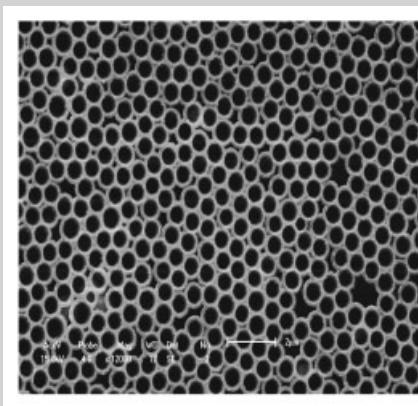


Summary: A general method for the generation of two-dimensional (2D) ordered, large-area, and liftable conducting polymer-nanobowl sheet has been demonstrated via chemical polymerization for the first time. The sheet is made using the monolayer self-assembled from polystyrene (PS) spheres at the aqueous/air interface as template, followed by depositing conducting polymer on the part of PS monolayer submerging in the aqueous phase via chemical polymerization, and core extraction. During the process of polymerization, no substrate is required, which caused the as-prepared patterned conducting polymer sheet can be easily lifted-off and deposited, in full size, on any flat substrate. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Fourier transform infrared (FTIR) spectrum were used to characterize the products.



Morphology of the polyaniline-CSA nanobowl sheet.

General Synthesis of Two-Dimensional Patterned Conducting Polymer-Nanobowl Sheet via Chemical Polymerization

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Introduction

At present, major goals in modern materials chemistry are represented by the ability to design, fabricate, and manipulate nanostructured systems to achieve well-tailored chemical-physical characteristics for advanced application. This conundrum has been addressed to some extent by many recent works describing the synthesis of two-dimensional (2D) well-patterned organic and inorganic thin sheets of micrometer and submicrometer dimensions with tailored structures and shapes for their wide applications in porous electrodes, photonic band crystals, separation media, catalysts, sensors, and nanodot patterns.^[1–9]

Among these methods, using polystyrene (PS) sphere as template to fabricate well-patterned organic and inorganic thin sheets becomes very popular due to their monodisper-

sity, low cost, and easiness to be extracted. Up to now, diverse methods have been developed to fabricate patterned functional sheets with PS as template, such as electron beam evaporation, vapor-liquid-solid growth, electrochemical polymerization, etc.^[10–12] However, all the patterned sheets fabricated via above methods were tightly connected with substrates, when separating them from the substrate, holes exist on the bottom of them, which would reduce their applications; at the same time, little attention has been put on using chemical polymerization to fabricate patterned sheets. So, it is foreseen that finding a general method to fabricate 2D organic patterned sheets with well-tailored properties will be very interesting.

In this study, a general synthetic method for 2D ordered, large-area, and patterned conducting polymer [polyaniline (polypyrrole) doped with-L-camphor sulfonate acid]

nanobowl sheet has been demonstrated with PS monolayer as template via chemical polymerization. During the chemical polymerization, no substrate is required, which causes the 2D patterned sheets can be easily transported on any flat substrate, in full size, without leaving holes on the bottom. We believe that our method will provide a powerful platform to construct other patterned polymer thin film for desirable applications.

Experimental Part

Preparation of 2D-Ordered Monolayer of PS Spheres at Aqueous/Air Interface

First, PS spheres with sulfonic acid groups on their surfaces were synthesized followed the paper.^[13] Then, 1 drop of 10 wt.-% PS spheres aqueous solution was dispersed in 2 ml ethanol. At the same time, 5 ml aliquot of solution A (containing 0.25 M aniline and 0.25 M L-camphosulfate, L-CSA) and 5 ml aliquot of solution B (containing 0.25 M ammonium persulfate, APS) were mixed at room temperature in a 20 ml beaker. Soon after that PS spheres suspension was gently dropped on the surface of the mixture with a pipette and the PS spheres spread on the surface to form a monolayer. It is important to emphasize that solution A and solution B have been both cooled to 5 °C before the mixing.

Fabrication of 2D Patterned Conducting Polymer-Nanobowl Sheet

5 h later, the PANI-PS composite layer was transferred onto a piece of Si wafer, washed with water, and dried in air at room temperature for 24 h. Then, the composite layer can be

obtained by submerging the conducting polymers-PS monolayer in tetrahydrofuran (THF) for 0.5 h and washing it with THF for two times to extract the PS sphere cores and drying in air at room temperature.

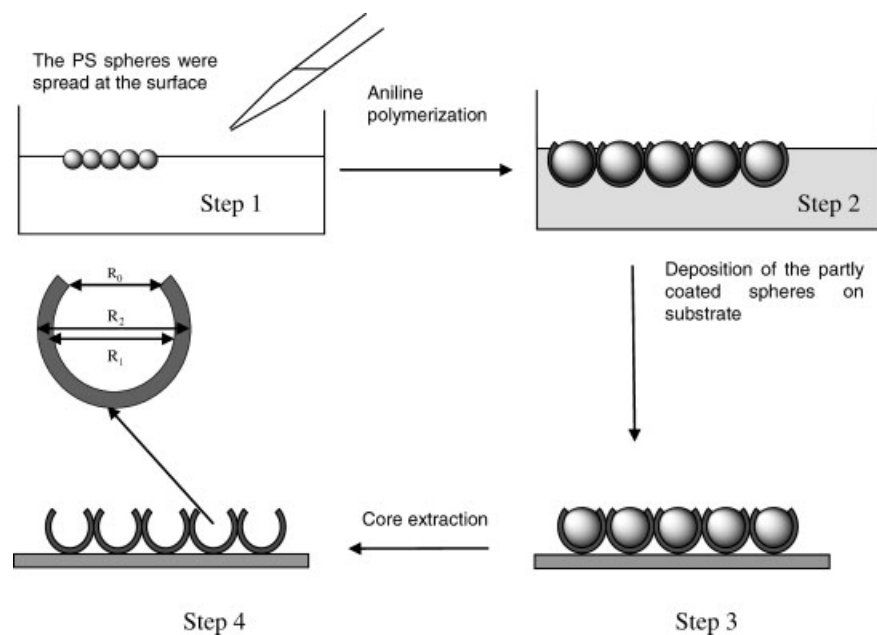
Characterization

Scanning electron microscopy (SEM) images of these samples were recorded on a SHIMADZU SSX-550, Japan. Transmission electron microscopy (TEM) images of these samples were recorded on a Hitachi S-570. Fourier transform infrared (FTIR) spectra of these samples were recorded on a BRUKER VECTOR22.

Results and Discussion

To clearly see the whole process, all the procedures have been illustrated in Scheme 1. First, a hexagon close-packed monolayer consisting of PS spheres was spread at the aqueous solution/air interface (step 1). During the process of chemical polymerization, conducting polymers were easily deposited on the hemisphere of the PS spheres submerging in the aqueous phase (step 2).^[14] 5 h later, the monolayer, consisting of conducting polymers and PS, can be transported on silicon wafer (step 3). Finally, 2D ordered, large-area, and patterned conducting polymers-nanobowl sheets were obtained by submerging the conducting polymers-PS monolayer in THF for 0.5 h and washing it with THF for two times to extract the PS sphere cores and drying in air at room temperature (step 4).

Figure 1 shows a typical SEM image of the hexagon close-packed PS monolayer, indicating that the 2D-ordered



Scheme 1. Schematic illustration of the process to fabricate 2D patterned conducting polymer-nanobowl sheet with PS spheres as template.

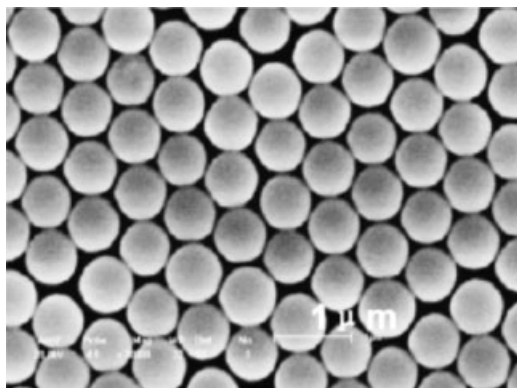


Figure 1. Morphology of the 2D-ordered PS monolayer obtained at the aqueous/air interface.

monolayer consisting of PS spheres (av. 660 nm) can be obtained through our method.

PANI-CSA sheet has been prepared first and characterized by SEM and TEM. Figure 2(a) shows the SEM image of the products at a low magnification, indicating the large-area 2D patterned polyaniline-CSA film made up of hollow polyaniline-CSA nanobowls with uniform openings on the top can be fabricated. From the cross section of the products [inserted in Figure 2(a)], it can be found that the structures of the products are very stable, the morphology of them can be even kept without any substrate. Enhancing the magnification [Figure 2(b)], it can be seen that their morphology is more like the honeycomb with uniform diameter (420 ± 10 nm) of the opening (R_0) on their top. To determine the accurate structure of the product, TEM has been used to characterize the products [Figure 2(c)]. It can be clearly detected that the inner diameter (R_1), the wall thickness, and the outer diameter (R_2) are 550 ± 20 , 100 ± 10 , and 750 ± 20 nm, respectively, and no hole exists on the bottom of the products. It can also be found that the inner diameter (R_1) of the samples is less than that of the template spheres, suggesting the shrinkage in the process of core extraction.^[12]

Our method can also be applied to fabricate patterned polypyrrole-CSA nanobowl sheet according to the same steps mentioned above. SEM investigations of the as-prepared sheet, with different magnifications, were also measured and shown in Figure 3. From these SEM images, it can be found that the morphology of polypyrrole-CSA nanobowl sheet is the same as that of the polyaniline, which can further prove that our method is a general method for fabricating conducting polymer-nanobowl sheet with uniform morphology.

Figure 4 shows the FTIR spectra of PANI-CSA sheet and PPy-CSA sheet. In the FTIR of PANI-CSA sheet as shown in Figure 4(a), the characteristic peaks at 1567 and 1483 cm^{-1} can be assigned to the stretching vibration of quinoid ring and benzenoid ring, respectively. The band observed at 1300 cm^{-1} corresponds to C–N stretch vibration of secondary aromatic amine. These characteristic vibration

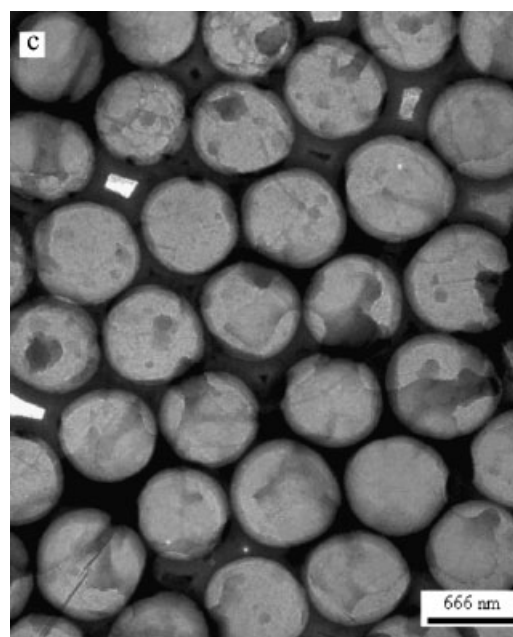
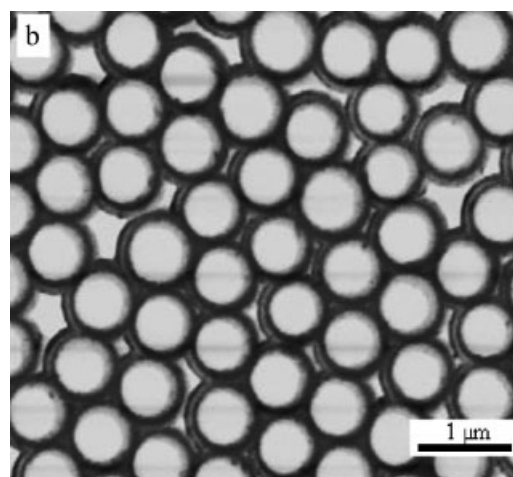
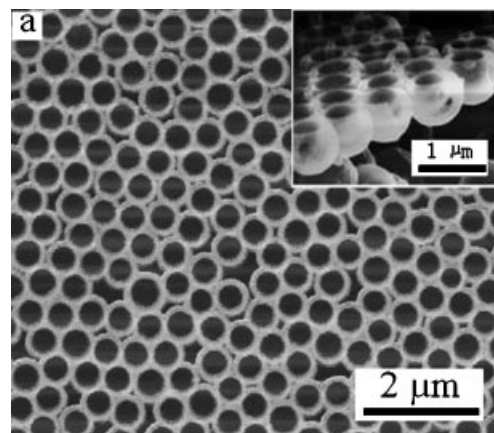


Figure 2. Morphology of the polyaniline-CSA nanobowl sheet. (a) and (b) are SEM images, (c) is TEM image.

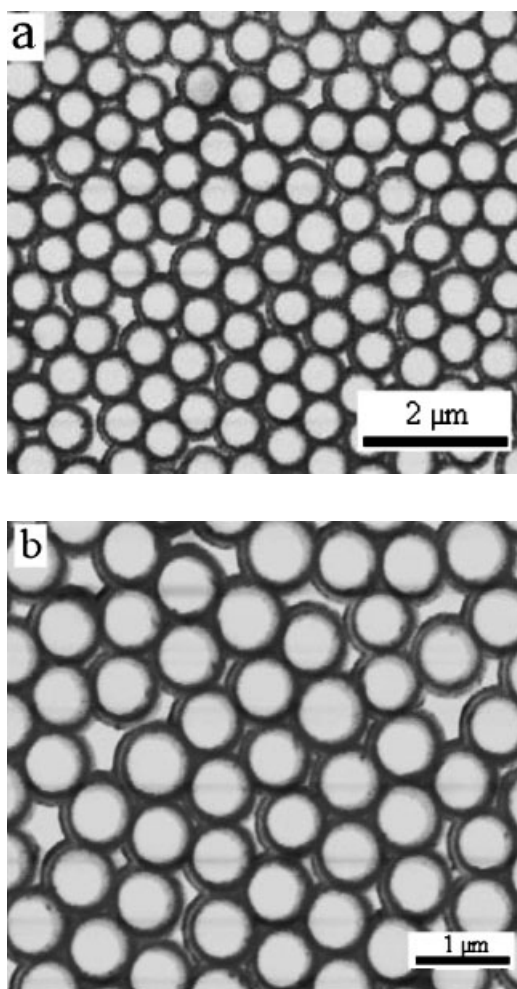


Figure 3. SEM images of the polypyrrole-CSA nanobowl sheet. The magnifications of (a) and (b) is $\times 12\,000$ and $\times 24\,000$, respectively.

peaks were identical to those of PANI prepared in common method.^[15] Figure 4(b) shows the FTIR spectrum of PPy-CSA sheet. The typical peaks can be observed at $1\,560$ and $1\,301\text{ cm}^{-1}$, which corresponded to the pyrrole ring stretching band and $=\text{C}-\text{H}$ vibration.^[16] The bands at $1\,138\text{ cm}^{-1}$ (a) and $1\,215\text{ cm}^{-1}$ (b) correspond to the $\text{S}=\text{O}$ asymmetric stretching vibration of sulfonic acid.

Conclusion

In conclusions, 2D ordered, large-area, and patterned polyaniline-CSA and polypyrrole-CSA nanobowl sheets have been successfully synthesized, for the first time, via chemical polymerization with PS spheres monolayer as template. Compared with the previous methods, our method is simpler and no holes exist in the bottom of the products, which can make our products good candidate for nanocontainers. Promoted by the bigger surfaces than that of the

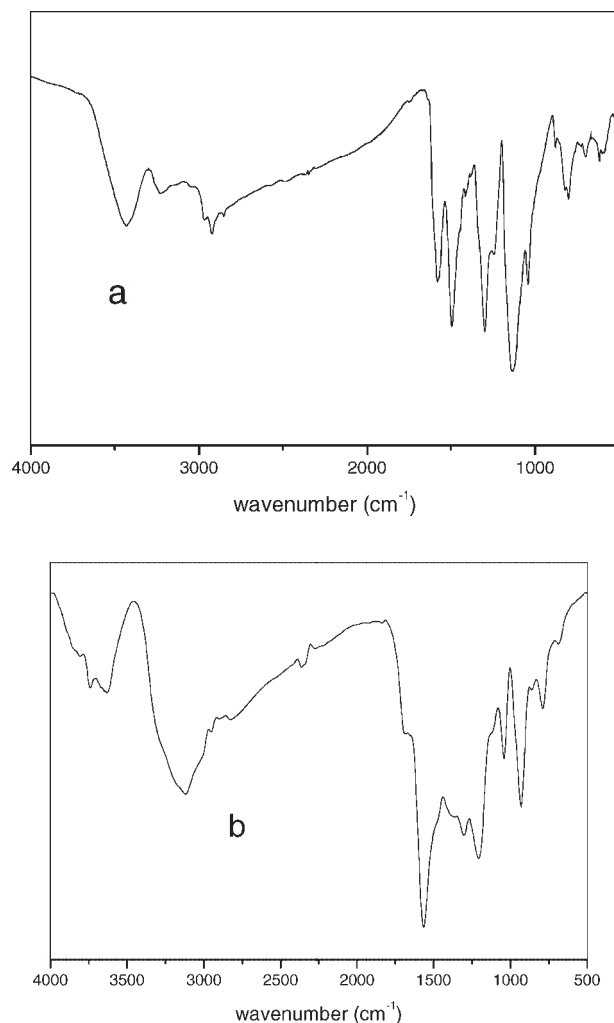


Figure 4. FTIR spectra of PANI-CSA sheet (a) and PPy-CSA sheet (b).

thin conducting polymer sheets, our products can be used as hypersensitive sensor. Most importantly, our method can provide a general method to construct other functional conducting polymer patterned sheets for desirable application.

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