

ARTICLES

One-Pot Synthesis and Characterization of Novel Silver–Gold Bimetallic Nanostructures with Hollow Interiors and Bearing Nanospikes**Yongdong Jin and Shaojun Dong****State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, Jilin, P.R. of China**Received: May 21, 2003; In Final Form: August 24, 2003*

One-pot preparation of shell-type silver–gold bimetallic nanostructures with hollow interiors and bearing nanospikes, based on colloid seed-engaged replacement reaction and colloid-mediated deposition reactions, has been reported. Heating-induced evolution of Ag–Au bimetallic nanoshells can lead to spontaneous production of nanospikes on the colloid surface. The hollow interior structure and bimetallic nature of the as-prepared colloids are characterized by transmission electron microscopy (TEM), UV–vis spectroscopy, and X-ray photoelectron spectroscopy (XPS).

Introduction

Inorganic nanoparticles of nonspherical shape have been of currently immense interest because of their shape-dependent unique properties and potential applications.¹ For example, in addition to semiconductor and metal nanowires and nanorods, a variety of shapes, including stars;² semiconductor and metal nanobelts;³ colloidal samples of Pt cubes and pyramids;⁴ and PbSe, CdS, and Ni triangles,^{5–7} had been prepared. Promising recent work has also resulted in methods for synthesizing distributions of arrow-, teardrop-, and tetrapod-shaped CdSe nanocrystals⁸ and even large quantities of triangular Ag nanoprisms.¹ Recently, nanostructures with hollow interiors have been an interesting emerging class of materials because they exhibit plasmonic properties completely different from those of solid nanoparticles.^{9,10} Although a significant amount of work has already been done in developing synthetic methods for hollow spheres, cubes, rods, and triangular nanoframes,¹⁰ it is still a significant challenge in the synthesis of nonclassical nanoparticles with a special shape or morphology. We report herein a simple method for preparing novel Ag–Au bimetallic colloids with hollow interiors and bearing nanospikes.

Recently Xia et al. reported a one-step approach to the large-scale synthesis of metal nanostructures with hollow interiors via a template-engaged replacement reaction.⁹ As an example, nanoscale shells of gold can be generated from silver colloid templates by simple addition of HAuCl₄ to a dispersion of silver nanoparticles and initiation of the replacement reaction. Similarly, silver nanoprisms were etched with HAuCl₄ to generate gold–silver alloy framework structures very recently in Mirkin's group.¹⁰ Herein, we extend the colloid silver template-engaged replacement reaction⁹ to prepare silver–gold bimetallic nanostructures with hollow interiors by adding a mild reducing agent, NH₂OH, during the synthesis process. Interestingly, heating-induced evolution of Ag–Au bimetallic nanoshells can lead to

spontaneous production of nanospikes on the colloid surface. The hollow interior structure and bimetallic nature of the as-prepared colloids are characterized by transmission electron microscopy (TEM), UV–vis spectroscopy, and X-ray photoelectron spectroscopy (XPS). To the best of our knowledge, this is the first example of bimetallic nanoparticles with hollow interiors and bearing nanospikes.

Experimental Section

Materials. The following analytical grade chemicals were all obtained from Aldrich and used without further purification: (3-aminopropyl)-trimethoxysilane (APTMS), HCl, HNO₃, HAuCl₄·3H₂O, tri-sodium citrate, hydroxylamine hydrochloride, and AgNO₃. Milli-Q grade water (>18 MΩ) was used for all solution preparation and experiments.

Preparation of Colloids and Colloid Monolayer Films. All glassware used in the following procedures were cleaned in a bath of freshly prepared 3:1 HCl:HNO₃ (aqua regia) and rinsed thoroughly in milli-Q grade water prior to use. The Ag nanoparticles were prepared by sodium citrate reduction of AgNO₃.¹¹ AgNO₃ (18 mg) was dissolved in 100 mL of H₂O and brought to boiling. A solution of 1% tri-sodium citrate (2 mL) was added, and the solution was kept on boiling for ca. 1 h. The final volume was adjusted to 500 mL. The Ag sols prepared were greenish yellow.

Both nearly smooth and surface nanospiked Ag/Au bimetallic nanoshells were synthesized based on colloid seed-engaged replacement reactions and colloid-mediated deposition reactions, in the presence of HAuCl₄ and NH₂OH, with the only variation in temperature treatment as described in context. In a typical experiment, the nearly smooth Ag/Au bimetallic nanoshells were prepared by adding quickly 0.50 mL of aqueous 0.1% HAuCl₄ and 0.10 mL of aqueous 0.02 M NH₂OH to 5 mL of as-prepared Ag sols under violent stirring at room temperature for ca. 30 min. The surface nanospiked Ag/Au bimetallic nanoshells were synthesized just by bringing the preformed suspension of the

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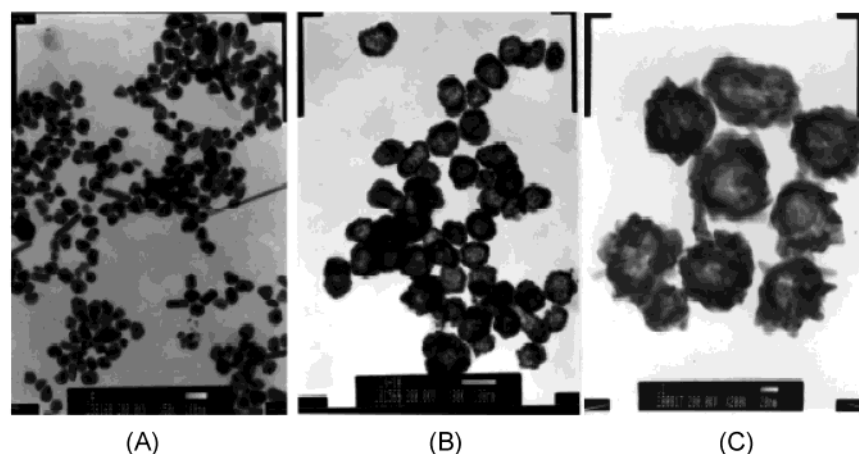


Figure 1. (A) TEM micrographs of Na_3 citrate prepared and faceted Ag nanoparticles; bar = 100 nm. (B) A TEM image of Ag–Au bimetal nanostructures (sample 1) showing the nearly spherical shell-type morphology; bar = 100 nm. (C) A TEM image of Ag–Au bimetal nanostructures (sample 1) after the heating treatment; bar = 20 nm. Note the spike-like knurl feature on nanoshell surface.

nearly smooth Ag/Au bimetallic nanoshells to heating and boiling for ca. 2 min, then stopping the heating, and letting it air-cool. Samples for TEM were prepared by placing a drop of suspension on a carbon-coated copper grid.

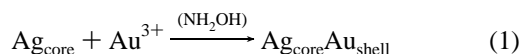
The colloid monolayer films for XPS characterization were prepared by placing a well-cleaned glass slide into a dilute solution of APTMS (0.3 mL of APTMS in 3 mL of CH_3OH) for 12 h and rinsing with copious CH_3OH upon removal.¹² The polymer-coated slides were subsequently immersed in as-prepared nearly smooth and surface nanopiked shell-type colloid suspensions, respectively, for 1 h for nanoparticle assembling. The monolayers were rinsed with water and dried under N_2 , and then they were ready for characterizations.

Instrumentation. Samples for TEM images were examined using a JEOL 2010 TEM operated at 200 KV. XPS analysis was performed on an ESCLAB MKII using Mg as the exciting source. Optical spectra were acquired on Carry 500 NIR–UV–vis spectrophotometer using 1 cm light path quartz cuvette.

Results and Discussion

Reaction Mechanism. The Ag colloids used as both templates and seeds were prepared by sodium citrate reduction of AgNO_3 solution¹¹ to generate faceted particles exhibiting a range of different morphologies, with a size of 60 ± 10 nm, as shown by transmission electron microscopy (TEM) image (Figure 1A). The central portions of these particles were darker than their edges due to a different thickness of silver along the path of the electron beam. The as-synthesized Ag colloids exhibited a greenish yellow tint, and its extinction spectrum (Figure 2, curve 1) displayed a sharp peak centered at ~ 440 nm.

To generate silver–gold bimetallic nanostructures with hollow interiors, NH_2OH was added to as-prepared colloidal Ag suspensions in addition to HAuCl_4 . In the method, three reactions coexist. First, the preformed Ag nanoparticles act as seeds and NH_2OH is thermodynamically capable of reducing Au^{3+} to bulk metal on colloid surface,¹³ as schematically denoted in reaction 1



Second, because the standard reduction potential of $\text{AuCl}_4^-/\text{Au}$ pair (0.99 V, vs SHE) is higher than that of Ag^+/Ag pair (0.80 V, vs SHE), silver nanoparticles suspended in solution

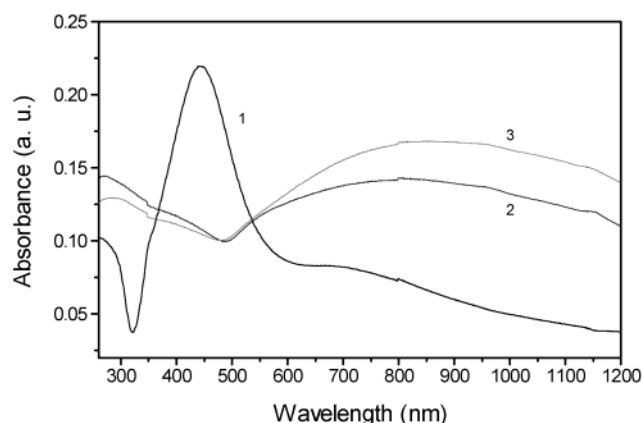
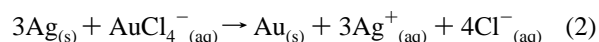
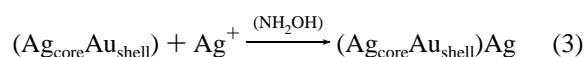


Figure 2. UV–vis–NIR spectra of a aliquot aqueous dispersion of precursor silver nanospheres before (1) and after reaction with 0.50 mL of aqueous 0.1% HAuCl_4 and 0.10 mL of aqueous 0.02 M NH_2OH for 1 h (2) and further heating treatment (3).

can be oxidized (or etched) by HAuCl_4 at the particle surface according to the following replacement reaction:⁹



In the same time, the chemically oxidized Ag^+ can be rereduced back to Ag at the colloid surface by NH_2OH , as schematically denoted in reaction 3



Because all of the reactions were confined to the vicinity of the colloid surface and Ag atoms migrate outward from the core during the colloid seed-engaged replacement reaction⁹ and colloid-mediated deposition/re-deposition reaction (NH_2OH seeding),¹³ the resultant nanoparticles are presumed to be bimetallic and with hollow interiors.

Synthesis and Characterization. In a typical experiment, 0.50 mL of aqueous 0.1% HAuCl_4 and 0.10 mL of aqueous 0.02 M NH_2OH were added quickly to 5 mL of as-prepared Ag sols under violently stirring at room temperature. Upon mixing, the solution produces the dramatic color change from greenish yellow to purplish blue. Figure 1B shows a TEM image of aforementioned colloid silver precursors after they have

completely reacted with the aqueous HAuCl_4 and NH_2OH solution at room temperature (sample 1). In this case, the center portion of most individual particle was lighter than its edge, indicating the formation of a shell-type nanostructures.⁹ The nanoshells with a core diameter of $\sim 60 \pm 10$ nm and shell thickness of ca. 10–15 nm have a morphology similar to that of the colloid silver precursors, with their core diameter (void size) mainly determined by the dimensions of colloid precursors.

Hollow nanostructures of noble metals are currently interesting to synthesize and investigate because they exhibit plasmonic properties completely different from those of solid nanoparticles (even made of the same metal).^{14,15} Metal nanoshells with shell layers consisting of metals with strong plasmon resonances exhibit a strong, plasmon-derived optical resonance, typically shifted to much longer wavelengths than the plasmon resonance of the corresponding solid metal nanosphere.¹⁶ Recent studies by Halas and co-workers, for example, reveal that the plasmon peak of spherical gold nanoshells could be conveniently tuned to cover the spectral regime from 600 to 1200 nm.¹⁷ In our case, the as-prepared metallic nanoshells exhibited a new and wide absorption peak centered at ~ 800 nm in the regime from visible to near-infrared (> 750 nm), having a full width at half-maximum (fwhm) of ~ 350 nm. The absence of absorption peak of Ag seed colloids around 440 nm in combination with TEM images (Figure 1, parts B and C) strongly indicated that the as-prepared metallic nanostructures are indeed nanoshells with hollow interiors.

The bimetallic nature of the as-prepared nanoshells was confirmed by X-ray photoelectron spectra (XPS) analysis of the self-assembled particle monolayers on 3-aminopropyltrimethoxysilane (APTMS) modified glass slides. The room temperature prepared nanoshell monolayers show both Ag 3d (370.8 eV) and Au 4f (87.0 eV) peaks with high intensity (Figure 3, curve 1), confirming the bimetallic nature of the nanoshells. The content of Ag and Au within the X-ray penetration depth (~ 3 nm) on the shell surface is quantified by Ag 3d and Au 4f peak areas, and an average composition of 1:3.1 (Ag:Au) is given. Curve 2 in Figure 3 shows XPS analysis of self-assembled monolayers of the aforementioned nanoshells after the heating treatment of the reaction solution. Irrespective of intensity difference due to different monolayer coverage and particle surfaces, the average surface composition of Ag:Au (1:1.8) is higher than that of room temperature prepared nanoshell monolayers and close to their stoichiometric ratio (Ag:Au = 1:1.4), further confirming the bimetallic nature of the as-prepared nanostructures and that heating prompts further surface alloying.

Interestingly, heating treatment can induce room temperature prepared sphere-like nanoshells to spontaneously evolve into novel nanostructures with hollow interiors and bearing nanospikes, as revealed by TEM analysis. Although the nanospikes bearing on the nanoshell (with a mean size of ~ 80 nm) surface were not well-evolved, a short spike-like knurl about 10–20 nm in length is evident (Figure 1C). This change in morphology after heating treatment was also reflected in the extinction spectrum (Figure 2, curve 3), as evidenced by an increase in intensity accompanied by a red shift in the central absorption band from ~ 800 to ~ 860 nm in the UV–vis spectrum of the solution.

In general, it was found that to a certain extent the addition of more HAuCl_4 leads to generate longer nanospikes. In a typical preparation, 2.0 mL of aqueous 0.1% HAuCl_4 and 0.10 mL of aqueous 0.02 M NH_2OH were added quickly to 5 mL of as-prepared Ag sols under violently stirring. After about 30 min, the reaction solution was heated to boiling and boiled for ca. 2

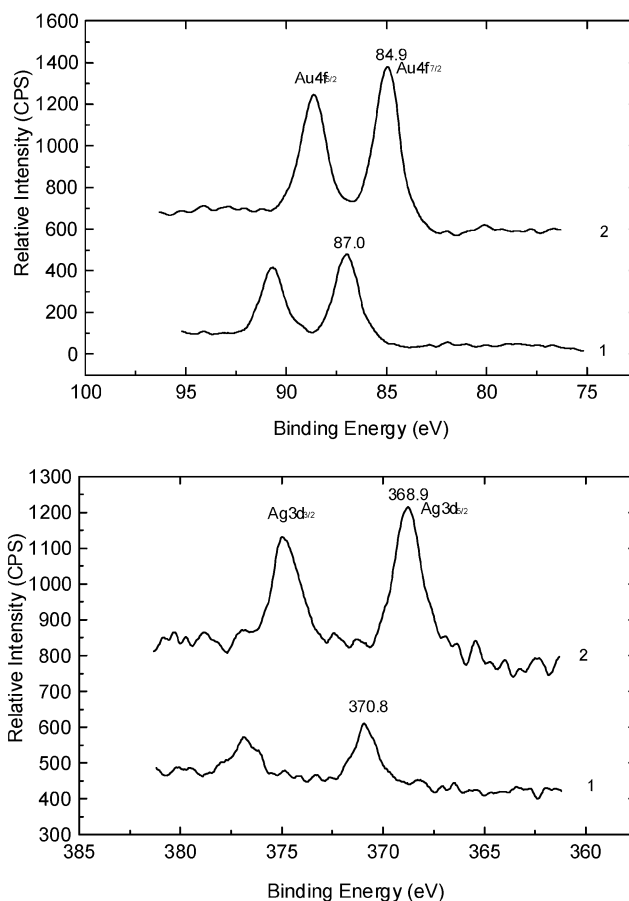


Figure 3. XPS analysis of self-assembled monolayers of resultant (1) spherical shell-type Ag–Au bimetal nanoparticles and (2) that bearing nanospikes before and after heating treatment of sample 1: (top) Au 4f and (bottom) Ag 3d. XPS analysis was performed on an ESCLAB MKII using Mg as the exciting source.

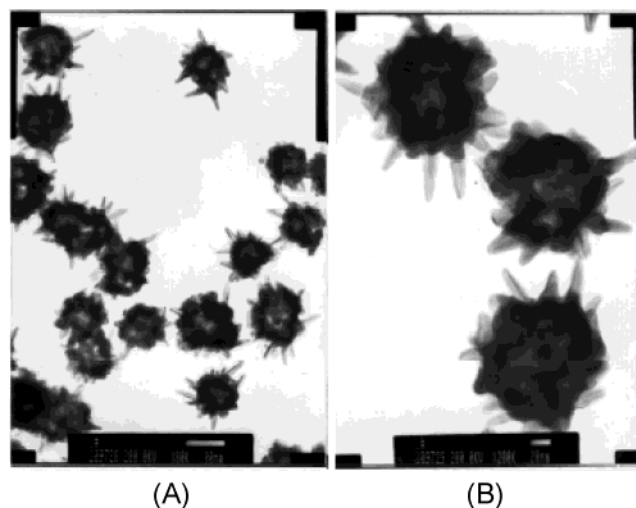


Figure 4. (A) Typical TEM image of as-prepared shell-type Ag–Au bimetal nanoparticles bearing nanospikes (sample 2); bar = 100 nm. (B) An enlarged TEM image showing the well-defined nanospikes and shell-type feature; bar = 20 nm.

min, then the heating was stopped, and we let it air-cool. The as-prepared colloid suspension shows interesting colors, which is henna under scatterance and shows dark blue against light transmission. TEM image in Figure 4A shows that the resulting bimetallic nanoparticles (sample 2) with a mean diameter of ~ 100 nm (not plus spikes) are well dispersed and consist of void cores (the center portion was lighter than edge, ~ 60 nm

in diameter), surrounded by a thicker shell coating (thickness ~ 20 – 30 nm) bearing nanopikes. The enlarged TEM image (Figure 4B) shows more clearly the spike-like knurl features, of which the nanopikes are typical about 40 – 60 nm in length. There are about 1 – 2 dozen nanopikes each as-prepared nanostructures. In another experiment, those shell-type particles bearing nanopikes also formed when the heating treatment was performed from the start stage of the colloid synthesis. Although the detailed physical evolution mechanism of the shell-like bimetal nanoparticles is not yet known, we assume that both the varied growth rates at different curvatures and planes of the precursor particles¹⁸ and surface free energy-driven metal island motion during the thermo-accelerated surface alloying¹⁹ may play an important role. In the control experiment, no nanopike features appeared, but enlarged sphere-like solid particles appear when we used Au sols with similar diameters as those of the seeds. It is also noteworthy to mention that the heating time is crucial to prepare the well-dispersed shell-type colloids bearing nanopikes. A relative long heating time causes the resultant nanoparticles to float up and liberate at the air/water interface, which results in the spontaneous formation of diffusion-limited aggregation (DLA)-defined fractal network aggregates²⁰ (even mesoscale porous thin films).

Conclusions

We have presented here a simple method, based on colloid seed-engaged/-mediated replacement/deposition reactions, to prepare shell-type Ag–Au bimetallic colloids with hollow interiors and demonstrated that heating treatment can lead to evolution of the shell-type Ag–Au bimetal colloids to spontaneously generate novel shell-type nanostructures bearing nanopikes. The hollow interior structure and bimetallic nature of the as-prepared colloids are characterized by TEM, UV–vis spectroscopy, and XPS. The as-prepared Ag/Au bimetal nanoshells bearing nanopikes could be promising building blocks for further constructing novel 3D nanostructures and would find potential applications. For example, the strong absorption of the as-prepared Ag/Au bimetallic nanoshells (and

even bearing nanopikes) in the near-infrared region (800 – 1200 nm, the transparent window of tissues) makes these nanomaterials ideal candidates for photothermally triggered drug releasing in tissues.^{21,22}

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