Fabrication of highly ordered porous structures

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(Received 16 August 2000; accepted for publication 11 October 2000)

We describe a simple method for the fabrication of highly ordered porous structures. That is, utilizing capillary forces, ultrafine particles are directly used to assemble themselves in the voids of template while the template is being assembled. The highly ordered porous structures with larger area and uniform orientation can be produced after removing the template. The majority of the single domains with uniform orientation prepared can reach 0.1 mm^2 in area. Scanning electron microscope images and transmission spectrum of these samples have confirmed the success of this simple method. © *2000 American Institute of Physics.* [S0003-6951(00)05350-X]

Currently, a great deal of attention is being paid to the fabrication of highly ordered porous materials[1–12] because of the wide range of possible applications.[13–19] For example, porous materials can be used as separation and adsorbent media,[14] catalytic surface and supports,[15,18] photonic crystal,[1,20] etc. In a popular preparation method, colloids are first crystallized as a template and then the porous structures are fabricated via a replication process. Although a variety of preparation methods have been developed, the creation of high quality porous structures with large areas is still an intellectually challenging problem.[20] The main barrier for fabricating high quality porous structures is that we must solve three challenging problems. These are (1) the fabrication of a high quality template, (2) complete infilling of the voids of the template, and (3) minimization of shrinkage after removal of the template. Since any one of these three factors can sensitively influence the final quality of the porous structure, all three of the requirements must be fulfilled at the same time. Now, large area three-dimensional templates can be fabricated by using the hydrodynamic flow method[21] or the vertical deposition method[22] and in a typical method for fabrication ordered porous structure, the voids of the template are completely filled with liquid precursors driven by capillary forces, after reaction of precursors to form the matrix, followed by the removal of the template to produce a porous structure. However, an important limitation of this method is its significant shrinkage.[6] Small shrinkage and perfect three dimensional porous structures of CdSe and CdS have confirmed the success of electrochemical method.[2] The key for the success of this method is that CdSe and CdS can be completely filled into the void of templates by electrodeposition processing. This method is very useful for fabricating semiconductor and metal-based porous structures. Another important approach is that ultrafine particles are directly used to fill the voids of the ordered template.[3,9,10] Small shrinkage after removing the template indicates that ultrafine particles are excellent candidates for fabricating porous structures. However, the random orientation of the samples fabricated by the filtration method[3] are a common situation and the gravity-sedimentary[9,10] sample generally contains polycrystalline domains of unknown size.[22] Therefore, it is not easy to fabricate highly ordered porous structures with large areas and uniform orientation by using these methods.[3,9,10] In this work, we describe a simple method to solve the three problems at the same time.

Our basic idea is to infill ultrafine particles into the voids of an ordered template directly by means of capillary forces. Figure 1 shows the schematic of the simple fabrication method used. The substrate is dipped into a slurry which contains polystyrene spheres and ultrafine particles. In contrast with the previously reported methods, we employed a vertical deposition technique, not only because the technique itself can fabricate high quality opal, but also because this fabrication method can help realize our overall strategy. The distinct feature of this method is that the fabrication of the template and the infiltration of ultrafine particles is carried out at the same time. Using this strategy, it is favorable for ultrafine particles to assemble themselves in the voids of

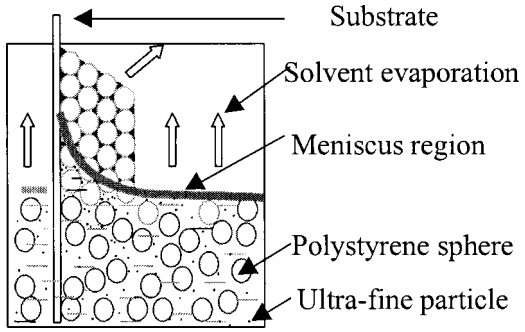

FIG. 1. Schematic of the simple method of assembly. Capillary forces are directly used to drive the ultrafine particles to assemble themselves in the ordered template while the template is being fabricated by using general vertical deposition method. The most important advantage is that this simple method can improve the assembly of the template itself due to synergistic effects.

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template, since they need only to move a short distance in the voids before assembling. Therefore, the voids can be completely filled by the ultrafine particles. Furthermore, spherical vacancies, which are common defects in samples fabricated using the self-assembly method,[22] can be immediately filled by ultrafine particles when the template is being assembled. This is favorable for the subsequent assembly of the template.

In our experiments, the monodispersed polystyrene particles were the product of Duke Scientific Corporation. Silica and titania dispersions were purchased from Catalysts and Chemical Ind. Co. Ltd. The mean size of the silica and titania particles used were 7 and 13 nm, respectively. The preparation method used was to first make a slurry by mixing the polystyrene dispersions with the silica or titania dispersions in the glass vial. Then a clean substrate was vertically dipped into the slurry in the glass vial. Subsequently the glass vial was covered with a plastic film punched through with a few fine holes to keep out any external airflow. Finally the glass vial was placed into a constant temperature and humidity chamber. The temperature and humidity was set to 50 °C and 30%, respectively. The area of the film fabricated by this method can reach about 0.5 cm^2 in 24 h. The number of layers (thickness) of the film can be controlled by the concentration of the polystyrene dispersion and by repeat deposition times using the same experimental conditions.[22] The films reported here were fabricated in a single deposition and the thickness of these films are about 3–6 μm. After removal of the template by calcination (the sample is slowly heated to 450 °C for 7 h), a high quality three-dimensional porous crystal was obtained.

Wide-view scanning electron microscope (SEM) images of the ordered porous silica structures on ITO/glass are shown in Fig. 2. The porous structures were prepared by using 406 nm polystyrene spheres and show large domains with excellent order, extending more than 100 μm [Fig. 2(a)]. Figures 2(a) and 2(b) show the presence of vertical cracks in the crystal, perpendicular to the substrate. The main feature of the domain boundaries is that they are regular, unlike classical grain boundaries. One explanation for the cracking is that it is due to the shrinkage after the removal the template by calcination. Figure 2(c) shows the highly ordered hexagonal array which is produced. The hexagonal orientation indicates the (111) plane of the fcc lattice. In Fig. 2(c) the holes connecting the pores are clearly visible. In particular, a regular triangular pattern below each hole in the first layer can be clearly observed. This is because along the (111) direction, each sphere rests on three neighboring ones below. The observation of a regular triangular pattern strongly confirms the perfect three-dimensional ordering of the structure. Figure 1(c) shows that one spherical vacancy defect in the template has been filled with ultrafine particles during the assembly process. It is this immediate mending process that greatly improves the quality of the template and the porous structure. The cracks in the porous structures are less than that in a polystyrene template fabricated under the same experimental conditions except for the absence of ultrafine particles in solution. Moreover, it has been found that through a careful observation of the entire sample by SEM, the area of the (111) orientation zone can extend to the order

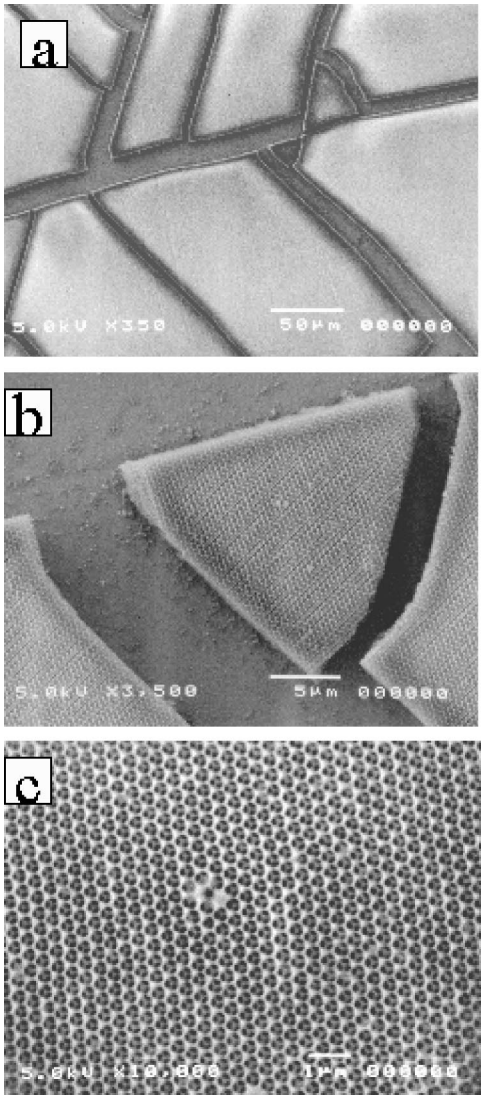

FIG. 2. (a)–(c) Scanning electron micrographs at different magnifications, illustrating the structure of the silica porous materials made using 406 nm polystyrene sphere templates on ITO/glass substrates. The initial sphere sizes were measured directly from the SEM images of ordered arrays of polystyrene spheres. All the SEM images in this study were taken with JSM-5400 scanning microscope.

of several tens of square millimeters. This suggests that the domain size for uniform structures can be potentially enhanced up to several tens of square millimeters.

Using the same experimental conditions, porous films were fabricated on quartz glass, which has a surface smoother than that of the ITO/glass substrate. From Fig. 3(a), it was found that the area of the single domains increases when compared to that on ITO/glass. The areas of most single domains exceeded 0.1 mm^2. One of the largest domains was about 0.4 mm^2. From Figs. 3(b) and 3(c), high magnification SEM images of the domain, we can clearly see the interconnecting network of macroporous structures with remarkable ordering in all three dimensions. This may be the largest single domain with uniformly oriented, highly ordered porous structure reported.[20] The results further confirm the success of our method. Similar results were obtained using different diameter polystyrene particles, or by using titania dispersions. The low shrinkage (between 3.2% and 4.6% for all the samples) confirms the high quality of infiltration using ultrafine particles.

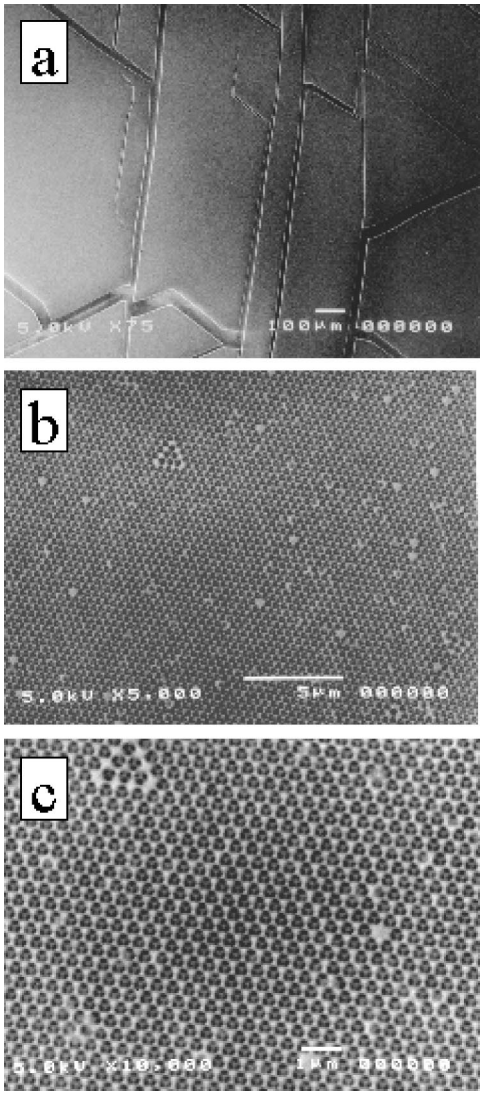

FIG. 3. SEM images of the silica porous materials made using 406 nm polystyrene sphere templates on quartz glass substrates.

Normal incidence transmittance spectra for silica samples are shown in Fig. 4 using different sizes of polystyrene spheres as templates. The first-order diffraction peaks can be clearly seen in the transmittance spectra. It should be noted that the spot size of the light beam in the transmission experiments is $12\,\text{mm}\times 2\,\text{mm}$. The results further confirm that the porous structures are highly ordered over a large area. The diffraction peak positions are at 488, 689, and 985 nm, respectively, for different ordered porous structures.

Using this simple, rapid, method we have realized the fabrication of large area, uniform orientation, highly ordered porous structures on different substrates using silica and titania. One important advantage of this simple method is that it can be used to produce porous structures using many different materials. We think this method will open up the avenue towards fabricating usable, highly ordered, porous materials, and promote more widely the various applications of porous materials.

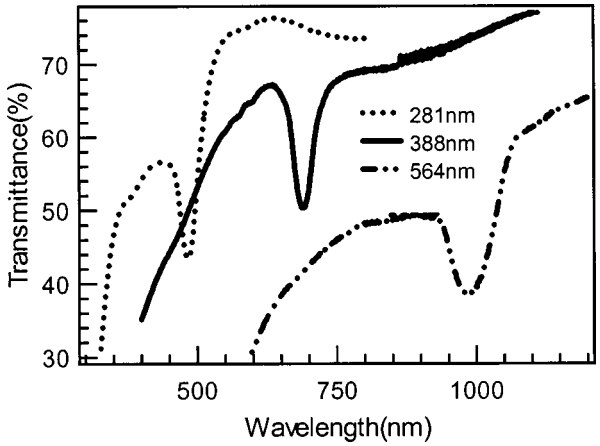

FIG. 4. Normal incidence transmission spectra of silica porous structures fabricated by using different sized polystyrene spheres as templates. The diameters of the air spheres were measured directly from the SEM images of ordered porous structures. The transmittance spectra were measured with a SHIMADZU UV-3100PC spectrometer.

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