

# Water-Assisted Fabrication of Polyaniline Honeycomb Structure Film

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An ordered honeycomb structure of 4-dodecylbenzenesulfonic acid (DBSA)-doped polyaniline (PANI) is fabricated in a humid atmosphere. By controlling both the relative humidity in the atmosphere and the concentration of the conducting polymer, different morphologies of the honeycomb structure can be obtained. The driving force of this procedure is capillary force (self-assembly), and water droplets serve as a template. Furthermore, the honeycomb structure film of PANI–DBSA is proved to be electroactive and exhibits semiconducting properties in the appropriate doping state.

## Introduction

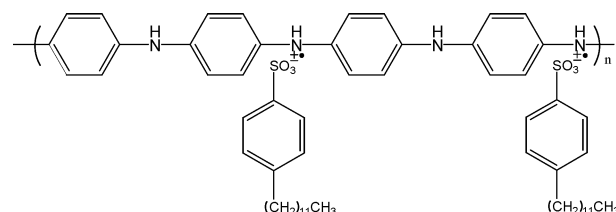
Ordered mesoporous/microporous solids are of interest in areas such as catalysis, sensors, size- and shape-selective separation media, adsorbents, and scaffolds for composite materials synthesis.<sup>1–5</sup> Therefore, microfabrication will be a key technology in providing novel interfacial functions on material surfaces. Photolithography and related techniques have been applied to the micropatterning of various surfaces and the fabrication of micromachines.<sup>6</sup> Furthermore, microporous structures can also be fabricated by the self-organization technique.<sup>7–11</sup> Polyaniline (PANI) is one of the most frequently investigated conducting polymers, and it can be made readily by chemical or electrochemical oxidation polymerization. Although the three-dimensional (3D) ordered network of PANI has been built by template synthesis techniques,<sup>12–15</sup> in this communication, the honeycomb structure film of 4-dodecylbenzenesulfonic acid-doped PANI (PANI–DBSA) is fabricated by a simple self-assembly method in a moist atmosphere, and its conductive property is investigated.

## Experimental Section

PANI–DBSA in chloroform was used as the film formation material, and its chemical structure is shown in Scheme 1. The conductivity of PANI–DBSA is 3.5 S/cm, as measured by a four-probe method, and details of the synthesis method can be found elsewhere.<sup>16</sup> Water was purified using a Milli-Q purification system (Millipore Corp., Bedford, MA) with a resistivity of 18 MΩ cm.

Ten microliters of the PANI–DBSA chloroform solution was cast on the hydrophilically treated substrates (glass or indium tin oxide (ITO)) at room temperature in a humid atmosphere with relative humidities of 70% and 90%, respectively, and honeycomb-patterned films can be obtained. Here, two different concentrations of the PANI–DBSA chloroform solution were

SCHEME 1: The Chemical Structure of PANI Doped with DBSA



chosen by dilution. For comparison, unpatterned films were fabricated by casting 10 μL of polymer solutions under ambient atmosphere (~55% relative humidity at 25 ± 1 °C).

Surface topographies of the as-prepared films were investigated by scanning probe microscopy (Seiko Instruments, Inc., model SPI3800N) in the tapping mode. A microfabricated silicon cantilever with a bending spring constant of 1.9 N/m and a resonance frequency of 25 kHz was used for imaging in the air with a 100-μm scanner at a scan rate of 0.50 Hz.

The conductivity of the honeycomb-structured PANI–DBSA film that was deposited on ITO glass was investigated by atomic force microscopy (AFM), using a conductive cantilever under the application of bias voltages. A commercially available conductive silicon cantilever coated with gold was used for imaging of the current signals. Prior to testing with conductive AFM, the sample was fixed on a metal that was plated with a conductive gel, to ensure an ohmic electrical contact between the sample and the stage on a piezo scanner. Bias voltages were applied to the thin film against the conductive cantilever.

The UV–vis spectra were measured using a Hitachi model U-3010 spectrophotometer.

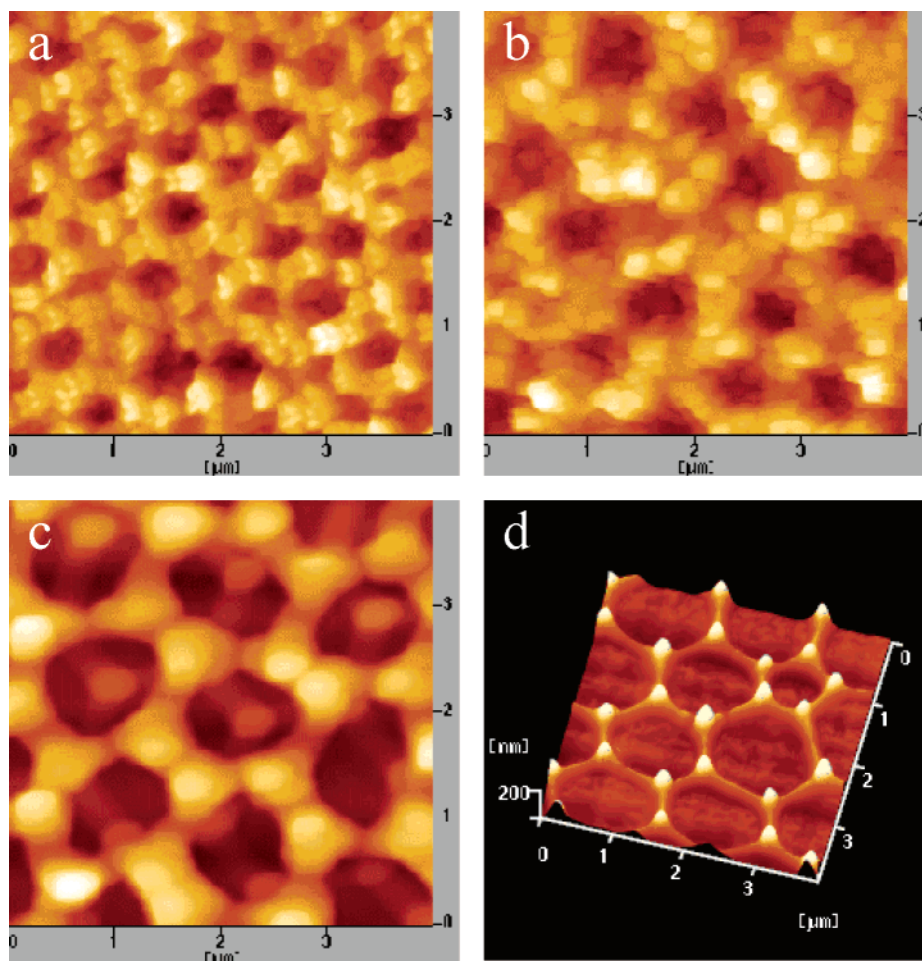
## Results and Discussion

There are several factors that influence the formation of the honeycomb structure and the different morphologies that can be obtained, including the concentration of the PANI–DBSA solution, the relative humidity in the atmosphere, the film formation temperature, the wettability of the substrates, etc. In this communication, the first two factors are studied in detail.

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**Figure 1.** AFM images of honeycomb structures under the following conditions: (a) the concentration of PANI–DBSA is 0.04 wt %, relative humidity of 90%; (b) the concentration of PANI–DBSA is 0.04 wt %, relative humidity of 70%; and (c) the PANI–DBSA solution was diluted 20 times at a relative humidity of 90% with bilayer structure. Panel (d) shows a three-dimensional (3D) image of the PANI–DBSA honeycomb structure, where the PANI–DBSA solution was diluted 20 times at a relative humidity of 90%.

Figure 1 shows AFM images of the as-prepared honeycomb structures of PANI–DBSA films in different concentrations of PANI–DBSA solution and in different humidities. Figures 1a and 1b are the patterns formed with relative humidities of 90% and 70%, respectively, while the concentration of PANI–DBSA is 0.04 wt %. Honeycomb structures clearly are formed, with an average pore diameter of 410.3 nm (see Figure 1a). The arrangement of the pores is relatively ordered, whereas the pore wall is composed of PANI–DBSA particles. Furthermore, when the relative humidity is 70%, the average pore size is 508.4 nm (see Figure 1b), which is relatively unchanged, compared to that shown in Figure 1a, but the pore interval distance is increased, because of the relatively lower density of the water droplet arrangement at lower relative humidity.

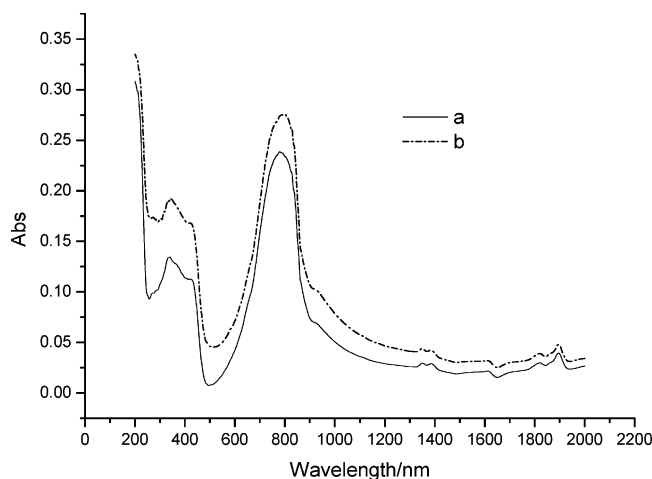
When the above-mentioned PANI–DBSA solution is diluted 20 times, a completely different morphology is obtained at a relative humidity of 90%; bilayer honeycomb structures with polygons (including mainly hexagons, pentagons, and even heptagons) are formed, showing beautiful patterns (see Figure 1c). In some other sections, only one layer of polygon structure can be observed. As shown in the magnified 3D image in Figure 1d, the diameter of the hexagon is ca.  $0.949\ \mu\text{m}$ , with a wall length of ca. 805.4 nm and a wall thickness of ca. 32.2 nm. There are crunodes in each polygon, with the average height of ca. 70.5 nm, indicating the shape of the close-packed water droplet. For comparison, the same experiments have been

conducted at a much lower relative humidity (55%), and no honeycomb structure can be obtained.

All of the previously mentioned phenomena can be well-understood, and the mechanism has been proposed elsewhere.<sup>11,17,18</sup> The high vapor pressure of the organic solvent drives solvent evaporation and rapidly cools the surface. This cooling leads to nucleation, and tiny water droplets cover the entire surface. Because of the incompatibility of the organic solvent and water, the polymer precipitates under this hydrophilic/hydrophobic balance and the polymer layer is formed. Only this “fast nucleation and slow growth” mechanism<sup>19</sup> provides the uniform size of the water droplet. These droplets are transported to the three-phase line and hexagonally packed by the capillary force generated at the solution front. After the film returns to ambient temperature, the condensed water and residual solvent evaporate, leaving behind the 3D polymer scaffold.

During this self-assembly process, two types of driving forces are observed: one is the surface tension between water and organic solvent, the other is the impulsive force of the water droplet.

When the concentration of PANI–DBSA is high, surface tension is the main driving force, and, thus, the shape of the pores is round. Furthermore, because the aggregation of polymer with high concentration is fast, the influence of the humidity on the pore size is not obvious. Because the concentration of PANI–DBSA is low, impulsive force of the water droplet is



**Figure 2.** UV-vis spectra of (a) PANI honeycomb-structured film fabricated at a relative humidity of 90% and (b) the ordinary PANI film produced by dripping PANI solution in air.

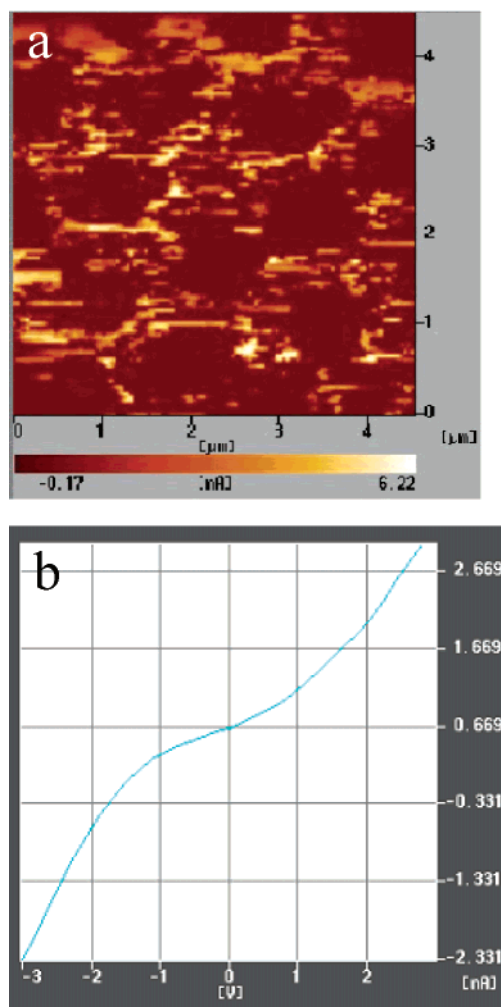
the main driving force; therefore, the pore shape is determined by the arrangement of water droplets, and, thus, the polygon structures are formed.

The UV-vis spectra of the honeycomb structure film and the flat film formed by a dripping process are given in Figure 2 (panels a and b, respectively). As shown, the absorption peaks of these two films are almost identical. There are two absorption peaks observed at 340 nm, with a shoulder at 420 nm and a distinct absorption maximum at 790 nm, which are typical of the absorption spectrum of PANI-DBSA. Because there is no peak of the emeraldine base form of PANI at 630 nm in Figure 2a, it can be concluded that no evident dedoping occurred during the fabrication of the honeycombs in the moist atmosphere, and this film theoretically should be electroactive.

Although the PANI-DBSA is a conducting polymer, the electric property of this as-prepared film is difficult to investigate using general measurements (such as the four-probe method), because of the limitation of the film thickness. In this work, the conductivity of the honeycomb-structured PANI-DBSA film that has been deposited on ITO glass with the diluted solution was investigated further by AFM, using a conductive cantilever under the application of bias voltages. The current image of the as-prepared thin films obtained at a bias voltage of  $-3$  V to  $+3$  V is shown in Figure 3a. The contrast observed in the conductive image is due to differences in the conductivity of the film, with a higher conductance corresponding to the honeycomb structured PANI-DBSA walls. The electrical characteristics of the bright regions were investigated using typical current-voltage ( $I$ - $V$ ) curves of several sites (shown in Figure 3b). As shown, the  $I$ - $V$  behavior of PANI-DBSA was almost exponential in the range of bias voltage between  $-3$  V and  $+3$  V, which is identical to that of the typical  $I$ - $V$  curves of organic semiconductors with lower conductance. The Schottky effect is also displayed, because the current increases dramatically as the bias potential increases.<sup>20</sup>

## Conclusions

A honeycomb structure of 4-dodecylbenzenesulfonic acid-doped polyaniline (PANI-DBSA) has been successfully fabricated via water-assisted self-assembly method for the first time. The humidity of the atmosphere and the concentration of PANI-DBSA each influence the morphology significantly. In addition, the as-prepared honeycomb structure film remains electroactive and exhibits semiconducting properties in the



**Figure 3.** Conductive property measured by conducting atomic force microscopy (AFM): (A) simultaneous current scanning image of the PANI honeycomb structure film with the dilute solution on ITO glass at bias voltage, and (B) a current-voltage ( $I$ - $V$ ) curve typical of several of the thin films.

appropriate doping state. The structures that have been fabricated are expected to be attractive candidates to manipulate photons in three-dimensional (3D) crystals. The ability to make 3D ordered macroporous structures with conducting polymers should lead to new applications in electronic and electrochromic devices.

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