Polyaniline self-organizes into honeycomb films for solar cell applications

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Exploiting the conductive properties of polymers to produce spatial patterning—the breath figure technique—produces microscopic mesh electrodes with tailored dimensions and adjustable void diameters.

Innovation of new photonics applications requires the development not only of new materials but also of novel methods to structure those materials. Many photonic and optical effects, like diffraction, photonic band gap formation, photon-induced charge separation, and so on depend both on the chemical nature of the material and spatial patterning.

In the past, we have been able to adsorb anionic DNA on cationic polymers such as poly(ethylene imine) using layer-by-layer adsorption. The success of this process suggested that it would be feasible to apply this technology to the development of patterned honeycomb film for use in solar cells and other electronic devices. Electrodes for dye-sensitized or polymer solar cells should be metal-free, lightweight, flexible, and recyclable; have low resistance; and, ideally, should feature new functions, such as the scattering of unabsorbed photons for a second path through the active layer in the thin-film solar cell. We are currently beginning to use such an electrostatic effect to adsorb DNA onto the porous electrode films produced by polyaniline, which will open new avenues for the electric and photonic applications of porous electrode films.

Pattern dimensions can range from molecular scales, as in the case of block-copolymer solar cells, to submillimeter scales, as in the case of metallic cloaking devices for electromagnetic radiation. Depending on the pattern size (from nano- to micrometer) and the chemical nature of the material (e.g., organic, ceramic, metal, or polymer), one can choose from an abundance of top-down and bottom-up patterning methods, each with its strengths and weaknesses. It would be unwise to restrict the methodology of patterning to only a few such materials because better methods could subsequently be found.

The pattern formation we focused on is the so-called breath figure technique (see Figure 1). By casting a solution of poly(styrene-co-maleic anhydride) that contains 10% by weight of an amphiphilic poly(ion complex) under high atmospheric humidity, it is possible to form structured, thin polymer films with a periodic hole array (see Figure 2).

The process is very simple and straightforward, but the biggest challenges for the preparation of regular hole patterns are preventing water droplet coalescence and tuning the droplet size. The water droplet coalescence is surface-tension driven. Larger droplets have smaller curvatures, and after two droplets coalesce, they have a larger volume-to-surface ratio and, therefore, are thermodynamically more stable than small droplets. Polymeric surface-active agents (SAA) decrease the surface tension.

Figure 1. Schematic of honeycomb film preparation by casting a polymer solution under high humidity.

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tension of the water droplets and also act as kinetic barriers that prevent droplet coalescence. Our task was to find the best SAA for the polystyrene copolymer/ethyl acetate solution combination. With time, the water droplets grow, but since they do not coalesce, their size distribution is small. With ongoing solvent evaporation, the polymer gels and the water droplets become fixed. After the water evaporates, a void is formed for each water droplet. We can control the size of the voids by controlling the polymer concentration, humidity, casting volume, and temperature. A higher concentration leads to a faster gelation of the polymer solution and, in turn, to smaller water droplets. Higher humidity leads to faster droplet growth and larger droplets. Generally, the void diameter can be adjusted from 500nm to 10 \mu m.

By placing such a honeycomb polymer film into a solution of aniline during oxidative polymerization in the presence of the emulsifier dodecylbenzene sulfonic acid (DBSA),\(^5\) we showed that the polyaniline prepared in situ is adsorbed onto the honeycomb film. The aniline in micellar form is polymerized and the cationic emeraldine salt is stabilized by the DBSA anion and, therefore, kept in solution for a certain time before precipitation. The timing of the insertion and withdrawal of the honeycomb substrate is crucial. The substrate should be inserted after the polyaniline starts forming and withdrawn before the precipitation of the colloidal polyaniline occurs.

Since only a portion of the polyaniline is precipitated, the film thickness is around a few 10–100nm. By repeating this process in a layer-by-layer fashion, we were able to produce thicker films (see Figure 3). Due to the nature of the adsorption from solution, the film grows not only in the axis normal to the film but also laterally. Thus, an increased number of polymerization/adsorption steps leads to a decrease of the diameter of the honeycomb voids, whereas the ‘bridge’ between the voids widens. The electric resistivity decreases with the number of layers and reaches a plateau at 1kOhm for four layers or more.

In summary, we exploited the electrostatic interactions between DNA and porous, anionic polyaniline films to produce hybrid materials that will open new avenues for the electric and photonic applications of porous electrode films. The electric properties of the DNA change after interaction with solutes, such as intercalators or metal complexes, and, therefore, such a hybrid film might be used as a sensor. This constitutes our ongoing research.

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References