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A versatile approach for the fabrication of Au hollow nanoparticles based on poly(styrene-*co*-2-aminoethyl methacrylate) template

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Abstract The hollow Au nanospheres were successfully prepared by the template method. The poly(styrene-*co*-2-aminoethyl methacrylate hydrochloride) (P(St-*co*-AEMH)) nanoparticles synthesized by the emulsion polymerization were used as the templates. After coating by Au colloidal nanoparticles and the formation of Au shells, the interior templates were etched out by sulfuric acid, leading to the formation of Au hollow nanospheres. The structure and morphology of the nanoparticles and hollow nanospheres were carefully investigated by the fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray analysis (EDX), wide-angle X-ray diffractometer (WAXD), and thermal gravimetric analysis (TGA) techniques.

Introduction

Hollow nanospheres have recently attracted a great deal of attention due to their wide variety of potential applications, including the delivery of drugs, catalysis, chemical storage, microcapsule reactors, as building blocks in the favorication of photonic band gap crystals, and so on [1–4].

Concerning the fabrication of hollow nanospheres, there are two main strategies such as the template-directed and emulsion methods [5–11]. For the template-directed strategy, the adsorption of nanoparticles or polymerization on modified polymeric or inorganic template surface was always performed, followed by the subsequent removal of the template by calcinations or dissolution with solvents [12–14]. In the emulsion strategy, the soft template was removed directly from the formed hollow nanospheres [15–18].

Au nanoparticles and nanoshells have been extensively studied and could find use in the field of catalysis, delivery of enzyme, optical imaging, and so on. The Au nanoshells could be prepared by the deposition of small gold nanoparticles on the surfaces of modified silica nanoparticles [9], or by layer-by-layer adsorption of polyelectrolytes and charged gold colloids to build shell-like structures around colloidal template particles [18]. In general, the inorganic templates were always difficult to erase, resulting in the destroying of the Au nanoshell structure.

In this article, in order to obtain more regular hollow Au nanospheres, the poly(styrene-*co*-2-aminoethyl methacrylate hydrochloride) P(St-*co*-AEMH) nanoparticles synthesized by the emulsion polymerization were used as the templates. The terminal amine groups acted as the anchor points for Au colloidal nanoparticles, serving as the nucleation sites for the growth of Au nanoparticles on the surface of the templates. After the formation of core–shell nanospheres, the polymer templates were selectively etched out, leading to the hollow nanospheres with Au shell.

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Experimental

Materials

Styrene was purified by distillation under reduced pressure. 2-Aminoethylmethacrylate hydrochloride (AEMH, Acros, 90%), divinylbenzene (DVB, Alfa Aesar, 80%), 2,2′-Azobis (2-methylpropionamidine) dihydrochloride (V50, Aldrich, 97%), chloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$), potassium carbonate, sodium borohydride, hydroxylammonium chloride, and sodium citrate were used without further purification.

Preparation of P(St-*co*-AEMH) nanoparticles by emulsion polymerization

Emulsion polymerization of styrene (St), divinylbenzene, and 2-aminoethylmethacrylate hydrochloride (AEMH) was carried out at 70 °C, using V50 as the initiator and deionized water as the dispersant. The monomer of St (1.33 mL), divinylbenzene (0.1 mL), and AEMH (0.2 g) were added drop-wise into the 100 mL flask containing 20 mL deionized water under vigorous stirring. After purging by argon for 15 min, V50 (0.02 g) dissolved in water (2 mL) was added into the mixture under vigorous stirring, and the mixture was heated and refluxed under nitrogen for 24 h. Latexes were collected by centrifuging and purified by re-dispersion and centrifuging in deionized water for several times. The received latexes were then dried at 110 °C under vacuum for 12 h.

Preparation of colloidal gold nanoparticles

The colloidal gold nanoparticles were prepared as described by Jana et al. [19]. Into a flask containing 100 mL water, $HAuCl_4 \cdot 4H_2O$ (0.027 g) and sodium citrate (0.019 g) were added under vigorous stirring, followed by the addition of freshly prepared sodium borohydride solution (5 mL, 0.1 M). Then, a solution of wine-red color was obtained.

Attachment of Au colloidal particles to P(St-*co*-AEMH) nanoparticles

To prepare the Au attached P(St-*co*-AEMH) nanoparticles, 0.2 g of P(St-*co*-AEMH) nanoparticles was added into the Au colloidal particles aqueous solution under vigorous stirring for 12 h. After the attachment of Au colloidal particles onto the amine groups of P(St-*co*-AEMH) nanoparticles, the objective nanoparticles were collected by centrifugation and re-dispersing method for several times. Finally, the received nanoparticles were dispersed in 50 mL water and the solution was transferred into the refrigerator aging for 7 days.

Preparation of P(St-*co*-AEMH)@Au core–shell nanoparticles

The P(St-*co*-AEMH) nanoparticles dressing by Au colloidal nanoparticles were used as seeds to prepare the P(St-co-AEMH)@Au core–shell nanoparticles. Into a reaction flask containing 100 mL water, 0.435 g of potassium carbonate was added. After stirring for 10 min, 10 mL of $HAuCl_4$ (70 mM) was added. The mixture exhibiting light yellow color gradually became colorless after stirring for 1 h. Then, the mixture was aged for at least 24 h in the dark. After mixing the above solution with P(St-*co*-AEMH) nanoparticles dressing by Au colloidal nanoparticles under vigorous stirring and 10 mL of freshly prepared hydroxylammonium chloride solution (1.87 mM) was added dropwise, leading to the formation of black precipitates. The precipitate was collected by the centrifuging and purified by re-dispersion and centrifuging process.

Preparation of the Au hollow nanospheres

The received P(St-*co*-AEMH)@Au core–shell nanoparticles (3.8 mg) were immersed into a 10 mL concentrated sulfuric acid for 7 days. After the inner polymer templates were etched out, the hollow Au nanoparticles were collected after washing by deionized water for five times.

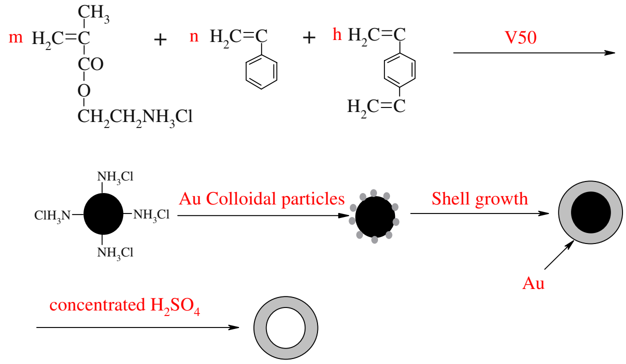
Characterization

The Fourier-transform infrared (FTIR) spectra were obtained in a transmission mode on a Shimadzu IRPrestige-21 FT-IR spectrophotometer. The morphology of the nanoparticles were studied by scanning electron microscopy (SEM), using a Hitachi S-4300 electron microscope. The nanoparticles were mounted on an aluminum alloy stub and sputtered with a thin layer of platinum. The SEM measurements were performed at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) analysis was also used to characterize the morphology of nanoparticles. In a typical experiment, several drops of the colloidal dispersion were introduced onto a carbon film supported by a copper grid. The droplet was allowed to dry in air, and then observed under a JEM-2010HR TEM operating at an acceleration voltage of 100 kV. The wide-angle X-ray diffraction (XRD) patterns of the specimens were recorded at room temperature using a Bruker D8 Focus X-ray diffractometer, equipped with Ni-filtered CuK_α radiation in the reflection mode with a wavelength of

0.154 nm. The scanning 2θ angle ranged between 3° and 90° with a step scanning rate of 2°/min. Thermogravimetry (TG) was performed under nitrogen with a Perkin–Elmer TGA 7 (heating rate 20 °C/min, sample size 8–10 mg).

Results and discussion

The synthetic pathway is composed of the fabrication of P(St-*co*-AEMH) nanoparticles by emulsion polymerization, followed by the attachment of Au colloidal nanoparticles onto the surface of the templates. Finally, hollow Au nanospheres were obtained by etching the inner polymer substrate in P(St-*co*-AEMH)@Au core–shell nanoparticles. The whole process for fabricating the Au nanoparticles is illustrated in Scheme 1.



Scheme 1 Schematic illustration of the preparation of hollow Au nanospheres

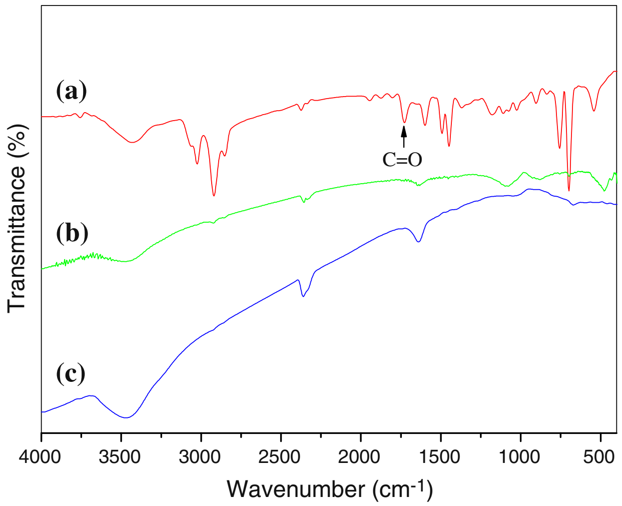


Fig. 1 FT-IR spectra of: (a) the P(St-*co*-AEMH) nanoparticles, (b) P(St-co-AEMH)@Au core–shell nanoparticles, and (c) hollow Au nanospheres

In Fig. 1, the absorption peaks at 1500 and 1600 cm^{-1} are assigned to the vibration of benzene ring, in addition to the absorption peak at 1730 cm^{-1} ascribed to the C=O stretch in P(St-*co*-AEMH). Furthermore, the relatively strong absorption peak at 2930 cm^{-1} is attributed to the aliphatic C–H vibration. The absorption peak at 3450 cm^{-1} is ascribed to the N–H vibration in AEMH segment. After the attachment of Au colloidal nanoparticles onto the P(St-*co*-AEMH) nanoparticles and the formation of Au shells, the FTIR spectra significantly changed. It is observed that the absorption peak at 2930 cm^{-1} became very weak due to the coating of Au colloidal nanoparticles onto the polymer templates. The other characteristic absorption peaks ascribed to the P(St-*co*-AEMH) were not observed either. The above results indicate that the Au nanoparticles were successfully coated onto the P(St-*co*-AEMH) nanoparticles. After etching out the inner polymer templates, the FTIR spectra of the resultant hollow Au nanospheres showed no significant difference as compared with former P(St-*co*-AEMH)@Au core–shell nanoparticles.

The morphology of the nanoparticles was investigated by SEM and TEM. It is observed from Fig. 2 that the P(St-*co*-AEMH) nanoparticles were spherical with rough surfaces, and the diameters of the nanoparticles were about 120 nm. After coating by Au colloidal nanoparticles, the shape and size of the resulting nanoparticles showed no serious change. The diameters of the hollow Au nanospheres were similar to those of P(St-*co*-AEMH) nanoparticles and the P(St-*co*-AEMH)@Au core–shell nanoparticles. Figure 3 shows the TEM graph for the hollow Au nanoparticles. The brightness in the inner part of the spheres represented that the polymer templates were removed during the etching process by sulfuric acid. The dark shells of the spheres are mainly composed of the Au nanoparticles and the thickness of the shell was in the size of about 20 nm.

Figure 4 shows the EDX spectra of pristine P(St-*co*-AEMH) nanoparticles, P(St-*co*-AEMH)@Au core–shell nanospheres, and hollow Au nanospheres, respectively. The EDX signals at 0.3 keV (attributable to C) and at 0.5 keV (attributable to O) are consistent with the presence of P(St-*co*-AEMH). Additionally, no signals ascribed to Au were observed in the spectra. After coating by Au colloidal nanoparticles, the signals at 0.3 keV and 0.5 keV ascribed to C and O, respectively, can still be observed. Furthermore, the appearance of the signal at 2.1 keV attributable to Au, indicated that the Au colloidal nanoparticles have been successfully anchored on the surface of the P(St-*co*-AEMH) nanoparticles. For the hollow Au nanospheres, the signal peak at 2.1 keV became stronger and the content of Au increased from 40% to about 87%. It is believed that the hollow nanospheres were mainly composed of Au. The above results are consistent with the results obtained from FTIR.

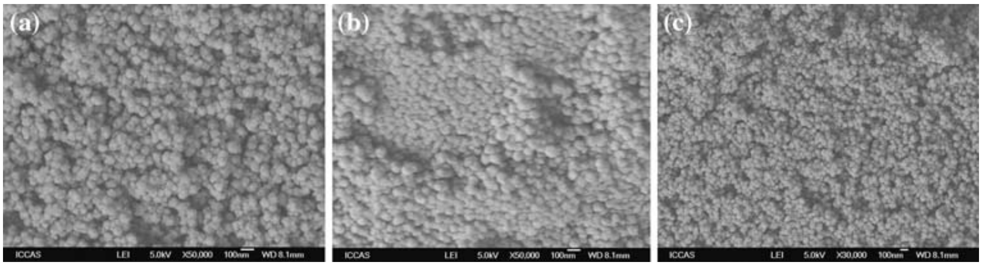


Fig. 2 SEM images of: **a** the P(St-*co*-AEMH) nanoparticles, **b** the P(St-*co*-AEMH)@Au core–shell nanoparticles, and **c** the hollow Au nanoparticles

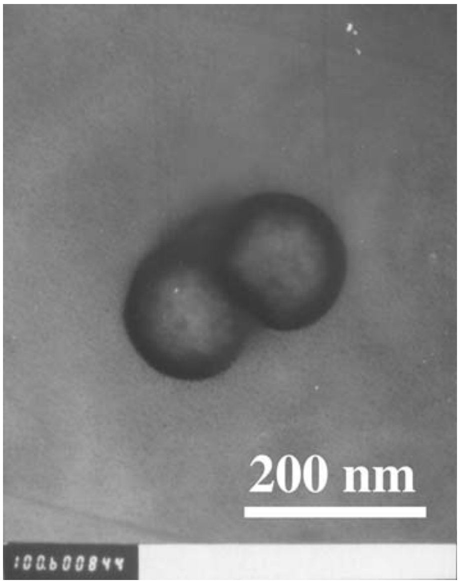


Fig. 3 TEM image of the hollow Au nanospheres

The crystalline structure of the nanoparticles was further investigated by WAXD. In Fig. 5, the pristine P(St-*co*-AEMH) nanoparticles exhibited round reflection peaks between 5° and 30°, indicating that the polymer template was amorphous. In contrast, the P(St-*co*-AEMH)@Au core–shell nanoparticles exhibited sharper reflection peaks. The appearance of reflection peaks at $2\theta = 38.2$, 44.5, 64.7, 77.8, and 81.9°, corresponding to the (111), (200), (220), (311), and (522) planes of Au, respectively, indicated that the surface of the P(St-*co*-AEMH) nanoparticles was coated by the Au shell. The results are consistent with those obtained by FTIR and EDX analysis.

In order to further analyze the component and structure of the nanoparticles, TGA was performed to investigate the degradation behaviors. It can be observed from Fig. 6 that the pristine P(St-*co*-AEMH) nanoparticles started to decompose at the temperature of 150 °C. Further increasing of the temperature led to the complete decomposition of the nanoparticles at about 500 °C. For the P(St-*co*-AEMH)@Au core–shell nanoparticles, almost about 25% weight was lost during the heating process, indicating that the content of the Au nanoparticles coated on the polymer templates was about 75%. As the hollow Au nanospheres were concerned, almost no weight loss was observed during the whole heating process, indicating that the resulting

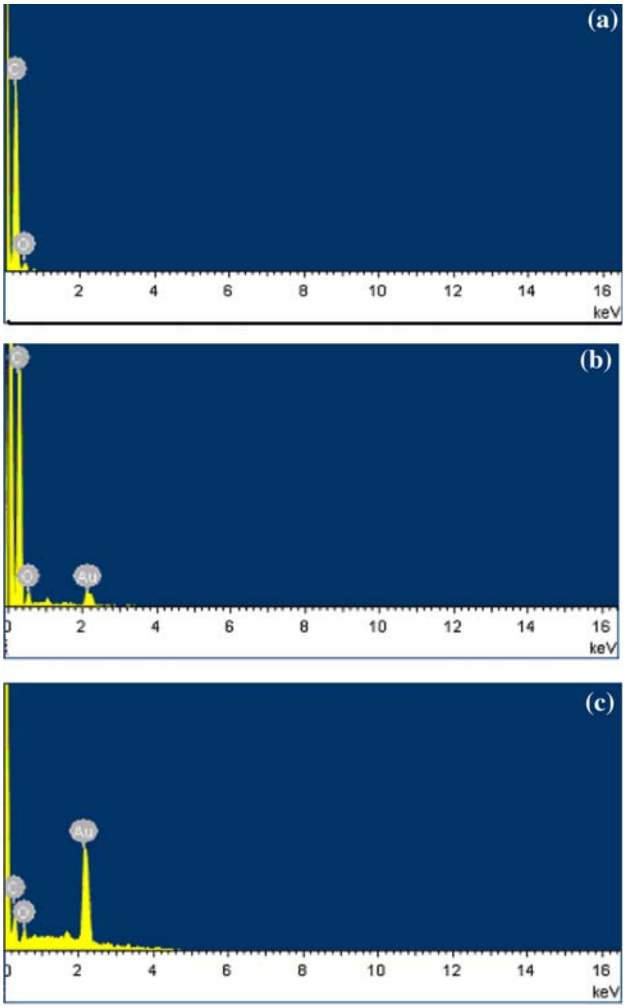


Fig. 4 EDX spectra of: **a** the P(St-*co*-AEMH) nanoparticles, **b** P(St-*co*-AEMH)@Au core–shell nanoparticles, and **c** hollow Au nanospheres

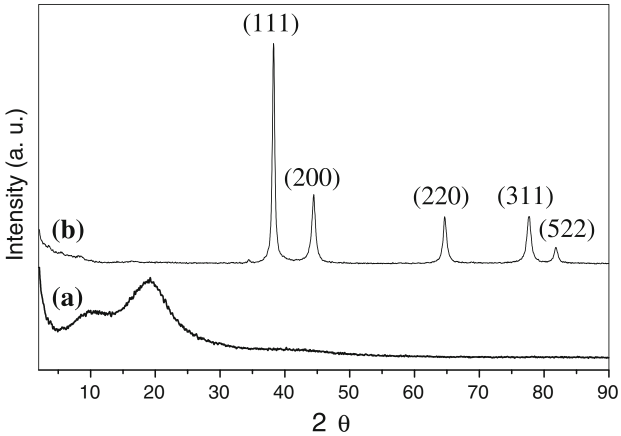


Fig. 5 X-ray spectra of: (a) the P(St-*co*-AEMH) nanoparticles and (b) P(St-*co*-AEMH)@Au core–shell nanoparticles

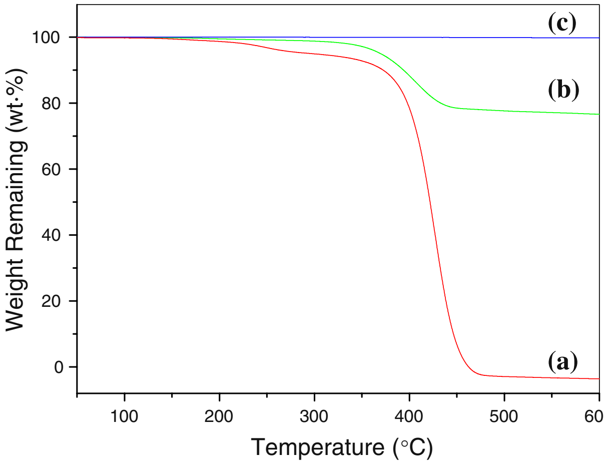


Fig. 6 TGA curves of: (a) the P(St-*co*-AEMH) nanoparticles, (b) P(St-*co*-AEMH)@Au core–shell nanoparticles, and (c) hollow Au nanospheres

nanoparticles were mainly composed of Au and the residual polymer templates were almost completely removed by the treatment of concentrated sulfuric acid.

Conclusions

The Au hollow nanospheres were successfully prepared by using P(St-*co*-AEMH) nanoparticles as templates, followed by etching out the inner polymer by concentrated sulfuric acid. The Au hollow nanospheres exhibited regular sphere shape, with the diameter determined to be about 120 nm and the thickness of the Au shell calculated to be about 20 nm. The method for preparing the Au hollow nanospheres based on the P(St-*co*-AEMH) nanoparticle template was demonstrated to be feasible and useful. The prepared Au hollow nanospheres may have potential use in the field of catalysis, biology, and so on.

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