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Preparation of silver hollow nanostructures by plasmon-driven transformation

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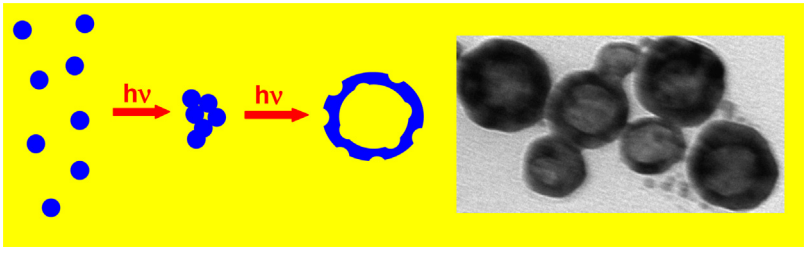
HIGHLIGHTS

- Silver hollow nanostructures were synthesized by plasmon-driven transformation.
- In contrast to typical methods, no auxiliary template structures are used.
- Plasmon-driven transformation was carried out in the presence of oxygen and citrate.

GRAPHICAL ABSTRACT



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ABSTRACT

Herein we demonstrate the synthesis of silver spherical hollow nanostructures by the plasmon-driven transformation (PDTr) of partially agglomerated silver sol. The PDTr process was carried out in the presence of oxygen and trisodium citrate using intensive 550–650 nm light. In contrast to typical methods of the synthesis of metallic hollow nanostructures, no auxiliary template structures are used. Therefore, the obtained nanoshells should be less contaminated, which may be beneficial to their catalytic and optical properties. The method is believed to open up a straightforward route to the fabrication of nanoshells from metals which support surface plasmon resonance.

1. Introduction

Metal nanomaterials with hollow interiors have found applications in areas including biomedical imaging [1], photothermal cancer treatment [2,3], drug delivery [4], surface-enhanced Raman scattering [5,6], and catalysis [7–12]. Because of their lower densities, which usually translate to a higher surface area than their solid counterparts, the hollow nanoparticles are especially promising in catalysis [10–12]. For instance, Pt hollow nanospheres are twice as active for methanol oxidation as solid Pt nanoparticles of roughly the same size [10]. Some hollow nanostructures also exhibit surface plasmonic properties superior to their solid counterparts [13–17]. For example, the position of the surface plasmon resonance (SPR) band for gold nanoshells can be changed by varying the shell diameter and its thickness in a significantly broader wavelength range than the SPR band of solid spherical gold nanoparticles [14–17]. The observed significant red-shift of the strong SPR band for very thin gold nanoshells significantly facilitates biomedical applications of such nanostructures, since it allows to tune maximum absorption/scattering of nanoparticles to the transparent window of biological tissues (800–1200 nm) [15–17].

Hollow nanostructures from noble metals are typically fabricated by the template-assisted selective etching of core–shell nanoparticles [12,18], or by the galvanic replacement reaction [18–22]. In the first approach the "auxiliary" core particle is overlaid with a shell of a noble metal and then the core is selectively

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removed by dissolution or calcination. In the second approach the metal nanostructures formed from a less noble metal are used as sacrificial templates to react with ions of a more noble metal. During the galvanic replacement the metal nanotemplates are dissolved and the more noble metal ions are reduced to elemental form, which subsequently deposits onto the surface of the templates and forms a shell [19–22]. Hollow silver nanostructures have been also synthesized using some more specific methods. For example, Moshe and Markovich produced hollow Ag nanoparticles by fast chemical reduction of Ag_2O nanoparticles capped with glutathione (reported transformation has been associated with the nanoscale Kirkendall effect [23]). Wang et al. synthesized various silver nanostructures with hollow interiors by the modification of the solid silver nanoparticles by dithiols, and subsequent dissolving of the interior metal and assembly of the outer surface [24]. Zheng et al. fabricated silver porous hollow spheres by ultrasonic spray pyrolysis of aqueous solutions containing $AgNO_3$ and glucose [25].

Many interesting metal nanostructures have been synthesized using photochemical reactions. Esumi et al. prepared rod-like gold nanoparticles by UV irradiation using some micelles as a template [26]. Shape-controlled synthesis of gold nanoparticles using UV irradiation has been also reported by many other groups [27–31]. Interesting application of light as a valuable tool for preparation of complex metal nanostructures was proposed by Mirkin et al. [32], who showed that upon illumination "almost spherical" solid silver nanoparticles are converted into triangular nanoprisms. Further investigations of this photo-transformation process showed that the size of formed nanoprisms strongly depends on the wavelength of the excitation radiation [33] and that by carrying out photochemical restructuring in the same conditions, but starting with different seeds, one may produce nanorods instead of nanoprisms [34]. Zhou et al. observed that when tartrate and citrate are used as structural-directing reagents, tetrahedral silver nanocrystals may be also obtained [35].

Briefly speaking, photochemical transformation process of silver clusters involves two steps: (i) partial dissolution of silver nanoparticles, and then (ii) photocatalytic reduction of Ag^+ to Ag^0, which causes the preferential deposition of silver at same places of silver nanoparticles [36,37]. The photocatalytic reduction of Ag^+ occurs preferentially at such places of the silver nanoclusters, at which strong surface plasmons are excited, and hence, this reconstruction process is called plasmon-driven transformation (PDTr). Herein, we report that PDTr of partially aggregated Ag sol leads to formation of hollow silver nanoshells. This new method of synthesis of hollow nanoparticles is believed to open up a simple route to fabrication of this important type of nanostructures from metals which support surface plasmon resonance.

2. Experimental

2.1. Materials

All materials were used as received without further purification or treatment. Tri-sodium citrate dihydrate, $AgNO_3$ and KCl (all pure p.a.) were purchased from POCH SA. $NaBH_4$ ≥99% were purchased from Fluka Analytical. Pyridine was purchased from Ubichem Limited. Water used for all experiments was purified in Millipore Milli-Q manner.

2.2. Characterization methods

The transmission electron microscopy (TEM) studies were performed on electron microscope LIBRA 120 (Zeiss, Germany) equipped with the In-column OMEGA filter and charge-coupled device (CCD) detector, working at an accelerating voltage of 120 kV.

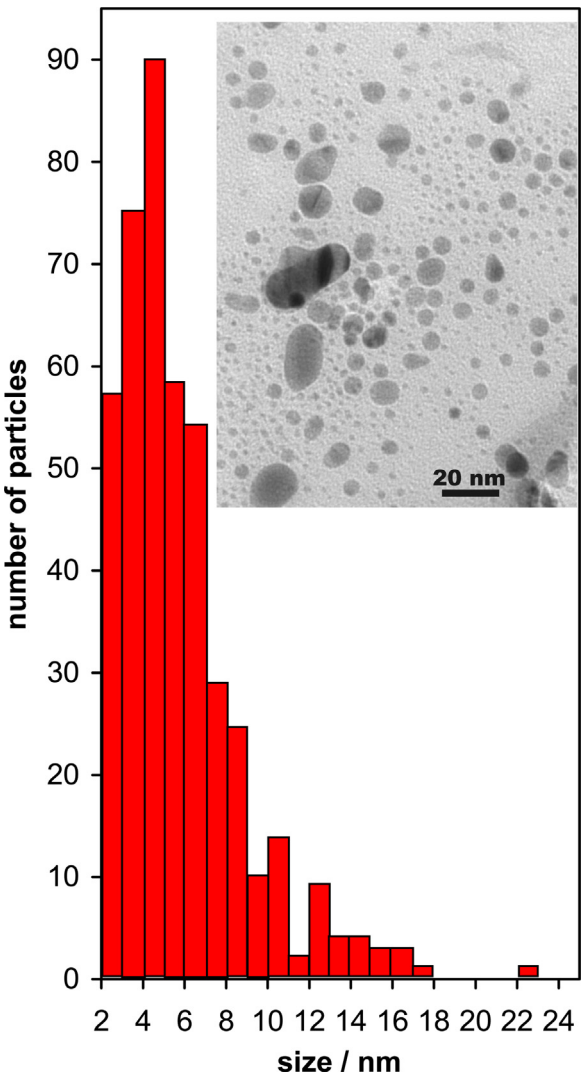

Fig. 1. Size distribution histogram of the silver precursor nanoparticles. The distribution histogram shows results from a larger number of nanoparticles (450) than shown on an example TEM micrograph (see inset).

The sample of synthesized Ag sol was dropped onto Formvar-coated 400-mesh nickel grids (Agar Scientific) and allowed to dry. UV–vis spectra were collected with a Shimadzu UV-2401PC spectrophotometer. Raman spectra were collected with a Horiba Jobin–Yvon Labram HR800 spectrometer equipped with a HeNe laser (632.8 nm), an Olympus microscope with a 50× long distance objective, holographic grating with 600 grooves/mm, and a Peltier-cooled (1024 × 256 pixel) CCD detector.

2.3. Synthesis of Ag precursor

Silver precursor nanoparticles for PDTr were prepared at the room temperature by the slow addition of 0.4 ml of 25 mM $NaBH_4$ aqueous solution to 20 ml of an aqueous solution of 1 mM $AgNO_3$ and 3 mM trisodium citrate under constant stirring. Fig. 1 shows size distribution histogram of the silver precursor nanoparticles and an example transmission electron microscopy (TEM) micrograph. The sizes of nanoparticles were measured for 450 randomly chosen silver nanoclusters using GIMP software. For the analyzed set of 450 silver nanoparticles the average size was 5.9 nm and the standard deviation of the measured size was 2.5 nm.