

Formation of Uniform Polyaniline Thin Shells and Hollow Capsules Using Polyelectrolyte-Coated Microspheres as Templates

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Received February 13, 2003

ABSTRACT: Multilayers of poly(diallyldimethylammonium chloride) and poly(sodium 4-styrenesulfonate) precoated onto melamine formaldehyde (MF) particles via the layer-by-layer (LbL) self-assembly procedure were used as templates for the subsequent deposition of polyaniline (PANI). Transmission electron microscopic (TEM) and scanning electron microscopic (SEM) images reveal that the as-prepared PANI-containing polyelectrolyte (PE)–MF core–shell particles are narrowly dispersed and possess uniform surface morphology. Intact hollow PANI/PE capsules can also be produced by extracting the MF cores in an acidic solution. FTIR spectra of the hollow capsules indicate that PANI and PE are both present and suggest that the PANI exists in the emeraldine form. The incorporation of PANI in the shells was found to enhance the rigidity of these composite materials, and the PANI/PE-coated MF core–shell particles have comparable conductivities with other PANI-coated colloidal particles. The amount of PANI incorporation was also found to increase with the PE layer number, suggesting that the LbL procedure for forming PE multilayers is a convenient method for modifying the colloidal particle surfaces for a favorable PANI film growth and for controlling the PANI thin shell thickness. The method developed is simple, versatile, and colloidal particle general.

1. Introduction

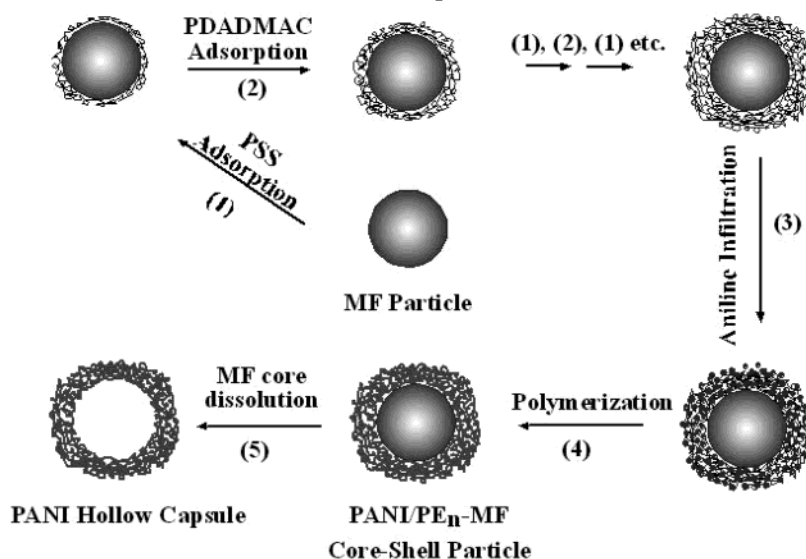
Synthesis of composite colloidal particles consisting of inorganic or polymeric cores uniformly coated with ultrathin films of materials has recently generated a great deal of interest.¹ These colloidal particles may find applications in areas as diverse as optical and electronic devices, catalysis, separation, and chemical and biological sensing.² Conductive polymer thin films coated onto colloidal surfaces have been of particular interest, owing to the expected improvement of polymer processability and unique properties intrinsic in dispersed nanometer- or micrometer-sized materials.^{3–5} Polypyrrole (PPY),^{6–8} polyaniline (PANI),^{3–5} and polythiophene⁹ have been deposited onto a variety of colloidal particles^{3–9} via chemical polymerization of the corresponding monomers. Despite a prodigious amount of work on the synthesis and characterization of colloidal particles coated with different conductive polymer shells, depositing thin uniform PANI films onto colloidal particles has proven to be challenging.¹⁰

It is established that self-assembled organic acid monolayers or surfactant bilayers on colloidal particles play an important role in the uniform growth of conductive PPY thin films with a desirable morphology.^{11,12} We envision that premodification of the particle surfaces might be a viable approach to prepare colloid-stable composite particles with uniform coating of conducting polymers. In this work, we assembled polyelectrolyte (PE) multilayers onto colloidal particles for the subsequent PANI deposition by the layer-by-layer (LbL) self-assembly technique.^{13,14} The immobilization of these PE multilayers serves two purposes. First, the PE coating thickness can be tuned at the nanometer level¹³ by altering the number of layers deposited. Second, these PE multilayers can serve as a nanometer-sized milieu

for confining the species from the solution and for performing the subsequent chemical derivatization.^{15–23} In a recent report, Caruso and Wang introduced metal oxides into the PE coatings on colloid particles via sol–gel reactions.²⁴ The PE multilayers would be particularly well suited for the PANI deposition, since several recent studies showed that PANI structures of a desirable morphology can be synthesized in a confined environment.^{25–30} For instance, Bein and co-workers prepared conducting PANI filaments in the ordered, nanometer-sized hexagonal channels present in a mesoporous aluminosilicate substrate.²⁵ Martin's group developed the membrane-based synthesis to create PANI nanotubes within the cylindrical pores of membrane templates.^{26–28} Lennox and co-workers synthesized PPY strands utilizing lipid tubule edges as a confined environment.²⁹

In addition, although water can be entrapped into PE multilayers,³¹ the interior of the multilayers is still relatively hydrophobic (reflected by the fact that most charges in the PE layers are neutralized to yield the water-insoluble PE multilayers), which might favor the growth of PANI into the PE multilayers. Moreover, the common problem of particle aggregation upon deposition of PANI could be overcome by localizing the aniline polymerization within the PE shells on colloids. This would significantly improve the colloid stability of the resultant PANI-coated particles. In the present study, we show that PE multilayers preformed onto micrometer-sized melamine formaldehyde (MF) particles can be utilized as a reaction vessel for forming uniform PANI coatings. Such coatings resulted in the production of colloid-stable, narrowly dispersed PANI-containing core–shell particles. We further demonstrate that intact hollow PANI capsules can be prepared by dissolving the MF core particles in acidic solutions. The methodologies described herein may afford new avenues for the fabrication of composites comprising conducting poly-

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Scheme 1. Schematic Illustration of the Procedure Used for Preparing PANI-Containing Core–Shell Particles or Hollow Capsules

mers of various sizes and structures and for tractability improvement of conductive polymer-based materials. These micrometer-sized PANI-containing colloidal particles might be amendable for the applications of separation media^{32–35} and “biomarker” particles for the purpose of biosensing.^{36,37}

2. Experimental Section

2.1. Materials. MF particles (diameter 3.0 μm , estimated from TEM images) were acquired from Microparticles GmbH (Berlin, Germany) as a 10 wt % aqueous solution. Polystyrene (PS) particles (diameter 1.1 μm , 4.0 wt %) were purchased from Interfacial Dynamics Corp. (Portland, OR). Poly(sodium 4-styrenesulfonate) (PSS, $M_w = 70\,000$) and poly(diallyldimethylammonium chloride) (PDADMAC, $M_w = 200\,000$) were obtained from Aldrich. Aniline hydrochloride was purchased from Sigma. Water was purified by a Millipore Milli-Q Plus 185 purification system with a resistivity of 18.2 $\text{M}\Omega\text{ cm}$.

2.2. Synthesis of PANI/PE-Coated MF Particles and Hollow PANI Capsules. *Assembly of PE Multilayers onto MF Particles.* The positively charged MF particles were first coated with several PE layers utilizing the LbL method (step 1 in Scheme 1).^{13,15–17} 50 μL of an MF solution was diluted to 1 mL with water, followed by addition of 1 mL of aqueous solution of PSS (1 mg/mL in 0.5 M NaCl). After adsorption for 15 min, the excess PSS was removed by three centrifugation (2000 rpm)/dispersion/washing cycles. This was followed by adding 1 mL of aqueous solution of PDADMAC (1 mg/mL in 0.5 M NaCl) to the PSS-modified MF particle suspension (step 2 in Scheme 1). The unadsorbed PDADMAC was removed after a 15 min adsorption step. These steps were repeated until a desired layer number was obtained.

PANI Deposition onto PE-Coated MF Particles and Formation of PANI Hollow Capsules. MF particles coated with different PE layer numbers, denoted as PE₁-MF (1 PE layer), PE₃-MF (3 PE layers), PE₅-MF (5 PE layers), PE₉-MF (9 PE layers), and PE₁₃-MF (13 PE layers), were separately exposed to 0.5 mL of a 0.2 M aniline hydrochloride (pH = 3) solution (step 3 in Scheme 1). The monomer/particle reaction mixture was cooled to 0 $^{\circ}\text{C}$ in an ice bath for at least 30 min prior to the addition of 0.5 mL of an ammonium peroxydisulfate solution (0.2 M, pH = 3). The mixture was not stirred,^{4,38} and under such an experimental condition the polymerization was usually completed in less than 1 h (step 4 in Scheme 1). The resulting dispersions were centrifuged and washed thoroughly with water to remove unreacted aniline monomers and PANI aggregates in the solution. The purified core–shell particle suspension was stored in water at room temperature. Accord-

ing to the method reported by Stejskal et al.,⁴ the conversion of aniline to PANI ranges 50–80%. The loading of PANI onto PE_n-MF particles was calculated using the following equation:

$$\text{PANI loading (\%)} = \{[W_t - W_0]/W_0\} \times 100\% \quad (1)$$

where W_t is the weight of PANI/PE_n-MF particles and W_0 is the weight of PE_n-MF particles. The PE_n-MF particle suspension was divided into two equal parts: one for the subsequent PANI deposition and the other for reference. Both portions were air-dried and weighed with an analytical balance.

For the production of hollow PANI capsules, the PANI-coated MF particles were treated with an HCl solution (pH 1.5) for 10 min (step 5 in Scheme 1).³⁹ The hollow PANI capsules produced were then centrifuged at 13 000 rpm for 10 min. After removal of the supernatant, the hollow PANI capsules were redispersed in water. These centrifugation/dispersion steps were repeated three times to remove the MF oligomers.

2.3. Instrumentation. *TEM and SEM Measurements.* TEM images were collected with a JEOL 1200 CX2 microscope operated at 120 kV. A solution containing PANI-coated MF particles (10 μL) was cast onto a Formvar-coated copper grid (Ted Pella Inc., Redding, CA), and the solvent was allowed to evaporate. SEM measurements were carried out with a Cambridge Stereoscan 250 instrument operated at 20 kV. SEM samples (on silicon substrates) were sputtered with a 5 nm thick Au coating.

FTIR Spectroscopy. Reflectance FTIR measurements were conducted with an Equinox 55 FT-IR (Bruker Optics Inc., Billerica, MA) housing a variable angle specular reflectance accessory (VeeMax II, Pike Instruments, Madison, WI). An average of 32 scans was performed to produce each spectrum. Suspensions of bulk PANI, hollow PANI capsules, and hollow PE multilayer capsules were cast onto the glass slides pre-coated with 120 nm thick Au films, air-dried, and stored in a vacuum desiccator prior to the FTIR measurements.

Flow Injection–Quartz Crystal Microbalance (FI-QCM). The QCM crystals were pretreated according to our published procedure.⁴⁰ To verify the formation of hollow PANI capsules, 25 μL of a PANI-coated MF particle (precoated with nine layers of PE multilayers) suspension was cast onto a gold crystal surface, and the solvent was allowed to evaporate. After the crystal was mounted onto the QCM flow cell, water was used as the carrier and introduced through a valve at a flow rate of 25 $\mu\text{L}/\text{min}$. The valve was switched to the inject position to divert 0.2 M HCl solution in a 100 μL loop into the QCM cell. At this flow rate, it takes about 100 s for the injected sample

to reach the QCM crystal and another 4 min for the carrier solution to completely replace the QCM cell content.

Conductivity Measurements. The PANI-coated MF particle suspensions were cast as a densely packed monolayer (confirmed by topographic atomic force microscopy images) across an 11 μm wide gap formed between two 9 mm wide and 20 nm thick Au stripes sputtered onto a glass slide.⁴¹ The film resistance (R) was measured using a digital multimeter (Keithley model 175A), and the conductivity (σ) was calculated from the equation $\sigma = d/RA$, where d is the particle diameter and A is the surface area covered by the particles.⁴²

3. Results and Discussion

3.1. Formation of PANI-Coated Melamine Formaldehyde (MF) Particles. To achieve a narrow dispersity or prevent agglomeration of the PANI-coated MF particles, uniform PANI coatings with a suitable thickness should be deposited. Armes and co-workers employed a solvated polymer layer as a steric stabilizer to form colloid-stable PPY-coated PS particles.^{37,43,44} However, deposition of uniform PANI thin layers onto PS particles has not been straightforward and generally led to patchy PANI films (57–59% coverage⁴⁵) with a relatively coarse surface morphology. It has been reported that charges on colloidal particles facilitate the formation of uniform conductive polymer thin films.^{4,45,46} For example, Garnier and co-workers⁴⁷ and Yamamoto and co-workers⁴⁸ have demonstrated that the presence of acidic functional groups (sulfonic or carboxylic acids) on the PS particles were responsible for the formation of uniform PPY coatings on PS particles. Furthermore, a relatively hydrophobic environment also promotes the growth of high-quality conductive polymer films.^{30,49–51} This aspect is manifested by the synthesis of conductive polymer nanowires⁵¹ and patterns³⁰ utilizing hydrophobic cavities in templates such as cyclodextrin and block copolymer micelles. Recently, we also demonstrated that PANI honeycomb films could be fabricated by electropolymerizing aniline into 2-D arrays of PE-coated polystyrene particles.⁵² Thus, we anticipate that the high surface charge density on MF particles rendered by the outermost PE layer and a somewhat hydrophobic microenvironment in the interior of the PE layers could be obtained. Therefore, a predetermined number of PE layers coated onto the MF particles can be used to control the ultimate amount of PANI deposition. Because PANI-coated MF particles differ from PANI aggregates in their densities and sizes, bulk PANI suspension can be conveniently removed by repeated centrifugation/washing/redispersion steps. Nearly 10% of the free PANI particles (estimated gravimetrically) were formed along with the core-shell particles, indicating that the aniline polymerization took place predominantly in or at the PE shells. These free PANI particles were removed to obtain the PANI/PE_{*n*}-MF core-shell particles. Through this procedure, we synthesized colloid-stable PANI-coated MF particles of an emerald color. The uniformity of the PANI-containing PE₅-MF and PE₉-MF particles is revealed by TEM images (Figure 1). Estimating from TEM measurements, we found that the diameter of a PANI/PE₉-MF structure produced using PE₉-MF as the template is about 8% greater than that of the counterpart fabricated with the PE₅-MF template. We should caution that TEM measurements of the changes in the thin shells coated onto a rather large core are only semiquantitative at best. Nevertheless, the TEM images show the uniformity in the morphology of the PE_{*n*} or PANI-PE_{*n*} ($n \geq 5$) coatings.

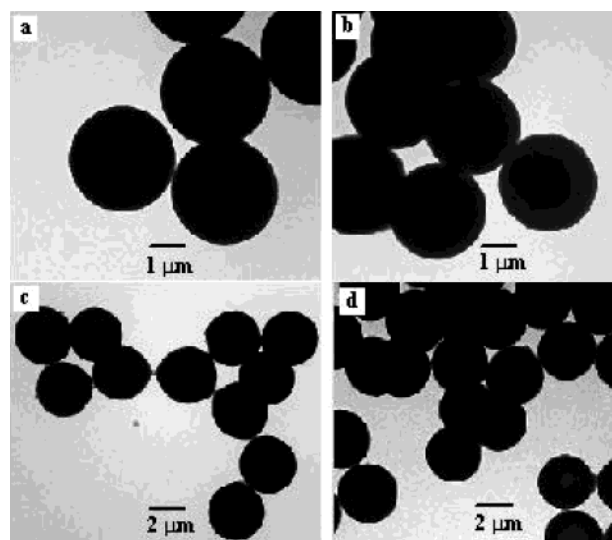


Figure 1. TEM images of MF particles coated with 5 (a) and 9 (c) layers of polyelectrolytes. Images (b) and (d) represent the TEM images of PANI-coated MF particles using 5 and 9 layers of polyelectrolytes as templates, respectively.

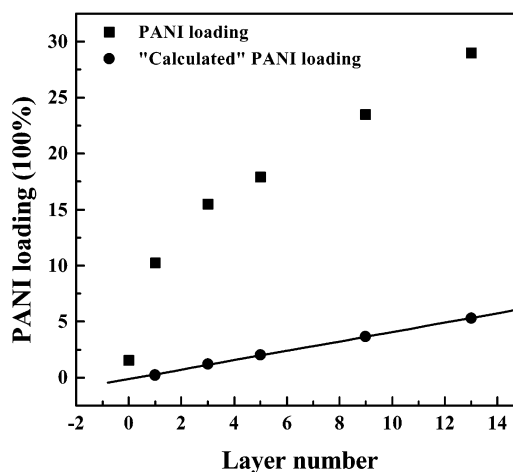


Figure 2. Plots of percent PANI loading measured experimentally and the "calculated" PANI loading as a function of the PE layer numbers.

As shown by eq 1, quantities of the PANI deposits at various PE_{*n*}-MF particles can be measured gravimetrically. A plot of the PANI loading (solid squares) vs the PE layer number, together with the "calculated" PANI loading in the PE shells corresponding to different PE layer number (solid circles), is shown in Figure 2. The relationship between the change of the PANI deposition (ΔW) and the variation of the PE layer number (Δn) is given by the following equation:

$$\Delta W/\Delta n = 4\pi L\rho(nL + r)^2 \quad (2)$$

where r is the radius of the MF particle (1.5 μm), n is the number of PE layers, L is the average thickness of each PE layer ($L \approx 2 \text{ nm}^{13}$), and ρ is the density of PANI (1.4 g/cm^3).^{3a} The above equation assumes that PANI fills the interior of the PE layers and does not extend out of the PE layers. Since $r \gg nL$, $\Delta W \approx 4\pi L\rho r^2 \Delta n$. Therefore, the PANI deposit should be proportional to the PE layer number, as depicted by the linearity of the "calculated curve" in Figure 2. Our experimental data, however, showed an initial rapid increase in the first two PE layers, followed by a gradual increase with

higher layer numbers. The latter increase had a slope comparable to that of the "calculated curve", suggesting that PANI deposition becomes layer-dependent when $n \geq 3$. The initial increase in the PANI deposition (for $n < 3$) is conceivable, because the large number of charges associated with the PE layers should favor conducting polymer attachment to colloidal particles.^{47,48} Therefore, only when n is small ($n < 3$), the PANI deposition may possibly extend out of the thin PE layers onto the surface of the colloidal particles. At greater n values, the larger volumes associated with the PE coatings may better confine the PANI deposition. In fact, SEM images (Supporting Information) show that the PANI/PE_{*n*}-MF ($n = 5$ and 9) particles are as uniform as the PE_{*n*}-MF particle templates. The difference between the actual PANI loading and the "calculated value" suggests that an expansion/swelling of the PANI/PE shells during the PANI growth may not be ruled out.

It is worthy to point out that the polarity of the outermost PE layer was found to affect the PANI loading. We carried out an FI-QCM experiment to monitor the incorporation of aniline monomers into PE multilayers preformed onto a QCM electrode (data not shown). When the outermost PE layer was PSS, we found that the protonated aniline monomers readily adsorbed onto/into the surface. Thus, it appears that the positively charged aniline monomers first bind to the outermost PSS layer via electrostatic interaction and subsequently infiltrate into the PE multilayers. The results are consistent with our previous studies related to the infiltration of charged inorganic, organometallic, and organic species into PE multilayered films^{15–17,52} as well as studies from other groups.^{18,22,53}

3.2. Formation of PANI Hollow Capsules. We further explored the formation of hollow PANI capsules by extracting the MF cores of the PANI/PE_{*n*}-MF structures using an HCl solution (pH = 1–1.7). To verify that the MF cores have indeed departed from the composite particles in the extraction step, we monitored the mass change of the PANI/PE₉-MF particles with FI-QCM. The abrupt mass loss accompanying the introduction of the acid into the cell (Supporting Information) is indicative of the instantaneous extraction of the core materials. In such an extraction, MF particles were decomposed to oligomers and released into the solution through the PANI/PE_{*n*} shells.^{54,55} Shown in Figure 3a is a TEM image of hollow PANI capsules prepared using the PE₉-MF templates. The hollow PANI capsules appear to be intact and narrowly dispersed (separate SEM images showing the dispersity are available as Supporting Information). Moreover, the solution of PANI capsules appears to be quite homogeneous and colloid-stable for at least 1 month. The interconnection of a few particles in Figure 3a (largely absent in the SEM images) might be attributable to the drying procedure in the TEM measurement. The size of the PANI/PE₉ hollow capsules (~4 μm) is greater than that of PANI/PE₉-MF core-shell particles. The penetration of the dissolved MF oligomers might have resulted in the expansion of the PANI/PE₉ shells. It is worth mentioning that, when PANI/PE₅-MF particles were exposed to an HCl solution, only fractured PANI/PE "rods" and "sheets" were produced (Figure 3b). These microscopic PANI/PE "rods" and "sheets" are probably the products of the PANI/PE₅ shell fragmentation during the MF core extraction. This implies that a thinner PE shell with a smaller amount of PANI loading is not sufficiently robust. Interestingly,

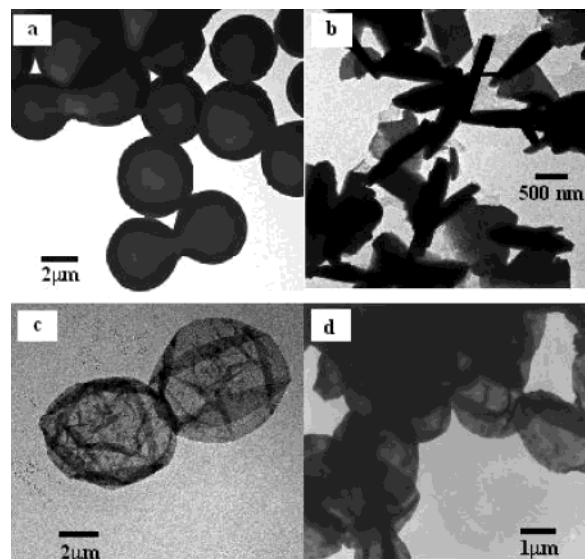


Figure 3. TEM images of hollow PANI/PE₉ capsules (a) and PANI/PE₅ composite fragments formed upon exposure to an HCl solution (b). Image (c) represents two hollow capsules comprising 9 PE layers, and image (d) shows the PANI/PE₉ hollow capsules formed by the aniline polymerization within the PE₉ hollow capsules.

similar to previous reports,⁵⁵ PE₅ hollow capsules can be produced by dissolution of the MF cores of the PE₅-MF particles (image not shown). These results again suggest that the PANI deposition into the PE shells took place, and the more compact structure has impeded the departure of the core materials from the center. Consequently, when the shells are relatively thin and compact, they could be ruptured by the core release.

The shape of PANI/PE₉ hollow capsules and that of capsules containing nine PE layers are contrasted by the two images presented in Figure 3a,c. While the former retains a somewhat spherical shape resembling that of the MF particles, the surface of the latter (Figure 3c) is distorted with abundant folds and creases (possibly produced by extraction of the solvent in the PE layers prior to the TEM measurement^{55,56}). The PE shells have semitransparent appearance, while PE hollow shells containing the PANI deposit are rigid and dense (reflected by the higher electron density of the shell in Figure 3a). Finally, we investigated whether preformed hollow PE capsules could serve as a template to incorporate the PANI deposit. Figure 3d shows a TEM image of hollow PANI/PE₉ shells produced from the PE₉ hollow capsules as the initial template. The dispersity of such PANI/PE₉ shells was found to be less satisfactory, because the hollow structures tend to be more oblong and conglomerate with one another, suggesting that high-quality hollow PANI capsules can only be obtained by decomposing the MF cores after aniline polymerization.

Although hollow PPY capsules have been produced (e.g., Marinakos et al. showed the preparation of PPY capsules using gold nanoparticles as a template⁶), attempts to synthesize PANI capsules or hollow spheres based on decomposing PANI-coated PS particles only resulted in the formation of broken PANI egg-shell structures or raspberry-like surfaces.^{3a,b} In a most recent report, Wei and Wan^{3c} synthesized PANI hollow microspheres using an aniline emulsion approach. Our approach thus provides an alternative route to the production of intact PANI hollow capsules based on

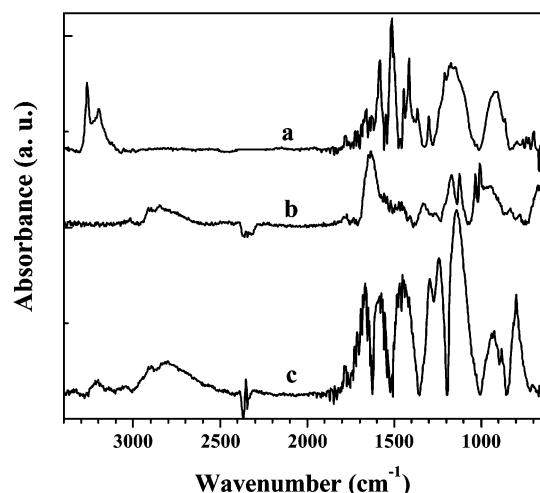


Figure 4. Reflectance FTIR spectra of (a) PANI powder, (b) PE₉ hollow capsules, and (c) PANI/PE₉ hollow capsules.

colloidal templating. We attribute the retaining of the enclosed structure to the robustness associated with the PE multilayers. To further investigate whether the formation of intact hollow PANI capsules is restricted only to MF particles, we prepared PANI/PE₁₀-PS particles (diameter 1.1 μm). Again, intact hollow PANI/PE shells were obtained by the subsequent exposure of the core-shell structure to tetrahydrofuran (image not shown). Therefore, our procedure represents a versatile and colloidal particle-general approach to produce narrowly dispersed PANI-containing core-shell and/or hollow structures.

3.3. Characterization of PANI/PE_n Composites.

Reflectance FTIR Measurements. To determine the composition of the as-prepared PANI/PE_n hollow capsules, reflectance FTIR spectra of bulk PANI powder, PE₉, and PANI/PE₉ composite hollow capsules were collected (Figure 4). The spectra of PANI only (spectrum a) and PANI/PE₉ capsules (spectrum c) both show three strong absorption bands attributable to PANI (at 1584, 1495, and 1147 cm^{-1}). The first two are associated with the quinonoid and benzenoid units, while the last one at 1147 cm^{-1} corresponds to the C–N stretching.^{52,57} In spectrum b, overlapping bands with weak intensities (at 2918 and 2850 cm^{-1}) and a stronger absorption band at 1320 cm^{-1} can be assigned to PSS,^{58,59} while the large peak at 1640 cm^{-1} is assigned to PDADMAC.⁶⁰ Thus, through the comparison of the bands around 2800 cm^{-1} , it is clear that PSS and PANI coexist in the PANI/PE₉ composite structure. In addition, the strong absorption at 1658 cm^{-1} in spectrum c and the band at 1640 cm^{-1} in spectrum b are in close proximity, indicating the presence of PDADMAC in the PANI/PE₉ shells. The band at 1290 cm^{-1} in spectrum c shows a distinctive shoulder that is originated from the PSS band at 1320 cm^{-1} (spectrum b). Overall, these FTIR spectra provide evidence about the composite nature of the emeraldine PANI/PE_n-MF particles or PANI/PE_n hollow capsules. More importantly, they provide supportive evidence about the existence of PANI within the PE thin shells and the absence of a large amount of PANI on the surface of the PANI/PE_n composite shells, because the signals associated with the PE layers would be overwhelmed if PANI were only deposited on top of the outermost PE layer.

Conductivity. Conductivity of the as-prepared PANI/PE_n-MF particles was measured.⁴¹ We found that the

conductivity of the core-shell particles increased with the PE layer number (e.g., from 1.1×10^{-3} S/cm for the PANI/PE₃-MF particles to 2.2×10^{-3} S/cm for the PANI/PE₅-MF particles). Since PE layers are not conductive, the conductivity enhancement suggests a greater amount of PANI incorporation into the thicker PE shells. Once the PE layer number exceeded 5, the increase in conductivity of the PANI/PE_n-MF particles became less drastic (e.g., the conductivity of the PANI/PE₅-MF particles is about the same as that of the PANI/PE₉-MF particles), suggesting that the PANI/PE_n ($n \geq 5$) composites became quite homogeneous in their compositions. Because of presence of the PE layers, the conductivity value (2.2×10^{-3} S/cm) is slightly lower than the PANI-coated colloidal particles reported by Armes and co-workers (5×10^{-2} – 1.5×10^{-1} S cm^{-1}),^{3a} but the morphology of the core-shell particles is much improved.

4. Conclusion

MF particles precoated with multilayers of polyelectrolytes (PEs) have been successfully employed as templates to produce PANI-containing core-shell or hollow capsule structures. The PE layers were found to significantly improve the uniformity of the PANI coating. Intact hollow PANI capsules can be prepared by decomposing the MF cores in an acidic solution. TEM images suggest that the PANI deposition increases with the thickness of the PE shells. The amount of PANI loading and the conductivity of the structures increase dramatically for the first three PE layer number, but the increase becomes less pronounced at higher PE layer number ($n \geq 5$). The FTIR peaks inherent with PEs and PANI provide clear evidence about the composite nature of the core/shell or hollow capsule structures. The presence of PEs in the composite materials was found to improve the ruggedness of the shells or hollow capsules. Tuning the shell thickness can be achieved through altering the number of PE adsorption cycles, whereas tailoring the dimensions of the structures becomes possible by utilizing core particles of different sizes. The procedure described herein is simple and colloidal particle general and represents a newly developed route for the fabrication of colloid particle-supported PANI thin shells. These structures could have potential applications as conducting fillers, separation media, and electrochromic components.

Acknowledgment. Financial support from the American Chemical Society-PRF funds (Grant 37899-AC5), the NIH-SCORE subproject (GM 08101), and the NSF-CRUI grant (DBI-9978806) is gratefully acknowledged.

Supporting Information Available: SEM images of MF particles coated with five and nine PE layers and PANI-containing PE₅-MF and PE₉-MF particles and an FI-QCM curve showing the extraction of MF cores by HCl. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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MA034185G