieved an enhancement factor of 10^8 for individual np-Au disks with benzenethiol as probe molecules.²² Yet, the recent reports are mostly substrate bound, limited control over the pore size (< 10 nm) and rely on dealloying approach which limit their practical and commercial applications.

Ability to control morphology of the np-Au nanoparticles with reduced symmetry while maintaining the mesoporosity (sub 10 nm pore size) remains challenging. Here, we demonstrate np-Au nanoparticles with reduced symmetry, will hold intense electromagnetic fields exploitable for location dependent single-particle SERS. The

fabricated np-Au nanoparticles with nanoscale porosity exhibit high SERS signal with good reproducibility. The intense SERS signal is attributed to both reduced symmetry and enhanced surface roughness resulting from ligaments and nanoscale porosity. We systematically study the SERS activity of np-Au nanoparticles with four geometries – nanocups, nanotubes with open and closed ends and plates. In general, nanopores on the surface of np-Au amplify the SERS signal at least five times compared to particles with smooth shell with similar size. Among the four different shapes of np-Au nanoparticles, cups with reduced symmetry show highest enhancement of the signal, 6×10^3 . In addition, we demonstrate a further 5-fold increase, 33×10^3 , in SERS enhancement resulting from open cavities when np-Au cups are facing up and at the open ends of np-Au tubes. These results put this substrate as a valuable and easy-to-fabricate tool for studying and detecting molecules on surfaces.

5.2 RESULTS AND DISCUSSION

Np-Au cups are synthesized by a seed mediated approach. Typically, np-Au cups are synthesized by selective reduction of HAuCl_4 onto preformed AgCl cube seed particles which is achieved by using PVP and hydroquinone (the mole ratio of hydroquinone to HAuCl_4 is 1:1) as capping and reducing agents respectively followed by removal of AgCl using NH_4OH .

Figure 1. Schematic geometry and SEM images of np-Au cups (A, B), rough Au cups (C, D), np-Au plates (E, F), np-Au tubes with open ends (G, H), np-Au tubes with closed ends (I, J) and rough Au tubes with closed ends (K, L).

Figure 1A-B shows a schematic geometry and SEM image of np-Au cups with outer diameter of 430 nm, a 388 nm cavity diameter and a 42 nm shell thickness. The

height of np-Au cups was determined by AFM as 240 nm, which have a diameter/height ratio of 1.8 compared to the value of 2 for an ideal semi shell. The morphology of nanoparticles is found to be highly dependent on mole ratio of hydroquinone to HAuCl_4 . By increasing mole ratio of hydroquinone to HAuCl_4 from 1 to 4 and maintaining all other conditions will result in Au nanocups with relatively smooth surface (Figure 1C-D).

The tailored synthesis of np-Au tubes (Figure 1G-H) at room temperature was achieved through selective growth of gold on AgCl nanowires, as sacrificial template, using PVP and hydroquinone as capping and reducing agents respectively. The inner and outer diameters of np-Au tubes were measured to be 240 nm and 340 nm, respectively. The average diameter is estimated to be about 340 nm. The enlarged SEM image on the sectional view of the nanowires (insert in Figure 1H) further reveals that they have a circular hole at the centre of the nanotubes.

It clearly presents a hollow interior, indicating that the gold is selectively grown on the surface of AgCl nanowires, upon removal of AgCl using concentrated NH_4OH . Similarly, the np-Au tubes with closed ends are achieved with increase of concentrations of hydroquinone and HAuCl_4 while maintaining their mole ratio at 1:1. As shown in Figure 1K-L, Au nanotubes with smooth surface are synthesized using mole ratio of hydroquinone to HAuCl_4 from 1 to 4.

Figure 2. Digital images (A) and UV-Vis-NIR extinction spectra (B) of np-Au cups (i), smooth Au cups (ii), np-Au plates (iii), np-Au tubes with open ends (iv), np-Au tubes with closed ends (v) and smooth Au tubes with closed ends (vi).

The optical properties of ensemble np-Au nanoparticles are investigated using UV-vis-NIR spectroscopy (Figure 2). For np-Au cups (Figure 2B-i), two well defined plasmon peaks are identified at 1165 and 674 nm. Despite of having a np-Au structure, they still display optical properties similar to Au semi-shell,²³⁻²⁵ where these two plasmon modes are assigned to the axial and transverse dipolar modes. We observed a red shift in the

plasmon modes in case of smooth Au cups (Figure 2B-ii). In case of other morphologies np-Au plates, np-Au tubes and smooth gold tubes, we observed a broadened and red-shifted plasmon resonance (Figure 2B-iii-vi) which is attributed to the polydispersity in size of the nanoparticles.

Figure 3. (A, B, C) Schematics showing the sample preparation, ligand exchange and SERS measurement

Following this, we investigated the we study the plasmonics properties of individual np-Au nanoparticles of four morphology – nanocups, nanotubes with open and closed ends and plates – particularly focusing on their single particle SERS performance under near-infrared excitation. In our SERS studies, 4-MBT was used as Raman reporter to evaluate the enhancements on single np-Au nanoparticles. 4-MBT is a non resonant molecule with negligible chemical enhancements under 785 nm laser excitation and is known to form self assembled monolayers on the gold nanoparticles with well-known packing density. For single particle measurements diluted ethanolic suspension of np-Au nanoparticles was drop-casted onto an oxygen plasma cleaned silicon wafer and allowed to dry. Typically, PVP molecules on the np-Au nanoparticle were exchanged with 4-MBT probe molecules by immersing substrate into an ethanol solution of 4-MBT (10 mM) with stirring at room temperature for at least 24 h. The 4-MBT exchanged np-Au substrates were then thoroughly rinsed with ethanol and dried under N₂ gas. To ensure that the spectra were collected from the single isolated np-Au nanoparticles, the area examined by

confocal Raman microscope were imaged by SEM to check the orientation of the particles.

Figure 4. (A, D) Schematic geometry of np-Au nanocups of different orientation, (B, E) SEM images of np-Au cups cavity facing down and facing up, (C, F) Overlaid SERS-SEM images of np-Au cups of two different orientations, (G) Raman spectra of 4-MBT on different positions of np-Au cups: on the surface (position I) and on the cavity (position II). Colors are assigned by the relative intensity of the vibrational mode at 1080 cm⁻¹ and (H) SERS enhancement factors of np-Au cups for two different orientations.

We examine the effect of shape, orientation and location on the SERS signals of the anisotropic np-Au nanoparticles. To investigate the SERS signal dependence on

orientation of the np-Au cups, we compare the SERS performance of our np-Au cups for two different orientations cavity down and cavity up (Figure 3B, E) by conducting SERS measurements at the single-particle level.

Figure 4(A,B,D and E) shows a schematic geometry and SEM image of np-Au cups with outer diameter of 430 nm, a 388 nm cavity diameter and a 42 nm shell thickness. Figure 4G shows a representative SERS spectra measured on a single np-Au cup, revealing strong Raman scattering peaks of 4-MBT. An intense Raman bands at 1080 cm^{-1} was observed in the SERS spectra, corresponding to the C–S stretching mode. Figure 4G shows the SERS signals recorded at two different positions on single np-Au cups. Fingerprint peak (1080 cm^{-1} for 4-MBT) were monitored to obtain a comparison of the intensity of the SERS signals. From figure 4G, it is obvious that when the np-Au cups in cavity up configuration (at position II), the SERS intensity (2094 ± 796 counts) increases rapidly and is at least 5 times larger when compared to that of np-Au cups face down (Position I, 379 ± 104 counts). This could be explained by the fact that the strong enhancement in the electric field (hot spot) at position II, due to localized charge at these positions. SERS spectra of 4-MBT SAMs on np-Au cups were collected for more than 50 particles for each sample. All the particles showed high Raman signals with a standard deviation of 38 % for face up and 27% for face down np-Au cups. In order to compare the SERS enhancements at different orientations of the np-Au cups, we calculated SERS enhancement factors using intensity of the peak at 1080 cm^{-1} . The SERS enhancement factor for np-Au cup in cavity up configuration is 3.3×10^4 (Figure 4H), which is nearly six times stronger compared to np-Au cup in cavity down, 0.6×10^4 .

Figure 5. (A, D) Schematic geometry of smooth Au nanocups of different orientation, (B, E) SEM images of np-Au cups cavity facing down and facing up, (C, F) Overlaid SERS-SEM images of smooth Au cups of two different orientations and (G) Raman spectra of 4-MBT on different positions of smooth Au cups: on the surface (position I) and on the cavity (position II). Colors are assigned by the relative intensity of the vibrational mode at 1080 cm^{-1} .

To illustrate the significance of nanoporous structure, we compare the SERS performance of np-Au cups with the relatively smooth Au nanocups in the following section. Figure 5(A, B, D and E) shows a schematic geometry and SEM image of smooth Au cups. On the contrary, to SERS of np-Au cups, we observe a much weaker signal from the isolated single smooth Au cups, measured at the same condition. On comparing smooth Au cups with two different orientations, we observe a higher SERS signal (195 ± 23 counts) in cavity up configuration (at position II), compared to when the cavity is facing down (Position I, 100 ± 26 counts) as indicated in figure 5G. This further highlights the necessity of having porous structure to stronger SERS signal. We collected SERS spectra from more than 50 particles and all the particles showed high Raman signals with a standard deviation of 11 % for face up and 27% for face down.

In the preceding section, we investigated the SERS performance of np-Au tubes with closed ends and compared to that of smooth Au tubes. Figure 6(A, B, D and E) shows a

schematic geometry and SEM images of np-Au tube and smooth Au tube. Unlike in Ag or Au nanowires where the signal is stronger at tips, we observed a uniformly distributed SERS signal along the whole surface of the np-Au tubes. The intensity of SERS signal is similar to that observed on np-Au cups when facing down. In case of smooth Au tubes we observed very weak SERS. It is clear from figure 6G that the SERS intensity from np-Au tubes surface (Position I, 400 ± 36 counts) is 19 time larger when compared to that of smooth Au tubes (Position II, 21 ± 6 counts). The SERS enhancement factor for np-Au tubes is 3×10^3 (Figure 6H), which is six times stronger compared to that of smooth Au tubes, 0.6×10^3 .

Figure 6. (A, D) Schematic geometry, (B, E) SEM images (C, F) Overlaid SERS-SEM images of np-Au tubes and smooth Au tube with closed ends, (G) Raman spectra of 4-MBT and (H) SERS enhancement factors on the surface of np-Au tube (position I) and

smooth Au tube with closed ends (position II). Colors are assigned by the relative intensity of the vibrational mode at 1080 cm^{-1} .

Following this, we investigate the effect of hollow cavity by considering the case of np-Au tubes with open ends. Figure 7A-B shows the schematic and SEM image of np-Au tubes with open ends. We observe an intense localization of the SERS signal at the open ends of the tube from overlaid SERS-SEM image of np-Au tube with open ends (Figure 7C). SERS signal intensity at the open ends is nearly 6 times larger than that on the surface of the np-Au tubes. In order to compare the SERS enhancements at different positions of np-Au tubes, we calculated SERS enhancement factors using intensity of the peak at 1080 cm^{-1} . The SERS enhancement factor at the open ends is 1.6×10^4 (Figure 7E), which is nearly six times stronger compared to that on surface, 0.3×10^4 .

Figure 7. (A) Schematic geometry, (B) SEM images (C) Overlaid SERS-SEM images of np-Au tubes with open ends, (D) Raman spectra of 4-MBT and (E) SERS enhancement factors on the surface of np-Au tube (position I) and at the open ends (position II). Colors are assigned by the relative intensity of the vibrational mode at 1080 cm^{-1} .

Figure 8(A, B, D, E) display the schematic and SEM images of np-Au and smooth Au plates. We observed strong signal on whole surface of the np-Au plates (Figure 8C). To show that np-Au structure is crucial for the enhancement of SERS signal, measurements were done Au plates with smooth surface. The Raman signal intensity of 4 MBT molecules absorbed on the roughened np-Au plates (487 ± 132) is 45 orders of magnitude higher than that of the smooth Au nanoplates (11 ± 2). The SERS enhancement factor of the np-Au plates was estimated to be 0.7×10^3 using intensity of the peak at 1080 cm^{-1} , which is seven times higher than that of smooth Au plates (0.1×10^3).

Figure 8. (A, D) Schematic geometry, (B, E) SEM images (C, F) Overlaid SERS-SEM images of np-Au tubes and smooth Au tube with closed ends, (G) Raman spectra of 4-MBT and (H) SERS enhancement factors on the surface of np-Au tube (position I) and

smooth Au tube with closed ends (position II). Colors are assigned by the relative intensity of the vibrational mode at 1080 cm^{-1} .

5.3 CONCLUSIONS

In conclusion, we have demonstrated location dependent single-particle SERS on the morphology controlled np-Au nanoparticles. Np-Au particles demonstrated at least 5-fold increase in SERS enhancements compared to that of smooth Au nanoparticles of similar dimensions. In general, we obtained similar SERS intensity on the surface of the np-Au nanoparticles. Np-Au cups display higher SERS enhancement, 6×10^3 , compared to that of other structures. In addition, we have demonstrated that a 5-fold increase in SERS enhancement achieved from the open cavities when np-Au cups are facing up and at the open ends of np-Au tubes (Figure 9).

Figure 9. SERS enhancement factors of the different morphologies of the np-Au nanoparticles as indicated in the figure.

5.4 EXPERIMENTAL METHODS

SERS measurements. For single particle measurements, diluted ethanolic suspension of np-Au nanoparticles was drop-casted onto an oxygen plasma cleaned silicon wafer and allowed to dry. Typically, PVP molecules on the np-Au nanoparticle were exchanged with 4-MBT probe molecules by immersing substrate into an ethanol solution of 4-MBT (10 mM) with stirring at room temperature for at least 24 h. Owing to a strong Au-S coordination bond, 4-MBT is known to form a self-assembled monolayer (SAM) on the nanoparticles. The 4-MBT exchanged np-Au substrates were then thoroughly rinsed with ethanol and dried under N₂ gas. The substrate drop-casted with nanoparticle was then rinsed with ethanol, and dried in nitrogen gas to remove unbound 4-MBT and solvent. SERS spectra were obtained using Ramantouch microspectrometer (Nanophoton, Osaka, Japan). A 785 nm laser was used as an excitation laser. The excitation laser light was focused into a line on a sample through a cylindrical lens and an air objective lens (LU Plan Fluor 100×NA 0.9). The back-scattered Raman signal from the line illuminated site was collected with the same objective lens, and a one-dimensional Raman image (1D space and Raman spectra) was obtained with a two-dimensional image sensor (pixis 400 BR, -70 °C, 1340 × 400 pixels) at once. Two-dimensional (2D) Raman spectral images were obtained by scanning the line-shaped laser focus in a single direction. The excitation laser power was 0.2 mW on the sample plane. The exposure time for each line and slit width of the spectrometer were 5s and 50 μm for 2D Raman imaging.

Calculation of enhancement factor (EF).

The enhancement factor is calculated by using the equation below:

$$EF = \frac{I_{SERS}}{I_{Normal}} \times \frac{N_{Normal}}{N_{SERS}}$$

We choose the peak at 1080 cm⁻¹ to calculate enhancement factor.

$I_{\text{SERS}} = 2094$ (on face up cups; measured using 100 $\times$ objective lens, XY Scanning, 5s integration time)

$I_{\text{Normal}} = 0.56$ (based on 0.1 M benzenethiol solution + 12 M NaOH, 100 $\times$ objective lens, XY-imaging, 5 s integration time)

N_{Solution} = number of molecules in solution within the measured laser spot

$$= V_{\text{solution}} \times \text{Concentration of molecules} \times \text{Avogadro's number}$$

$$V_{\text{Solution}} = \pi \times a \times b \times h \text{ (} a=0.91/2=0.455 \text{ } \mu\text{m, } b=0.68/2=0.34 \text{ } \mu\text{m, } h=4.32 \text{ } \mu\text{m)}$$

$$= 3.142 \times (455 \text{ nm}) \times (340 \text{ nm}) \times (4320 \text{ nm}) = 2.1 \times 10^9 \text{ nm}^3$$

$$N_{\text{Solution}} = 2.1 \times 10^9 \text{ nm}^3 (= 2.1 \times 10^{-18} \text{ m}^3) \times 0.1 \text{ M (= } 100 \text{ mol/m}^3) \times 6.022 \times 10^{23}$$

$$= 1.26 \times 10^8$$

N_{Surface} = number of molecules on the surface of nanoparticles within the measured laser spot

$$\text{Surface area of one np-Au cup} = 74.94 \times 10^4 \text{ nm}^2$$

$$\text{Surface area of one np-Au plate} = 88.9 \times 10^5 \text{ nm}^2$$

$$\text{Surface area of one np-Au tube} = 159 \times 10^4 \text{ nm}^2$$

$$\text{Surface area of methyl benzenethiol} = 2.3 \times 2.3 \text{ } \text{\AA}^2/\text{molecule} = 0.0529 \text{ nm}^2/\text{molecule}$$

$$N_{\text{Surface}} = 74.94 \times 10^4 / 0.0529 \text{ nm}^2/\text{molecule} = 1.41 \times 10^7 \text{ molecules}$$

$$EF_{\text{cups face up}} = [2094/0.56] \times [1.26 \times 10^8 / 1.41 \times 10^7]$$

$$= 3739.28 \times 8.898$$

$$= 33273 = 3.3 \times 10^4$$

$$EF_{\text{cups face down}} = [379/0.56] \times [1.26 \times 10^8 / 1.41 \times 10^7]$$

$$= 676.78 \times 8.898$$

$$= 6021.98 = 0.6 \times 10^4$$

$$EF_{\text{tubes at hole}} = [2143/0.56] \times [1.26 \times 10^8 / 3 \times 10^7]$$

$$= 3826.78 \times 4.2$$

$$= 16072 = 1.6 \times 10^4$$

$$EF_{\text{tubes at surface}} = [400/0.56] \times [1.26 \times 10^8 / 3 \times 10^7]$$

$$= 714.28 \times 4.2$$

$$= 3000 = 0.3 \times 10^4$$

$$EF_{\text{smooth tubes at surface}} = [21/0.56] \times [1.26 \times 10^8 / 8.57 \times 10^6]$$

$$= 37.5 \times 14.7$$

$$= 551 = 0.5 \times 10^3$$

$$EF_{\text{plates}} = [487/0.56] \times [1.26 \times 10^8 / 1.68 \times 10^8]$$

$$= 869.64 \times 0.75$$

$$= 652.23 = 0.0652 \times 10^4$$

$$EF_{\text{plates smooth}} = [11/0.56] \times [1.26 \times 10^8 / 0.188 \times 10^8]$$

$$= 19.64 \times 6.7$$

$$= 131.62 = 0.0131 \times 10^4$$

Characterization. SEM images were obtained with a JEOL 7600F SEM operating at 5 kV in LBE mode. UV/Vis – NIR spectra were measured using SHIMADZU UV-3600

UV-VIS-NIR Spectrophotometer. SERS spectra were obtained using Ramantouch microspectrometer (Nanophoton, Osaka, Japan).

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Chapter 6

CONCLUSIONS AND OUTLOOK

The main goal of this thesis is to design and develop synthesis methods which enable the preparation of more efficient noble metal nanoparticles with tailored morphologies for optical, catalytic and SERS applications.

First part of the thesis presents a new approach to synthesize spiky nanoparticles with tunable spike length and to study their fundamental optical properties. Spiky nanoparticles exhibit higher overall plasmonic excitation cross sections than their non-spiky peers. In this work, we demonstrate a two-step seed-mediated growth method to synthesize a new class of spiky Ag–Au octahedral nanoparticles with the aid of a high molecular weight PVP polymer. The length of the nanospikes can be controlled from 10 to 130 nm with sharp tips by varying the amount of gold precursor added as well as the injection rates. Spatially resolved EELS study on individual spiky Ag–Au nanoparticles illustrates multipolar plasmonic responses. While the octahedral core retains its intrinsic plasmon response, the spike exhibits a hybridized dipolar surface plasmon resonance at lower energy. With increasing spike length from 50 to 130 nm, the surface plasmon of the spike can be tuned from 1.16 to 0.78 eV. The electric field at the spike region increases rapidly with increasing spike length, with a 10^4 field enhancement achieved at the tips of 130-nm spike. The results highlight that it is important to synthesize long spikes (>50 nm) on nanoparticles to achieve strong electric field enhancement. A mechanism for the formation of sharp spikes is proposed based on our studies using XPS, SEM, and high resolution TEM.

The second part of this thesis focuses on the design and wet-chemical synthesis of np-Au nanoparticles and their application in catalysis. np-Au with networks of interconnected ligaments and highly porous structure holds stimulating technological implications in fuel cell catalysis. Current syntheses of nanoporous gold mainly revolve around de-alloying approaches that are generally limited by stringent and harsh multistep protocols. Here we develop a one-step solution phase synthesis of zero-dimensional hollow np-Au nanoparticles with tunable particle size (150–1,000 nm) and ligament thickness (21–54 nm). With faster mass diffusivity, excellent specific electroactive surface area and large density of highly active surface sites, our zero-dimensional np-Au nanoparticles exhibit 1.4 times' enhanced catalytic activity and improved tolerance towards carbonaceous species, demonstrating their superiority over conventional np-Au sheets. Detailed mechanistic study also reveals the crucial hetero-epitaxial growth of gold on the surface of silver chloride templates, implying that our synthetic protocol is generic and may be extended to the synthesis of other nanoporous metals via different templates.

The third part of this thesis focuses on tailored synthesis of morphology controlled np-Au nanoparticles with tunable ligament sizes. Precise control of ligament size and porosity in np-Au nanoparticles allows for enhanced catalytic activities as well as utilization efficiencies. Currently, np-Au is synthesized using the dealloying approach; however, the fast diffusion of gold atoms at the alloy-electrolyte interface limits formation of small ligaments and pores. Hence, high yield syntheses of np-Au nanoparticles with tunable ligament size, porosity and morphology are yet to be realized. Here, we report a simple wet-chemical approach to synthesize np-Au nanoparticles with tailored morphology. We use a two-step seed-mediated method, with silver templates as sacrificial seeds, hydroquinone and PVP as reducing agent and shape directing agent respectively. Our synthetic protocol is robust, rapid, and reliable. This method is effective in achieving large scale synthesis of np-Au particles (~0.4 g) with well-defined morphology in a cost-

effective and time-saving manner (<30 min). We systematically tailor the size of the ligament 21 to 6 nm by varying the final concentration of hydroquinone in the solution. Furthermore, we study the detailed mechanism for the formation of np-Au nanoparticles by evaluating the role of individual reactants, such as reducing agent, PVP, seed particles their shape and composition, on the formation of np-Au nanoparticles. We evaluate the electrochemical properties of these np-Au nanoparticles as a function of morphology and ligament size. Np-Au nanoparticles with a ligament size of 8 nm exhibits 2 times increase in electro active surface area ($20.3 \text{ m}^2.\text{g}^{-1}$) compared to that of 21 nm ($10 \text{ m}^2.\text{g}^{-1}$). These results highlight the importance of having sub 10 nm ligament sizes to improve the catalytic activity of np-Au nanoparticles.

Finally, we demonstrate that np-Au nanoparticles with reduced symmetry posses intense electromagnetic fields that can be exploited for location dependent, single particle SERS. We study the plasmonic properties of individual np-Au nanoparticles of four geometries – nanocups, nanotubes with open and closed ends and plates – particularly focusing on their SERS performance as substrates for single particle sensing under near-infrared excitation. Np-Au particles demonstrated at least 5-fold increase in SERS enhancements compared to that of smooth Au nanoparticles of similar dimensions. In general, we obtain similar SERS intensity on the surface of the np-Au nanoparticles, with np-Au cups displaying higher SERS enhancement, 6×10^3 , compared to that of other structures. Furthermore, we demonstrate an additional 5-fold increase in SERS enhancement resulting from the open cavities when np-Au cups are facing up and at the open ends of np-Au tubes.

As a future work, we believe our synthesized np-Au nanoparticles can be applied in the other real applications, which include the following:

1. Fabrication of nanoporous nanoparticles of other noble metals and compositions to meet the current requirements in fuel cell catalysis

The synthetic protocols demonstrated in this dissertation can be extended to other metal nanoparticles by selecting adequate metal precursor and reducing agent. In addition, our current understanding could be employed for the controlled synthesis of nanoporous metal nanoparticles with different morphologies and composition. We are particularly interested in achieving nanoporous gold composite nanoparticles such as Au-Pt, Au-Ru, Au-Pd, Au-Pt-Ru and Au-Pt-Ru which can hold a great promise in fuel cell catalysis.

2. SERS monitoring of chemical reactions catalyzed by nanoporous gold

SERS spectra can offer the molecular information down to a single molecule sensitivity which can be utilized to track the catalytic reactions. However, the monitoring of chemical reactions catalyzed by gold nanoparticles by SERS remains a great challenge. Generally, gold nanoparticles are catalytically active when size is <10 nm but they are inefficient for SERS because of small scattering cross-sections. Hence, fabrication of gold nanoparticles with the integration of both catalytic and SERS ability can resolve this problem. In my thesis, I have demonstrated the superior electrocatalytic as well as SERS activity of nanoporous gold nanoparticles. Therefore, nanoporous nanoparticles could be a potential candidate for label-free monitoring of catalytic chemical reactions.

3. Contrast enhancement agents for biomedical imaging

An ideal contrast enhancement agent for biomedical imaging should possess the following properties: (i) strong NIR absorption where tissue is transparent, (ii) biocompatibility, (iii) good photothermal conversion efficiency, and (iv) real time

monitoring of nanoparticles delivery, distribution and their performance. Multifunctional contrast agent holds great advantages in nanomedicine by simultaneous detection and treatment. Nanoporous gold nanoparticles with tunable surface plasmon resonance in the NIR region, strong SERS hotspots within the particle and control over ligament size will be interesting for theranostic applications.

4. Systematically investigate and understand the optical as well as photo-thermal properties of nanoporous gold nanoparticles as a function of ligament size

To utilize our nanoporous nanoparticles in biomedical applications we first should understand their optical and photothermal properties. Hence, we should systematically investigate the plasmonic and photothermal properties of nanoporous gold nanoparticles both as a function of particle size and ligament size.

LIST OF PUBLICATIONS, CONFERENCES AND AWARDS

PUBLICATIONS

1. Wee Shern Chew, **Srikanth Pedireddy**, Yih Hong Lee, Weng Weei Tjiu, Yejing Liu, Zhe Yang, Xing Yi Ling. "Nanoporous Gold Nanoframes with Minimalistic Architectures: Lower Porosity Generates Stronger Surface-Enhanced Raman Scattering Capabilities." *Chem. Mater.* **2015**;
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3. Srikanth Pedireddy, Xing Yi Ling. "One-step synthesis of zero-dimensional hollow nanoporous gold nanoparticles with enhanced methanol electrooxidation performance." Poster presented at 8th Asian Photochemistry Conference 2014, Trivandrum, India.
4. Srikanth Pedireddy, Xing Yi Ling. "One-step synthesis of zero-dimensional hollow nanoporous gold nanoparticles with enhanced methanol electrooxidation performance." Poster presented at Humboldt Kolleg-2014, International Symposium on Environment and Health in 21st Century, Singapore.
5. Srikanth Pedireddy, Xing Yi Ling. "Synthesis of Spiky Ag–Au Octahedral Nanoparticles and Their Tunable Optical Properties." Oral presented at ICMAT-2013, 7th International Conference on Materials for Advanced Technologies, Singapore.
6. Srikanth Pedireddy, Xing Yi Ling. "Synthesis of Spiky Ag–Au Octahedral Nanoparticles and Their Tunable Optical Properties." Poster presented at ASC-2013, 4th Asian Spectroscopy Conference, Singapore.

SELECTED HONORS AND AWARDS

1. Awarded Best Paper award for title entitled "One-step synthesis of zero-dimensional hollow nanoporous gold nanoparticles with enhanced methanol electrooxidation performance" in the 8th Asian Photochemistry Conference 2014.
2. Awarded CBC Laboratory Teaching Assistant Award for excellent performance in the undergraduate teaching laboratory, Nanyang Technological University.
3. Awarded Best Paper award for title entitled "Synthesis of Spiky Ag–Au Octahedral Nanoparticles and Their Tunable Optical Properties" in the 4th Asian Spectroscopy Conference 2013.