Introduction

The organic/inorganic nanocomposites with different combinations of the two components have attracted significant academic and technological attention because they have interesting physical properties and potential applications. The incorporation of metallic or semiconducting nanoparticles in conducting polymers, such as polypyrrole and polyaniline, is of interest because of the strong electronic interaction between the nanoparticles and polymer matrixes. The ability to control the shape and size of nanocomposites is an important factor for defining their properties, such as the electronic band gap, conductivity, and light-emission efficiency. Nanocomposite hollow spheres have broad applications in catalysis, delivery and controlled release, optoelectronics, and microcavity resonance. There has been increasing interest in the fabrication of composite hollow spheres with enhanced optical and electrical properties, which remains scientifically challenging.

Polyaniline (PANI) is one of the most important conducting polymers because of its high conductivity, ease of preparation, good environmental stability, and large variety of applications such as electrochromic devices, secondary batteries, catalysis, and electrostatic discharge protection. PANI is unique among polymers because of its high conductivity, ease of preparation, and electrostatic discharge protection. Polyaniline (PANI)/Au composite hollow spheres were successfully synthesized using polystyrene/sulfonated polystyrene core/shell gel particle templates. The PANI shell thickness and the number of Au nanoparticles decorating the PANI could be controlled effectively by adjusting the experimental conditions. The morphology, composition, and optical properties of the resulting products were characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, thermogravimetric analysis, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, and ultraviolet–visible absorption spectra. It was found that the electrical conductivity of the PANI/Au composite hollow spheres was more than 3 times higher than that of the pure PANI hollow spheres. Furthermore, PANI/Au composites were immobilized on the surface of a glassy carbon electrode (GCE) and applied to construct a sensor. The obtained PANI/Au-modified GCEs showed one pair of redox peaks and high catalytic activity for the oxidation of dopamine. The possible formation mechanism of the PANI/Au composite hollow spheres was also discussed.

Polyaniline/Au Composite Hollow Spheres: Synthesis, Characterization, and Application to the Detection of Dopamine

Xiaomiao Feng, Changjie Mao, Gang Yang, Wenhua Hou,* and Jun-Jie Zhu*

Key Laboratory of Mesoscopic Chemistry and Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

Received December 15, 2005. In Final Form: February 16, 2006

Polyaniline (PANI)/Au composite hollow spheres were successfully synthesized using polystyrene/sulfonated polystyrene core/shell gel particle templates. The PANI shell thickness and the number of Au nanoparticles decorating the PANI could be controlled effectively by adjusting the experimental conditions. The morphology, composition, and optical properties of the resulting products were characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, thermogravimetric analysis, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, and ultraviolet–visible absorption spectra. It was found that the electrical conductivity of the PANI/Au composite hollow spheres was more than 3 times higher than that of the pure PANI hollow spheres. Furthermore, PANI/Au composites were immobilized on the surface of a glassy carbon electrode (GCE) and applied to construct a sensor. The obtained PANI/Au-modified GCEs showed one pair of redox peaks and high catalytic activity for the oxidation of dopamine. The possible formation mechanism of the PANI/Au composite hollow spheres was also discussed.

* Corresponding author. E-mail: whou@nju.edu.cn; jjzhu@nju.edu.cn.

hollow spheres were immobilized on the surface of a glassy carbon electrode, and it was found that the PANI/Au-modified electrode showed enhanced bioelectrocatalytic activity for the oxidation of dopamine compared with that of the pure PANI-modified electrode. The electrical conductivity of PANI/Au hollow spheres was more than 3 times higher than that of the pure PANI hollow spheres. The morphology, optical properties, and composition of the resulting composites were characterized by SEM, TEM, FTIR, UV–vis, XRD, TGA, and XPS. The possible formation mechanism of the composite hollow spheres was also discussed.

**Experimental Section**

**Materials.** Aniline, styrene, sulfuric acid (H₂SO₄), potassium persulfate (K₂SO₄, KPS), ammonium persulfate ((NH₄)₂SO₄, APS), tetrahydrofuran (THF), trisodium citrate, and HAuCl₄ were purchased from the Shanghai Chemical Reagent Company. Aniline and styrene were distilled under reduced pressure, and other reagents were used as received without further treatment.

**Preparation of Polystyrene Particles.** Monodispersed polystyrene (PS) particles (340 nm in diameter) were prepared according to the following procedure. Styrene monomer (10 g) was added to 140 g of distilled water under stirring for 10 min at 70 °C in a nitrogen atmosphere. An aqueous solution of initiator (10 g containing 0.23 g of potassium persulfate) was added, and the reaction was held for 24 h.²² Finally, the emulsion was naturally cooled to ambient temperature, and the monodispersed PS colloid was obtained. The diameter of PS colloid particles could be controlled by changing the experimental conditions.

**Preparation of PS/Sulfonated PS Core/Shell Gel Particles.** The above PS colloid (10 mL with a solid content of 0.3 g/mL) was centrifuged (9000 rpm, 10 min) and washed with distilled water. The wet PS particles were dispersed in 30 mL of concentrated sulfuric acid. The sulfonation reaction was allowed to proceed at place near 40 °C for 4 h. The product was centrifuged and washed with distilled water. Wet PS/sulfonated PS core/shell gel particles were then obtained.

**Preparation of PANI Hollow Spheres.** The above wet core/shell gel particles were directly dispersed in 20 mL of water, and 1 or 3 ml of aniline monomer was added to the mixture under stirring. Stirring was continued for 10 h. An aqueous solution of APS (5 mL, 1:1 molar ratio of APS to aniline) was added, and the reaction was allowed to proceed for 12 h. The reaction solution was centrifuged, and the precipitate was washed with distilled water and ethanol several times. The final product was dried in vacuum at 40 °C for 24 h. The PANI-coated PS core/shell particles were then obtained. The PANI hollow spheres were prepared by dissolving PS cores from the PANI-coated PS particles in THF.

**Preparation of PANI/Au Hollow Spheres.** The Au colloid was prepared according to the reported method by boiling HAuCl₄ aqueous solution with trisodium citrate.²³ The average diameter of the prepared Au nanoparticles (NPs) is about 30 nm. PANI hollow spheres were added to the Au colloid at a concentration of 1.0 mg/mL under stirring. The reaction was allowed to proceed for 12 h, and the resultant product was centrifuged and dried. Au NPs could be adsorbed on the surface of PANI, leading to the formation of PANI/Au composite hollow spheres. The amount of Au NPs adsorbed on the PANI surface could be controlled by adjusting the concentration of PANI in the Au colloid.

**Preparation of PANI/Au and PANI-Modified Glassy Carbon Electrodes.** The glassy carbon electrodes (GCE, 3 mm in diameter) were polished with 1.0, 0.5, and 0.05 μm alumina slurry followed by rinsing with doubly distilled water and drying at room temperature. PANI/Au and PANI hollow spheres were dispersed in distilled water to form a 1.0 mg/mL solution and ultrasonically treated for 30 min. The colloidal solution (5 μL) was dropped onto the pretreated GCE surface and allowed to dry under ambient conditions.

**Characterization.** The morphologies of PANI and PANI/Au hollow spheres were observed by scanning electron microscopy (SEM, LEOM300VP) and transmission electron microscopy (TEM, JEOL JEM-200CX). X-ray diffraction patterns were taken on a Philips X’Pert X-ray diffractometer with a Cu Kα X-ray source. Ultraviolet–visible (UV–vis) absorption spectra of PANI/Au dispersed in distilled water through ultrasonic irradiation were recorded on a UV-2401PC spectrometer. All Fourier transform infrared (FTIR) spectroscopic measurements were performed on a Bruker model VECTOR22 Fourier transform spectrometer using KBr pressed disks. X-ray photoelectron spectroscopic (XPS) analysis was carried out on a ESCALAB MK II X-ray photoelectron spectrometer. The amount of Au within the composite was determined by thermogravimetric analysis (TGA) on a Shimadzu TGA-50 instrument from room temperature to 800 °C at a heating rate of 10 °C/min in an air atmosphere. The conductivity was measured by a four-probe method on a WR-2B digital multimeter at room temperature using the compressed pellets of powders. For each value reported, at least three measurements were averaged. Electrochemical experiments were conducted with an Autolab PGSTAT 30 system (Ecochemie, The Netherlands). All electrochemical experiments were performed in a cell containing 20.0 mL of phosphate buffer solution (PBS, 0.1 M) at room temperature, using a coated platinum wire as the auxiliary electrode, a saturated calomel electrode (SCE) as the reference electrode, and the PANI/Au- (or PANI-) modified electrode as the working electrode.

**Results and Discussion**

PANI/Au composite hollow spheres were successfully synthesized by using the PS/sulfonated PS core/shell gel particles as the template. Figure 1 shows the typical SEM and TEM images of PANI/Au and PANI hollow spheres. The obtained PANI hollow spheres are uniform in size and morphology, with an average shell thickness of 30 nm. The outside particles in Figure 1B and the corresponding dark spots in Figure 1D are Au NPs. It can be seen from Figure 1B and 1D that Au NPs are successfully modified onto the PANI surface. The possible mechanism for the formation of PANI and PANI/Au hollow spheres is shown in Scheme 1. The PS/sulfonated PS core/shell gel particles were prepared by an inward sulfonation from the surface of polystyrene particles. The sulfonation of polystyrene is very important for the synthesis of PANI/Au hollow spheres. The shell thickness of gel particles is determined by the sulfonation time and temperature.²⁴ In this experiment, polystyrene particles were sulfonated with concentrated sulfuric acid at 40°C for 4 h in order to keep the shell thickness of sulfonated polystyrene gel particles invariable. Aniline can be adsorbed in the gel shell and further in-situ polymerized along the gel shell when the oxidant is added, resulting in the formation of PANI/PS capsules. The PANI hollow spheres were produced by exposing the PANI/PS particles to THF. It can be seen from Figure 1 that the PS core could be successfully removed. The shell thickness of PANI could be controlled by changing the amount of aniline monomer. As shown in Figure 2, when the amount of aniline monomer is tripled, the shell thickness of PANI and PANI/Au composite hollow spheres is increased from ca. 30 to ca. 100 nm. When the polycationic PANI hollow spheres were introduced into the Au colloid, Au-decorated PANI composite hollow spheres were formed by an electrostatic effect because the surface of citrate-stabilized Au NPs was electronegative. During the formation of PANI/Au hollow spheres, the number of Au NPs adsorbed onto

---

the surface of PANI hollow spheres would be increased if the concentration of PANI hollow spheres in Au colloid decreased (Figure 3).

The X-ray diffraction patterns of PANI and PANI/Au hollow spheres with different contents of Au NPs are shown in Figure 4. In the case of PANI, only a broad band appears at a 2\(\theta\) value of 25°, which is ascribed to the periodicity parallel to the polymer chains of PANI.\(^{25}\) In Figure 4b and c, besides the PANI peak, three additional peaks at 38, 43, and 65° representing Bragg reflections from (111), (200), and (220) planes of Au are observed, showing the existence of Au NPs in the PANI/Au composite. The relative diffraction peak intensity for Au NPs in Figure 4c is increased compared with that in Figure 4b. When the concentration of PANI hollow spheres in the Au colloid is decreased, the content of Au NPs in the composite would be increased, leading to an increase in the relative peak intensity.

The composition of PANI/Au composite hollow spheres was determined by TGA (Supporting Information). Because Au does not qualify as a loss under the experimental conditions, the residual weight percentage (wt %) can be referenced to the content of Au in the composite. All TGA curves of PANI and PANI/Au with different contents of Au show a two-step weight loss. The weight loss in the first step is attributed to the loss of residual water. The second step that is started around 250 °C corresponds to the degradation of polymer and the departure of acid dopant.\(^{26}\) The total weight loss of intrinsic PANI is 100% under the experimental conditions. When the concentration of PANI in the Au colloid is 0.5 mg/mL, the residual weight percentage of PANI/Au is about 10.3%. As the concentration of PANI in Au colloid is doubled, the residual weight percentage of PANI/Au is about 5.7%.

Proof of the sample’s nature and removal of the PS core were provided by FTIR spectra shown in Figure 5. In the spectra of PANI and PANI/Au hollow spheres, the characteristic peaks at 1583 and 1494 cm\(^{-1}\) correspond to the C\(_{\text{d}}\)C stretching of quinoid and benzenoid rings,\(^{27}\) peaks at 1303 and 1243 cm\(^{-1}\) are related to the C–N and C\(_{\text{d}}\)N stretching modes,\(^{28}\) the peak at 1150 cm\(^{-1}\) is assigned to the in-plane bending of C–H,\(^{29}\) and the peak at 826 cm\(^{-1}\) is attributable to the out-of-plane bending of C–H.\(^{30}\) The band at 1042 cm\(^{-1}\), which is ascribed to the absorption of the –SO\(_3\)H group, is also observed in Figure 5b and c, confirming that PANI is doped with –SO\(_3\)H directly.\(^{31}\) In the spectrum of PANI/PS (Figure 5a), the typical PS absorption bands at 1583, 1494, 1452, 757, and 698 cm\(^{-1}\) are clearly seen.\(^{32}\) The typical absorption peaks of PANI are also displayed. Two peaks (1452 and 757 cm\(^{-1}\)) of PS that do not overlap with the peaks of PANI have completely disappeared and the band at 698 cm\(^{-1}\) becomes very weak in the spectra of PANI and PANI/Au.

hollow spheres. It is evident that the PS core is successfully removed after the above-described extraction.

UV–vis absorption spectra of PANI and PANI/Au are shown in Figure 6. The insets show the UV–vis spectra of the as-prepared colloidal gold solution (A) and the gold solution after reaction with PANI and centrifugation (B). The characteristic peak of citrate-stabilized colloidal Au NPs appears at 510 nm. It is caused by the surface plasmon resonance. A great loss in the intensity of the surface plasmon resonance at 510 nm was
Dopamine (DA) is an important neurotransmitter in mammalian central nervous systems, and the loss of DA-containing neurons may lead to serious diseases including Parkinson’s disease. The detection of DA has therefore been a subject of considerable interest. It is well known that PANI bears good electrochemical behavior and has been applied to the field of chemically modified electrodes. In this work, PANI/Au composite hollow spheres were immobilized onto the surface of a glassy carbon electrode, which was taken as an example of developing a possible application as a dopamine biosensor. The GCE was previously tested in pH 3 PBS buffer before the PANI/Au composites were drop coated on it. It presented no redox process in the potential range studied. The working electrode coated with PANI/Au (PANI) was immersed in the electrolyte solution for 30 min prior to the measurement to ensure the diffusion of the solution to the interlayer space and permit better ionic exchange.

The effect of the potential scan rate (v) on the peak current for the PANI- and PANI/Au-modified electrodes was studied in the range of 20–500 mV/s (Supporting Information). The anodic peak current for PANI is increased linearly with the square root of the scan rate (v)^1/2, indicating that the peak current is diffusion-controlled. A broad redox peak is found for each sample with a redox potential of around 280 mV. This redox peak is the overlap of two redox processes (i.e., leucoemeraldine to emeraldine salt and emeraldine salt to the permigraniline state). This phenomenon is normally found for the PANI system under acidic conditions, as confirmed by the redox behavior of the PANI/Au measured in different pH buffer solutions (Supporting Information). PANI shows two separate redox peaks in pH 1 PBS buffer. The first oxidation wave around $E_{GCE} = 0.13$ V is assigned to the transition of leucoemeraldine to emeraldine salt, and the second oxidation wave around $E_{SCE} = 0.59$ V is due to the transition from emeraldine salt to the permigraniline state. However, these two pairs of redox peaks move closer as the pH of the solution is increased to 2, and finally they merge to show only one broad redox peak when the pH is 3. This electrochemical behavior of PANI/Au is also similar to that of PANI/carbon nanotube multilayer films prepared via the layer-by-layer assembly method.

In the potential range of 0.8 to −0.4 V, the cyclic voltammograms of PANI/Au- and PANI-modified electrodes in PBS and after the addition of DA are shown in Figure 8A and B, respectively. The oxidation peak in the presence of DA appears at 565 and 682 mV for the PANI/Au- and PANI-modified GCEs, respectively, and is attributed to the oxidation of DA to dopaminequinone. The anodic current of the PANI-modified GCE is observed at a more positive potential compared with that of PANI/Au-modified GCE, implying that the composites have a strong catalytic effect on the oxidation of DA. It can also be seen that the oxidation peak current is increased with the gradual addition of DA, showing the catalytic property of the modified electrode in the oxidation of DA. Furthermore, the electrocatalytic anodic current in the PANI/Au system is about 2.8-fold higher than that in the PANI system. For example, at a DA concentration of 10 mM, the PANI/Au system generates an anodic current of 54.1 μA, whereas the PANI system yields a current of 19.4 μA. For comparison, the oxidation of DA in the Au NPs-modified GCE was also studied. Figure 8C shows that the Au NPs-modified composite hollow spheres with a shell thickness of 30 nm is 8.74 S/cm; it is 3.88 times higher than that of pure PANI. When the content of Au NPs is increased from 5.7 to 10.3%, the conductivity of the composite is improved from 8.74 × 10⁻³ to 9.83 × 10⁻³ S/cm. Because gold is a conductor, it is beneficial for improving the conductivity of PANI when PANI is combined with gold. Therefore, with increasing gold content, the conductivity of PANI/Au composites would be enhanced.

References:

GCE has no electrochemical response in the absence of DA. A pair of redox peaks appear in the presence of DA, and the catalytic peak current intensity is much lower than that of PANI/Au-modified GCE at the same concentration of DA, implying that Au NPs can act as a catalyst for the oxidation of DA. To confirm the effect of Au NPs in the PANI/Au composite on the electrocatalytic oxidation of DA, the CVs of PANI/Au with different sizes and numbers of Au NPs were compared. It can be found that the catalytic peak current increases with the number of Au NPs. When the size of Au NPs is less than 30 nm, the catalytic current is increased with the size of Au NPs. However, it decreases drastically when the size of Au NPs is larger than 30 nm. The catalytic effect of Au NPs on the oxidation of DA can lead to the effective electrocatalytic oxidation of DA by PANI/Au-modified GCE. At the same time, the improved electrocatalytic oxidation of DA in the PANI/Au-modified electrode may also be due to the fact that the charge transport is enhanced through the PANI/Au composite system, which facilitates the electrical contacting of the redox DA with the electrode. The enhanced electron transfer in the PANI/Au system is attributed to the charge hopping through the metallic conductor Au NPs that mediate the effective charge migration through the polymer. It is well known that Au is one important type of conductor. Although Au NPs do not make a continuous electron path, the incorporated Au NPs generate many active sites for charge transfer through the interface inside the electrode by making good contact with the PANI matrix. The effective transport of the electrons to the electrode in the PANI/Au matrix leads to the efficient electrocatalytic oxidation of DA.

Additional experiments were done to test the reproducibility and stability. It was found that the catalytic peak current retained 99 and 98% of its initial response for PANI/Au- and PANI-modified GCEs, respectively, after 100 cycles at a DA concentration of 2 mM (scan rate 100 mV/s). In addition, no obvious change was found after the modified electrodes were immersed in PBS and stored in the refrigerator at 4 °C for 20 h. The relative standard deviations of the catalytic peak current (RSDCPC) in six successive determinations at a DA concentration of 2 mM were 0.4 and 0.5%, respectively, for PANI/Au- and PANI-modified GCEs. Furthermore, five PANI/Au-modified GCEs and five PANI-modified GCEs were fabricated independently. The corresponding RSDCPC values determined at a DA concentration of 2 mM were 3.4 and 10.2%, respectively.

**Conclusions**

We have synthesized PANI/Au composite hollow spheres with controllable shell thickness. By incorporating Au NPs onto the PANI surface, the electrical conductivity of the composites was improved compared with that of the pure PANI hollow spheres. Furthermore, this kind of material could be applied to the chemically modified electrode. The PANI/Au-modified electrode showed enhanced electrocatalytic activity for the oxidation of DA compared with that of the pure PANI-modified electrode. This method could be extended to prepare other composite hollow spheres with different compositions.

**Acknowledgment.** This work is supported by the National Natural Science Foundation of China (grant nos. 20325516 and 20575026) and the Modern Analysis Center of Nanjing University.

**Supporting Information Available:** TGA curves of PANI and PANI/Au hollow spheres. Cyclic voltammograms of PANI- and PANI/Au-modified GCEs. This material is available free of charge via the Internet at http://pubs.acs.org.

LA053403R