Insight into the formation of hollow silver nanoparticles using a facile hydrothermal strategy

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ABSTRACT

A facile hydrothermal approach is used to synthesize hollow silver nanoparticles, labeled as hAgNPs, involving an initial formation of metal complexes from Ag^+ ion precursors and dodecylamine in a water/ethanol mixture at room temperature and a subsequent reduction in an autoclave at elevated temperature. A number of characterization techniques are used to characterize the structure and chemical composition of the as-formed hAgNPs, and to understand the mechanism behind the formation. The notable simplicity renders this synthetic approach promising for creating hAgNPs on a large scale for a given technological application, and the mechanistic understanding may provide new opportunities to design and fabricate other hollow nanostructures.

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Introduction

The synthesis of noble metal nanoparticles with hollow structures (hNMNPs) is of great interest because of their immense potential in catalysis (Kim, Kim, Lee, & Hyeon, 2002; Liang et al., 2004; Yang, Lee, Too, & Valiyaveettil, 2006; Peng, Wu, & Yang, 2009; Bai et al., 2011; Liu, Ye, & Yang, 2014; Chen, Cui, He, Liu, & Yang, 2014; Chen et al., 2015; Deng & Lee, 2014), optics (Chen et al., 2005; Kundu, Le, Nordlander, & Halas, 2008; Bardhan, Grady, & Halas, 2008; Park et al., 2008; Acevedo, Lombardini, Halas, & Johnson, 2009; Zhang et al., 2010), and therapeutics (Chen et al., 2007; Gobin et al., 2007; Song, Kim, Cobley, Xia, & Wang, 2008; Zhang, 2010; Xia et al., 2011). Commonly, the hNMNPs are produced by template-assisted selective etching of core-shell particles (Yang et al., 2006; Peng et al., 2009; Bai et al., 2011; Liu et al., 2014; Chen et al., 2014, 2015; Liu et al., 2012; Hou, Cui, Liu, Li, & Yang, 2015), wherein the core particle is overlaid with the desired noble metal material or its precursor and is then selectively removed by calcination or with a solvent. A specific method based on galvanic replacement is also capable of generating hNMNPs from such metals as Au, Pt, and Pd by templating against Ag nanostructures (Chen et al., 2005, 2008; Skrabalak et al., 2008; González, Arbiol, & Puntes, 2011). In contrast with the abundance of studies on hNMNPs from metals such as Au, Pd, Pt, Rh, and Ru produced by template-assisted selective etching

or by galvanic replacement reaction, the present literature on hollow Ag nanoparticles (hAgNPs), an important type of nanostructure with tunable optical properties, is scarce owing to its synthetic inaccessibility. The limited examples for hAgNP synthesis include the *in situ* replacement reaction with Co nanoparticles in the aqueous phase (Chen & Gao, 2006), the dissolution of the interior metal and assembly of the outer surface for solid Ag nanoparticles modified by dithiols (Wang, Chen, & Liu, 2008), the fast chemical reduction of Ag_2O nanoparticles capped with glutathione (Ben Moshe & Markovich, 2011), and the plasmon-driven transformation from Ag nanoparticles (Stasieńko, Krajczewski, Wojtysiak, Czajkowski, & Kudelski, 2014). Unfortunately, these preparative protocols are either time-consuming (typically requiring days) or are only capable of fabricating hAgNPs on a very small scale.

Herein, we demonstrate a facile hydrothermal approach for the fabrication of hAgNPs based on the reduction of metal complexes formed by Ag^+ ion precursors and dodecylamine (DDA) at an elevated temperature. This very simple protocol involves mixing an aqueous solution of Ag salt with an ethanol solution of DDA, then heating the mixture in an autoclave. One of the notable characteristics of this strategy is that no additional templates are needed during the synthesis. The purpose of our work is method development and, specifically, the synthesis of hAgNPs based on a hydrothermal approach. Therefore, we focus on the characterization of the as-prepared Ag products with a hollow interior and the discussion on the formation mechanism of the hollow structure. Considering the remarkable simplicity of this synthetic approach, it may be promising for generating hAgNPs on a large scale for

a given technological application. Additionally, this hydrothermal approach enriches the strategies for producing hAgNPs, and the mechanistic understanding may provide new opportunities to design and fabricate other hollow nanostructures, although the physical/chemical properties of the as-prepared hAgNPs are not presented in this work.

Experimental

Materials

Silver nitrate ($AgNO_3$, ACS reagent, ≥99.0%) from Sigma-Aldrich (St. Louis, USA), ethanol (99.5%) from Beijing Chemical Works (Beijing, China), and dodecylamine (DDA, 98%) from J&K Scientific Ltd. (Beijing, China) were used as received. All glassware and the autoclave Teflon® liner were cleaned with aqua regia followed by copious rinsing with deionized water before drying in an oven.

Synthesis of hAgNPs

In a typical synthesis of hAgNPs, 34 mg (0.2 mmol) of $AgNO_3$ was dissolved in 20 mL of deionized water, after which 20 mL of DDA/ethanol with a volume ratio of 1/5 was added. After magnetic stirring for about 20 min, the mixture was transferred into an autoclave with a volume of 50 mL and kept at an elevated temperature (120 °C or higher) for 8 h. After this hydrothermal process, the autoclave was cooled down to room temperature naturally and the precipitates were collected by centrifugation and washed with deionized water and pure ethanol several times. Finally, the hollow nanoparticle products were dried in vacuum for 12 h.

Characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on a JEOL JEM-2100 electron microscope (Japan) operating at 200 kV with software supplied for automated electron tomography. For the TEM measurements, a drop of the nanoparticle solution was dispensed onto a 3-mm-diameter carbon-coated copper grid, whereupon any excess solution was removed by absorbent paper and the sample was dried at room temperature in air. Fourier transform infrared spectroscopy (FTIR) analysis was performed on a Bruker Alpha RT-DLATGS spectrometer (USA), and the spectra were collected over the range of 400–4000 cm^{-1} in the transmission mode. Powder X-ray diffraction (XRD) measurements were carried out on a Bruker D8 focus X-ray diffractometer (USA) using Cu-Kα radiation (λ = 1.5406 Å), and X-ray photoelectron spectroscopy (XPS) spectra were collected using a Thermo Scientific K-Alpha XPS spectrometer (USA).

Results and discussion

It is well known that DDA can interact with noble metal ions to form metal ion-DDA coordination compounds. These compounds are often used to transfer noble metal ions, including Ag$^+$ ions, from the aqueous phase to a non-polar organic solvent such as toluene, hexane, or chloroform for the production of noble metal nanoparticles or noble metal-semiconductor nanocomposites (Yang, Lee, Deivaraj, & Too, 2004; Yang & Ying, 2009; Yang, Sargent, Kelley, & Ying, 2009; Yang, Lee, & Ying, 2011; Liu, Ye, Ma, Cao, & Yang, 2013). In this work, mixing the aqueous solution of $AgNO_3$ and an ethanolic solution of DDA forms coordination compounds composed of Ag$^+$ ions and DDA, wherein the ethanol is used to promote sufficient contact between Ag$^+$ ions and DDA because it is water-miscible and a good solvent for DDA. The formation of Ag$^+$-DDA coordination compounds can be verified by the FTIR spectra of the compounds recovered from the mixture of aqueous $AgNO_3$ solution and ethanolic DDA solution. As shown by Fig. S1 in the Supplementary materials (SM), the FTIR spectra of pure DDA exhibits bands at 3330, 2920, and 1492 cm^{-1} that are attributed to the stretching vibrations of C—N, C—H, and N—H, respectively. Comparing the FTIR spectrum of Ag$^+$-DDA coordination compounds with that of pure DDA, apparent differences can be identified in the C—N and N—H stretching vibrations, while other FTIR characteristic peaks exist in the spectra of Ag$^+$-DDA coordination compounds (SM Fig. S1). This again demonstrates that Ag$^+$-coordination compounds are formed through the interaction between the amino group (—NH$_2$) of DDA and the Ag$^+$ ions.

The Ag$^+$ ions in Ag$^+$-DDA coordination compounds are then reduced by DDA at elevated temperatures, resulting in the generation of Ag nanoparticles with a hollow interior (hAgNPs) protected by DDA. After being recovered from the reaction system via centrifugation, the hAgNPs are subjected to washing with deionized water and pure ethanol several times to remove the free DDA from the particle surface. Fig. S2 in the Supplementary materials shows the FTIR spectrum of the as-prepared hAgNPs where, although the signals are weak, the remaining infrared fingerprints of DDA can be identified, indicating that DDA is present on the surface of the hAgNPs and serves as a capping agent for the latter. The FTIR peaks of DDA in the hAgNP samples are shifted to slightly higher wavenumbers (SM Fig. S2) compared with those of pure DDA (SM Fig. S1), suggesting a DDA coordination to the surface of the hAgNPs, analogous to the FTIR spectrum of ethylenediamine on the Ru nanoparticle surface (Lee, Yang, Deivaraj, & Too, 2003).

A typical TEM image of the hAgNPs as-prepared at 150 °C and a histogram of the particle size distributions are shown in Fig. 1(a) and (b), respectively, which suggest that quasi-spherical nanoparticles with an average diameter of 44.2 nm are the dominant products, with a small portion (*ca.* 6%) of particles possessing rod-like morphologies. A hollow interior with an average diameter of 24.5 nm and a standard deviation of 5.6 nm (SM Fig. S3) can be clearly discerned in each Ag nanoparticle by the strong intensity contrast between the central and surface regions in the TEM image. The XRD pattern of the hAgNPs was collected to confirm their phase purity (Fig. 1(c)), where it can be seen that the lines of the {1 1 1} (2θ = 38.2°), {2 0 0} (2θ = 44.3°), {2 2 0} (2θ = 64.5°), {3 1 1} (2θ = 77.4°), and {2 2 2} (2θ = 81.6°) diffractions match well with the face-centered cubic (fcc) Ag phase (JCPDS card No. 870579, plotted in Fig. 1(c)), with no other XRD peaks observed. A local HRTEM image (Fig. 1(d)) with its Fourier transform diffraction pattern (Fig. 1(e)) reveal the lattice planes in these hAgNPs, confirming that these hollow particles are of high crystallinity. The interplanar spacings of 0.24 and 0.20 nm indicated in the HRTEM images of the hAgNPs correspond to the {1 1 1} and {2 0 0} planes of fcc Ag, respectively. However, as displayed by the magnified TEM image (SM Fig. S4(a)), twinning defects in the shell region are still visible although the hAgNPs are of high crystallinity. This indicates that the final hollow Ag products have a polycrystalline nature, which is consistent with the irregular pattern of the corresponding Fourier transform (Fig. S4(b)).

The chemical compositions of the hAgNPs as-synthesized at 120 °C by the hydrothermal approach also underwent XPS analysis. As shown in the SM Fig. S5, a set of doublet peaks at 368.7 and 374.7 eV in the energy range of the Ag 3d signal ($3d_{5/2}$ and $3d_{3/2}$, respectively), which represents the zero valence state of Ag (Wagner et al., 2003; Yang, Lee, & Too, 2007; Ye, Liu, Huang, & Yang, 2014), can fit the XPS spectrum very well. This indicates that the oxidation state can be neglected in DDA-capped hAgNPs prepared through the hydrothermal approach.

To understand the formation mechanism of the hAgNPs, TEM was used to follow the particle growth process, and the results are shown in Fig. 2. After the reduction of Ag$^+$-DDA coordination