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Preparation of novel silver–gold bimetallic nanostructures by seeding with silver nanoplates and application in surface-enhanced Raman scattering

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Abstract

Novel silver–gold bimetallic nanostructures were prepared by seeding with silver nanoplates in the absence of any surfactants. During the synthesis process, it was found that the frameworks of silver nanoplates were normally kept though the basal plane of silver nanoplates became rugged. The real morphology of these nanostructures depended on the molar ratio of gold ions to the seed particles. When the molar ratio of gold ions to silver atoms increased from 0.5 to 4, porous or branched silver–gold bimetallic nanostructures could be made. The growth mechanism was qualitatively discussed based on template-engaged replacement reactions and seed-mediated deposition reactions. Due to the unusual structures, they exhibited interesting optical properties. Moreover, they were shown to be an active substrate for surface-enhanced Raman scattering measurements.

Keywords: Silver nanoplates; Seed-mediated growth; Silver–gold bimetal; Surface-enhanced Raman scattering; Branched particles

1. Introduction

Shape-controlled syntheses of metal nanoparticles have attracted a great deal of attention because their optical, electronic and magnetic properties are strongly dependent on the size and shape of the particles [1–5]. Many nonclassical nanoparticles, such as nanorods [6,7], nanowires [8–10], nanoplates [11,12], nanocubes [13–15], etc., have been synthesized and characterized. To further explore their fascinating shape-dependant optical and electric properties, it is still a challenge to develop simple synthetic approaches to produce novel nanostructures for both fundamental studies and potential applications.

Recently, it has been an interesting subject to construct novel metal nanostructures by use of metal particle as templates Sun et al. presented a general approach to generate nanoscale hollow structures of metals by reacting solutions of appropriate salt solutions with solid template of a more reactive metal [16]. For example, Au–Ag nanoboxes [16] could be formed through galvanic replacement reaction between silver nanocubes and HAuCl [4]. Our group also reported a simple method for preparing novel Ag–Au bimetallic colloids with hollow interiors and bearing nanospikes by seeding with citrate-reduced silver nanoparticles [17]. Dumbbell-shaped Au–Ag core–shell nanorods were produced using gold nanorods as the seeds [18].

As one of two-dimensional nanomaterials, silver nanoplates are highly oriented single crystals with (111) planes as the basal plane. The sides or edges of nanoplates are bound by (200) or (111) planes [19,20]. Owing to their unique structure, they had been applied as templates to make novel metal nanostructures with unusual optical properties, for instance, single crystalline gold nanorings could be produced using silver nanoprisms as templates [19a,21]. With the assist of the surfactant cetyltrimethylammonium bromide (CTAB), corrugated bimetallic particles [22] or multipod gold nanocrystals [23] could be made from silver nanoprisms or nanoplates. Silver nanoprisms could also be used as a template to generate gold–silver alloy framework structures [24]. Herein, we take advantage of the anisotropic structure of silver nanoplates as seeds to prepare novel silver–gold bimetallic nanostructures without any surfactants. By controlling the molar ratio of gold to silver, porous or branched silver–gold bimetallic particles

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can be synthesized. These unusual structures are difficult to be achieved by the normal methods. The modified shapes of the silver nanoplates directly influence their optical properties as well as the surface-enhanced Raman scattering (SERS) properties. We also stressed that our results were different from those described for triangular and corrugated core–shell nanoparticles obtained when using seed-mediated growth approach in the presence of CTAB [22] as well as for the triangular nanoframes made of gold and silver through etching with $HAuCl_4$ and subsequently reducing the metal ions in the aqueous solution by ascorbic acid [24].

2. Experimental

2.1. Materials

$NaBH_4$ (98%) and 4-aminothiophenol (4-ATP) were from Acros. The following analytical grade chemicals were purchased from the domestic and used without further purification: $AgNO_3$, hydrated hydrazine, HCl, HNO_3, NaOH, tri-sodium citrate, hydroxylamine hydrochloride, $HAuCl_4$. Milli-Q grade water (>18 MΩ) was used for all solution preparation and experiments.

2.2. Syntheses of silver nanoplates

Silver nanoplates were synthesized according to a modified procedure developed by our group. First, silver seeds were synthesized as follows: 0.5 mL of 59 mM $AgNO_3$ and 1 mL of 34 mM sodium citrate were added to 98 mL of aqueous solution. The solution was further stirred for several minutes. Then, 0.5 mL of an aqueous 0.02 M $NaBH_4$ solution, which had been aged for 2 h, was added all at once. The resultant solution was stirred for 1 h and aged for 24 h at room temperature before use. From transmission electron microscopy (TEM) measurements, the silver seeds were nearly spherical with the diameter of 8.5 ± 3.5 nm and one SPR band at 392 nm. Then, silver nanoplates were prepared by enlarging these small silver seeds in the presence of citrate. Typically, two sets of solutions (**1** and **2**) were prepared. Solution **1** was prepared by injecting 900 μL of an aqueous 40 mM hydrated hydrazine, 300 μL of an aqueous 40 mM Na_3 citrate and 200 μL of silver seeds to 60 mL aqueous solution. Solution **2** was prepared by adding 300 μL of aqueous 59 mM $AgNO_3$ into 30 mL of aqueous solution. Then solution **2** was dropwise (1 mL/min) added into solution **1** under strong stirring. After the addition of solutions **2** to **1** was finished, stirring was continued for 10 min. After aging 24 h, these nanoplates were purified by centrifugation (8000 rpm, 8 min). Then all solid portions were collected and redispersed into pure water. The final volume of silver nanoplates was fixed to be 75 mL. At last, 300 μL of an aqueous 40 mM Na_3 citrate was dropwise added into the nanoplate solution as stabilizers.

2.3. Syntheses of silver–gold alloy nanostructures

Two sets of solutions (**A** and **B**) were prepared. Solution **A** was prepared by 100 μL of aqueous 80 mM $NH_2OH{\cdot}HCl$, 100 μL of aqueous 80 mM NaOH and different amount of silver nanoplates. The final volume of solution **A** was kept to 25 mL by adding pure water. Solution **B** was prepared by injecting 100 μL of aqueous 25 mM $HAuCl_4$ into 10 mL of aqueous solution. Then solution **B** was dropwise (1 mL/min) added into solution **A** under strong stirring. After the addition of solutions **B** to **A** was finished, stirring was continued for 30 min. Four samples (**S1** to **S4**) were prepared by adding 20, 10, 5 and 2.5 mL of purified silver nanoplates into solution **A**, i.e., the corresponding molar ratios of Au ions/Ag atoms were 0.5, 1, 2, and 4, respectively (the Au ions/Ag atoms molar ratios were calculated with the nominal silver concentration (∼0.25 mM)). All the experiments were performed at room temperature ($14 \pm 2\,^{\circ}C$).

2.4. Instrumentation

Samples for TEM images were examined using a JEOL 2010 TEM operated at 200 kV. They were prepared by directly placing 5 μL of the as-prepared samples on a carbon coated copper grid and dried at room temperature. For each sample, usually over 200 particles from different parts of the grid were used to estimate the mean diameter and size distribution of particles. Energy-dispersive X-ray spectroscopy (EDS) was made on an XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. Samples were made by placing 10 μL of the as-prepared samples on an indium tin oxide (ITO) glass slide and air-dried at room temperature. Optical spectra were acquired on Cary 500 NIR-UV–vis spectrophotometer using 1 cm light path quartz cuvette. Power X-ray diffraction (XRD) measurements were performed on Rigaku D/max 2000 X-ray diffractometer using Cu$K\alpha$ radiation. The Raman instrument includes a FT-Raman spectrometer (Thermo Nicolet 960) equipped with an InGaAs detector and a Nd/VO4 laser (1064 nm) as an excitation source. The laser power was about 500 mW. The resolution of the Raman instrument was 4 cm^{-1}. All FT-SERS spectra were recorded by averaging 512 scans. To analyze the SERS activities of these samples, 4 mL of them was concentrated by centrifugation (8000 rpm, 10 min). The upper part of the colorless solution was removed and the solid portion was redispersed in 0.1 mL of pure water. Then 10 μL of these concentrated colloids was directly cast on the clean glass slide (1 cm × 1 cm) and let dry in air. Finally, 10 μL of a 1 mM ethanol solution of 4-ATP was cast onto the colloid films formed on the glass slide, and allowing the solvent to evaporate. The SERS signal of different points (more than 10) on these colloid films was tested and the highest SERS signal was recorded.

3. Results and discussion

3.1. Characterizations of silver nanoplates

As shown in Fig. 1A, the dominant products were thin nanoplates with a truncated triangular or hexagonal outline. A small percent of other shapes like faceted silver nanoparticles (<10%) were also found in this TEM image. The size of these