

1. Introduction

It has long been recognized that performing reactions in a confined nanometer- or micrometer-sized environment may result in the formation of new materials of desired properties. A wide range of nanomaterials consisting of metals, inorganic oxides, and polymers has been produced using various reaction vessels of micrometer or nanometer dimensions. These include nanocapsules, nanobubbles, and block copolymers. Another area that is currently under active pursuit is the use of nanospheres as templates for the fabrication of well-ordered structures. This approach appears to be a new avenue for the synthesis of new materials that combine the unique properties of conductive polymers and the controllability of template-directed surface reactions.
environment using this templating strategy. For instance, Wu and Bein reported the template-directed preparation of conducting polyaniline (PANI) filaments by taking advantage of the nanometer-sized hexagonal channels in mesoporous aluminosilicate substrates. Martin developed the membrane-based procedure to create PANI nanotubes within the cylindrical pores of membrane templates. Such arrays or materials may find applications in areas as diverse as catalysis, biosensing, and development of nanoelectronics and optical devices.

Recently, polyelectrolyte (PE) multilayers and related capsule systems have emerged as a useful medium for material synthesis. Dahne et al. fabricated hollow PE capsules to carry out the “ship in a bottle” synthesis of copolymers. Sukhorukov and co-workers utilized PE multilayered capsules as nanoreactors to synthesize iron oxide nanoparticles. The PE multilayers or capsules are formed by the stepwise adsorption of oppositely charged polyions via the layer-by-layer (LbL) self-assembly procedure. The LbL procedure permits a fine control of PE multilayered capsules as nanoreactors to synthesize within the cylindrical pores of membrane templates.2,3 The membrane-based procedure to create PANi nanotubes conductive honeycomb films with various dimensions.46 Deposited PANi within the interstitial voids to form thin assembled PE-coated spheres onto Au substrates and metal composite materials.39 Because it is known that the diffusion of precursor species into the PE multilayers is slow, the relatively small number of PE layers was chosen in this work to facilitate the penetration of the aniline molecules into the layers as well as to sustain the regularity of the packing order. In addition to the development of the synthetic protocols and the characterization of the resultant structures, evidence supporting the impregnation of the PE thin shells with the aniline monomers is also presented.

2. Experimental Section

2.1. Materials. Aniline hydrochloride was purchased from Sigma. Poly(sodium 4-styrenesulfonate) (PSS, average Mw = 70,000) and poly(diallyldimethylammonium chloride) (PDADMAC, Mw = 200,000) HClO4, NaCl, and toluene were all acquired from Aldrich (Milwaukee, WI). The PS nanospheres with a diameter of 600 nm were obtained from Interfacial Dynamics, Inc. (Portland, OR), as a 0.8 wt% solution in water. All of the solutions were prepared with water purified by a Milli-Q Plus 185 purification (Millipore Corp.) system.

2.2. Electrodes. AT-cut 9.995-MHz crystals coated with gold film in a keyhole shape (quartz crystal microbalance, QCM, active area = 0.212 cm²) were acquired from ICM Technologies (Oklahoma City, OK). Gold film substrates for self-assembling PE-coated particles were prepared by sputtering 60-nm-thick gold films with a 5-nm-thick underlayer of chromium onto thin glass slides. Both the gold-coated QCM crystals and the gold slides were cleaned with a piranha solution and rinsed with deionized water. CAUTION: Piranha solution reacts violently with organic solvents and is a skin irritant. Extreme caution should be exercised when handling piranha solution. A Pt coil and a Ag/AgCl electrode were used as the auxiliary and reference electrodes, respectively.

2.3. Instrumentation. A CHI 440 electrochemical workstation (CH Instruments, Austin, TX) was used for monitoring the aniline electropolymerization and the QCM characterization. For the flow-injection QCM (FI-QCM) experiment, the QCM flow cell, the QCM controller, and the computer were all housed in a Faraday cage (Elchema, Inc., Potsdam, NY), and the delivery of carrier solution to the flow cell was accomplished with a syringe pump (Harvard Apparatus, Holliston, MA). The QCM instrument was calibrated by comparing the mass changes of the silver deposition/stripping processes measured voltammetrically and microgravimetrically, and a sensitivity of 0.81 ng/Hz was determined. Reflectance fourier transform infrared spectroscopy (FTIR) measurements were conducted with an Equinox 55 FTIR (Bruker Optics, Inc., Billerica, MA) housing a variable angle.

specular reflectance accessory (VeeMax II, Pike Instruments, Madison, WI). An average of 32 scans were performed to produce each spectrum. Atomic force microscopy (AFM) was carried out in the contact mode (Molecular Imaging, Phoenix, AZ). Scanning electron microscopy (SEM) was performed with a Hitachi S4100 instrument operated at 5–15 kV. Assembling well-ordered arrays of PS particles coated with different numbers of PE layers was achieved with a modified Langmuir–Blodgett “mini-trough” system (KSV Instruments, Helsinki, Finland).1,52

To measure the film conductivity, the aniline monomers were infiltrated into the truncated PE eggshell structures that had been predeposited across an 11-μm gap separating two 1.8-cm-wide and 20-nm-thick Au stripes.5,40 Upon electropolymerization, the resistance of the film was measured using a digital multimeter (Keithley model 175A). We measured the conductivity in the dry state on the basis of the assumption that the void spaces were considered as part of the films. The average thickness used in the calculation was obtained from the AFM measurements.

2.4. Procedures. Self-Assembly of well-ordered Truncated Eggshell Structures coated on Au Substrates. PS nanoparticles were first coated with a predetermined number of PE layers utilizing the previously reported LbL self-assembly procedure.46,51,52 PS particles with PE shells of different layer numbers (PE1–PS, denoted as PE1–PS (n = 2 PE layers), PE2–PS (n = 4 PE layers), and PE4–PS (n = 6 PE layers) were diluted with water (10%). These particles were then allowed to self-assemble onto the gold film substrates or QCM crystals following the reported procedures.46,51,52

Lithographic Patterning of Surfaces with Truncated Eggshell Structures Containing PE Multilayers and the Subsequent Infiltration of the Aniline Monomers. Gold films or QCM crystals coated with arrays of PE1–PS nanoparticles were immersed in toluene for 24 h. Upon removal of the PS core, a 0.2 M aniline hydrochloride solution was allowed to infiltrate into the resultant truncated eggshell structures of the PE multilayers for 30 min. This infiltration step was followed by sequentially dipping the substrate into three separate beakers filled with deionized water.5,40

In quantifying the infiltrated aniline monomers by FI-QCM, water was used as the carrier and the 0.2 M aniline monomer solution was introduced into the flow cell housing a crystal covered with the truncated eggshell structures. A flow rate of 1 mL/h was used, and the sample injection was accomplished via a 250-μL loop on a six-port rotary injection valve (Valco Instruments, Houston, TX).

Electropolymerization of Aniline Monomers within the Truncated Eggshell Structures. Substrates covered with truncated eggshell structures of PE multilayers that had been impregnated with aniline monomers were transferred into an electrochemical cell containing 0.5 M HClO4. Electropolymerization of the aniline monomers was carried out by cycling the electrode potential between −0.1 and +0.8 V.

3. Results and Discussion

3.1. Fabrication of Well-Ordered Truncated Eggshell Structures of PE–PAni Composites. Figure 1 schematically illustrates the procedure for the construction of well-ordered arrays of truncated eggshell structures containing PE–PAni. Prior to self-assembly, the PS particles were coated with a predetermined number of PE layers by sequential exposure to PDADMAC and PSS solutions. A hexagonally close-packed pattern of the PE-coated PS particles was then formed on a gold substrate (step 1). The PS cores were extracted by immersing the surface in toluene, leaving an array of “deflated” PE thin shells behind on the substrate (step 2). As will be discussed in connection with the description of the surface characterization, extraction of the PS cores results in the rupture of the apices of the spherical PE shells and an expansion of the PE shells along the surface. While the hexagonal pattern was retained, the original PE spheres had been converted into a uniformly truncated PE eggshell structure. In step 3, the resultant structure was brought into contact with an aniline hydrochloride solution. The aniline monomers, being positively charged, were attracted to the negative charges residing on the outermost PE shell and eventually infiltrated into the void spaces within the PE multilayers. Finally, the array of the truncated PE eggshell structures containing aniline monomers was thoroughly rinsed with water to rid the nonspecifically adsorbed aniline of the surface and transferred to an aniline-free 0.5 M HClO4 solution for electropolymerization (step 4). This electropolymerization reaction is confined within the deflated PE shells, eventually producing an array of the PE–PAni composite.

3.2. Impregnation of the PE Thin Shells and Electropolymerization of Aniline. As shown in Figure 1, the organization of the final PE–PAni composite film is highly dependent on the regularity of the template (i.e., the array of the truncated eggshell PE structures). We have shown that it is possible to produce a highly ordered two-dimensional array of PE-coated PS particles onto a substrate surface.46,52 Figure 2a is a representative scanning electron micrograph of a PE2–PS particle assembly over a 16 × 16 μm area. Clearly, the PE coating on the PS particles does not significantly impede the hexagonal close-packing of the colloidal particles across a large area.46,52,53,54 We should note that the use of a Langmuir–Blodgett trough for the PE-coated NSL was found to improve the regularity of the array over a larger surface area (Figure 2b). Figure 2b shows a topographical AFM image of the surface resulting from exposing the substrate to toluene. The dissolution of the PS cores had two consequences: (1) as described in our previous report,2 the apices of the PE shells tend to be ruptured by the departing core materials and (2) the “deflated” PE shells expanded somewhat along the substrate surface, enlarging the shell thickness. Interestingly, the rupture force appears to be rather uniform because the cross-sectional contour of the PE shell structure in Figure 2b clearly shows the

Figure 1. Schematic illustration of the procedure for the formation of the truncated eggshell structures of PE multilayers, the impregnation of the structures with aniline monomers, and the electropolymerization of the monomers confined within the PE shells to produce the PE–PAni composite.
regularity in the truncation. Moreover, the small expansion of the PE layers associated with the PS core extraction did not disrupt the organization of the hexagonal packing. Similar trends were observed for the PE4 and PE6 arrays (images not shown). From Table 1, there was a decrease in the pore diameter and an increase in both the pore depth and the PE shell width as we increased the PE number on the spheres.

To demonstrate that aniline monomers can be attracted to the surface of these truncated PE eggshell structures and subsequently be incorporated into the PE shells, we carried out a FI-QCM experiment. Figure 3 is an overlay of three time-resolved frequency measurements performed on QCM crystals covered with arrays of truncated PE$_2$, PE$_4$, and PE$_6$ eggshell structures. The time lapse between the injection of the aniline solution (indicated by the arrow on the left) and the onset of the frequency decrease correlates well with the time needed for the injected sample plug to reach the crystal surface from the sample loop, suggesting a rapid adsorption of the aniline monomers onto the outermost PE layer. The adsorption may be followed by a slow inward diffusion of the aniline monomer into the interior of the thin PE layers, which would not cause any additional frequency change in the FI-QCM response. In our previous work, we have attributed such a rapid uptake to the electrostatic attraction between the positively charged aniline monomers and the negatively charged PS outer layer. At the end of the injection (indicated by the arrow on the right), the frequency remained quite steady, suggesting that the PE shells retained the aniline monomers. The frequency (mass density) changes (see Table 2 for the average values) of the aniline monomer incorporation into the PE$_2$–PS, PE$_4$–PS, and PE$_6$–PS arrays were found to be 61 ± 3, 101 ± 9, and 113 ± 5 Hz, respectively. The fact that the PE$_6$–PS array caused the greatest amount of aniline infiltration is conceivable because the volume associated with a thicker PE multilayer will be higher for monomers containing aniline. We should point out that, given the porosity and

<table>
<thead>
<tr>
<th>PE$_n$</th>
<th>pore diameter$^a$ (nm)</th>
<th>pore depth$^a$ (nm)</th>
<th>shell thickness$^a$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE$_2$</td>
<td>310 ± 14/272 ± 22</td>
<td>47 ± 15/49 ± 9</td>
<td>184 ± 11/202 ± 15</td>
</tr>
<tr>
<td>PE$_4$</td>
<td>290 ± 15/266 ± 10</td>
<td>52 ± 17/54 ± 26</td>
<td>195 ± 13/227 ± 24</td>
</tr>
<tr>
<td>PE$_6$</td>
<td>258 ± 20/246 ± 21</td>
<td>59 ± 11/55 ± 9</td>
<td>207 ± 12/267 ± 14</td>
</tr>
</tbody>
</table>

$^a$ Before/after aniline electropolymerization.

Figure 3. Overlays of time-resolved QCM responses to the injection of a 0.2 M aniline monomer solution into a flow cell housing crystals coated with the truncated eggshell structures composed of (a) PE$_2$, (b) PE$_4$, and (c) PE$_6$ layers. The arrow on the left indicates the time when the injections were made, and the arrow on the right corresponds to the time when the aniline solution had completely exited the flow cell. The flow rate used was 1 mL/h.

<table>
<thead>
<tr>
<th>PE$_n$</th>
<th>conductivity (S cm$^{-1}$)</th>
<th>aniline loading$^a$ (Hz)</th>
<th>PAni loading$^b$ (ng/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE$_2$</td>
<td>2.24 × 10$^{-3}$</td>
<td>61 ± 3</td>
<td>9.0</td>
</tr>
<tr>
<td>PE$_4$</td>
<td>3.34 × 10$^{-3}$</td>
<td>101 ± 9</td>
<td>19.9</td>
</tr>
<tr>
<td>PE$_6$</td>
<td>3.07 × 10$^{-3}$</td>
<td>113 ± 5</td>
<td>31.8</td>
</tr>
</tbody>
</table>

$^a$ Calculated from average QCM infiltration curves. $^b$ Calculated from charges for polymerization of aniline into PE$_n$ layers.
morphology of the eggshell structure, the film cannot be considered as a rigid layer. Consequently, the viscoelastic effects associated with a nonrigid film will make the Sauerbrey equation semiquantitative at best. Nevertheless, the QCM results are a qualitative or semiquantitative measure of the mass change accompanied by the aniline infiltration process. For example, Rickert et al. have shown that, for a nonrigid film that is highly solvated, despite that the resonance frequency measurements by QCM can deviate from the true mass change by as much as 4 times, QCM can still give a relatively reliable indication of the adsorption process occurring at the solid/solution interface. It should also be noted that the change in density from that of pure water to that of 0.2 M aniline is ~1.8%, which may introduce a small uncertainty in the frequency measurements. However, such an uncertainty is much smaller than the differences exhibited by the FI-QCM curves displayed in Figure 3.

We have observed a trend similar to that in Figure 3 at thin PE shells coated onto melamine–formaldehyde particles in a colloidal solution. The FI-QCM results support the notion that aniline monomers have penetrated into the PE shells and remained in the layers long enough for the subsequent electropolymerization step. Table 2 lists the average amounts of aniline loading in the arrays. When we turn our discussion to the electrochemical QCM (E-QCM) experiments, which further verified the retention of the monomers by the truncated PE eggshell structures. Upon immersion in a 0.2 M aniline monomer solution, substrates were transferred into an aniline-free 0.5 M HClO₄ solution. Shown in Figure 4 are the voltammograms (panel a) recorded for 19 potential cycles between –0.1 and +0.8 V in a HClO₄ solution and the corresponding frequency–potential diagrams (panel b). The two distinctive redox waves at about 0.2 and 0.65 V are characteristic of the aniline monomer oxidation and PANi formation. In Figure 4a, each additional potential cycle leads to smaller redox peaks, while the concurrent frequency change measured (panel b) shows a gradual buildup of the PANi deposit at the surface. The cyclic voltammetry responses are in contrast with those commonly observed for the electrochemical oxidation of aniline monomers present in solution. This observation suggests that a finite amount of aniline monomers was present within the structures after the substrate transfer to an aniline-free solution. During the potential cycling, they were accessible for the electron-transfer reactions with the substrate electrode to polymerize. As the electropolymerization proceeds, the aniline monomers are rapidly consumed and eventually exhausted. The sharp decline in the frequency value in the first few potential cycles (e.g., the first three to five cycles) is somewhat surprising because the polymerization of the monomers confined in the PE shells should not cause an increase in the overall film mass. We postulate that, upon the application of an oxidation potential, some aniline monomers may diffuse to the boundary between the PE shell and the gold substrate and the electropolymers propagate from the boundary toward the bulk of the eggshell structure. The closer proximity of the poly-merization to the QCM sensing surface and the greater rigidity of the PANi/PE composite with respect to the aniline-containing PE shell could cause an enhanced QCM sensitivity. It can be seen from Figure 4b, for the electropolymerization of aniline within the PE4 array, that the magnitude of the frequency change precipitously decreases after the initial four to five cycles. We also attempted a QCM experiment in which the possible mass change upon exposing PE thin shells impregnated with aniline monomers to a K₂S₂O₈ solution (0.1 M) was monitored. Unfortunately, the PE shells were found to peel off the surface, making the microgravimetric measurements unreliable. Unlike the electrochemical polymerization that occurs at the gold substrate/PE shell interface, the chemical oxidation of the infiltrate aniline would first take place at the top of the PE shells. Probably because of the difference in the locations of polymerization, the mechanical stability of the former is better because of the formation of the more rigid PE/PAni composite film close to the substrate surface.

![Figure 4. Nineteen consecutive cyclic voltammograms (a) and the corresponding frequency–potential diagrams (b). The voltammograms were obtained in a 0.5 M HClO₄ solution on a QCM crystal covered with truncated eggshell structures of PE4 impregnated with aniline monomers. The scan rate used was 0.05 V/s, and arrows indicate the scan directions.](image-url)

Similar EQCM behavior was observed for the electropolymerization of aniline monomers within the PE2 and PE6 arrays (data not shown). For all three types of arrays, the mass of aniline infiltration measured by FI-QCM (Figure 3) is considerably less than the amount of PANi formed within the PE shell (estimated by integrating the charges of the peaks as previously reported). Again, this discrepancy can be attributed to the inaccuracy in

(60) Buttry, D. A. Applications of the Quartz Crystal Microbalance to Electrochemistry; Marcel Dekker: New York, 1991; Vol. 17.
Thus, it appears that the PAni deposition within the PE thin shell yielded an expansion of the eggshell structure, possibly as a result of the stiffening of the PE eggshell structures by the PAni formation.

To probe the regularity of the truncated eggshell structures composed of both PAni and PE, we utilized SEM to image arrays across a larger surface area than those examinable by our AFM. To contrast the influence of the PE layer number on the ordering of the composite structures, two SEM images are presented in Figure 5c,d (corresponding respectively to the counterparts shown in Figure 5a,b). Two points are worth noting. First, both surfaces display regular porous structures across a large area, with the PE2 structure possessing a greater periodicity. However, when the array of the PE6 eggshell structure was used as the template, some defects (i.e., the "cracks" shown in the inset of Figure 5d) were observed. We have noted in our previous report about the effect of a thicker PE coating on the organization of arrays of PE−PS particles.46 These defects appear to have an implication in the observed decline in the film conductivity described in the following section.

3.3. Characterization of the Truncated Eggshell Structures of PE−PAni Composites. AFM and SEM Characterizations. We also employed AFM and SEM to monitor the morphological changes of the array surfaces following each step of the scheme in Figure 1. Figure 5a,b are AFM images of arrays of truncated PE2−, PE4−, and PE6−PAni eggshells, respectively. As a result of the interaction between the AFM tip and the electrostatic charges and elasticity of the PE shell, a substantial frictional force was created as the tip scans over the sample, causing the image to be somewhat blurry. A comparison of these images to Figure 2b reveals that the electropolymerization step has not significantly altered the surface morphology of the original PE−eggshell arrays. Thus, another piece of evidence suggesting that the aniline monomers are confined in the interior of the PE thin shells9 because the growth of the polymer films out of the monomers adsorbed onto the surface of the PE shells would produce a different morphology and dimension. Table 1 lists the geometric parameters of the various arrays. While the variation in the parameters between these arrays is small, a close examination of the pore diameters and the thickness of the eggshell structures indicates that the PE shell thickness and pore depth increase slightly with the layer number. The trend is understandable because the expansion of the thin shell (due to electropolymerization of aniline) should propagate in both directions along the surface. This is in contrast to our previous work46 on the electropolymerization of aniline in the interstitial voids of the PE-coated PS particle arrays (where the polymerization takes place in an aniline solution). In the present work, extraction of the core precedes the PAni deposition.


...
peaks associated with the PE molecules suggests that a large amount of PANi is absent within the PE network because the absorption peaks associated with the PE layers would be overwhelmed if PANi were only deposited on top of the outermost PE layer.

4. Conclusions

This work demonstrates that arrays of PE-coated colloidal particles can be self-assembled by NSL and converted to arrays of uniformly truncated PE eggshell structures by exposing the original template to an organic solvent (e.g., toluene). The utilization of a Langmuir–Blodgett trough in the procedure was found to improve the regularity of the arrays across a large surface area that is not easily obtained with the casting procedure typically used in NSL. The truncated PE eggshell structures were shown to be viable vessels for the extraction and storage of charged aniline monomers from solution. The extent of aniline infiltration was found to be dependent on the thickness of the PE shells, suggesting that the LbL
deposition of alternating PE layers is a convenient technique for varying the volume of the nanometer-thick storage vessels. EQCM experiments show that the aniline monomers are retained by the PE shells and can be electropolymerized to PANi inside the structure. AFM, SEM, and reflectance FTIR measurements also provide direct or indirect evidence about the coexistence of PANi and PE and formation of PANi in the interior of the PE multilayers. Templating surfaces with evenly truncated PE eggshell structures affords an attractive route for combining a well-ordered system with the unique properties of conductive polymers.

**Acknowledgment.** We gratefully acknowledge support from the American Chemical Society-PRF funds (Grant 37899-AC5), a Henry Dreyfus Teacher-Scholar Award (TH-01-025), and a NSF-CRUI grant (DBI-9978806). We also thank the two anonymous reviewers for their constructive suggestions on some of our data interpretations.

Figure 6. Reflectance FTIR spectrum of a two-dimensional array of a truncated eggshell structure containing the PE$_4$-PAni composite.