Facile preparation of gold nanocages and hollow gold nanospheres via solvent thermal treatment and their surface plasmon resonance and photothermal properties

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A B S T R A C T

Although template etching method is one of the most common ways of preparation of hollow gold nanostructures, this approach still requires further improvements to avoid the collapse of gold shells after the cores were removed. In this work, an improved template etching method, with which hollow gold nanostructure is fabricated by etching Polystyrene (PS) cores from PS@Au core–shell nanospheres with solvent thermal treatment in N,N-Dimethylformamide (DMF), is demonstrated. When PS cores were removed by a thermal treatment process, gold nanoshells reconstruct and the collapse of the nanoshells is avoided. Gold nanocages and hollow gold nanospheres are easily obtained from the various structures of PS@Au core–shell nanospheres. These hollow nanostructures represent special near infrared (NIR) optical property and photothermal property. Compared with hollow gold nanospheres, the gold nanocages show higher temperature increase at the same particle concentration.

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1. Introduction

Hollow gold nanostructures (especially gold nanocages and hollow gold nanospheres) exhibit unique optical property due to their tunable surface plasmon resonance (SPR) absorptions, and have attracted extensive research attentions [1–3]. The SPR absorptions can be tuned from the visible region to the near-infrared (NIR) region by changing the size and thickness of gold shells [4–6]. The hollow gold nanostructures have potential applications in cell imaging [7–9], biosensor [10], photothermal therapy of cancers [11,12], controllable drug release [13,14] and catalysis [15–17]. Currently, a series of methods on preparation of hollow gold nanostructures with tunable optical property have been researched in some groups. The most common approaches for the preparation of hollow gold nanostructure involve growing gold nanoparticles on soft surfactant aggregates templates [18],

galvanic replace reaction by using sacrificial metal templates [4,19,20], and selective etching or calcination gold core–shell nanostructures [21–24]. As to the selective etching and calcination methods, hollow gold nanostructures were usually fabricated by depositing gold shells on PS sphere templates, and then selectively removed templates via calcination or chemical etching. PS sphere templates have easily functionalized surface and broad size range and have therefore been frequently used [25,26], and the way of fabricating gold core–shell nanostructures on colloidal surfaces has been widely researched since Halas' pioneering work on preparation of gold core–shell nanospheres [3]. However, the gold shells of hollow nanostructures would be collapsed or destroyed after the PS cores were selectively removed. The main challenge in the preparation of hollow gold nanoshells is the difficulty of removing PS templates. There are reports on successfully removing PS templates by calcination at high temperature (above 300 °C), but the processes are rather complex because the gold shells would be destroyed if they are not protected before calcination [27–30]. Other method is dissolution of PS core into an organic solvent. Even though PS can be easily dissolved in Tetrahydrofuran (THF) and Dimethylformamide (DMF), gold shell would collapse after the PS cores were removed due to its low mechanical strength [31,32]. To date, most PS@metal core–shell nanostructures have been applied without core removed, and caused performance

degradation of the core–shell nanostructures [33]. Therefore, it is essential to develop an effective and facile method of fabricating hollow gold nanostructures. Compared with the calcination method, the chemical etching method will be a promising route to remove PS templates at low temperature, if troubles of shell collapse are solved. As well known, metal nanoparticles grow larger by Ostwald ripening at the expense of smaller ones due to chemical potential energy difference. Moreover, metal nanoparticles would reconstruct at lower temperature than the melting point of blocks. There are reports on reconstructing gold nanoparticles upon the thermal treatment [34–38]. In our work, to achieve perfect hollow gold shells, the thermal treatment process was used in solvent etching method to solve the trouble of gold shell collapse. When PS@Au core–shell nanospheres were treated by heating in DMF solvent, PS cores were etched out and gold nanoshells reconstructed to improve their mechanical strength, so the gold nanoshells would not collapse after PS cores were removed.

Herein, we report on the preparation of gold nanocages and hollow gold nanospheres from PS@Au core–shell nanospheres by solvent thermal treatment in DMF. In this process, gold nanoshells reconstruct in Ostwald ripening process by thermal treatment (below 120 °C). Hollow gold nanostructures are obtained without shells collapse. Moreover, various shell structures of hollow nanostructures (nanocages or hollow nanospheres) are controllably obtained from variable surface structures of PS@Au core–shell nanospheres. The SPR features of these hollow nanostructures are investigated, and they have strong SPR absorption in NIR region. In addition, these hollow gold nanostructures have stable photothermal effect, and hollow gold nanocages have higher temperature increase than that of hollow gold nanospheres at the same particle concentration.

2. Experimental section

2.1. Materials

PS spheres (about 260 nm in diameter) were used as received. $HAuCl_4 \cdot 4H_2O$ was obtained from Shanghai Reagent Company. Poly (ethyleneimine) branched (PEI, Mn = 10,000) was purchased from Sigma–Aldrich. N,N-Dimethylformamide (DMF) and potassium carbonate (K_2CO_3), ammonium hydroxide ($NH_3 \cdot H_2O$, 28–30%), formaldehyde (HCHO 37%), sodium borohydride ($NaBH_4$), and polyvinypyrrolidone (PVP, Mw = 30,000) were received from Beijing Chemical Company. All chemicals were analytical grade and used without further purification. Deionized water used for all experiments was treated with a Millipore water purification system (Millipore Corp.).

2.2. Preparation of the PS@Au core–shell nanospheres

The PS spheres were modified with PEI layer via electrostatic interaction before used. 2.5 mL suspension of negatively charged sulfate-stabilized PS spheres (87 mg mL^{-1}) was added to excess positive charged PEI solution (10 mL, 0.6 mg mL^{-1}), and was mixed for 30 min. The PEI modified PS spheres were purified by repeated centrifuging (10,000 rpm, 20 min). Then the PEI modified positive charged PS spheres (PS-PEI) were redispersed into 25 mL water (8.7 mg mL^{-1}). PVP protected gold nanoparticles were prepared according to the literature [39] and were used as seeds. Gold seeds were absorbed on modified PS spheres as following: 200 μL, PS-PEI was added to 8 mL newly prepared gold sol quickly. After 30 min, the excess gold sol was removed by centrifuging (8000 rpm, 5 min) and washed one time. Then, gold seeds on PS spheres (PS@Au seeds) were obtained. PS@Au core–shell nanospheres were prepared via a seeding-mediated growth approach in 0.3 mM $HAuCl_4$ growth solution. Growth solutions were prepared as

following [40]: 50 mg of K_2CO_3 was dissolved in 200 mL water. After 10 min of stirring, 1.41 mL of $HAuCl_4$ (48 mM) was added. The solution became colorless after 30 min and was aged for 24 h in the dark for use in subsequent steps. PS@Au core–shell nanospheres were fabricated by adding former PS@Au seeds to 10 mL growth solution with PVP (1 mg mL^{-1}) as stabilizer, and 50 μL $NH_3 \cdot H_2O$ (28–30%) was added to adjust pH. Then, 60 μL formaldehyde was added and reacted for 12 h. Different PS@Au core–shell nanostructures were obtained by adjusting the volume of $HAuCl_4$ (5 mL, 10 mL, 15 mL, 20 mL, 25 mL, and 40 mL) and formaldehyde (Table S1 in Supporting Information). Finally, PS@Au was washed three times by centrifuging (5000 rpm, 5 min), and redispersed into water.

2.3. Preparation of Au nanocages and hollow Au nanospheres

Hollow gold nanostructures were obtained by removing the PS templates in heated DMF. PS@Au core–shell nanospheres (prepared in 20 mL growth solution) were added into 20 mL DMF with stirring. With the heating for 12 h at 120 °C, the PS templates were removed and hollow gold nanostructures were obtained. Gold nanocages and hollow gold nanospheres were prepared from variable PS@Au core–shell nanostructures. Gold nanostructures were washed with DMF to remove the PS in solution by centrifuging (5000 rpm, 5 min) three times, and redispersed into water. Effects of temperature and time of thermal treatment were also investigated.

2.4. Photothermal conversion analysis

The photothermal experiments of gold nanocages and hollow gold nanospheres were carried at the same particle concentration. The same amounts of PS spheres were used at all the core–shell nanostructures, so the corresponding hollow gold nanostructures were the same particle concentration. The suspensions of gold nanocages and hollow gold nanospheres were irradiated at a power density of 0.5 W cm^{-2} by 808 nm laser. The laser spot was altered to cover the surface of the suspensions. The temperature increases of the suspensions were recorded as a function of the irradiation time. Stability test was carried by recording the temperature increase after irradiating the suspensions for 5 min, and re-irradiating the suspensions after their temperature deceases to room temperature. This process was repeated for 8 times.

2.5. Characterization

Scanning electron microscopy (SEM) images were obtained by using a Hitachi S-4800 field emission microscope operated at 10 kV. Transmission electron microscopy (TEM) images were obtained with a JEOL model JEM 1011 operated at 100 kV and high-resolution transmission electron microscopy (HRTEM) images were obtained by using a JEOL model JEM 2100F operated at 200 kV. UV-vis-NIR spectra measurements were characterized on U-2800 (400–1000 nm) and lambda 950 (400–1400 nm) (PerkinElmer UV WinLab). Size and zeta potential analysis were recorded at 25 °C on Malvern ZetaSizer Instruments. Power X-ray diffraction (XRD) measurements were recorded on an EMPYREAN Diffractometer system with Cu Kα radiation (λ_1 = 1.540598 Å, λ_2 = 1.544426 Å, intensity ratio λ_2/λ_1 = 0.5) with samples on glass holder.

3. Results and discussion

3.1. Preparation of PS@Au core–shell nanospheres

Scheme 1 illustrates the preparation procedure of hollow gold nanostructures. PS@Au core–shell nanostructures are fabricated