



Effect of Metal Concentration on Shape and Composition Changes in Gold-Silver Bimetallic Systems

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Abstract

Ag-Au alloy nanoparticles with tunable shape and composition were prepared by a replacement reaction between Ag nanoparticles and chloroauric acid at one hundred and fifty degree celsius temperature under oilbath heating. The replacement reaction between silver nanostructures and chloroauric acid solution has recently been demonstrated as a versatile method for generating Au-Ag alloy nanostructures via galvanic reaction. Here we describe the results of a systematic study detailing the morphological, structural, compositional involved in such a heterogeneous reaction on the nanoscale.

This method leverages upon the rapid interdiffusion of Ag and Au atoms in the reduced dimension of a nanoparticle in the replacement reaction. This method of preparation has several notable advantages: (1) independent tuning of the shape, size and composition of alloy nanoparticles; (2) production of alloy nanoparticles in high concentrations; (3) general utility in the synthesis of alloy nanoparticles that cannot be obtained by the co-reduction method.

1. Introduction

The properties of alloy nanoparticles can be very different from the properties of the component monometallic nanoparticles. This provides yet another dimension in tailoring the properties of nanomaterials besides the usual size and shape manipulation. Ag-Au alloy nanoparticles can be prepared by a number of methods, the most common one being the co-reduction of the corresponding metal precursor salts in the presence of a stabilizing agent. [1] Water in oil microemulsions have also been used by Chen to produce Ag-Au alloy nanoparticles. [2] In the digestive ripening method of Klabunde and coworkers, [3] Ag-Au alloy nanoparticles were formed by refluxing Ag and Au nanoparticles in 4-tert-butyltoluene in the presence of an alkanethiol. Other methods of preparation of a more physical nature include laser ablation [4] and evaporation condensation. [5] Despite a myriad of methods of preparation, the large scale synthesis of alloy nanoparticles with good control of size and composition remains a challenge. First, size tuning by chang-

ing the synthesis conditions is more complex for the alloy nanoparticles than for the monometallic nanoparticles. This is because the synthesis conditions affect the reduction potentials and the effectiveness of the stabilizing agent in different ways. Second, most current methods of preparation are unable to decouple shape, size and composition control, which increases the difficulty in producing alloy nanoparticles with the same composition but different sizes, or the same size with different compositions. In addition, silver ion has the propensity of forming insoluble halide precipitates whenever the synthesis involves the use of a halogen containing metal precursor salt (e.g. chloroauric acid). The precipitation of AgCl contaminates the alloy nanoparticles formed and further complicates the control of alloy composition.

Here, we report a polyol synthesis of monodisperse Au-Ag alloy nanoparticles through interface diffusion of auric ions and Ag atom of spherical and/ decahedron Ag nanoparticles. We first prepared spherical Ag nanoparticles by thermal reduction of silver nitrate in ethylene glycol (EG)

under Ar gas bubbling in presence of PVP for 50 min heating. These Ag nanoparticles were then used as seeds (sacrificial template) on which Au was deposited by reduction of chloroauric acid in EG under various metal concentrations at one hundred and fifty degree celsius. Spherical Ag seeds, chloroauric acid and PVP in EG are heated at one hundred and fifty degree celsius to facilitate Ag and Au diffusion in Ag seeds for the formation of Au-Ag alloy nanoparticles. In the synthesis, EG and PVP are used as reducing agent and stabilizing surfactant respectively.

Our results clearly demonstrated that the template engaged replacement reaction proceeded through two distinctive steps: (i) the formation of seamless hollow structures (with the walls made of Au-Ag alloys) via a combination of galvanic replacement (between Ag and chloroauric acid) and alloying (between Au and Ag) under Ar gas bubbling. Metal concentrations and operating gas bubbling Ar are seemed to play the most important role in determining the final morphology of the product because the solubility product constant of AgCl and the nature of gas bubbling. This method can also be used to produce other alloy nanoparticles, even those which cannot be obtained by the co-reduction method, e.g. Ag-Pd alloy nanoparticles.

2. Experimental Procedure

2.1 Preparation of Ag Seeds:

15 mL of EG solution was preheated at one hundred and fifty degree celsius and maintained at this temperature for 60 min under Ar gas bubbling. Then a mixture of silver nitrate and PVP (Mw = 40 k in term of monomer units) as a polymer surfactant in 5 mL of EG was added and

further heated at one hundred and fifty degree celsius for 50 min under Ar gas bubbling. The products were collected by centrifugal separation at 12000 rpm three times for 30 min to remove all byproducts produced in the supernatant.

2.2 Shape and Component Changes in Products by the Addition of Ag Particles to $H AuCl_4.PVP.EG$ Solution under Ar Gas Bubbling:

A solution of chloroauric acid in EG was mixed with prepared solution (250 mM PVP in 20 mL EG) contained Ag seeds. It was heated from room temperature to one hundred and fifty degree celsius in oilbath heating for 60 min under bubbling gas Ar with sampling 10, 30 and 60 min. The final concentrations of chloroauric acid, silver nitrate and PVP were 2.4, 24 and 250 mM (Mw = 40 k in term of monomeric units) respectively.

When the effects of concentration of Au and Ag precursor salts were examined, the concentration of chloroauric acid was changed from 2.4 mM to 1.2 or 4.8 mM for Au and from 24 to 12 or 48 mM for the preparation of Ag seeds. The Ag/chloroauric acid and PVP/chloroauric acid molar ratios were kept at the same values as those used at initial condition. The solution temperature was increased from room temperature to one hundred and fifty degree celsius by heating for 6 min; it was kept at that temperature for 60 min with sampling at 10, 30, and 60 min. The total flow rate of gas bubbling was kept at 150 sccm using mass flow controllers.

2.3 Analyses of Shape and Component of Products:

For TEM (200 kV, JEM-2000XS; JEOL) observations Ag and Au-Ag bimetallic particles were ob-

tained from ethanol solution by centrifuging the colloidal solution at 15,000 rpm for 30 min three times. The TEM-EDS data were also measured (200 kV, 2100F; JEOL).

3. Result and Discussion

Galvanic replacement reaction has been demonstrated as a general and effective means for preparing metallic nanostructures (e.g., thin films) by consuming the more reactive component. We have focused on spherical Ag particles because this class of nanostructures provides a model system with monodispersed size and well-defined facets. Since the standard reduction potential of chloroauric ion/Au pair (0.99 V vs standard hydrogen electrode, SHE) is higher than that of the silver ion/Ag pair (0.80 V vs SHE), silver would be oxidized into Ag cation when silver nanostructures and chloroauric anion are mixed in organic polyol medium.

3.1 Morphological and Structural Changes Involved in the Reaction:

Both TEM and TEM-EDS were used to follow the morphological and structural changes involved in various stages of the replacement reaction between spherical/decahedron Ag particles (templates) and chloroauric acid solution.

3.2 Shape and Component Changes in Products under Ar Gas Bubbling:

We used oilbath heating for the synthesis of Au-Ag alloy particles using a mixture of spherical Ag nanocrystals as an sacrificial template and chloroauric acid/PVP in EG solution under Ar gas bubbling at one hundred and fifty degree celsius. Most of Ag seed particles are twin particles (decahedron) in which twin lines

are appeared under oil-bath heating of silver nitrate/PVP(40K)/EG solution with Ar gas bubbling at one hundred and fifty degree celsius for 50 min.

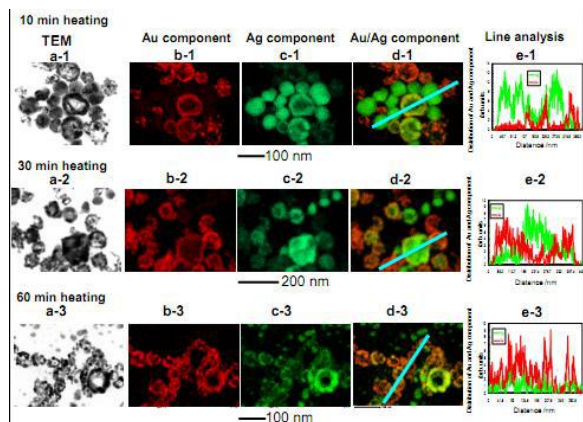


Fig. 1: Typical TEM and TEM-EDS images of Au-Ag bimetallic products obtained after heating Ag seeds. HAuCl_4 .PVP.EG solution under Ar gas bubbling.

Fig. 1 depicts TEM-EDS image of Ag nanoparticles (all started with the same amount), they had reacted with 2.4 mM chloroauric acid at one hundred and fifty degree celsius under Ar gas bubbling. Fig. 1a-1 gives a typical TEM image of spherical Ag nanoparticles, indicating the monodispersity that could be achieved using the modified polyol process, where twin decahedron and spherical particles with average size 18 nm are observed. In most Ag particles, five-twin lines are observed, (see also fig. 2) indicating that they are seeds of five-twin decahedral particles. After the Ag structures had reacted with 2.4 mM

chloroauric acid solution in presence of PVP under Ar gas bubbling for heating 10 min, a pin hole is formed at a specific site of the surface, indicating that the replacement reaction was initiated locally rather than over the entire surface. As shown in fig. 1a-1, the holes can be clearly observed as on the surfaces of spherical particles. This observation suggested that only one hole is formed on each particle because each polycrystalline particles have planer defect on their surfaces, from which the pin hole would be originated via replacement reaction. The newly formed surfaces containing holes should represent the most active sites for further replacement reaction.

To obtain more information related to distributions of Au and Ag components in the product particles at different heating times, TEM-EDS measurements and line analysis were conducted for 10 min heating in figs. 1a-1-1e-1. These data clarify that the particles along diagonal lines are uniform Ag-rich Ag/Au alloys and the atomic ratio of Ag : Au in porous particles was 75 : 25 %. EDS data show that porous particles are Ag rich Ag/Au alloy particles which are similar with concept of line analysis along porous ring like particles spectra in fig. 1e-1. The fluctuation of Au spectra is much higher than 10 min that means the percentage of Au atom increases with increase of heating time for 30 min in figs. 1a-2-1e-2 under the same experimental condition. After 60 min heating, the atomic ratio of Au : Ag was 62 : 38 in final product particles due to more replacement reaction between Au and Ag atoms in fig. (1a-3-1e-3). The residual Ag atoms are dissolved and rereduced to small Ag particles dispersed in solution that are observed in high contrast fig. 3.

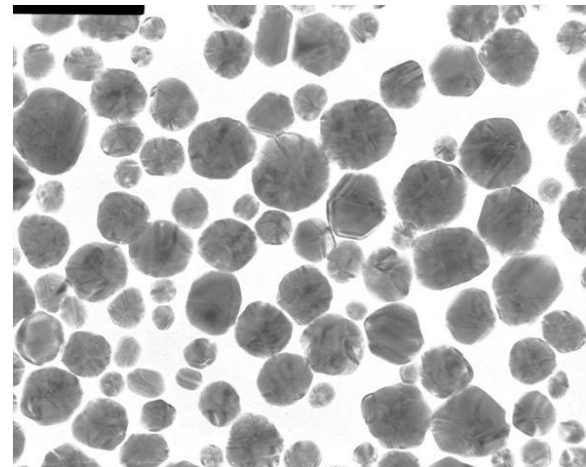


Fig. 2: TEM image Ag nanoparticles obtained from AgNO_3 .PVP.EG solution after heating for 50 min under Ar gas bubbling.

3.3 Effect of Precursor Salt Concentrations:

The effects of precursor salt concentration were examined by changing chloroauric acid and silver nitrate concentrations from 2.4 mM to 1.2 or 4.8 mM and from 24 to 12 or 48 mM to prepare Ag seeds as templates respectively. The molar ratio of Au, Ag precursor and PVP was kept constant as 24 mM for the preparation of Ag seed and in the galvanic reaction medium. Figs. 4 and 5 show TEM and TEM-EDS data at 1.2 and 4.8 mM of chloroauric acid solution after heating for 60 min. At 1.2 mM, no significant shape and composition change occur in Ag templates but major products are spherical Ag rich Ag/Au particles and few numbers of ring-like particles are produced. The distribution ratio of Ag:Au was 95 : 5 as

shown in line analysis in fig. 4. It is reasonable to assume that below 2.4 mM chloroauric acid solution is not appropriate amount for galvanic reaction to produce ring-like or ribbon type Au/Ag particles.

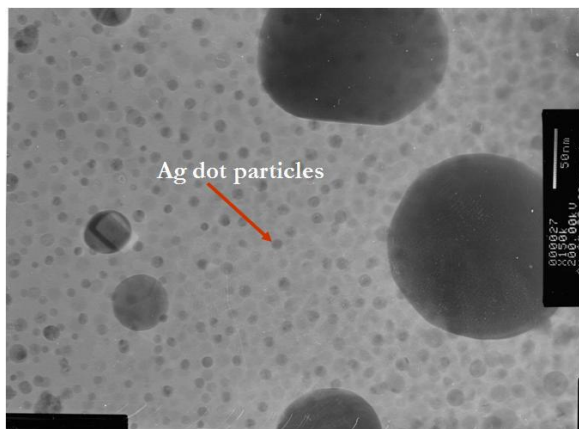


Fig. 3: TEM image of small Ag particles for 48 nm concentration of silver nitrate

At 4.8 mM, a drastic changes in shape, size and component for spherical Ag templates to Au rich Au/Ag alloy particles produced after heating for 60 min in fig. 5. Major products (yield: 99 %) were spherical or decahedral Au-rich Ag/Au alloy particles. The atomic ratio of Au : Ag in Ag/Au alloy particles was 97 : 3. That atomic ratio was nearly opposite at low concentration of chloroauric acid. The Ag atoms from the template are dissolved in solution in presence chloroauric anion.

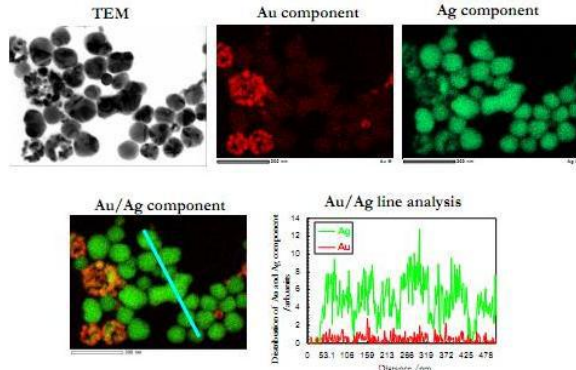


Fig. 4: Typical TEM and TEM-EDS images data obtained after heating for 60 min. The chloroauric acid concentration for galvanic reaction with Ag seeds was 1.2 mM.

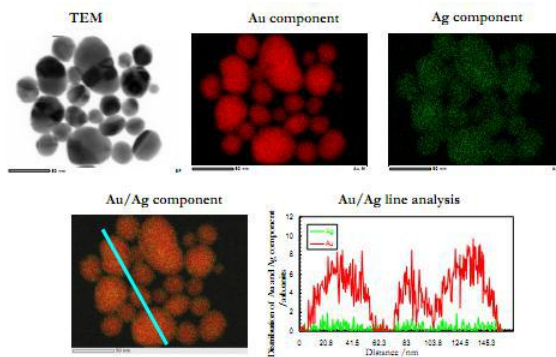


Fig. 5: Typical TEM and TEM-EDS images data obtained after heating for 60 min. The chloroauric acid concentration for galvanic reaction with Ag seeds was 4.8 mM.

The dissolved silver ion is reduce to small Ag particles (5nm) that are abundantly dispersed in solution shown in fig. 6. These results imply that shape, size, and component distributions of the product depend on the metal precursor concentration and higher chloroauric acid concentration than 2.4 mM are favorable for the preparation of Au rich Au/Ag alloy particles with initial shapes just like Ag templates.

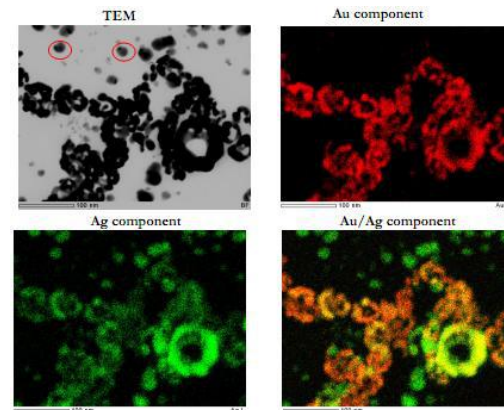


Fig. 6: Expanded of Fig. 1a-3-d-3

4. Conclusion

In summary, we have demonstrated that a change between Au deposition and Ag oxidation in galvanic replacement reactions can lead to differences in the morphology, composition of the resultant hollow nanostructures. When spherical Ag particles were heated with chloroauric acid/PVP/EG solution at one hundred and fifty degree celsius under Ar gas bubbling then different types of

Au/Ag alloy particles were formed at the early stages of galvanic replacement reaction. Metal concentrations are played an important role on the preparation of Au/Ag alloy particles. Au-Ag alloy nanoparticles were prepared by the replacement reaction between Ag nanoparticles and chloroauric acid at one hundred and fifty degree celsius. In case of 4.8 mM concentration of chloroauric acid, the Au distribution in Au-Ag alloy had more intensive peak than that of 1.2 mM and 2.4 mM concentration of chloroauric acid. TEM-EDS confirmed the formation of homogeneous Au/Ag alloy nanoparticles. The alloy nanoparticles were formed by the rapid interdiffusion of Au and Ag atoms as a result of the reduced

dimension of the Ag nanoparticles., The method has several notable advantages such as the ease of independent control of both size and composition of the alloy nanoparticles, and the production of the alloy nanoparticles in relatively high concentrations. This method is a versatile method for synthesizing these nanostructures as well as tuning their LSPR peaks for use in controlled release of drugs, optical sensing, and photothermal therapy.

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