Self-assembly and Characterization of Polypyrrole and Polyallylamine Multilayer Films and Hollow Shells

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Conductive multilayer films have been fabricated from the alternating adsorption of the charged polymers, polypyrrole (PPy) and polyallylamine hydrochloride (PAH), on planar substrates as well as onto the surfaces of melamine formaldehyde (MF) microparticles based on the sequenced electrostatic layer-by-layer assembly technique. Hollow microcapsules are achieved after the removal of MF cores by dissolution in acid solution. The structure and conductive properties of the multilayer films and the hollow shells were characterized by UV−visible spectroscopy, phase contrast optical microscopy, atomic force microscopy, transmission electron microscopy, and scanning electron microscopy, respectively. The conductivity of all the composite films calculated from the measured resistivity is about 0.007 S/cm, which is comparable to other conductive polyelectrolyte films. The measurement of cyclic voltammetry showed that the PPy/PAH planar multilayer films, PPy/PAH-modified colloid particles, and hollow shells maintained their oxidative stability and electrochemical properties.

Introduction

Polypyrrole (Ppy) is an inherently conductive polymer due to interchain hopping of electrons, which has been studied extensively during the past decades.[1] However, like many other conducting polymers, PPy always exists in an intractable state and suffers from poor processability, mainly because of its rigid, highly conjugated backbone.[2] As an insoluble material in most solvents, it is always to be prepared in functional materials such as thin films by standard electrochemical techniques.[3] The surface charge characteristics of PPy can be modified by changing the dopant anion, which is incorporated into the material during synthesis.[4]

Compared to other conducting polymers, polypyrrole has a much higher chemical stability and has no toxicity.[5,6] These advantages make it have more potential applications in the fields of physics, chemistry, and especially medicine.[7,8] Furthermore, with the inherentlyconductive property, materials of PPy have been exploited to locally enhance nerve regeneration, which shows significant advantages over other systems such as electromagnetic fields, external electrodes, and piezoelectric materials.[9]

Polypyrrole can be water-soluble and negatively charged when doped with organic acid (Aldrich product), which still retains the conductivity. The water-soluble PPy is tractable and suitable for the layer-by-layer self-assembly technique.[10]

The layer-by-layer (LbL) technique based on electrostatic or other molecular forces creates an advantageous approach to construct different types of assembled materials [11−13] Since the technique was first developed by Decher and others, it has been extensively applied in preparing various materails.[14−17] It is also a typical approach to modify colloidal particles at a micro-nanoscale.[18] Layer-by-layer assembly of conductive polyaniline (PANI)/PSS thin planar films and PANI/PSS

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microcapsules have been reported by Rubner and co-workers[19,] and Caruso and co-workers.[20]

Armes and co-workers fabricated PPy-coated PMMA and PBMA particles by in situ chemical polymerization of pyrrole monomers adsorbed onto charged colloid particle surfaces.[21]

In the present work we introduced an approach toward fabricating conducting capsules by alternating layer-by-layer deposition of PPy and polyallylamine hydrochloride (PAH) on MF particles and following the removal of the cores. As described previously,[16,17,20] this technique provides the ability to incorporate various composites into the assembled multilayer film, which may modify the physicochemical properties of the assembled capsules.

Here, we applied the self-assembly technique with soluble PPy solution to construct conductive planar multilayer films and conductive film modified microparticles. Linear polyelectrolyte PAH was used as a counterion of PPy as well as a co-dopant. It is found that the PPy/PAH film assembly is convenient and stable without the requirement of adjusting pH values to offer higher charge density.[22,23]

The characteristics of the PPy/PAH planar multilayer films, as well as modified colloid particles and PPy/PAH hollow shells, were measured by UV, optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The electric conductivity and electrochemical properties of these materials were also detected by a digital multimeter and an impedance analyzer (CV).

Experimental Section

Materials. The water-soluble polypyrrole (PPy) (5 wt % in water) doped with organic acid and poly(allylamine hydrochloride) (PAH) were purchased from Aldrich and used without further purification. The positively charged MF particles (diameter 5.7 μm) were acquired from Microparticles GmbH (Berlin, Germany) as a 10% aqueous solution. Water used in all the experiments was purified through a Millipore Milli-Q Academic system with a resistivity of 18.2 MΩ cm.

Self-assembly of PPy/PAH Multilayer onto Quartz Plates and Positively Charged MF Spheres. The PPy and PAH solution were prepared by dissolving the reagents in 0.5 M NaCl aqueous solution at a concentration of 1 mg/mL. Both polyelectrolyte solutions were neutral without adjusting their pH values. The hydrophilic quartz plate was dipped in PAH solution for 15 min for sufficient electrostatic absorption and subsequently rinsed with deioned water to remove the excess PAH.[24] Then the plates coated with positively charged PAH were deposited into PPy solution for the same time. Alternately dipping the PPy/PAH-coated quartz plate, we obtained the multilayers with a required layer number.

The positively charged MF microspheres with uniform size were first coated with one layer of negatively charged PPy by being added in 1 mg/mL PPy solution in centrifuge tubes, allowing 15 min for abundant adsorption, coupled with stirring frequently to block them from congregation and sedimentation. Then excess PPy was removed by three repeated centrifugation (10000 rpm, 5 min)/water wash/redispersion cycles. The deposition of PAH layer was carried out using the same method. By repeated consecutive assembly of PPy and PAH, we obtained the desired number of PPy/PAH multilayers on the MF particle surface.

Formation of PPy Hollow Capsules. The $(PPy/PAH)_8$ film coated MF particles were dissolved by using 0.1 M HCl solution under the conditions of ultrasonic stirring for 1 h and heating to about 80 °C. Then the samples were washed three times by centrifugation (7000−10000 rpm, 5 min) and redispersed into pure water.

Instrumental Characterizations. The UV spectra of PPy/PAH multilayer films on quartz plates as a function of different layers were recorded by a UV−visible spectrophotometer (HITACHI model 3310). Atomic force microscopy (Di, USA) images were recorded by using a tapping mode. The optical microscopy (Olympus IX 70) was used for measuring the thickness of planar PPY/PAH films deposited and afterward lacerated on a quartz plate. The thickness of each PPy/PAH film with different layers was obtained by a surface profiler (Ambios XP-2). The phase contrast optical microscopy images of PPy/PAH-coated MF particles and hollow capsules were determined by dropping the coated particles solution and the capsules dispersion on the quartz plates, respectively. Both SEM (JSM-6301F) and TEM (Philips Tecnai 20) techniques were applied to further characterize the morphology of the PPy/PAH-coated particles and hollow capsules. Samples for SEM measurement (on silicon wafers) were sputtered with a 5 nm thick Au coating. TEM samples were prepared by casting a solution containing PPy-coated MF particles or hollow spheres on a carbon-coated copper grid and air-dried in a desiccator.

The cyclic voltammetery measurements were performed by an impedance analyzer (BAS-Zahner IM6e). A standard three-electrode configuration was used, where samples on an ITO glass plate acted as a working electrode, platinum wire as a counter electrode, and Ag/AgCl as a reference electrode. The medium is 1 M NaCl aqueous solution.

Electric Conductivity Measurements. The quartz plates deposited with PPy/PAH multilayers as a function of different numbers were Au-gilded through an interdigitated mask as electrodes with fixed sizes and equal separation from one tract to another. Then the electric resistance (R) was measured using a digital multimeter (solartron, 7081 precision), and the conductivity (σ) was calculated from the correlative equation.

Results and Discussion

PPy/PAH Multilayers on Planar Substrates. UV−visible spectra of planar composite films on quartz were carried out to study the deposition ability of PPy and PAH. Figure 1 shows the spectra of PPy/PAH as a function of the number of bilayers from 1 to 8. The adsorption peak at 237 nm can be attributed to a $\pi-\pi^*$ transition centered on the pyrrole ring (interband transition). UV absorbance increases gradually with the increase of the number of PPy/PAH bilayers, indicating the successive deposition during the LbL assembly process. In the UV spectra, the adsorption increases steadily from the third bilayer, whereas the adsorption intensity in the first and second bilayers is weaker than

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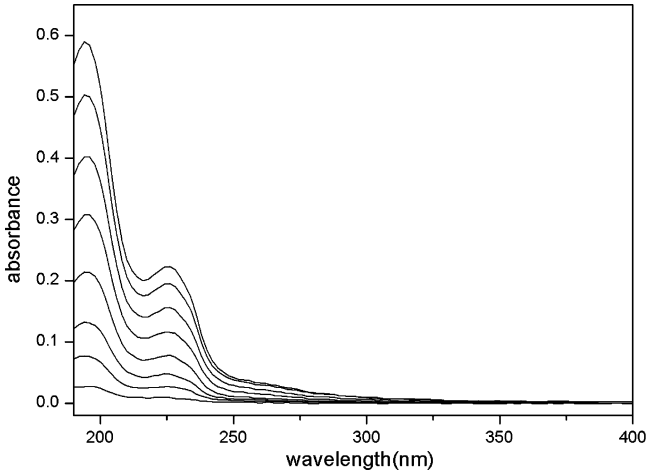

Figure 1. UV spectra of PPy/PAH film as a function of the number of bilayers from the bottom to the top corresponding to 1 to 8 bilayers. The composite films were deposited on quartz plates by the LbL technique via electrostatic adsorption.

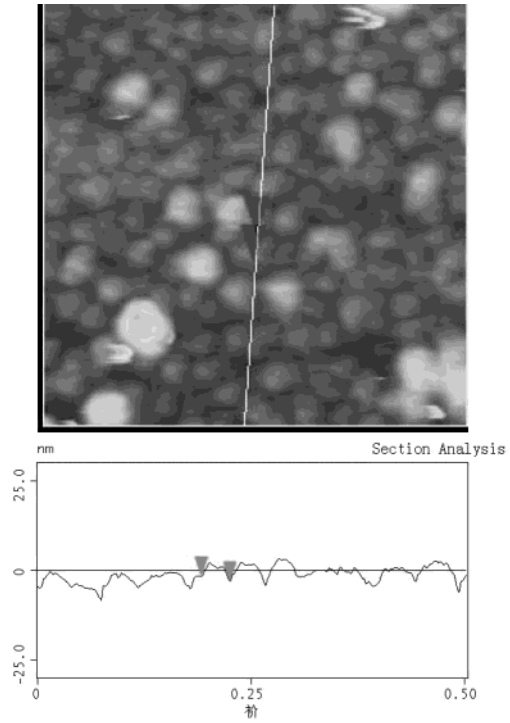

Figure 2. AFM image of $(PPy/PAH)_4$ films deposited on a silicon oxide substrate with cross-sectional analysis. The image dimension is 0.5×0.5 μm^2.

those in the subsequent ones. The reason for this is that the first polyelectrolyte-coated surface provides a higher charge density, which creates a stronger electrostatic adsorption for the later bilayers.

The surface morphology of the PPy/PAH multilayer film was investigated by atomic force microscopy (AFM). Figure 2 shows the surface topography of a 0.5×0.5 μm^2 dimension of a 4-bilayer PPy/PAH dry film on silicon surface, where a condensed film with nearly equal grain size can be observed. The mean grain size of the 4-bilayer film is about 30 nm in diameter and 3 nm in height. Owing to the rigid pyrrole ring in the conjugated polypyrrole, the surface of the film will be rougher than that of the flexible linear polymers such as poly(styrene sulfonate) (PSS). As mentioned above, a complete and continuous thin conductive (PPy/PAH) film could be obtained by the LbL technique via electrostatic adsorption, which may be considered to fabricate conductive hollow capsules.

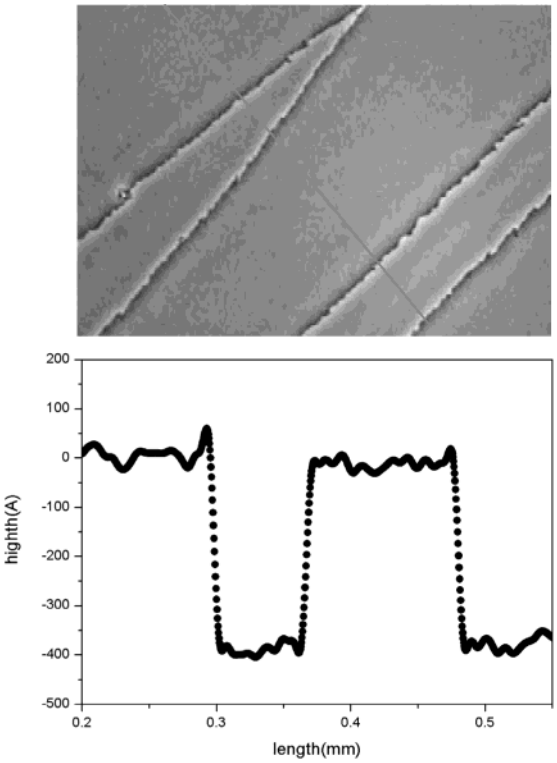

Figure 3. (a) Optical microscopy image of 8-bilayer PPy/PAH films on a quartz plate. (b) Thickness of $(PPy/PAH)_8$ film determined by the profile of the microscopy image.

Figure 3 shows the optical microscopy image of an 8-bilayer (PPy/PAH) film on a quartz plate with gaps (Figure 3a). By measuring the defected edge along the line shown in Figure 3a, one can obtain the thickness of the planar $(PPy/PAH)_8$ multilayers. Figure 3b displays the profile of 8 (PPy/PAH) bilayers. The estimated film thickness is about 40 nm, indicating that the thickness of each bilayer is about 5 nm. This value is very consistent with the reported thickness of a polyelectrolyte bilayer.[17,20] By using a similar approach, we measured the thickness of 4, 12, 16, and 20 (PPy/PAH) bilayers as 20, 60, 80, and 120 nm, respectively. It demonstrates that every adsorption polymer bilayer has a uniform thickness.

PPy/PAH Multilayer Assembly on MF Spheres. The morphology of the (PPy/PAH)-coated MF spheres was examined by both SEM and TEM. Figure 4 shows the SEM images of an uncoated MF particle with a smooth surface (Figure 4a) and $(PPy/PAH)_8$-coated MF spheres (Figure 4b). It is seen that the PPy/PAH-coated MF particle has a rougher surface covered by nanosized grains due to the coverage of (PPy/PAH) multilayer. The TEM image (inset Figure 4b) of a selected core−shell sphere displays the coating of the 8-layer composite film (arrows). The increased particle size observed might be due to some polydispersity of MF particles. The dried hollow shells shrink to 3.5 μm in diameter estimated from Figure 4c. The folds of the capsule wall were observed during the drying process.

The removal process of MF core was also observed by optical microscopy. Figure 5a shows the optical image of $(PPy/PAH)_8$-modified MF particles with a diameter

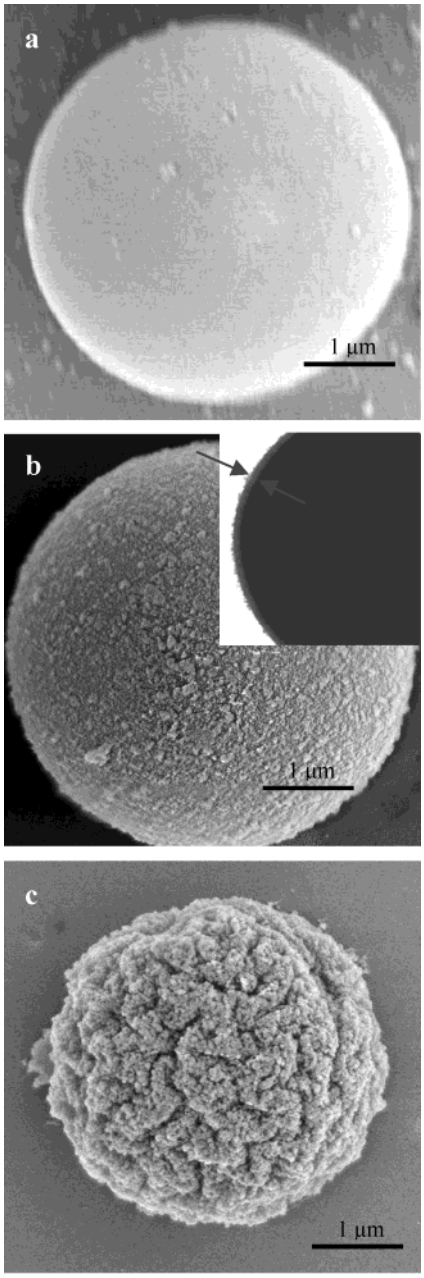

Figure 4. SEM images of (a) pure MF particle with a diameter of 5.7 μm, (b) $(PPy/PAH)_8$-coated MF sphere, and (c) hollow $(PPy/PAH)_8$ capsule after the core removal by acid with the help of heating and ultrasonication.

slightly larger than 5.7 μm. The hollow shells dispersed in water have a larger size (ca. 9 μm) (Figure 5b) due to the extension of the whole wall and exhibited a transparent and hollow state.

Conductivity Measurements. To further understand the electric properties of the PPy/PAH composite films, we carried out the conductivity measurements by a voltmeter on interdigitated electrodes with fixed sizes and equal separation from one tract to another. Owing to the larger size of the (PPy/PAH) shells, we presume that the shells have the identical density and conductivity to the flat multilayers deposited on planar substrates. So the conductivity measurement was performed on the planar (PPy/PAH) film of 2−8 bilayers. It is found experimentally that the resistance of a multilayer film reduces with the increase of the bilayers number. The average conductivity calculated for the (PPy/PAH) films is about 0.007−0.008 S/cm. Such a value of conductivity is comparable to that obtained for the (PANI/PSS) film prepared with a similar technique.[25]

Electrochemical Property. The electrochemistry of the PPy/PAH planar multilayers, PPy/PAH-coated MF particles, and hollow capsules were measured by the cyclic voltammetry. The PPy/PAH planar film was prepared by depositing the 8-bilayer polyelectrolyte layers onto the ITO glass by the LbL technique. The modified particles and hollow capsules were also transferred onto the surface of the ITO glass as well by casting the suspension. To avoid the effect of the bare glass surface upon the preciseness of the measurements, we deposited 4-bilayer PSS/PAH polyelectrolyte film on the ITO glass surface. Figure 6 shows the cyclic voltammogram (CV) curves of (a) the $(PPy/PAH)_8$ flat multilayer film, (b) the $(PPy\text{-}PAH)_8$-coated MF particles, and (c) the $(PPy/PAH)_8$ hollow capsules in a 1 M NaCl aqueous solution at a scan rate of 20 mV/s. Platinum wire was used as the counter electrode and Ag/AgCl as the reference electrode. The difference of the peak current scale is owing to the different amounts of samples during the course of specimen preparation. The peaks are associated with the oxidation and reduction processes of PPy films. The three CV curves show a reduction peak at −0.69, −066, and −0.70 V, with the oxidation peak at −0.31, −0.30, −0.28 V , respectively. The positions of the peaks are similar within the experimental error range, which allows the conclusion that the PPy/PAH film has identical electrochemical properties in the planar state as well as in a curved particle surface after removal of the cores. Even the oxidation peak appears at a negative voltage, so in the natural state PPy exists in a highly stable oxidative

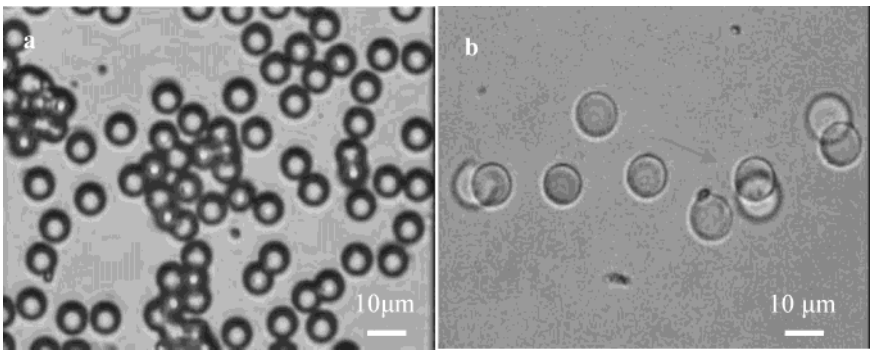

Figure 5. Optical microscopy images of (a) $(PPy/PAH)_8$-coated MF particles with a diameter of 5.8 μm; (b) hollow $(PPy/PAH)_8$ capsules dispersed in pure water.

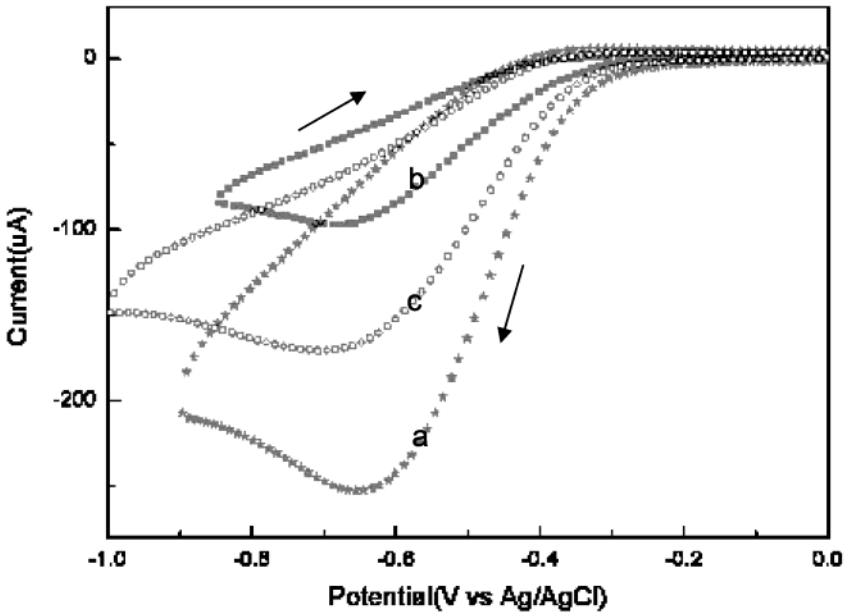

Figure 6. Cyclic voltammogram curves of (a) $(PPy/PAH)_8$ films deposited on ITO glass, (b) $(PPy/PAH)_8$-coated MF particles on ITO glass, and (c) hollow $(PPy/PAH)_8$ capsules on ITO glass in a 1 M NaCl aqueous medium at a scan rate of 20 mV/s. Platinum wire was used as the counter electrode and Ag/AgCl as the reference electrode.

form doped by organic acid as counteranions. The reduction and reoxidation process of PPy are accompanied by the de-insertion and re-insertion of the counteranions or the insertion and de-insertion of the countercations (Na^+). The latter explanation is a more likely fit to the case of the electrochemically polymerized PPy film investigated by others.[26]

Conclusions

We demonstrate that PPy/PAH conductive planar films and hollow microcapsules can be fabricated with the layer-by-layer technique. The conductivity of the PPy/PAH films was measured as 0.007 S/cm. Cyclic voltammetry studies indicate that flat multilayer film, $(PPy/PAH)_8$-coated particles, and the hollow $(PPy/PAH)_8$ shells have identical electrochemical properties and high stability in the oxidative state. This approach provides an easy route to construct conductive PPy multilayer films and maintain their high oxidative stability.

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