



Tuning the shell thickness-dependent plasmonic absorption of Ag coated Au nanocubes: The effect of synthesis temperature



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ABSTRACT

The temperature dependent synthesis and plasmonic optical properties of Ag coated Au nanocubes have been investigated experimentally. It has been found that the Au nanocubes with more uniform morphology and higher yield could be obtained by decreasing the growth temperature. Because of the non-spherical symmetry of the particles shape and the plasmon coupling between Au–Ag interface and outer Ag surface, four absorption peaks at most have been observed. As the Ag coating thickness is increased, the absorbance intensity of these plasmon peaks gets intense greatly, and the absorption peak at longest wavelength blue shifts firstly and then red shifts. The non-monotonous plasmonic shift has been attributed to the competition between the increase of Ag composition and the enlargement of the particle size. What's more, the wavelength region of both blue shift and red shift could also be enhanced by decreasing the temperature.

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1. Introduction

In recent years, Au–Ag bimetallic core–shell nanoparticles have received great attention owing to their novel optical and electronic properties different from the solid metallic nanoparticles with individual metals. As is known that the collective electron oscillation induced surface plasmon resonance (SPR) is the base of other optic features of noble metallic nanoparticle, such as light absorption, resonance light scattering, local field enhancement and fluorescence quenching [1–4]. Because of having different bulk metal dielectric function and plasmon frequency, the plasmonic properties of Au and Ag nanoparticles including absorption intensity and resonance wavelength are different [5]. On the other hand, the core–shell structure leads to the plasmon coupling from different metal surface and better tenability [6–8]. Therefore, Au–Ag bimetallic core–shell nanostructures usually have more abundant SPR modes and broader shift region from visible to infrared.

Au–Ag bimetallic core–shell nanoparticle with spherical morphology is one of the most simply nanostructure [9–12]. In the report of Csapó et al., Ag–Au core–shell nanoparticles were synthesized using only sodium citrate as reductant without any stabilizers

[13]. The high-resolution transmission electron microscopy images clearly confirm the core–shell structure of the bimetallic nanoparticles. In the study of Pyne et al., synthesis of Ag shell with increasing thickness has been done by reducing Ag ions over the Au colloid in the presence of mild reducing ascorbic acid [14]. The blue shift of SPR band with increasing Ag mole fraction has been observed, which is in agreement with the theoretical calculation result [15]. By using the replacement reaction between hydrophobized Ag nanoparticles and hydrophobized AuCl_4^- , core–shell Ag–Au nanoparticles have also been synthesized [16]. It has been found the significant plasmonic red-shift is more resulted from the shape and chemical composition changes rather than Au nanoshell formation. By using unmodified apoferritin as a template, Au-core Ag-shell nanoparticles with a size range from 1 to 5 nm have been synthesized by Li et al. [17]. And the Ag shell thickness could be controlled from one layer to several layers by varying the loading Ag amounts. Anomalous infrared and visible light absorption of Au–Ag core–shell nanoparticles have been reported by Suzuki et al. [18]. They found the effect of a thinner metal shell is slight in the visible absorption spectra, whereas the effect appeared strongly in the infrared absorption spectra. Au–Ag core–shell nanoparticles have also been proposed as candidates for obtaining Fano resonances [19]. Pal et al. demonstrated that Au–Ag core–shell nanoparticles with typical shell thickness below 5.0 nm produce a well defined and measurable Fano profile in the far-field. In the report of Gui et al., human serum albumin-stabilized fluorescent Au–Ag core–shell nanoparticles have been prepared in water,

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and the excellent photoluminescence properties could be used for highly sensitive and selective sensing of copper ions [20].

Besides of spherical morphology, bimetallic core-shell nanoparticles with non-spherical metal core or non-spherical metal coating have also been widely studied. By using a two-step method, shape-dependent Au–Ag core-shell nanoparticles have been synthesized [21]. In the prepared Au–Ag core-shell nanostructure, Au nanocores have various shapes including octahedron, triangle or hexagon plate, and decahedron. It has been found that the shapes of formed Ag shells strongly depend on shapes of initiated Au nanocores. Wagner et al. studied the formation of star-like core-shell Au–Ag nanoparticles [22]. These dendrit-like bimetal nanoparticles were formed by the reduction of mixtures of tetrachloroaurate and Ag nitrate solutions with ascorbic acid in two- and three-step procedures. Cardinal et al. described the modulation of localized SPR and SERS response in Au nanodumbbells by stepwise Ag coating [23]. Park et al. reported the shape evolution of Au–Ag core-shell nanopolyhedrons [24]. It has been found that the addition of the silver led to continuous shape evolution from gold seeds to silver spheres, cuboctahedrons, and cubes, respectively. Furthermore, the optical properties of the bimetallic nanoparticles could be fine tuned with the overgrowth of Ag shells. Hong et al. reported the shape control of Ag shell growth on Au nanodisks [25]. They found that the presence of iodide ions could greatly affect the growth direction of the Ag shell on the Au nanodisks.

The preparation and plasmonic optical properties of rod-like Au–Ag core-shell nanoparticles have also been widely studied [26,27]. In the report of Liu et al., Au–Ag core-shell nanorods with different Ag shell thickness were synthesized by chemically depositing Ag on Au nanorods surface [28]. Both the plasmonic absorption and light scattering spectral properties have been studied. By using Au nanorods as the cores, Au–Ag core-shell nanorods with varying Ag shell thicknesses were also prepared by Jiang et al. [29], and the nature of the SPR in this nanostructure has also been studied. By chemically depositing Ag on Au nanorods, Au–Ag core-shell nanoshuttles with sharp tips at both ends have been synthesized [3]. Strong local field enhancement in the Au–Ag core-shell nanoshuttles at the longitudinal SPR was observed. Contreras-Caceres et al. developed an easy and reproducible strategy for the immobilization of Au–Ag core-shell nanorods onto macroscopic substrates [30]. In order to investigate the SERS responses, two different controllable Ag nanoshells were successfully coated on the Au nanorod surface.

Because of having the square cross sections and sharp corners, metallic nanocubes are particularly attractive for plasmonic optics and related applications [31–33]. Halder et al. presented an alternate approach for producing Au nanostructures with different shapes and sizes from cube-shaped crystalline intermediates [31]. Zhang et al. reported the synthesis of Ag nanobars with different aspect ratios using a seed-mediated method [32]. They also found that the SERS enhancement of the Ag nanobar was dependent on its aspect ratio, orientation, and the excitation wavelength. Recently, Yao et al. reported the fabrication of hollow $\text{Cu}_2\text{O}/\text{CuO}$ nanocube-supported Au–Pd alloy nanoparticles [34]. By using the galvanic replacement reaction, Au–Pd alloy nanoparticles with a mean diameter of 15 nm have been deposited on the hollow $\text{Cu}_2\text{O}/\text{CuO}$ core-shell nanocubes. Au–Ag core-shell nanocubes containing varying shaped cores have been synthesized by Gong et al. [35]. They found that the Au–Ag core-shell nanocubes exhibit very abundant and core-shape dependent SPR properties. Ma et al. also studied the synthesis and optical properties of Au–Ag core-shell nanocubes [36]. In the prepared bimetallic nanoparticles, the Au core is spherical and the cubical Ag shell has an edge length controllable in the range of 13.4–50 nm. Although many experimental conditions have been developed to control the structure and optical properties of the core-shell type Au–Ag nanoparticles, the effect

of temperature on the Au nanocube growth, Ag shell coating and plasmonic shift is still a new topic. In the study of Yao et al., it has been found that the DMF-protected Au nanoparticles with different particle sizes could be prepared by controlling the reaction temperatures and times [37]. So we think that the growth of cube-shaped Au nanoparticles and the Ag coating could also be affected by the reaction temperature. In this paper, we report on the SPR absorption characters of Ag coated Au nanocubes. It has been found that both the corner geometry of the Au nanocubes and the Ag coating dependent absorption enhancement and plasmon shift are greatly dependent on the growing temperature of the Au nanocubes.

2. Experimental

2.1. Chemicals and reagents

Cetyltrimethylammonium bromide (CTAB, 99%) was purchased from Sigma (USA), silver nitrate (AgNO_3 , >99%), sodium borohydride (NaBH_4 , 98%), ascorbic acid (AA, 99.99%) were purchased from Shanghai Aladdin Industrial Corporation, China, chloroauric acid tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$) was purchased from Sinopharm Chemical Reagent Co. Ltd., China, sodium hydroxide (NaOH , >96%) was purchased from Tianjin HengXing Chemical Reagent Co. Ltd., China. All chemicals were used as received without further purification. And all water used was deionized (DI) water with a resistivity of $18.2 \text{ M}\Omega \text{ cm}$.

2.2. Preparation of gold nanocubes

We employ a seed-mediated growth method to prepare Au nanocubes in aqueous cetyltrimethylammonium bromide (CTAB) solution [38–40]. Firstly, very small Au nanocrystallines used as seed were synthesized by quickly injecting freshly prepared, ice cold NaBH_4 (0.01 M, 0.3 mL) into the mixture solution composed of HAuCl_4 (0.01 M, 0.125 mL) and CTAB (0.1 M, 3.75 mL), followed by a minute of vigorous stirring. The color of the solution changed from dark yellow to brownish yellow indicating the formation of the gold seed. Then the resulting solution was aged for 1 h at room temperature in order to decompose excess borohydride. Secondly, the growth solution was prepared by injecting CTAB (0.1 M, 19.2 mL), HAuCl_4 (0.01 M, 2.4 mL) and ascorbic acid (0.1 M, 11.4 mL) into deionized water (96 mL) in order. The mixed solution was shaken violently. The color of the solution turn from dark yellow to colorless after the addition of ascorbic acid due to the reduction of Au^{3+} to Au^+ [40]. The seed solution was diluted 100 times with deionized water, and then 600 μL of the diluted seed solution was added into the growth solution at once followed by gently shaken. Then the resultant solutions were placed in the water bath set at 25°C , 45°C and 65°C respectively and left undisturbed overnight to ensure the full growth of Au nanocubes.

2.3. Preparation of silver coated gold nanocubes

Ag coated Au nanocubes with different thickness of Ag shell were formed by depositing Ag on the as-prepared Au nanocubes according to a method which was reported previously [27] with some minor changes. In a typical synthesis, Au nanocubes solution was centrifuged at 7500 rpm for 20 min in order to remove the unreacted materials. The precipitate was redispersed into the same volume of 0.08 M CTAB (the capping agent) after discarding the supernatant. One minute of ultrasonic of the mixture solution is needed to ensure the uniform mixing. Then AgNO_3 (the precursor to elemental Ag) and ascorbic acid (the reducing agent) were added into the mixture solution containing Au nanocubes. After vigorous stirring for one minute, 0.6 mL of 0.1 M NaOH was quickly injected

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