



Synthesis of mesoporous silica hollow nanospheres with multiple gold cores and catalytic activity



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ABSTRACT

The core-shell Au@resorcinol-formaldehyde (RF) nanospheres with multiple cores have been successfully synthesized by a modified Stöber method. After coating mesoporous silica and the calcination, the Au@meso-SiO₂ hollow nanospheres with multiple gold cores can be obtained, which have a high surface area (~537 m²/g) and uniform pore size (~2.5 nm). The Au@meso-SiO₂ hollow nanospheres can be used as a catalyst for the reduction of 4-nitrophenol by NaBH₄ into 4-aminophenol, and exhibit excellent catalytic performance.

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1. Introduction

In recent years, a special class of core-shell structures with core@void@shell configuration (the hollow nanospheres with cores) has attracted considerable attention because of the following advantages. (I) The moveable cores can afford much more exposed active sites to interact with the guest molecules more effectively. (II) The outer shells can prevent the aggregation of neighboring nanoparticles. (III) The hollow spaces between the cores and the shells can provide large space for loading functional molecules. Due to the functionalities of the freely movable cores, the protective shells and the spaces between them, hollow nanospheres have been widely applied in the fields of catalysis, biomedicine, lithium-ion batteries and so on [1–13].

Up to now, a variety of synthetic strategies have been developed to fabricate hollow nanospheres with metal cores. According to the sequence of preparing cores and shells, the methods can be classified into pre-shell/post-core and pre-core/post-shell approaches. In the pre-shell/post-core approaches, the metal ions are reduced to grow metal cores in the pre-formed hollow shells [14–17]. Most of the hollow nanospheres are synthesized by pre-core/post-shell approaches, firstly, a sandwich structure (core/template/shell) is fabricated by using hard or soft templates, and then, the voids can be formed via selectively removing the intermediate sacrificial template layer, using a solvent or calcination [18–24].

Generally, the inner sacrificial shells are composed of silica or carbon precursors for the hard-templating method. The silica shells can be selectively removed by NaOH [21], NH₃·H₂O [10], Na₂CO₃ [25], NaBH₄ [19,26], H₂O [11,27] and organosilane [16,28]. However, compared with etching silica in solution, calcination in air to remove the carbonaceous shells is much more simple. Many carbon precursors can be used to fabricate carbon-based nanospheres, such as resorcinol-formaldehyde (RF) resin [29–32], phenol-formaldehyde resin [33,34], saccharide [35,36], and polydopamine [37]. Among them, RF resin, a three-dimensional (3-D) network structured polymer, has been paid much attention due to the attractive properties such as low cost, controllable morphology and outstanding stability.

Until now, various porous shells have been fabricated to encapsulate metal nanoparticles, such as SiO₂, ZrO₂, TiO₂ and C [3,5,38–44]. The porous outer shells can provide convenient channels for the diffusion and transport of reactants to reach the surface of the active cores, and protect the active metal cores from leakage. In particular, mesoporous silicas have been paid much attention because of their high surface area, large pore volume, tunable uniform pore size, high stability, controllable morphology, facile surface functionalization and high biocompatibility [45].

The Stöber method has attracted many interests for the fabrication of silica shells on nanoparticles through the facile hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in basic aqueous solutions [46]. Functional nanoparticles have been encapsulated in silica to form the core-shell structures, including noble-metal nanoparticles, metal oxides, and quantum dots

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[25,47–49], because the encapsulated nanoparticles can maintain their specific catalytic, magnetic, electronic or optical properties. Among them, gold@silica nanospheres have been applied in many fields such as catalysis, drug delivery and bioimaging [15–17,22,50]. In the case of nanocatalysts, the strategy of encapsulating gold nanoparticles in hollow mesoporous silica nanospheres is a good way to obtain great catalytic performance, because the gold cores can move freely inside the cavity of the shells to sufficiently expose the surface of the active cores.

Herein, we demonstrate the one-pot synthesis of the core–shell Au@RF nanospheres with multiple gold cores by a modified Stöber method, using resorcinol and formaldehyde as the precursors, $\text{NH}_3\cdot\text{H}_2\text{O}$ as the catalyst, surfactant CTAB and F127 as the costabilizers. After the core–shell Au@RF@meso-SiO₂ nanospheres were calcined, Au@meso-SiO₂ hollow nanospheres with multiple gold cores could be achieved. The obtained Au@meso-SiO₂ hollow nanospheres have a high surface area ($\sim 537 \text{ m}^2/\text{g}$) and uniform pore size ($\sim 2.5 \text{ nm}$). Furthermore, the Au@meso-SiO₂ hollow nanospheres were successfully employed in the catalytic reduction of 4-nitrophenol as a model reaction.

2. Experimental

2.1. Chemicals

Cetyltrimethylammonium bromide (CTAB, 99.0 wt%), formaldehyde solution (37.0 wt%), resorcinol (99.0 wt%), aqueous ammonia ($\text{NH}_3\cdot\text{H}_2\text{O}$, 25.0 wt%) and chloroauric acid tetrahydrate ($\geq 47.8 \text{ wt\% Au}$) were purchased from Sinopharm Chemical Reagent Company. Tetraethyl orthosilicate (TEOS, 98.0 wt%), NaBH_4 (99.0 wt%), 4-nitrophenol (4-NP, 99.0 wt%) and absolute anhydrous ethanol (99.7 wt%) were obtained from Shanghai Chemical Company. Tri-block copolymer Pluronic F127 ($\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$, EO = ethylene oxide, PO = propylene oxide, 99.0 wt%) was purchased from Sigma–Aldrich. All chemicals were used without additional purification. Deionized water was used for all experiments.

2.2. Synthesis

2.2.1. Synthesis of core–shell Au@resorcinol–formaldehyde polymer (Au@RF) nanospheres

In a typical synthesis, 0.125 g of F127 and 0.05 g of CTAB were dissolved in the solution containing 10 mL of deionized water and 4 mL of ethanol. After stirring at 30 °C for 15 min, 0.05 mL of $\text{NH}_3\cdot\text{H}_2\text{O}$ was added. After further stirring for 50 min, 0.1 g of resorcinol was added. Stirring for additional 30 min, 0.14 mL of formaldehyde solution was added. The mixture was stirred for 24 h at 30 °C, then, 0.5 mL of 0.1 M HAuCl_4 aqueous solution was added. After stirring for 30 min, the mixture was transferred to a Teflon-lined auto-clave and heated for 24 h at 100 °C under static conditions. The products were centrifuged, washed three times with water and once with absolute ethanol, and then dried at 60 °C overnight, after which the core–shell Au@RF nanospheres were obtained.

2.2.2. Synthesis of core–shell Au@RF@meso-SiO₂ nanospheres

The core–shell nanospheres with double shells were prepared through a surfactant-templating sol–gel approach by using CTAB as a template. In a typical synthesis, 0.075 g of CTAB was dissolved in the solution containing 25 mL of deionized water and 13 mL of ethanol. After stirring at 30 °C for 15 min, 1 mL of an ethanol dispersion solution containing 0.05 g of Au@RF nanospheres was added. The mixture was homogeneously dispersed by ultrasonication for 15 min, followed by the addition of 0.25 mL of $\text{NH}_3\cdot\text{H}_2\text{O}$. Stirring for additional 10 min, a solution containing 0.11 g of TEOS

and 1.0 mL of ethanol was added dropwise with continuous stirring for 1 min. After reaction for 6 h, the products were centrifuged, washed for three times with water and once with absolute ethanol, and then dried at 60 °C overnight, after which the core–shell Au@RF@meso-SiO₂ nanospheres were obtained.

2.2.3. Synthesis of Au@meso-SiO₂ hollow nanospheres

Removal of the polymer shells and surfactants was achieved by the calcination of the core–shell Au@RF@meso-SiO₂ nanospheres in air from room temperature to 550 °C for 6 h at a rate of $1 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$, after which the Au@meso-SiO₂ hollow nanospheres were obtained.

2.3. Catalytic reduction

The catalytic reduction process of 4-nitrophenol (4-NP) was carried out in a quartz cuvette and monitored by *in situ* measuring the UV–vis absorption spectra. At first, 0.125 mL of 0.2 M freshly prepared NaBH_4 solution was added in the solution containing 0.0125 mL of 0.005 M 4-NP and 1.0 mL of deionized water. Subsequently, 0.05 mL of aqueous dispersion of 0.0125 wt% Au@meso-SiO₂ hollow nanospheres was added, and the reaction started immediately. The gradual change of the solution color from light bright yellow to colorless was observed during the reaction. To study the recyclability of the catalysts, the used Au@meso-SiO₂ hollow nanospheres were separated from the reaction mixture by centrifugation at the end of each run, washed once with absolute ethanol and once with deionized water, then re-dispersed in water by ultrasonication and added in a fresh reaction solution. After reaction for 20 min, the solution was measured using UV–vis spectroscopy.

2.4. Characterization

Scanning electron microscopy (SEM) images were obtained on a FE-SEM S-4800 microscope (Hitachi, Japan) operated at 1 kV. Transmission electron microscopy (TEM) images were taken by a JEM-2011F microscope (JEOL, Japan) operated at 200 kV. The samples for TEM measurements were dispersed in ethanol, and then dipped and dried on holey carbon films supported on a Cu grid. Energy dispersive X-ray spectroscopy (EDX) was recorded on an IET-200 EDX instrument (Oxford, England). Thermogravimetric analysis (TGA) was monitored by using a Mettler Toledo TGA/DSC 1 analyzer (Switzerland) from 30 to 600 °C under air ($40 \text{ mL}\cdot\text{min}^{-1}$) with a heating rate of $5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$. X-ray diffraction (XRD) patterns were recorded on a D8 advance X-ray diffractometer (Bruker, Germany) with Ni-filtered Cu K α radiation (40 kV, 40 mA). Nitrogen adsorption/desorption isotherms were measured with a Tristar II 3020 analyzer (Micromeritics, USA) at 77 K. Before the measurements, the samples were degassed in vacuum at 180 °C for at least 6 h. The surface area and pore size were obtained by using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. The carbon contents of the samples were measured on a Vario EL III elemental analyzer (Germany). The UV–vis spectra were collected using a UV-3600 spectrophotometer (Shimadzu, Japan).

3. Results and discussion

SEM images (Fig. 1a) show that the Au@RF nanospheres have well spherical morphology, the size of the core–shell Au@RF nanospheres is quite uniform with the average diameter of about 850 nm. The monodispersed spherical morphology of the core–shell Au@RF nanospheres can be further confirmed from the TEM images (Fig. 1b). TEM images display that many gold nanoparticles

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