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Short Communication

Au and Ag/Au double-shells hollow nanoparticles with improved near infrared surface plasmon and photoluminescence properties

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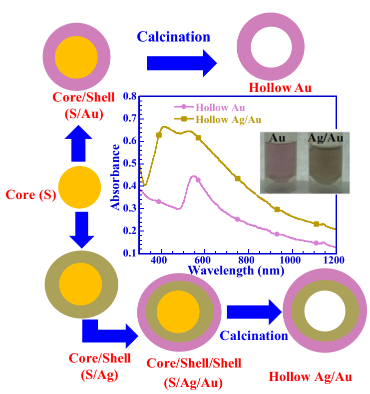
GRAPHICAL ABSTRACT



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ABSTRACT

Metallic hollow nanoparticles have been continuously drawing researcher's attention because of their excellent improved performance compare to the spherical particles in catalysis, photonics, information storage, surface-enhanced Raman scattering, and sensors applications. In this article we demonstrate a novel route for the synthesis of single and double-shells Au and Ag/Au bimetallic hollow nanoparticles using elemental sulfur as a sacrificial core. We also investigate the optical properties of these new hollow particles and compare with that of pure spherical nanoparticles. The surface plasmon resonance spectra of solid Au, hollow single shell Au, and double shells Ag/Au nanoparticles show that there is gradual shifting of Au peak position towards the higher wavelengths for these three nanoparticles respectively. A similar observation was also found for photoluminescence spectra. In case of double-shells Ag/Au hollow nanoparticles the emission spectrum shifts towards the NIR region with significant higher intensity, which is beneficial for in vivo biomedical applications of these particles.

1. Introduction

The hollow structured nanoparticles (NPs) are extremely important compare to the solid nanoparticles from the application perspective, mainly because of the high specific surface area, porosity and low density. The noble metal nanoparticles are always drawing researcher's attention because of their excellent optical and catalytic properties, especially the hollow structures show improved performance in catalysis, electronics, photonics, information storage, surface-enhanced Raman scattering (SERS), and sensors applications [1–5]. The surface plasmon resonance (SPR)

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is one of the most important properties of the noble metals and it has been observed that, in addition to enhanced surface area [6–8], the presence of sharp edge, rough surface, and porous structure are also equally important to enhance the electromagnetic (EM) field to improve the SPR intensity [9–11]. As a consequence, the hollow Au nanoparticles have a higher surface plasmon field generated by photon excitation, and this field is responsible for the higher SPR intensity than solid Au particles [2,12–14]. Hollow Au nanoparticles with larger particle size but lower shell thickness (nano shells) are also able to shift the light absorbance peak position, SPR peak intensity, and photoluminescence peak to the infrared region which is useful for sensor applications in the biomedical field [15,16]. Similar to hollow Au nanoparticles, the noble bimetallic nanoparticles in the forms of alloy, core/shell, and hollow multi-shells hetero-structures are also equally important because of their similar improved optical properties. Especially, Au–Ag combination, in the forms of alloy or core/shell particles can enhance the optical properties, the SPR, and photoluminescence peak position shift towards extended visible or NIR regions which in turn more useful for the biomedical imaging applications [17]. Especially the photoluminescence property of these hollow noble nanoparticles at the NIR region is mostly useful for the optical imaging in biomedical field for in vivo application as blood and plasma are inactive in this optical region.

Metallic hollow nanoparticles were synthesized by Kirkendall effect, galvanic replacement, and Ostwald ripening [18]. However, similar to other materials these metallic hollow nanoparticles have been also synthesized by sacrificial core removal technique, either using inorganic or organic sacrificial templates [1,17,19–21]. The most commonly used core particles can be broadly divided in two groups, soft [22–24] or hard core [1,15,19,25,26]. Generally, soft core are easily deformable and easy to remove; such as gas bubbles, surfactant micelles, enzymes or organic cores are under this group. But most of the cases hard cores mostly inorganics material such as Ag, AgCl, ZnO, SiO_2 or organic polymers are used for the synthesis of hollow Au nanoparticles in which these cores are removed by dissolution using acid/alkali or by calcination at higher temperature. The synthesis of hollow Au nanoparticles by galvanic replacement method using Ag as sacrificial core is the most common method [1,19,27], but in recent study, direct synthesis of hollow Au nanoparticles is another new approach without using any template [28]. In this method different sized sub-100 nm (5, 10, and 20 nm) hollow Au particles were synthesized without any template in the presence of semifluorinated oligo (ethylene glycol) ligands [28]. Whereas, hollow bimetallic (Au–Ag, Ag–Pd, and Ag–Pt) nanoparticles were synthesized by partial removal of Ag through galvanic replacement [29–34] and the presence of Au or Ag enhance the optical property which ultimately enhance photo induced catalytic reaction [29,32,35].

In this work we report a new synthesis technique and optical properties of pure (Au, Ag), bimetallic composite (Au–Ag), hollow Au, and hollow bi-layer Ag/Au nanoparticles in aqueous surfactant micellar media. Herein, the hollow Au and Ag/Au nanoparticles are synthesized using sulfur as a sacrificial core through the formation of S/Au and S/Ag/Au core/shell/shell types of particles respectively. Finally, comparative optical (SPR and photoluminescence) properties have been studied of these hollow nanoparticles with respect to solid Au, Ag, and Au–Ag composite nanoparticles.

2. Experimental section

2.1. Materials

The required chemicals were purchased from the following sources: sodium thiosulphate ($Na_2S_2O_3$, $5H_2O$) from Rankem, Sodium dodecylbenzene sulfonate from Sigma Aldrich (Technical grade, Cat no. 28995-7), cetyltrimethyl ammonium bromide (CTAB) of 99% purity from Sigma Aldrich, nitric acid (HNO_3) from Merck, silver nitrate ($AgNO_3$) of 99.9% purity from Ranbaxy, chloroauric acid ($HAuCl_4 \cdot xH_2O$) of 49% assay from Loba Chemei, and sodium borohydride ($NaBH_4$) of >98% purity from Acros Organic. All the chemicals were used as it is received without any further purification. Ultrapure water of 18.2 MΩ cm resistivity, 71.5 mN/m surface tension, and 6.4–6.5 pH was used for all the experiments. The constant temperature 25 ± 0.5 °C was maintained throughout the experiments.

2.2. Synthesis techniques

Pure Au, Ag nanoparticles were synthesized by the reduction of respective precursor ($HAuCl_4$ and $AgNO_3$) with varying concentration whereas composite Au–Ag nanoparticles were formed by the reduction of $HAuCl_4$ (0.1 mM) and $AgNO_3$ (0.1 mM) respectively using $NaBH_4$ as reducing agent in respective surfactant media. Whereas hollow Au and Ag/Au nanoparticles were synthesized using sulfur as sacrificial template. Core sulfur nanoparticles were synthesized by HNO_3 catalyzed disproportionation reaction of sodium thiosulphate (5 mM) in CTAB media (2.7 mM) according to our previous study [36]. After the completion of core formation, the nanoparticles suspension was half diluted with CTAB solution to maintain same surfactant concentration and then diluted sulfur suspension was sonicated by a probe sonicator of capacity 260 W for 20 min, then finally core sulfur particles were coated with Au (0.1 mM Au precursor concentration) for synthesis of S/Au core/shell nanoparticles or coated with successive Ag and Au layers for the synthesis of S/Ag/Au core/shell/shell nanoparticles by the reduction of corresponding metal salt precursors. For the synthesis of double-shells nanoparticles, initially Ag precursor (0.1 mM) was added to core suspension and then after complete coating of Ag shell, finally Au precursor (0.1 mM) was added for external coating. Then after completion of reaction, the particles were separated by centrifugation at 25,000 rpm for 20 min, washed thrice by water ethanol mixture (1:1, v/v), and finally the collected washed particles were calcined at 450 °C for 30 min in air to remove the sulfur core for the formation of hollow particles.

2.3. Particle characterization

Particle size measurement was carried out by the dynamic light scattering (DLS) using Malvern Zeta Size analyzer (Nano ZS), with the help of cumulant fitting model and intensity distribution within the media. The size and shape of the particles were observed by transmission electron microscope (Tecnai S-twin). Hollow particles were also characterized by UV–vis–NIR Spectroscopy (Shimadzu-3600), fluorescence spectroscopy (Hitachi-7000), and X-ray diffraction (XRD) (Philips, PW 1830 HT).

3. Results and discussion

3.1. Pure nanoparticles

To make a comparative studies on the optical properties of the pure (Au, Ag), bimetallic composite (Au–Ag), hollow Au, and hollow double-shells Ag/Au nanoparticles, initially pure Au and Ag nanoparticles were synthesized and the optical properties were studied. Pure Au and Ag nanoparticles were synthesized in CTAB and SDBS surfactant micellar media with varying precursor concentration and the particles were characterized by UV–vis spec-