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Preparation of Au/Ag Nanoshells Through a Galvanic Replacement Reaction

A Project Submitted to:

Governors State University

By: Elizabeth Maschmeyer

In partial fulfillment of the requirement for the Master of Analytical Chemistry

May 2017

Governors State University

University Park, Illinois

This is dedicated to everyone in my life who has believed in me to pursue my education from elementary school to Governors State University.

Acknowledgements

My most heartfelt thanks to my research professor who has been there to help me every step of the way, and my family who never stops believing in me. We also greatly acknowledge our collaborators for the TEM measurements.

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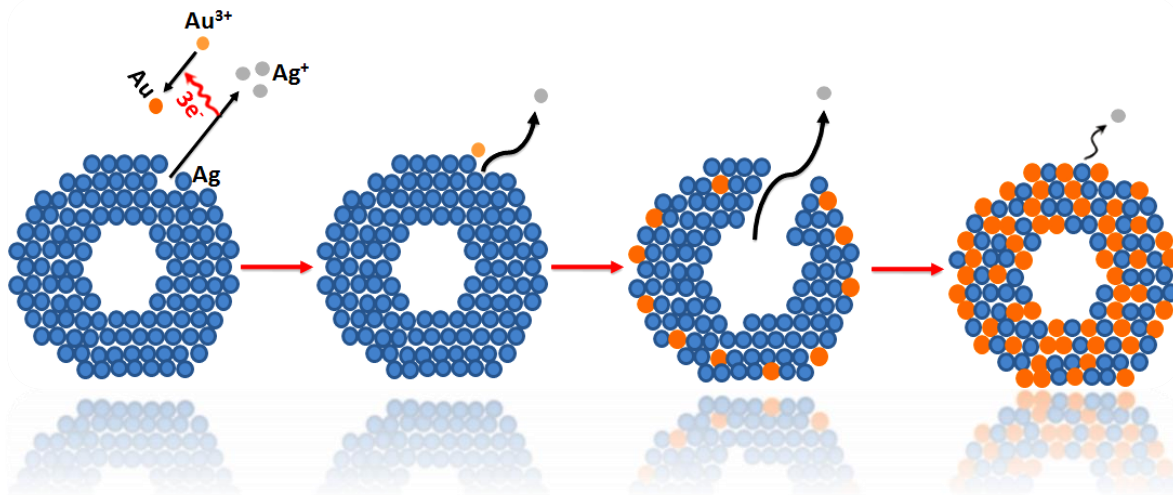
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Abstract

It generally requires solid metal templates of hollow metal structures with uniform morphology by the present galvanic replacement mediated-growth approaches. In this project report, we present a new and simple approach for the controllable synthesis of Au/Ag alloy nanoshells (NSs) by applying galvanic replacement reaction on hollow Ag template in the presence of gold salt. High quality thiol-coated spherical shape Au/Ag NSs were produced via this new synthetic approach and the hollow interior of the Ag template is very well preserved during the galvanic replacement reaction. Plasmonic property measurements reveal that Au/Ag NSs exhibit strong absorption peak and more importantly, these can maintain their optical properties even after several months. These nanoshells were studied by TEM to elucidate their structure. These studies show that the nanostructures are hollow and do not consist of a Ag core surrounded by a Au shell. The excellent stability along with the ability to maintain long lasting plasmonic features make these Au/Ag NSs useful candidates to test for fascinating application in surface plasmonics, surface-enhanced Raman scattering, chemical and biological sensing and optical labeling.



Scheme I Schematic illustration of the structural evolution at different stages of the galvanic replacement reaction between Ag hollow particle and HAuCl_4 in an aqueous solution.

Introduction

The novel physical properties observed in nanoparticle are attributed to the dramatic changes in the electronic structure.¹ Metal nanoparticles play important roles in many areas of modern science and technology. They have been widely used in photography², catalysts³, optoelectronics⁴, information storage⁵, and surface enhanced Raman scattering(SERS)⁶. The properties of metal nanoparticles are determined by the size, composition, shape, crystallography, and the type of structure. It is interesting to notice that one could control these parameters to fine tune the properties of this metal nanoparticle. In addition to that shape control of nanoparticles is important to understand basic size and shape dependent properties. These properties have led to the further development of synthetic methods that permit exquisite control of their dispersity on the nanometer scale⁷. Several methods can be produced in large quantities through solution phase methods⁸. It is possible to control the reaction and diffusion processes of room temperature to produce polymetallic hollow nanoparticles with very different morphology and composition by employing simultaneous sequential action of galvanic replacement and the Kirkendall effect⁹.

The Kirkendall effect occurs when there is a movement of the boundary layer between two metals. This motion is due to the different diffusion rates of metal atoms. This method was conceived in 1942 and was verified in 1947.¹⁰ The initial experiment used copper and brass welded to each other and was exposed to higher temperatures. The movement of the boundary layer was seen between the two since zinc diffuses into copper faster than copper into zinc. The experiment proved that diffusion of the two metal atoms included defects that help atomic jumps. These defects are called vacancies that are empty lattice sites. Creating the vacancies weakens the bonding strength of the bond-pad interface. This weakening often causes wire failures that

engineers try to prevent. This is done by diffusion layer barriers. Contrary to engineers, chemists utilize the weakening bond strength effect to create hollow nanostructures. The hollow nanostructures occur when the vacancies combine into one hollow core.¹¹

Aldinger was the first person to pursue an interest in the hollowing of silver nanoparticles caused by the Kirkendall effect.¹² He used beryllium micro particles covered with Co by evaporation or Ni by electroplating to form shell particles. He found that vacancies crash at the shell interface when a structure has any flaws. These imperfections cause the occurrence of stress cracks that separates the core from the shell. By using the nanoscale, scientists are able to use the perfection of the nanoparticle and the abundance of single crystal metal nanoparticles.¹³ This process makes the Kirkendall effect form smooth and uniform-sized hollow compound nanocrystals. To get pure-phase hollow nanocrystals, an appropriate amount of shell material compared to the starting crystals is needed. This reaction is less favorable in a solid-solid reaction. A vapor or solution phase is often more favorable. This is because the source of the shell material is continuous and sufficient.

In the beginning, the Kirkendall effect came from metal alloys, but it has now taken part in compound systems in the form of oxides and nitrides.¹⁴ In these oxides and nitrides, oxidation or nitridation of the metal element occurs quickly with a fast diffusion rate of the metal through the compounds. This was shown in a reaction of Co nanocrystals in solution in an elemental S or O₂/Ar ambient that caused the formation of hollow Co₃S₄ or CoO NPs.¹⁵ The experiment has suggested the size of the ending vacancy was smaller when compared to the beginning Co NP. The discovery has shown there was an inward growth of the product shell, because of the sulfur anions and the outdiffusion of Co cations.

The Kirkendall effect method for making hollow nanoparticles (NPs) been beneficial. The most commonly used procedure uses polystyrene and silica spheres as the sacrificial model.¹⁶ Due to the inherent size of the polystyrene and silica spheres, they usually make big hollow structures. Colloidal metal nanocrystals are able to be made with a high yield. This results in crystalline hollow NPs even in the quantum range because the colloidal metal nanocrystals are mixed with the Kirkendall diffusion. Also, the Kirkendall method is a one-step mass synthesis with almost 100% purity, which is highly favored over the many step purification routes taken in other methods.¹⁷

The plasmonic properties of noble metal nanoparticles are extremely sensitive to their size and shape. Gold nanospheres have characteristic red color but anisotropic gold nanorods have different colors. The color is due to collective oscillation of electrons in the conduction band known as surface plasmonic oscillation. The collective oscillation of the conduction electrons in resonance with certain frequencies of incident light leads to an excitation known as surface Plasmon resonance (SPR).¹¹ The resonance condition is established when the frequency of the light photon match with the natural frequency of the surface electron oscillation. Plasmonic properties of silver nanoparticles (AgNPs) have been extensively studied for their superior performances that exceed those of other metals with a surface plasmonic resonance (SPR) in the visible range like gold.¹² The plasmonic response depends on the size, shape, dielectric environment, and on mutual electromagnetic interactions among particles in close proximity.¹¹ Correlating the NPs plasmonic properties with their morphology is a fast and easy way for in situ monitoring of the synthesis by UV–visible spectroscopy.¹⁹ This is very useful in the early stages of wet chemistry synthesis, when many different chemicals are present in solution and especially sample preparation for transmission electron microscopy analysis.¹⁵

Galvanic replacement reaction (GRR) was known to be a powerful synthetic technique for converting solid metal nanostructures into hollow ones. It has been frequently employed to synthesize hollow Au/Ag nanostructures of various shapes. In this case, the driving force for the galvanic replacement reaction is the difference in the reduction potential of gold and silver metals where the deposition of the gold with a higher reduction potential onto a solid template nanostructure of silver (with a relatively lower reduction potential) occurs. This difference in the reduction potential drives the oxidation of solid silver template by the gold salt precursor to form a fully enclosed hollow Au/Ag nanostructure. The most common way of forming Au/Ag nanostructure is achieved via the reaction between HAuCl_4 and Ag nanoparticle template where the oxidation of Ag nanoparticle template, reduction of AuCl_4^- and subsequently alloying of the deposited Au with the remaining Ag in the template occur. The resultant nanoparticles are expected to be bimetallic and with hollow interiors.¹⁶ This approach has been successfully used to produce hollow bimetallic nanostructures of many different noble metals using solid Ag nanoparticle template, yet to date there has been no evidence of the forming bimetallic hollow nanostructures from a hollow Ag nanoparticle template. In addition, to best of our knowledge, no attempt has been made to synthesize hollow Au/Ag nanostructures, starting from hollow Ag nanoparticles as sacrificial templates. Attempting to make fully enclosed hollow Au/Ag nanostructure out of a hollow Ag template rather than a solid Ag template appears to be challenging since it is required to preserve the hollow template during the galvanic replacement reaction as the oxidation of remaining Ag template can cause the nanoshell (NS) to etch. Therefore, the conditions of galvanic replacement need to be adjusted in a way that the deposition of Au on the hollow Ag template nanoparticle occurs as an effective way of stabilizing the template too.

Based on the previous work done by Sanedrin et al. and Aherne et al., one possible way of protecting the Ag template against oxidation during the galvanic replacement is by maintaining a sufficiently high level of reducing agent in the reaction mixture.²⁰⁻²¹ This will guarantee that enough Ag is present in the template as the availability of reducing agent minimize the level of Ag^+ ions in the reaction mixture during the reaction. Taking the advantage of this scenario, we studied the use of silver hollow spheres as sacrificial templates to generate Au/Ag hollow spheres with well define shape and hollow structure. This attempt resulted in the formation of thiol-coated spherical shape Au/Ag hollow particles for the first time by employing galvanic replacement reaction on spherical shape Ag hollow particle as the sacrificial template.

Here, we have prepared Au/Ag hollow particles that are produced by adding HAuCl_4 to thiol-coated Ag hollow particle solution in the presence of excess reducing agent, ascorbic acid. Since substantial amount of materials are needed for the gel formation, scaled up reactions were carried out by increasing the amounts of starting materials by 10times compared to the literature synthetic method²² while keeping other manipulations the same.

Experimental Section:

I. Materials:

Silver nitrate (99.9%) and sodium borohydride (98%) were purchased from Strem Chemicals. L glutathione reduced (98%) were purchased from Sigma-Aldrich. Sodium hydroxide was purchased from VWR, and L(+) ascorbic acid (99%) and HAuCl_4 (49.0% Au) were purchased from Acros.

II. Synthesis of Ag Hollow Particles:

The silver hollow particles were synthesized following a literature synthetic method.²² with several modifications to prepare bigger particles in a larger scale. In a typical synthesis 2.6mL

millipore water was added to a 10-mL round bottom flask and it was kept in the freezer for nearly an hour until ice cubes were formed on the surface. To this ice-cold water, appropriate volumes of 10 mM silver nitrate and glutathione were added while stirring. After ~4 minutes, 0.1M sodium hydroxide (0.1M) was poured into the above mixture while vigorous stirring. After ~4 minutes a freshly prepared 10 mM sodium borohydride solution was injected quickly. The resulting mixture was stirred slowly for nearly an hour.

III. Synthesis of Au/Ag Hollow Particles:

Au/Ag alloy hollow particles were prepared by employing galvanic replacement reaction. To the as-prepared silver hollow particle solution, ascorbic acid solution (200 μ L, 10 mM) was added and then a solution of HAuCl_4 (8 mL, 0.5 mM) was added at a rate of 1 mL min^{-1} using a syringe pump. The resulting solution was stirred slowly for few hours. The color change from orange to bright blue indicates the formation of Au/Ag alloy.

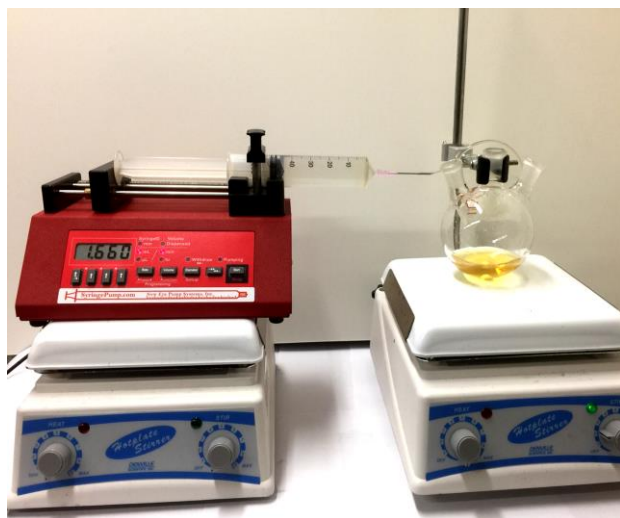


Figure 1. Programmable syringe pump used to gradually add small amounts of solution at a desired rate.

IV. Characterization:

Spectroscopic Instrumentation and Methods:

A PerkinElmer Lambda 35 UV-Vis spectrophotometer was used for optical absorption measurements on Ag NSs and Au/Ag NSs. The absorption spectrum of the silver seeds solution was measured without dilution while the silver nanoprism and Ag/Au hollow nanoprism solutions were diluted $\times 3$ in Millipore water and measured from 700 to 300 nm.

Transmission Electron Microscopy (TEM)

The TEM analysis was performed by using JOEL JEM-1230 analytical electron microscope with Gatan ultra scan 4000 camera operating at a 120-kV acceleration voltage. One drop of AgNS or Au/Ag Ns solution was added onto a carbon-coated copper TEM grid and the solvent was allowed to evaporate few hours before introduction to the instrument.

Results and Discussion

Thiol-coated spherical shape Ag NSs were prepared by employing fast reaction diffusion process as reported in the literature.²² In addition, Ag NSs with different sizes were also prepared by employing the same synthetic method by changing the ratio of reactants. Since substantial amount of materials are needed for the property characterization, scaled up reactions were carried out by increasing the amounts of starting materials by 20 times compared to the reported procedure while keeping other manipulations same. Ag NSs were produced by the formation of Ag₂O first by reacting AgNO₃ with sodium hydroxide in the presence of glutathione followed by the reduction of preformed Ag₂O by freshly prepared sodium borohydride solution. This two-

step reaction is signified by turning the yellow color solution of Ag_2O into dark orange color. This scaled up reaction still produce narrowly distributed Ag NSs in a rapid and reproducible manner under ambient condition. In search of clear relationship in shift in the SPR peak, several experiments were carried out by varying the amounts of glutathione, silver nitrate, sodium borohydride, and sodium hydroxide. The first comparison was done by varying amount of AgNO_3 while keeping every other component in the solution same. In order to accomplish this, series of samples were prepared by adding increasing amounts of AgNO_3 (90 μL , 120 μL , 150 μL , 180 μL , 210 μL , 240 μL , 270 μL , and 300 μL). By preparing a series of samples in this manner we could monitor the variation in the formation of the hollow sphere. The reaction progress was monitored by measuring the evolution of SPR. As shown in Figure 2, there is an initial red-shift at for first there reactions and this is followed by a slight blue shift as increased amounts of AgNO_3 were reacted. However it is difficult to identify a significant relationship as the position of the SPR peak vary between a narrow range (475 – 510 nm).

We also prepared series of samples by varying the glutathione content while keeping other manipulations constant (10 μL -168 μL). As shown in Figure 3, there is a significant initial red-shift and broadening of the SPR but this is followed by a progressive blue shift as increased amounts of glutathione were reacted. The evolution of the SPR can be correlated to the changing structure of the nanoparticles during the reaction by looking at transmission electron microscopy (TEM) data of each sample.²¹

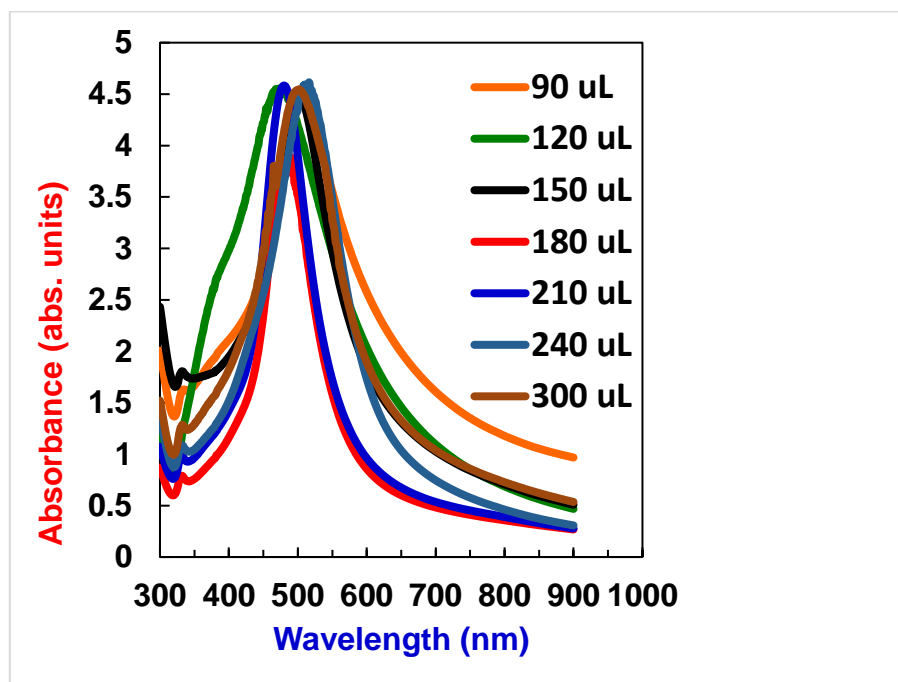


Figure 2. UV-Visible absorption spectra of the series of Ag hollow particles obtained by using different volumes of AgNO₃ solution: 90 μ L, 120 μ L, 150 μ L, 180 μ L, 210 μ L, 240 μ L, 270 μ L, and 300 μ L.

We also prepared another series of samples (Table 1) by varying the AgNO₃ (10 μ L-168 μ L) and glutathione (18 μ L-100 μ L) at the same time while keeping other manipulations constant. The positions of the main SPRs of these samples are well separated as can be seen in Figure 4. It has been reported that the spectral position of the SPR can be tuned by controlling the size of the Ag nanoprism without any significant variation in thickness.²² Accordingly one can think of the different peak positions of the samples and the different colors as shown in Figure 4 are due to different sizes and thicknesses of silver hollow particles prepared according to the conditions given in the table 1.

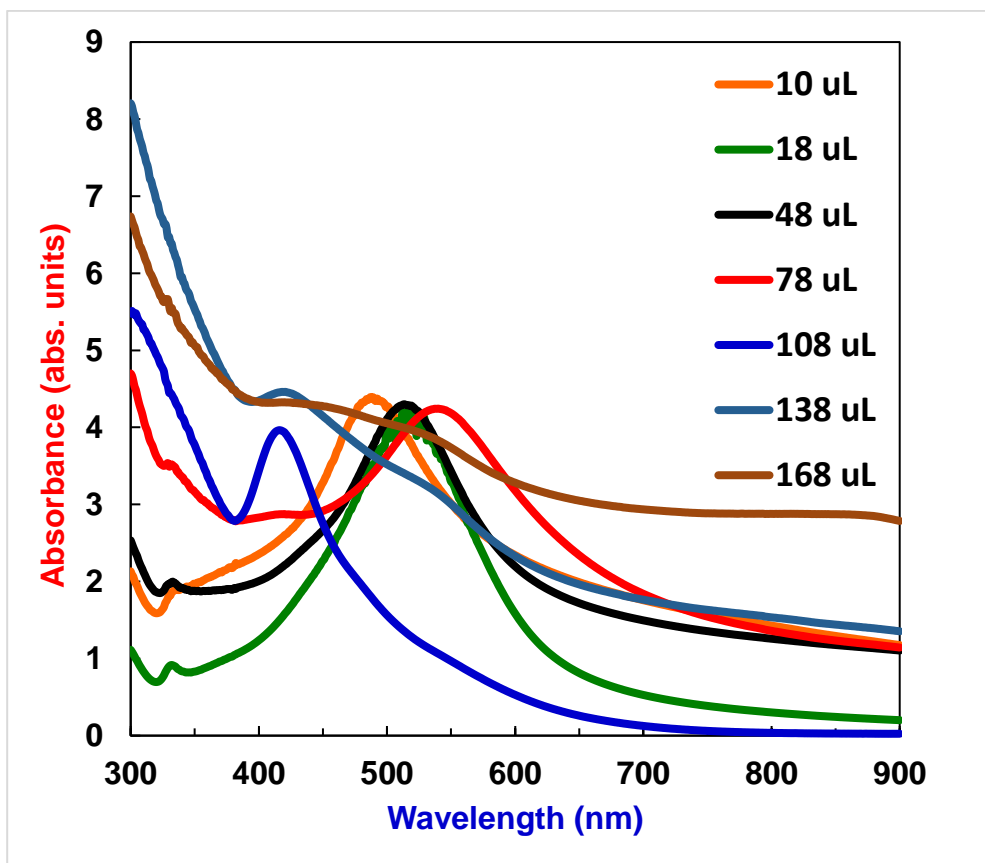


Figure 3. UV-Visible absorption spectra of the series of Ag hollow particles obtained by using different volumes of glutathione solution: 10 μ L, 18 μ L, 48 μ L, 78 μ L, 108 μ L, 138 μ L, and 168 μ L.

To characterize the hollow particles produced by this method and to explore the relationship between nanoparticle dimensions and the position of the main SPR, TEM analysis of statistically significant numbers of particles from samples need to be carried out and such measurements will be done in the future.

Table 1. Volumes of AgNO₃, Glutathione, NaOH, and NaBH₄ Used in the Synthesis of Ag Hollow Particles

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Water	2.6 mL	2.6 mL	2.6 mL	2.6 mL	2.6 mL
10 mM AgNO ₃	150 μL	150 μL	300 μL	300 μL	500 μL
10 mM Glutathione	18 μL	55 μL	60 μL	75 μL	100 μL
0.1 M NaOH	500 μL	500 μL	500 μL	500 μL	500 μL
10 mM NaBH ₄	180 μL	180 μL	180 μL	180 μL	180 μL

Since substantial amount of materials are needed for the gel formation, scaled up reactions were carried out by increasing the amounts of starting materials by 10 and 20 times compared to the literature synthetic method²² while keeping other manipulations the same (Table 2). Figure 5 displays absorption spectra of the samples prepared in larger scale compared to the original sample. It is interesting to notice that the hollow nanoparticles prepared in larger scale too exhibit sharp plasmon resonance absorption peaks around 480 nm.

Table 2. Volumes of AgNO₃, Glutathione, NaOH, and NaBH₄ Used in the Synthesis of Ag Hollow Particles in larger scale.

	Original	10 time scale up	20 time scale up
Water	2.6 mL	25 mL	50 mL
10 mM AgNO ₃	150 μL	1.5 mL	3 mL
10 mM Glutathione	18 μL	180 μL	360 μL
0.1 M NaOH	500 μL	5 mL	10 mL
10 mM NaBH ₄	180 μL	1.8 mL	3.6 mL

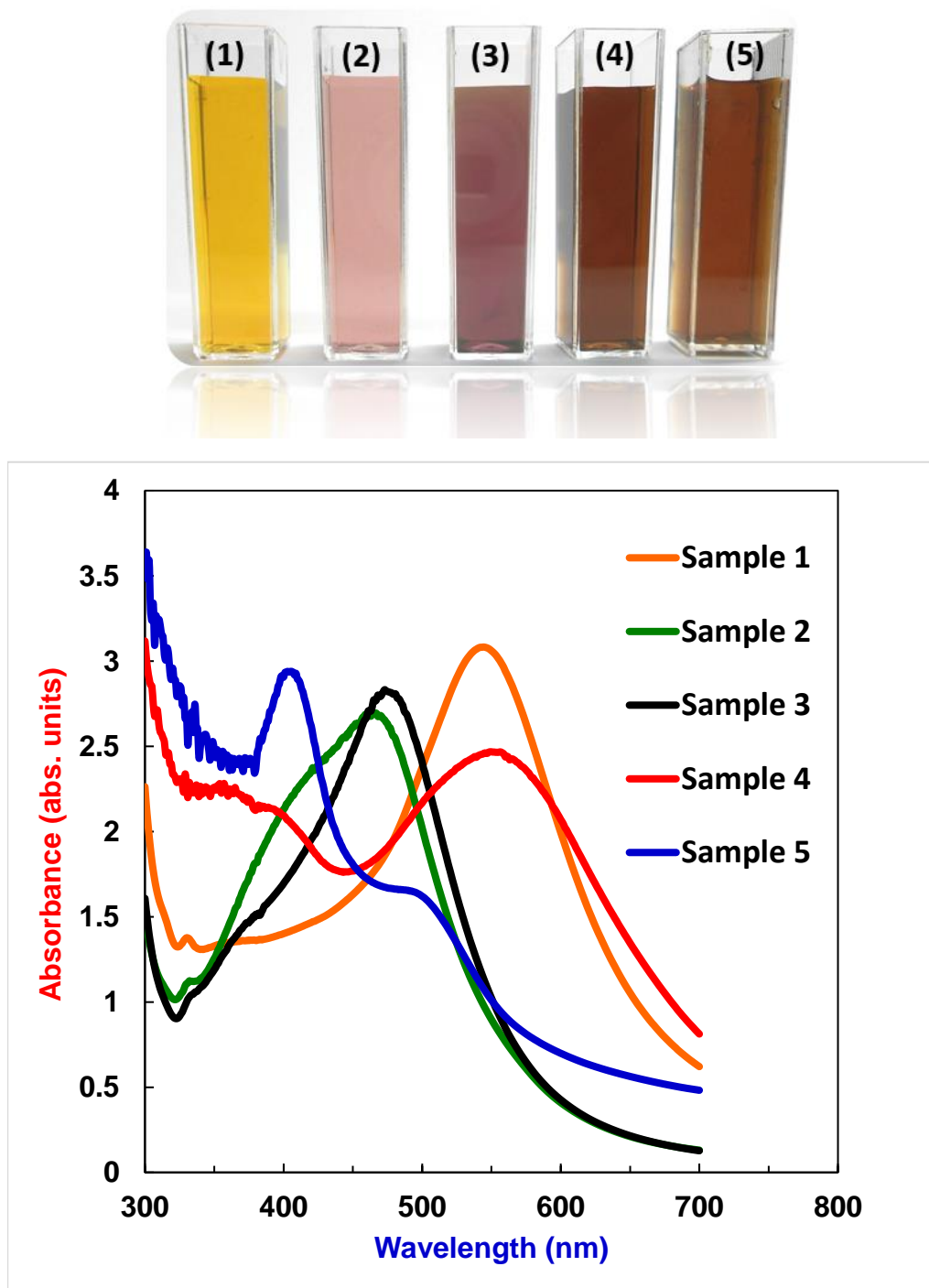


Figure 4. Photograph of series of samples illustrating range of colors obtained (top). Normalized spectra of a series of as-prepared five samples obtained using different volumes of AgNO_3 and Glutathione(bottom).

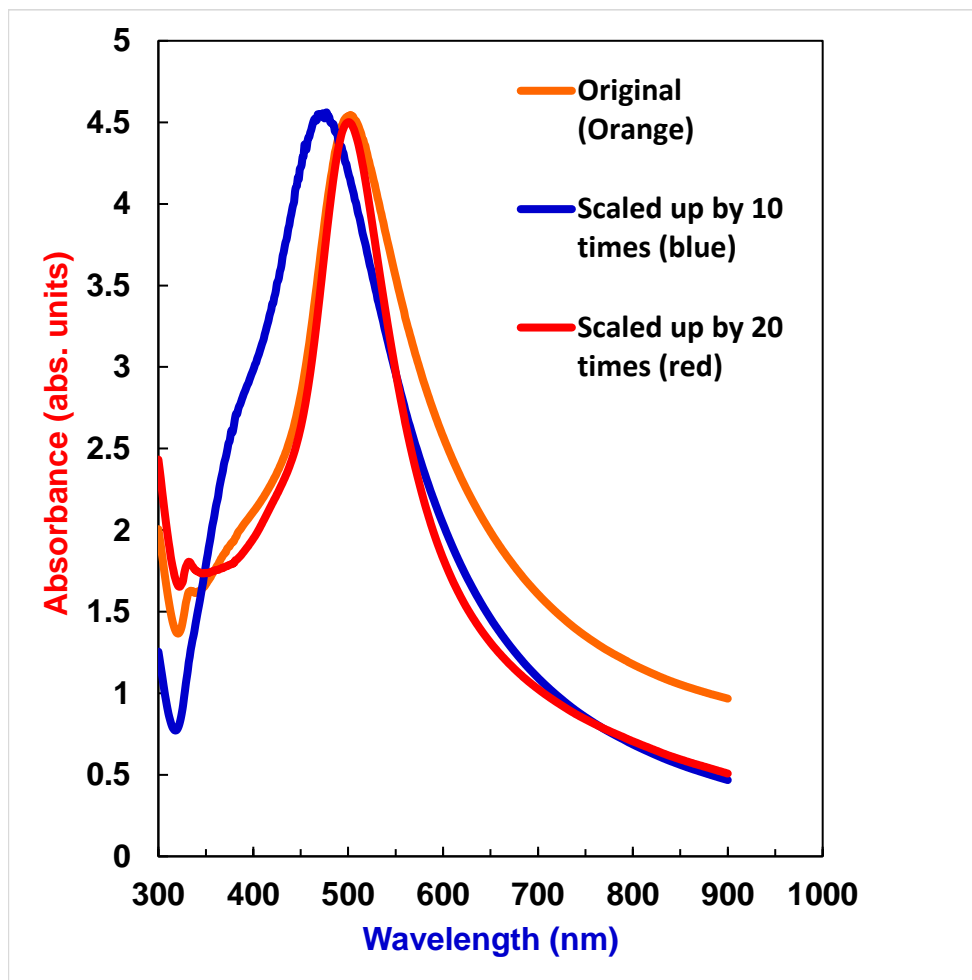


Figure 5. UV-Visible absorption spectra of three different samples: original silver hollow particles showing SPR peak around 480 nm (orange), hollow silver nanoparticles prepared by increasing the amounts of reactants by ten times compared to original sample (blue), and the sample prepared by increasing the amounts of reactants by twenty times (red).

The Ag hollow particles grown by this route (scaled up by ten time) display a narrow Surface Plasmon Resonance (SPR) maximum at ~480 nm. Initially, the galvanic replacement reaction

was attempted. However, as shown in Figure 6, it was realized that this route was less productive to form Au/Ag hollow nanostructures since the pores of the hollow particles start to collapse as the reaction goes leading us to believe that the size and the thickness of the Ag nanoshell (NS) might be playing important role to preserve the hollow interior enabling the hollow structure to be maintained during the galvanic replacement reaction. This initial sturdy however resulted in the formation of Au/Ag alloy nanoparticles. Therefore, we were induced to prepare Ag hollow particles with different sizes employing the same synthetic method by changing the ratio of reactants (Table 3) and reacting those as prepared Ag nanoshells with appropriate amounts of HAuCl_4 in the presence of ascorbic acid.

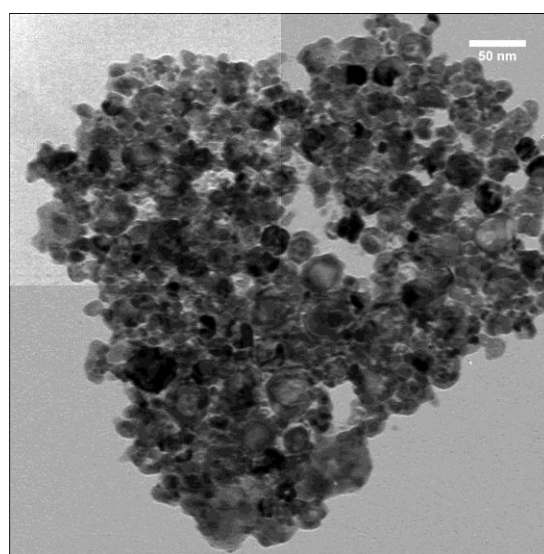


Figure 6. TEM image showing pores of the Ag NSs start to collapse as the reaction with HAuCl_4 proceeds and eventually resulting in the formation of Au/Ag alloy nanoparticles.

Table 3. Volumes of AgNO₃, Glutathione, NaOH, and NaBH₄ Used in the Synthesis of Ag Hollow Particles

Sample #	H ₂ O/ml	AgNO ₃ /mL	HS-G /mL	NaOH/mL	NaBH ₄ /mL
Sample 1	25	1.5	0.15	5	1.8
Sample 2	25	0.5	0.05	2.5	1.8
Sample 3	25	0.35	0.05	5	1.8

Since the optical properties are strongly dependent on the structure and composition of the nanostructure, searching for bimetallic hollow nanostructures with accurately controlled structures and compositions is very useful to obtain such materials with interesting properties. It has been demonstrated that surface plasmon resonance peaks of the hollow Au/Ag bimetallic nanoparticles could be tuned across the visible spectrum region by controlling the Au:Ag ratio in the galvanic replacement reaction.¹⁶ Knowing this fact, we decided to study how the size and position of the plasmon resonance of our Au/Ag NSs can be controlled through the adjustment of reaction condition. For this study Ag NSs showing SPR ~550 nm was prepared by employing the condition given for sample 3 in table 3 where silver nitrate (350 μ L, 10 mM), glutathione (50 μ L, 10 mM), sodium hydroxide (5 mL, 0.1M) and a freshly prepared sodium borohydride solution (1.8 mL, 10 mM) were reacted. Attempts were made to prepare Au/Ag alloy nanoshells with different sizes by adding different amounts of HAuCl₄ to as prepared Ag NS template solution in the presence of reducing agent, ascorbic acid (200 μ L, 10 mM). By preparing a series of samples

in this manner, one can also monitor the progress of the Au/Ag NS formation. At first to Ag NSs showing SPR ~ 550 nm, solution of HAuCl_4 (8 mL, 0.5 mM) was added at a rate of 1 mL min^{-1} . The resulting Au/Ag NS sample display a slight progression in color as the SPR red-shifted and exhibit maximum surface plasmon resonance peak at 570 nm as shown in Figure 7. Transmission electron micrographs (TEM) show that almost all the individual Ag NSs consist of significantly larger single hollows in the center of the nanosphere (Figure 8A). The Ag NSs grown by this route exhibit an average outer diameter of 63.7 ± 10.5 nm and shell thickness of 12.4 ± 2.4 nm and these are much bigger than the Ag NSs prepared by literature synthetic method where those showing SPR at 480 nm possess the outer diameter of 24.1 ± 4.5 nm and shell thickness of 5.8 ± 0.9 nm.²¹ Transmission electron micrographs (TEM) show that in almost all the individual Au/Ag nanoshells, significantly larger single hollows have been created as indicated by variation in the degree of contrast between edges and middle of the nanosphere.

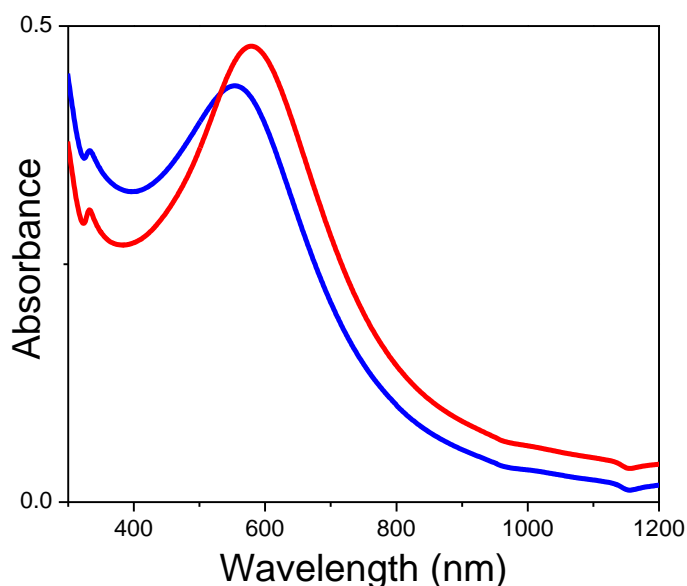


Figure 7. UV-Visible absorption spectra of Ag nanoshells (left) and Au/Ag alloy nanoshells (right) produced by galvanic displacement of the pre-formed Ag nanoshells.

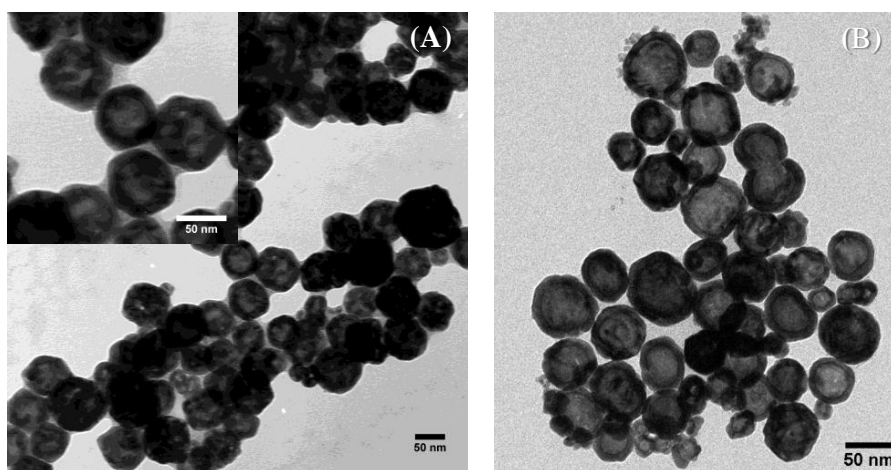


Figure 8. TEM images of Ag nanoshells (A) and Au/Ag alloy nanoshells (B) produced by galvanic displacement of the Ag nanoshells.

It is interesting to notice that as shown in Figure 8B, Au/Ag nanoshells still retain the spherical shape after the galvanic displacement reaction and the shell thickness uniformly distributed around the hollow interior of the particles. This suggests that oxidation of Ag template initiated uniformly over the entire core of the particle. This is quite a remarkable finding and indeed this is the first time that such Au/Ag nanoshells have been formed from a Ag NS template. Based on a calculation from about 100 Au/Ag nanoshells, the outer diameter and shell thicknesses were obtained as 60.9 ± 10.8 nm and 9.0 ± 1.9 nm, respectively. It is reasonable to believe that due to the presence of sufficient amount of reducing agent (ascorbic acid), after initial oxidation of silver from Ag NSs by galvanic replacement reaction, alloy Au/Ag nanoshells

are formed by coreduction of Ag^+ and AuCl_4^- as suggested by Aherne et al. to explain how the alloying of Ag with Au occur when there is excess ascorbic acid at the low temperatures.²¹ This ascorbic acid-mediated co-deposition facilitates the formation of well-defined Au/Ag NSs. Our ability to form Au/Ag hollow structure using Ag hollow particles as sacrificial template by employing a general experimental approach allowed us to gain insight regarding the mechanism of Ag-Au alloying as illustrated in scheme I. Galvanic replacement reaction included two stages. At the initial stage, replacement reaction starts at specific sites with relatively high surface energies and then seamless hollow nanostructures with smooth Au–Ag alloy walls were evolved through an integration of galvanic replacement with alloying.²⁴ Ag atoms also simultaneously migrate into the Au shell to form a seamless, hollow nanostructure with Au–Ag alloy wall. This mechanism for galvanic replacement is applicable irrespective of the morphology and composition of the sacrificial templates as long as the presence of appropriate reduction potentials difference between the two metals involved.

Conclusion

In conclusion, this work makes it clear that from a hollow Ag nanoparticle template, chemical synthesis of bimetallic hollow nanostructures with well-controlled shapes, sizes, and structure is a practical reality. The major requirement seems to be the adjustment of the reaction conditions to preserve the hollow template during the galvanic replacement reaction. We studied the wide tunability of the plasmonic features of Ag hollow particles by engineering the size of the particles through varying the reaction conditions. According to the study of optical property measurements on Ag hollow samples with increasing glutathione content, it can be seen that surface plasmon resonance peaks of the Ag hollow particles prepared with higher glutathione

content lie at longer wave lengths and are red-shifted compared to the surface plasmon resonance of AgNS template and then blue shift. We successfully prepared thiolate-capped Au/Ag alloy particles in large scale by employing galvanic replacement reaction of Ag hollow particles. Our success in preparing Au/Ag alloy will be helpful in constructing similar nanostructures such as Pt/Ag, Pd/Ag bimetallic alloy.

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