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A Facile Method for Fabrication of Ordered Porous Polymer Films

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In the past decade, the strategy to fabricate two- or three-dimensionally ordered porous polymer films has attracted considerable attention since these films have some important potential applications, such as photonic crystals, biosensors, templates, catalysis, size- and shape-selective separation media,[1−9] and even in paints, photonic papers, and cosmetics due to their structural colors, etc.[10,11]

A variety of methodologies have been developed to create micro- or nanoscale ordered porous polymer films, including direct writing of polymer patterns,[12] soft-lithographic methods,[13,14] the use of photo- or electrochemically polymerizable precursors,[15,16] and electric-field-induced patterning of block copolymers.[17,18] In particular, the templating method and "breath figure" approach are two of the most widely used techniques for fabrication of ordered porous polymer films. In the templating method, uniform and spherical particles (usually silica[19] or polymer spheres[20]) are first assembled into crystalline arrays; the void spaces between spheres in the colloidal crystal template are then infiltrated by any type of fluid (e.g., oligomners, cross-linkable resins, or precursors) that penetrates the template and can be converted into a solid. The templating spheres are finally removed to cause ordered porous polymer films.[21−24] The major advantage of this method is that it provides a simple and effective route to the fabrication of two- or three-dimensionally ordered porous polymeric materials with controlled pore sizes, but the preparation processes seem to be very time-consuming and toilful. First, multistep processes, e.g., the assembly of template spheres, the infiltration of fluids, and the solidification of fluids by chemical or physical treatment, are needed for preparation of the template-contained polymer films. Second, in order to obtain the ordered porous films, removal of the templates by etching or by calcination or pyrolysis processes is usually indispensable. Recently, a template-free method called the "breath figure" approach has been developed and used to produce periodic porous polymer films.[25−30] This approach utilizes the condensation of water vapor on the surface of a polymer/organic solvent solution. The droplets of the condensed water self-assemble into a hexagonally ordered array at the air/solution interface. After complete evaporation of the solvent, the water droplets remain in the polymer films, forming well-ordered porous polymer structures.[26] However, this method is known to require precise control over the processing environmental conditions: the amount of water condensation from humidity or the humid air flow rate, the evaporation rate, and the polymer concentration all have a serious impact on precisely controlling the pore size and distribution. Moreover, this approach cannot be employed for mass of production for porous polymer films, and a lot of organic solvent in the polymer solution would seriously damage the environment. Therefore, how to develop facile and feasible processes for fabrication of ordered porous polymer films remains a great challenge to material scientists.

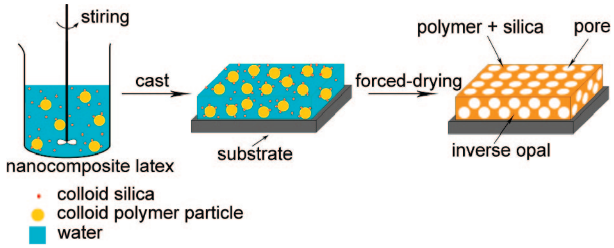

Figure 1. Fabrication diagram of well-ordered porous nanocomposite polymer films.

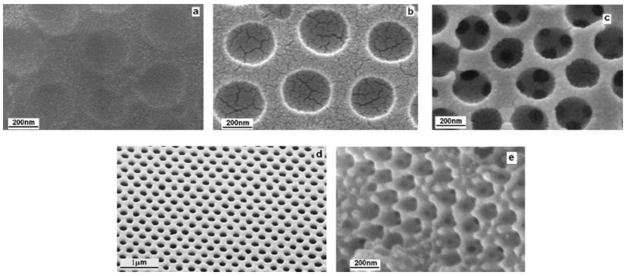

Figure 2. SEM images of polymer films from various drying temperature: (a) 20 °C, 1 day; (b) 60 °C, 2 h; (c) 120 °C, 2 h; and (d) larger surface from (c, e) typical SEM image of the cross section of a porous film.

In this paper, we report for the first time the fabrication of ordered porous polymer films via the "forced drying" of waterborne nanocomposite polymer latex. Our approach has several important advantages over the previous techniques: (i) the well-ordered porous films can be fabricated via one-step, neither complicated steps (assembly, infiltration, solidification, and removal of templates) nor organic solvent is necessary, so the whole process is really simple, cost-efficient, and environmentally friendly; (ii) the nanocomposite latex can be cast on any kind of and any size of substrates, so this method can be used for mass of production of ordered porous films; (iii) the matrix is composed of organic and inorganic components, so the composition and properties of the film can be tunable.

Figure 1 schematically describes a brief procedure for fabrication of the well-ordered porous structure. First, a monodisperse poly(styrene−butyl acrylate−acrylic acid) latex is blended with colloidal silica to prepare nanocomposite polymer latex and then cast on any substrates (glass, silicon wafer, plastic, and so on) by pouring, spin-coating, or brush-coating method. When the substrate cast with nanocomposite polymer latex is directly dried in an oven at comparatively high temperatures (for example, 120 °C or much higher) for a period of time without predrying at ambient temperature (we would call it a "forced-drying" process), a three-dimensionally periodic porous structure is directly obtained.

Figure 2 shows the SEM images of the nanocomposite polymer films with 20 nm of silica obtained from various drying temperatures. When a film was dried at 20 °C, shallow cavities were unveiled on the surface of a flat film (Figure 2a). However, when a film was dried at 60 °C, ordered cavities appeared

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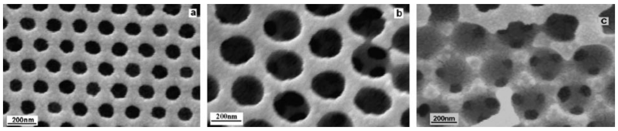

Figure 3. Electronic micrographs of polymer films dried at 120 °C for 2 h: (a) from 160 nm polymer latex, (b) from 270 nm polymer latex, and (c) artificially broken film from 390 nm polymer latex.

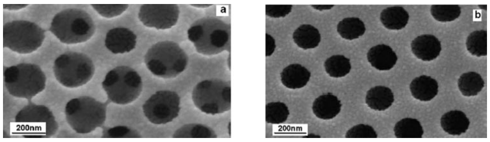

Figure 4. SEM images of polymer films with various thickness: (a) 55 μm, (b) 10 μm. Drying conditions: 120 °C for 2 h.

(Figure 2b). When this film was dried at 120 °C or higher, a periodic array of pores in the size of 200 nm was observed (Figures 2c,d). The typical cross-sectional SEM view (Figure 2e) displays that this film has a periodic structure of three-dimensionally porous array. Moreover, this ordered porous film has a typical face-centered cubic structure, in which each pore is surrounded by six equal pores and the neighboring two pores are separated from each other by a wall of less than 100 nm. The film was further scanned by XPS and exhibited C, O, and Si elements (see the XPS surveys in Supporting Information, Figure S1), indicating that the matrix of the ordered porous film is composed of both polymer and colloidal silica particles.

The pore size and the distance between neighboring two pores can be modulated by the particle size of polymer latex, as demonstrated in Figure 3. When the particle size of polymer latex was 160 nm, the mean pore size was around 105 nm with an average distance of around 160 nm. When the particle size of polymer latex was increased to 270 nm, the mean size of pores was 210 nm with a distance of around 280 nm. When the particle size of polymer latex was increased to around 390 nm, the mean size of pores was increased to around 280 nm and the distance between neighboring two pores was increased to around 370 nm. The SEM image of the artificially broken film in Figure 3c further confirms that this ordered porous film has a face-centered cubic structure.

The particle size of colloidal silica seems to have little influence on the mean size of pores, but the content of colloidal silica has a crucial influence on forming this periodic structure; no or too much colloidal silica would not cause this structure (see Supporting Information, Figure S2). As the film thickness decreased, the periodic pores became even shallower (Figure 4).

To further understand the formation mechanism of this ordered porous structure, the effect of drying time on the porous structure of the nanocomposite films was also investigated. The orderly array of pores appeared even after dried at 120 °C for 10 min, extending drying time seemed to cause much deeper pores and a flatter framework (see Supporting Information, Figure S3).

Figure 5 further presents the typical reflectance peak change of the porous film as a function of incident angle by optical reflectance measurement and band structure calculations using a plane wave expansion method. Figure 5a shows the experimental result with different incident angle in color scale; the red color indicates high reflection, which has a very good agreement with the theoretical result, as indicated by Figure 5b with the line of the center band gap around point L of the Brillouin zone. These experimental and theoretical results further confirm that the films fabricated by our method have very beautiful iridescence phenomena and regular periodicity.

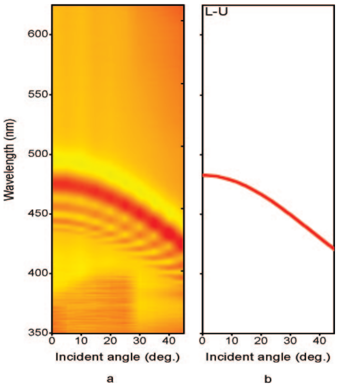

Figure 5. Reflectance peak change as a function of incident angle by measurement and calculation: (a) by optical reflectance measurement; (b) by calculation.

The exact formation mechanism of this ordered porous structure is still unclear at present. The possible formation mechanism could be deduced as follows based on the above results and discussion. When the poly(styrene−butyl acrylate−acrylic acid) latex was blended with colloidal silica particles, the colloidal silica particles tended to locate around the ploymer particles due to the interaction between the −SiOH groups of silica and −COOH groups of polymer (see the TEM image of nanocomposite latex in Supporting Information, Figure S4). When this nanocomposite latex was cast on a substrate and forced to dry at high temperatures, as water evaporated, both colloidal silica and polymer beads codeposited. The colloidal silica particles tended to self-organize into silica framework through the hydrogen bonds or the condensation of −SiOH groups between colloidal silica particles. And this self-assembly occurred mainly around the polymer latex spheres due to the affinity of the silica particles to polymer beads. This self-assembly of colloidal silica particles caused a lot of voids and interstitial spaces, which were infiltrated by the highly mobile polymer chains (polymer latex particles with $T_g = 26$ °C). This process finally formed a periodic pore array with a comparable pore size to that of polymer beads since both the polymer spheres and colloidal silica particles were monodisperse. To confirm this possible formation mechanism, some control experiments were carried out: When the nanocomposite polymer latex was dried at room temperature for a long time (e.g., 7 days), no pores were observed in the film possibly because neither self-assembly of colloidal silica nor movement of polymer chains had happened. When either acrylic acid or colloidal silica was absent, no periodic array of pores was obtained probably because no interaction between polymer spheres and silica particles or no self-assembly of colloidal silica had ever occurred. When a polymer with much higher T_g was used, it was difficult to form this structure. Thus, the above mechanism seems to be reasonable.

In summary, in this Communication, a simple method to fabricate ordered porous polymer films has been proposed which we call the “forced drying” of water-borne nanocomposite polymer latex. In this approach, a monodisperse polymer latex and colloidal silica is blended first and then forced-drying on a substrate under relatively high temperatures to obtain the well-ordered porous polymer film directly. This process needs neither complex processes nor removal of any templates like the templating method or an organic solvent like the “breath figure” approach; therefore, it is really feasible, inexpensive, and environmentally friendly. In addition, this process can be used for a large-scale fabrication of ordered porous polymer films on any substrates (see Supporting Information, Figure S5), and the matrix of the film is composed of organic and inorganic phases. Thus, the composition and performances of the obtained porous films can be modulated. This technique presents a new paradigm in the preparations of ordered porous polymer films and may be applicable to prepare other porous films with functional organic (e.g., biocompatible, hydrophobic) and inorganic (e.g., high refractive index, magnetic, electric) components. This kind of ordered porous polymer films not only can be used in electronic devices, supports, biosensors, templates, catalysis, size- and shape-selective separation media, etc., but also the ordered porous surface structure could cause some specific surface properties; a related investigation is under way.

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Supporting Information Available: Detailed preparation procedures and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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