

A Simple One-Step Chemical Route to Gold/Polymer Core/Shell Composites and Polymer Hollow Spheres

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ABSTRACT: Au/poly(*o*-toluidine) (POT) core/shell composite spheres have been successfully fabricated by chemical polymerization route in aqueous solution without the aid of surfactant or functional acids using HAuCl₄ as the oxidant. By altering the concentration of oxidant, the amount of Au nanoparticles inside each POT sphere can be tuned from tens to one. Moreover, uniform POT hollow spheres with one opening in each polymer surface can be obtained under extremely low concentration of oxidant.

The chemical structures of Au/POT composites were confirmed by Fourier transform infrared (FTIR), UV-vis, and X-ray diffraction (XRD) spectroscopies. Moreover, the formation mechanisms of Au/POT core/shell composites and POT hollow spheres were also discussed. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1244–1249, 2009

Key words: composites; conducting polymers; gold nanoparticles; hollow spheres; TEM

INTRODUCTION

Composites consisting of polymer matrix filled with nanosized particles are attracting a great deal of interest because of their importance in applications such as optical and electrical devices, catalysts, sensors, and so on.^{1–3} Moreover, they hold the long-term stability and will offer new routes to influencing the interactions that may take place between the matrix and the nanoparticle.^{4,5} The clever combination of different nanoscale materials can lead to the development of multifunctional nanomaterials.⁶ Recently, conducting polymer of polyaniline (PANI) has been widely studied because of their novel properties of high environmental stability, controllable electrical conductivity and interesting redox properties associated with chain nitrogen,^{7–9} and extensive applications ranging from batteries to light-emitting devices.¹⁰ Many inorganic nanoparticles, such as TiO₂,¹⁰ NiO,^{11,12} Fe₃O₄,¹³ V₂O₅,¹⁴ Ag,^{15–17} have been encapsulated in PANI. Among the various inorganic nanoparticles, Au nanoparticles are the most stable metal nanoparticles and exhibit many chemical and physical properties in different contents, such as catalysis, surface-enhanced Raman phenomena, and applications to optical devices.^{18,19} Composites of Au/PANI with different morphology have been

reported using different synthetic strategies. Zhu and coworkers²⁰ reported that Au/PANI composite nanotubes and nanofibers could be obtained by a self-assembly process in the presence of camphorsulfonic acid and hydrochloric acid. Kleinermanns and coworkers²¹ developed a micelle-assisted one-pot synthesis of water soluble Au/PANI composites particles with tetrahedron shape. Chen and coworkers²² have reported the preparation of high conductive Au/PANI nanocables. In most of the aforementioned routes, surfactants or functional acids are often used to assist the formation of Au/PANI core/shell structures. Moreover, Au/PANI composites hollow spheres²³ could be synthesized when PANI hollow spheres were introduced to Au colloid, and PANI nanofibers decorated with gold nanoparticles could be fabricated with γ radiolysis.¹⁶

Recently, we have reported that a series of hollow spheres of PANI derivatives, such as poly(*o*-toluidine) (POT), poly(*o*-methoxyaniline) and poly(*o*-phenylenediamine), can be synthesized through the chemical polymerization of monomers in aqueous solution using ammonium persulfate (APS) as the oxidant without the aid of surfactant or functional acid, where the monomer droplets were considered to act as template to the formation of hollow structures.^{24–26} In this article, we report the interesting finding that well-defined Au/POT core/shell composite spheres can be successfully prepared through the chemical polymerization of *o*-toluidine monomers in aqueous solution using HAuCl₄ instead of APS as the oxidant. By adjusting the concentration of HAuCl₄, Au/POT core/shell composite spheres and POT hollow spheres with holes in their surfaces

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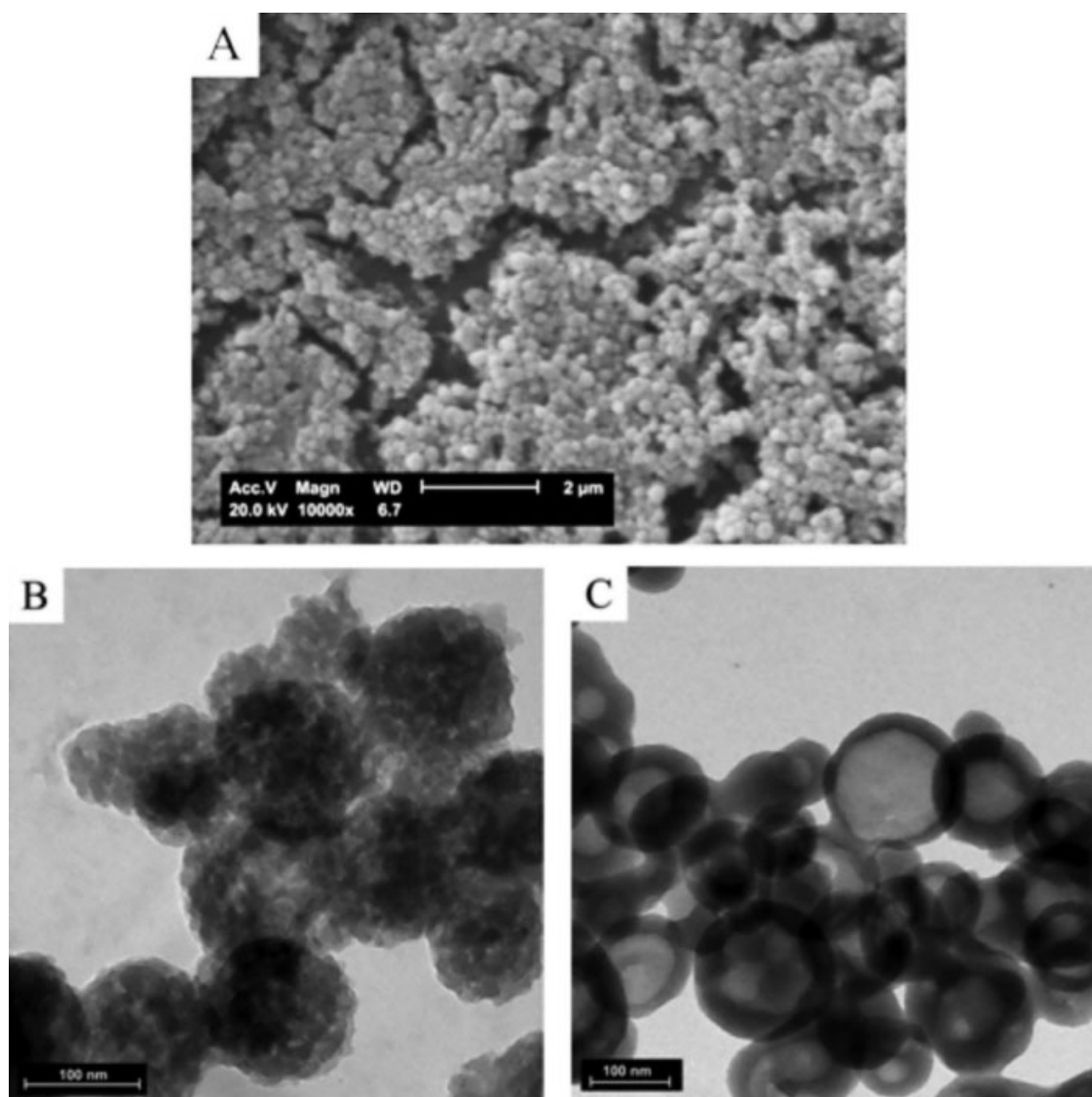


Figure 1 (A) SEM and (B) TEM images of Au/POT composites; (C) TEM image of POT hollow spheres when Au/POT composites (Fig. 1A,B) were dissolved with saturated I_2 solution to leach out the Au cores. Synthetic conditions: [*o*-toluidine] = 160 mM; [HAuCl₄] = 40 mM; 20°C.

can be formed. The proposed strategy possesses the advantage of simple synthetic procedures and also this is an environmentally friendly way to the fabrication of gold/conducting polymer composites as surfactants and functional organic acids are not used in the synthesis. The products were characterized by Fourier transform infrared (FTIR), UV-vis, and X-ray diffraction (XRD) spectroscopy. Moreover, the formation mechanisms of Au/POT core/shell composite spheres and POT hollow spheres were also discussed.

EXPERIMENTAL

Materials

o-Toluidine (Shanghai Chemical Co., Shanghai, China) was distilled under reduced pressure before

use. HAuCl₄·3H₂O (Shanghai Chemical Co.) and other reagents were used as received.

Synthesis of Au/POT core/shell composites

In a typical synthesis, *o*-toluidine (45 mg, 0.42 mmol) and quantitative amount of HAuCl₄·3H₂O were dissolved in 2 mL and 1 mL deionized water, respectively, with magnetic stirring at room temperature for 10 min. These two solutions were then mixed at room temperature (20°C). The resulting solution was stirred for another 0.5 min to ensure complete mixing and then the reaction was allowed to proceed without agitation for 12 h at 20°C. Finally, the precipitates were washed with deionized water and ethanol till the filtrate became colorless and then dried in vacuum at 60°C for 24 h.

Characterization

The morphologies of products were examined by a scanning electron microscopy (SEM, XL-30E Philip Co., Holland) and a transmission electron microscopy (TEM, Tecnai-12 Philip Apparatus Co., USA), respectively. The FTIR spectra of products were recorded in the range of 400–4000 cm^{-1} using FTIR spectroscopy (TENSO2 27, Bruker, Germany), with samples prepared in pellet form using spectroscopic grade KBr. The UV-vis spectra (UV-2501, Shimadzu Corp., Japan) of products dissolved in water was measured in the range between 250 and 850 nm. The XRD patterns were recorded on a German Bruker AXS D8 ADVANCE X-ray diffractometer.

RESULTS AND DISCUSSION

Morphology studies

When the oxidant of HAuCl_4 was added to the aqueous solution of *o*-toluidine monomer, dark green products were formed promptly. The typical SEM and TEM images of the products are shown in

Figure 1. As seen in Figure 1(A), the products are uniform spherical structures with an average diameter of 150 nm. The TEM image [Fig. 1(B)] shows that Au nanoparticles with an average diameter of 15 nm are well-dispersed in the POT matrix, and tens of Au nanoparticles are buried inside each POT sphere. As we know, Au can be easily oxidized into Au^{3+} ions in saturated I_2 solution.²² When the Au/POT core/shell composites are dissolved in saturated I_2 solution, uniform POT hollow spheres with shell thickness of about 30 nm can be obtained [Fig. 1(C)]. The results further confirm the existence of Au nanoparticles inside POT spheres.

Effect of oxidant concentration

The concentration of HAuCl_4 was found to have significant influence on the morphology of Au/POT core/shell composites. As compared with Figure 1, when the concentration of HAuCl_4 decreases to 10 mM, Au/POT core/shell composites with only one Au core of irregular shape were found as seen in Figure 2(A). The size of Au nanoparticles is about

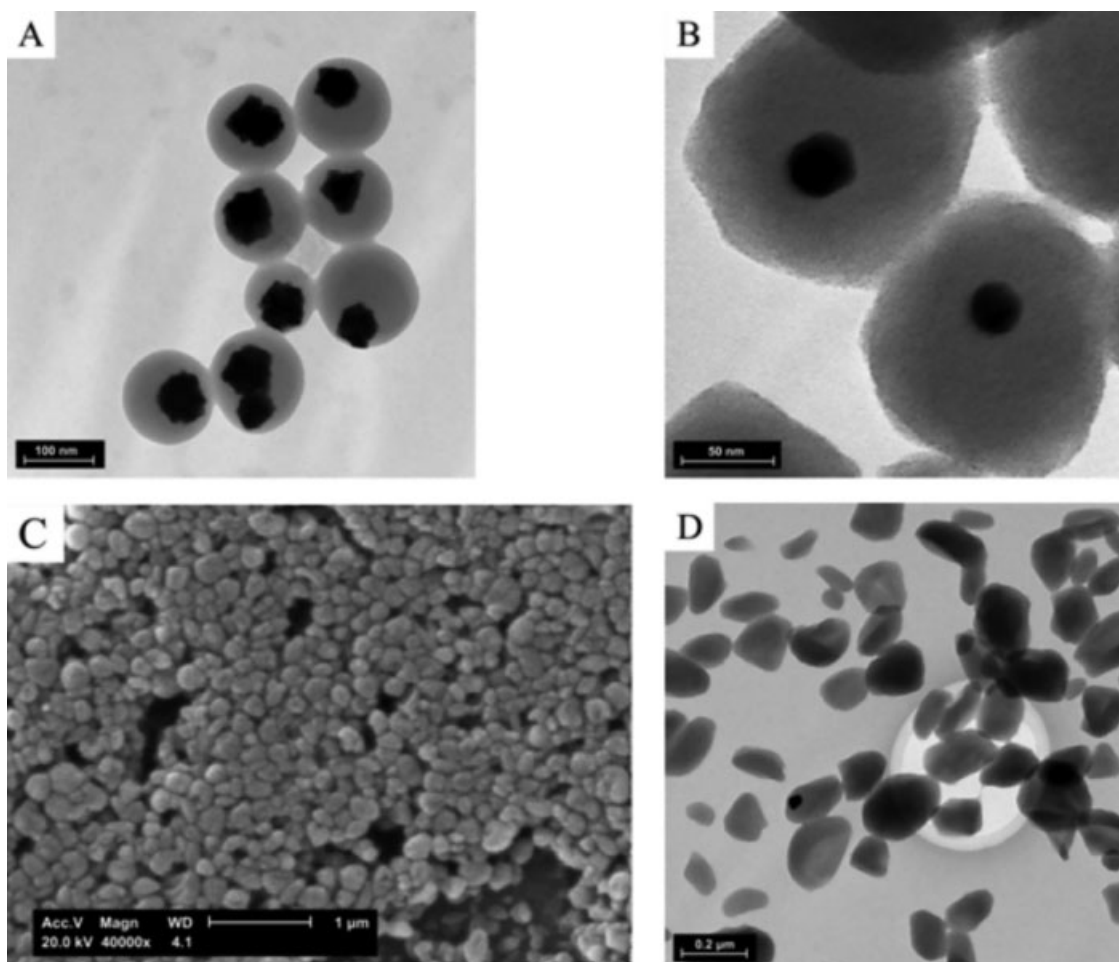


Figure 2 (A, B, D) TEM and (C) SEM images of Au/POT core/shell composites synthesized at different concentrations of HAuCl_4 (mM): (A) 10; (B) 4.0; (C, D) 2.0. Other synthetic conditions: [*o*-toluidine] = 160 mM; 20°C.

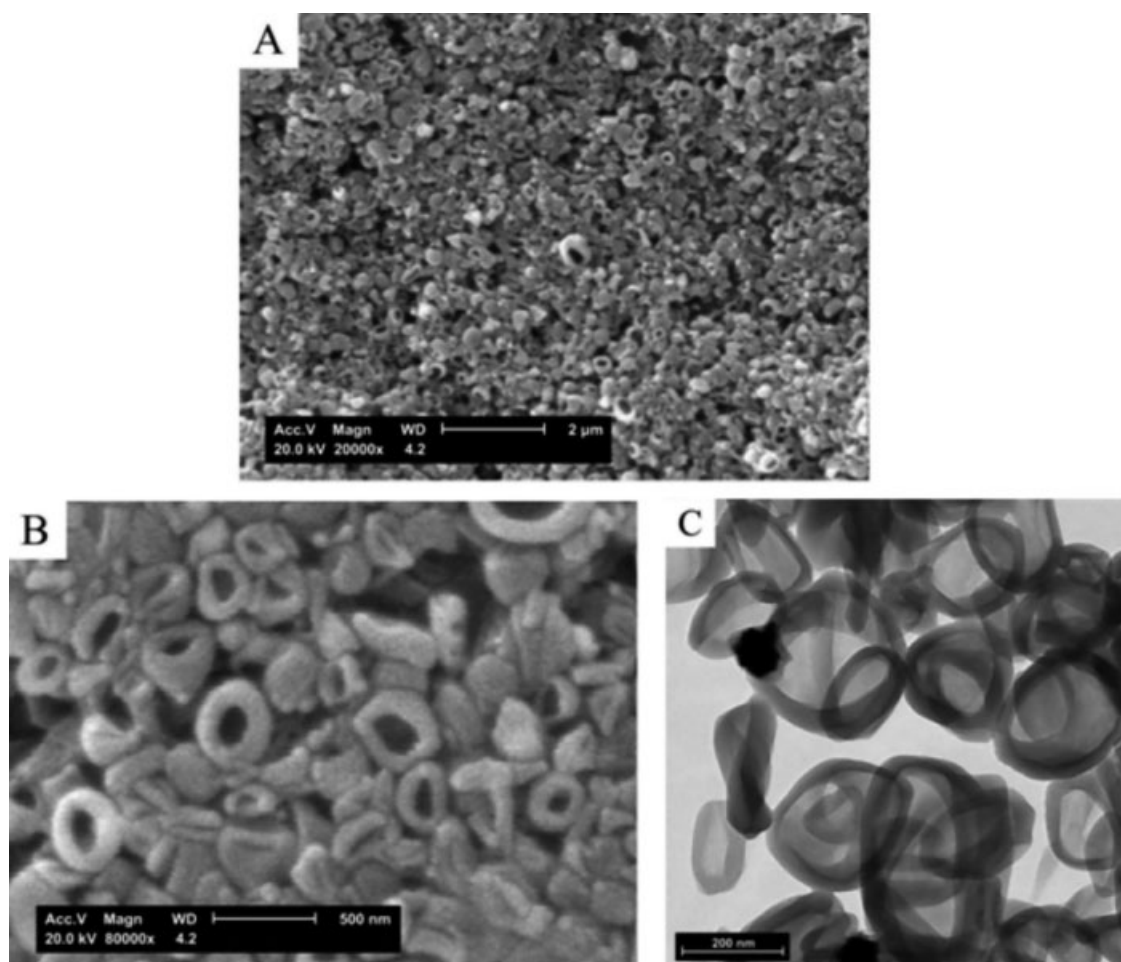


Figure 3 (A, B) SEM and (C) TEM images of POT hollow spheres with holes in their surfaces. Synthetic conditions: [*o*-toluidine] = 160 mM; [HAuCl₄] = 0.8 mM; 20°C.

70 nm. By further decreasing the concentration of HAuCl₄ to 4.0 mM, the size of Au core can be tuned to about 30 nm, and the morphology of Au core changes to spheres [Fig. 2(B)]. If the concentration of HAuCl₄ is maintained at 2.0 mM, some sunken POT particles are observed as shown in Figure 2(C). Figure 2(D) clearly reveals that some of the POT particles are hollow inside. Under this condition, only a small portion of POT particles are observed to have Au nanoparticles buried inside.

Interestingly, if the concentration of HAuCl₄ decreases further to 0.8 mM, well-defined POT hollow spheres with one hole in the each surface are found [Fig. 3(A)]. The magnified SEM image as given in Figure 3(B) shows the size of POT hollow sphere is about 300 nm and the size of hole is about 200 nm. Some wrinkles of the polymer shells are also found and no fracture fragments are observed as revealed in this figure, from which we can conclude that such polymer shells show excellent flexibility. The hollow structures are further confirmed by TEM image as shown in Figure 3(C), where the

shell thickness is estimated to be 50 nm. In addition, a small proportion of Au nanoparticles covered with POT are also discovered.

Formation mechanism

As we have reported,²⁴ because of the amphiphilic structure of *o*-toluidine monomer, droplets formed by monomers themselves will exist in the aqueous solution. Therefore, we speculate that the formation of Au/POT core/shell composite spheres and POT hollow spheres may be formed with the aid of monomer droplet template. The schematic illustration of the formation of Au/POT core/shell composite spheres and POT hollow spheres are given in Figure 4. When the oxidant of HAuCl₄ is added to monomer aqueous solution, gold nanoparticles and *o*-toluidine oligomers are simultaneously formed. The originally formed Au nanoparticles will locate in the inner part of monomer droplets because of their hydrophobic feature.^{10,11} The morphology of product is evidently related to the concentration of HAuCl₄.

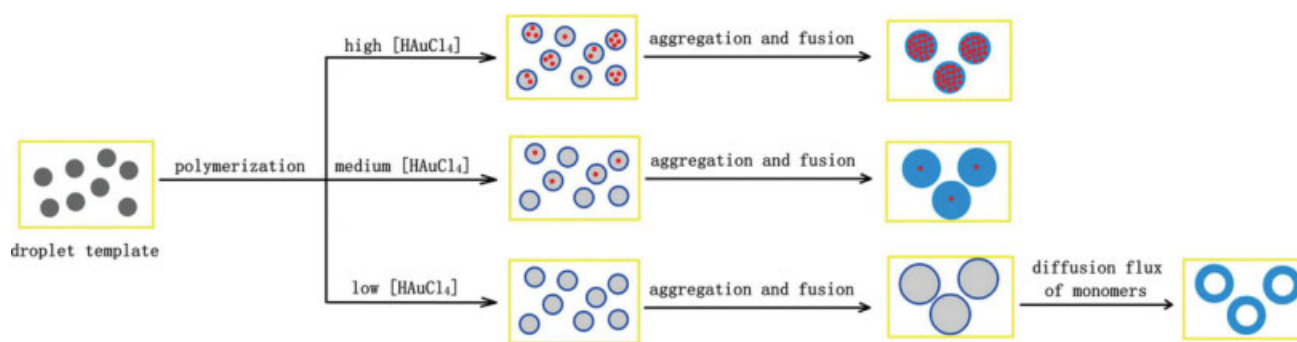


Figure 4 Schematic illustration of the formation of Au/POT core/shell composite spheres and POT hollow spheres. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

At high concentration of HAuCl_4 , a large amount of Au nanoparticles are formed, and the monomer droplets will have one or more Au nanoparticles. With the polymerization proceeding, the Au/oligomer core/shell droplets will aggregate and fuse together. At last, POT spheres filled with Au nanoparticles are formed. When the concentration of HAuCl_4 is relatively low, only a small portion of monomer droplets include Au nanoparticles because of the low concentration of Au nanoparticles. The aggregation and fusion processes are more likely happened between Au/oligomer core/shell droplets and pure monomer droplets, which will lead to the formation of Au/POT core/shell spheres with only one Au core in each POT sphere. If the concentration of HAuCl_4 is extremely low, the situation is just like using APS as the oxidant, as the originally formed Au nanoparticles can be ignored because of their very low concentration. Then the droplets formed by monomers themselves will act as template to the formation of hollow spheres and the diffusion flux of monomers during the polymerization process is re-

sponsible for the formation of hole in the surface of each hollow sphere.²⁴

Polymer characterization

The chemical structures of Au/POT core/shell composites were confirmed by XRD, FTIR and UV-vis spectroscopy. There are five main peaks in the XRD patterns (Fig. 5), which correspond to (111), (200), (220), (311), and (222) Bragg reflection of Au,²⁷ indicating the presence of Au particles in POT matrix. Moreover, a broad band centered at $2\theta = 15\text{--}30^\circ$ is also observed in each samples, which reveals that the polymer shells are all amorphous. Besides, the relative intensity of the characteristic peaks of gold decreases with decreasing oxidant concentration, confirming the decreasing amount of gold in polymer matrix, which is consistent with the results of TEM observations.

In the FTIR spectrum (Fig. 6), the characteristic peaks of POT,^{24,28–30} such as the N-H stretching vibrations in the range of $3200\text{--}3500\text{ cm}^{-1}$, C-N stretching vibration of benzenoid and quinoid rings

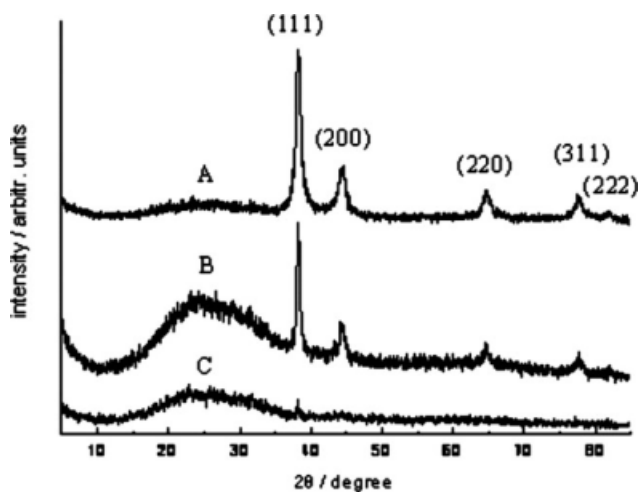


Figure 5 XRD patterns of Au/POT composites synthesized at different concentrations of HAuCl_4 (mM): (A) 40; (B) 4.0; (C, D) 0.8.

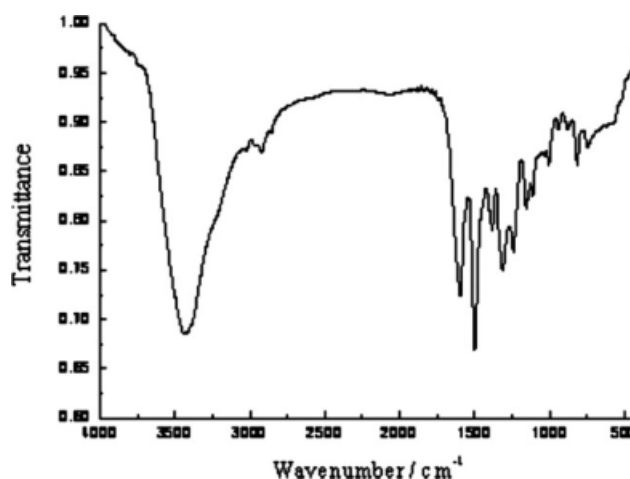


Figure 6 FTIR spectrum of Au/POT core/shell composite spheres.

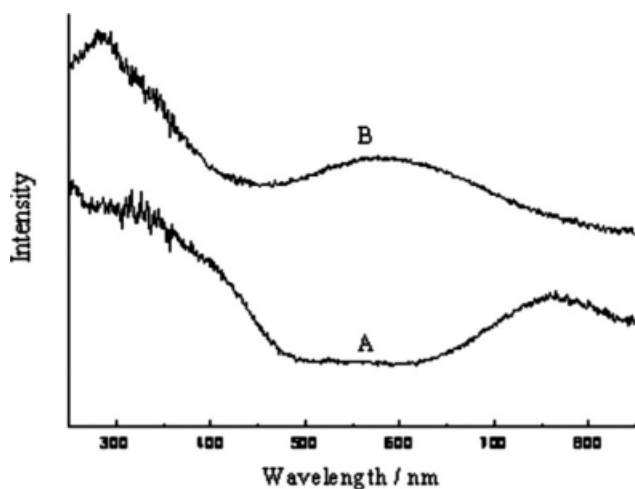


Figure 7 Uv-vis spectra of (A) doped and (B) dedoped Au/POT core/shell composite spheres.

centering at 1597 cm^{-1} and 1498 cm^{-1} are observed. Moreover, the band at 878 cm^{-1} ascribed to the methyl group attached to the phenyl ring is also observed. For Au/POT core/shell spheres and POT hollow spheres as mentioned above, the FTIR spectra are almost identical to each other, which reveal that the molecular structures of POT in each sample are the same.

As the doping acid is not used in our reaction system, then the doping/dedoping experiments were conducted to see whether the Au/POT composites can still be reversibly doped and dedoped. The corresponding UV-vis spectra are shown in Figure 7. After doping with 1.0M HCl(aq) , the bands at 300–400 and 765 nm are observed, indicating the emeraldine salt form of POT [Fig. 7(A)]. When dedoping with $0.1\text{M NH}_4\text{OH(aq)}$, the Uv-vis spectrum of Au/POT composites shows only two peaks at 306 nm and 590 nm [Fig. 7(B)], which are assigned to the $\pi\text{-}\pi^*$ benzenoid transition and the benzenoid to quinoid excitotic transition, respectively,³¹ indicating the emeraldine base form of POT. The results reveal that the polymer shells can be reversibly controlled between the conducting and insulating forms.

CONCLUSIONS

In conclusion, Au/POT core/shell composite spheres and POT hollow spheres with holes in their surfaces have been successfully synthesized through chemical polymerization of *o*-toluidine monomers in aqueous solution using HAuCl_4 as the oxidant. With the decreasing concentration of HAuCl_4 , the number of Au nanoparticles inside each POT spheres decreases from tens to one, and extremely low concentration of HAuCl_4 will lead to the formation of POT hollow

spheres. The droplets formed by the monomers themselves are proposed to act as template to the formation of Au/POT core/shell composite spheres and POT hollow spheres. Moreover, this simple chemical route may also be applied to synthesize other Au/PANI derivative composites, such as Au/poly(*o*-methoxyaniline).

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