Section 3. Synthesis and processing – carbon

Template-directed synthesis of periodic macroporous organic and carbon aerogels

Theodore F. Baumann *, Joe H. Satcher Jr.

Lawrence Livermore National Laboratory, Chemistry and Material Science Directorate, P.O. Box 808, L-092, Livermore, CA 94550, USA

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Abstract

We describe a general procedure for the synthesis of ordered macroporous resorcinol–formaldehyde (RF) and carbon aerogels (CA) in which colloidal crystals of polystyrene (PS) spheres were used as templates. With this approach, ordered arrays of PS spheres are infused with a resorcinol–formaldehyde sol–gel solution. Following gelation of the sol, the RF/PS composite was washed with toluene to remove the template. Periodic macroporous RF aerogels were obtained after supercritical drying with liquid carbon dioxide. These materials can then be carbonized under a nitrogen atmosphere to afford the corresponding macroporous CAs. Scanning electron microscopic examination shows that both the organic and carbon materials consist of many hexagonally ordered domains of spherical cavities with different crystal orientations, reflecting the symmetry of the original PS template.
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1. Introduction

The synthesis of periodic macroporous solids [1] is currently an active area of research since materials of this type are being investigated for a wide range of applications including catalysis, separation technology, energy storage and conversion, photonic crystals, and nanoelectronics. A common method for the preparation of the three-dimensionally ordered macroporous solids utilizes close-packed arrays of monodisperse spheres (typically silica or polystyrene) as templates. In this approach, the interstitial regions of the colloidal crystals are infused with a reaction solution of the material that will eventually comprise the replicate structure. Once the composite forms, the template is removed, either chemically or thermally, yielding the macroporous replicate solid with periodic voids in the 0.1–1 μm size range. A variety of macroporous materials have been prepared by this method, including silica [2–8], metal oxides [9–18], metals [19–28], carbon [29–32], polymers [33–39] as well as other materials [40,41]. A promising extension of the template approach towards ordered porous materials of higher complexity is the development of methods that allows one to tailor composition and porosity of the wall structure defining the macropores. Such an advance will be extremely important in the design of new ordered macroporous materials for catalysis, separations, and sensor applications.

With the work presented here, our goal was to apply organic sol–gel chemistry to the template-assisted preparation of periodic macroporous materials. Since organic sol–gel chemistry provides a straightforward method to control the textural porosity and the composition of the aerogel matrix, utilization of this technique in the preparation of ordered macroporous solids should provide control over the properties of wall structure in these materials. For example, organic aerogels are typically

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* Corresponding author. Tel.: +1 925 423 5543; fax: +1 925 423 4897.
E-mail address: baumann2@llnl.gov (T.F. Baumann).

prepared through the base-catalyzed sol–gel polymerization of resorcinol with formaldehyde in aqueous solution to produce gels that are dried in a supercritical fluid [42]. The mesoporosity of the resultant aerogel is determined by the resorcinol-to-catalyst (R/C) ratio used in the sol–gel reaction [43]. Therefore, using this technique in the preparation of ordered macroporous solids, materials with bimodal pore structures can be prepared in which the large ordered cavities are continuous and interconnected, and the smaller mesoporous channels interconnect the macropores throughout the structure. Materials with such hierarchical pore structures are advantageous for a number of applications due to the increased mass transport of the large ordered cavities and the high specific surface area of the meso- and micropores of the wall structure. In addition, we have demonstrated that the composition of organic and carbon aerogels can be tailored through the sol–gel polymerization of resorcinol derivatives [44,45]. With this approach, inorganic or organic species can be homogeneously incorporated into the aerogel matrix in a uniform fashion. To demonstrate the flexibility associated with organic sol–gel chemistry in the preparation of ordered macroporous materials, we recently reported the first examples of ordered macroporous carbon aerogels that contained homogeneously incorporated metal nanoparticles and exhibited high surface areas [46]. The work presented in this paper describes a general procedure for the synthesis of ordered macroporous resorcinol–formaldehyde (RF) and carbon aerogels in which colloidal crystals of polystyrene spheres were used as templates. The physical characterization of these ordered porous materials will also be presented.

2. Experimental

2.1. Sample preparation

The suspensions of monodisperse polystyrene (PS) spheres (300 and 450 nm) were obtained from Duke Scientific Corporation (Palo Alto, CA). All other chemicals were obtained from Aldrich and used as received. The resorcinol–formaldehyde sol–gel (RF) solution was prepared by dissolving resorcinol (1.23 g, 0.011 mol), a 37% solution of formaldehyde (1.79 g, 0.022 mol), and $Na_2CO_3 \cdot H_2O$ (40 mg, 0.32 mmol) in 0.7 ml of distilled water. This particular formulation gels in ∼4 h at RT so the sol–gel solution was typically prepared 0.5 h before the template was ready for infiltration. The PS spheres (0.1 vol.% solution in water) were filtered through a 25 mm diameter polycarbonate membrane (100 nm pore size), which was mounted on a filter stand with a stainless-steel membrane support. A small pressure drop across the membrane sustained the filtration. The PS particles accumulated on the membrane surface

as closely packed 3-D ordered layers, the thickness of which depends on the duration of filtration. Layer thickness of 20–30 μm can be collected in ∼3 h, while layers thickness of 1–2 mm required 2–3 d. The ordered lattice was washed briefly with water and the sol–gel solution was infused into the interstitial regions of the template using filtration. When infiltration of the RF solution into the PS template was complete, the filtration was stopped, the apparatus was sealed with a septum, and the RF solution was allowed to gel at room temperature overnight. The PS/RF composite was then removed from the filtration apparatus and the pinkish monolith was soaked in toluene for 24 h to remove the PS template. The wet RF gel was washed with acetone to exchange toluene and residual water and the part was then dried with supercritical CO_2 ($T_c = 31.1$ °C, $P_c = 7.4$ MPa). The dried aerogel was obtained as a pink monolith that exhibited opalescence when illuminated with white light. The macroporous RF aerogel was carbonized under N_2 at 2 °C min^{-1} to 1050 °C followed by a 3 h hold at 1050 °C, affording the material as a black monolith.

2.2. Physical characterization

Bulk densities of the untemplated and templated aerogels were determined by measuring the dimensions and mass of each monolithic sample. Surface-area determination and pore-volume and -size analysis were performed by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods using an ASAP 2000 Surface Area Analyzer (Micromeritics Instrument Corporation) [47]. Samples of approximately 20 mg were heated to 100 °C under vacuum (10^{-5} Torr) for at least 24 h to remove all adsorbed species. Nitrogen adsorption data were then taken at five relative pressures from 0.05 to 0.20 at 77 K to calculate the surface area by BET theory. Scanning electron microscopy (SEM) of the macroporous solids was performed on a Hitachi S-4500 cold field-emission scanning electron microscope. Secondary electrons were used for imaging at acceleration voltages between 1.8 and 2.0 kV. Samples were examined as received and no conductive coatings were applied.

3. Results

The first step in the preparation of the macroporous aerogels is the assembly of the colloidal crystal template. Formation of an organized 3-D array was achieved by increasing the volume fraction of monodisperse PS particles against a flat surface. This approach has been used previously to assemble templates for the preparation of other ordered macroporous materials [3]. Filtration of a dilute solution of either 300 or 450 nm PS particles

through a smooth narrow-pore membrane allowed for the accumulation of closely-packed 3-D ordered layers on the membrane surface. We chose to prepare our template by filtration over other methods, such as sedimentation or centrifugation, for three reasons: (1) the template could be assembled in a short period of time; (2) we could control the thickness of the template; and (3) filtration could be used to infuse the RF sol–gel solution into the template. Examination of a dried colloidal crystal by scanning electron microscopy (SEM) showed that the template was composed of completely crystalline domains with different orientations, most of which exhibit hexagonal packing of the latex spheres. The dried templates also exhibited bright red and green reflections due to the diffraction of light in the ordered lattices. These results are in agreement with other reports that used filtration to organize latex templates.

Once assembled, the interstitial regions of the crystal template were infiltrated with a freshly prepared RF sol–gel solution (Fig. 1). Penetration of the RF sol into the template occurred quite rapidly using filtration and, after gelation, the resulting latex/RF composites were obtained as thin monolithic disks. The template was removed from the aerogel by washing with toluene and the replicate gel was dried using supercritical carbon dioxide. The macroporous organic aerogel was isolated as a pinkish monolith that exhibited an opalescent sheen when illuminated with white light (Fig. 2). The bulk density of the macroporous RF monolith was determined to be 250 mg cm^{-3}. On the basis of the work with untemplated RF gels prepared by the same formulation, the skeletal density of the porous aerogel is estimated to be ~600 mg cm^{-3}. Pyrolysis of the material at 1050 °C under nitrogen carbonizes the aerogel matrix, generating

Fig. 2. Photograph showing the opalescence of an ordered macroporous RF aerogel. While the entire monolith is templated, only the center of the material appears opalescent at this angle when illuminated with visible light due to surface curvature. The dark material around the edge of the disk is untemplated RF aerogel.

the macroporous carbon aerogel (CA) as a black disk that did not show the opalescence of the pre-carbonized material. Following pyrolysis, the bulk density of the macroporous carbon monolith was measured at 400 mg cm^{-3}, while the skeletal density of the material was ~1000 mg cm^{-3}.

The macropore architectures of the ordered RF and carbon aerogels were examined using SEM (Figs. 3 and 4). From the micrographs, it can be seen that both the RF and carbon aerogels are macroporous materials consisting of large 3-D ordered arrays of spherical cavities. The micrographs show that the macropore structure in both aerogel samples consists of hexagonally ordered domains of spherical cavities with different crystal orientations, reflecting the symmetry of the original PS template (Fig. 3(a)). For the RF aerogel, the sizes of the voids are close to the size of the original PS spheres, indicating that template removal through dissolution with toluene does not significantly perturb the overall void network (Fig. 3(b)). It is these ordered lattices of voids that are responsible for the opalescence observed in these materials. An untemplated RF aerogel is typically dark red in color, yet the templated aerogel exhibits brightly colored reflections when illuminated with white light. Within each void are smaller circles that represent interconnections to neighboring spherical void. These points correspond to regions where the polystyrene spheres were in contact with one another in the colloidal crystal. Apparently, the RF solution was unable to completely penetrate the narrow regions around the contact points between latexes in the template. Interconnections of this type have been observed in other replicate solids prepared using colloidal crystal templates.
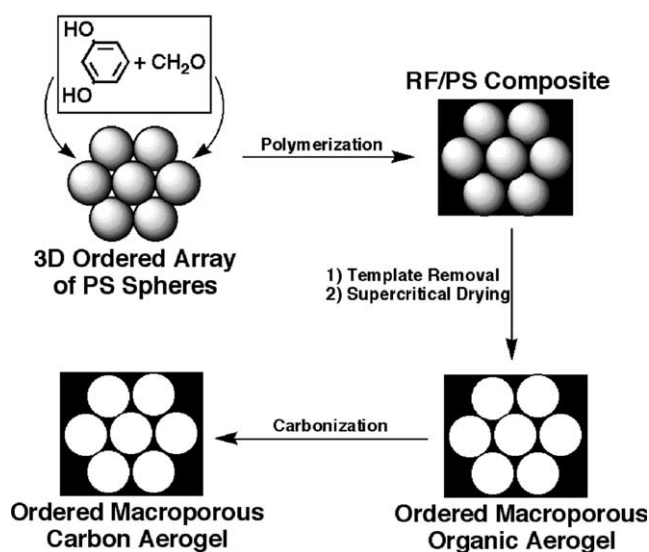

Fig. 1. Schematic illustration for the template-assisted preparation of the ordered macroporous organic and carbon aerogel using colloidal crystals of polystyrene spheres as the template.
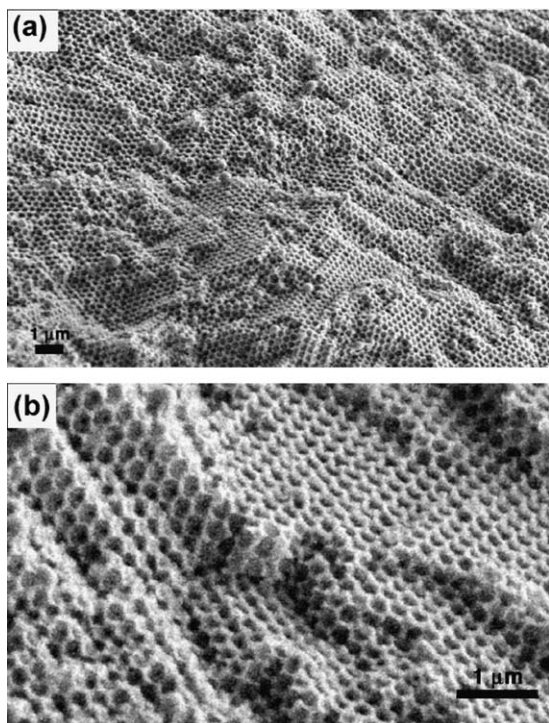
Fig. 3. Scanning electron micrographs of the replicate RF aerogel prepared using ordered arrays of 300 nm PS spheres as a template: (a) typical low magnification image and (b) higher magnification micrograph of a domain of highly ordered pores.
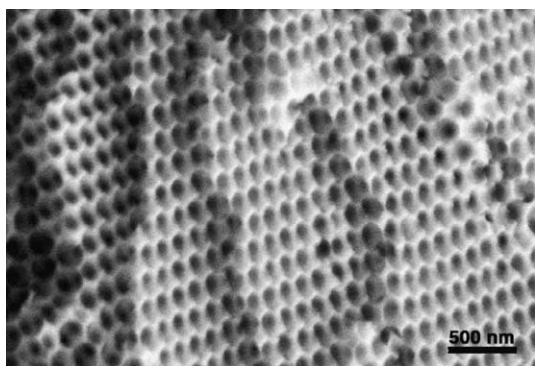

Fig. 4. Scanning electron micrograph of a macroporous carbon aerogel following pyrolysis at 1050 °C under nitrogen of the ordered macroporous RF aerogel formed using ordered array of 300 nm PS spheres as a template.

The overall macroporous structure of the RF aerogel is retained in the carbonized material (Fig. 4). The main difference between the two systems is that the sizes of the macropores in the carbonized material are 40–50% smaller than the sizes of the voids in the uncarbonized material. The shrinkage of the ordered lattices in the carbon material is most likely related to the carbonization process. During pyrolysis, carbon aerogels undergo significant mass loss, leading to volumetric shrinkage and densification relative to their pre-carbonized counter-

parts. For the material presented here, the shrinkage of the aerogel architecture during carbonization results in a reduction of the void sizes in the macropore network. This change, however, occurs in a uniform fashion and does not significantly alter the spherical shape of the voids. We also prepared macroporous CAs by an alternative method in which the RF/PS composite was dried using supercritical CO_2 and the template was removed thermally during the carbonization step. The SEM examination of that material reveals ordered arrays of macropores similar to the aerogels in which the template was removed chemically (Fig. 5). This method, however, does appear to generate some deformation of the voids in the hexagonal lattice. This approach of RF carbonization with concomitant PS template removal has been reported previously for the preparation of non-ordered mesocellular carbon foams [48].

The textural properties of the macroporous organic and carbon aerogels were characterized by nitrogen adsorption/desorption techniques. Both sets of aerogel materials exhibited a Type II nitrogen isotherm, consistent with a macroporous adsorbent [49]. In the case of the ordered macroporous RF aerogel, the isotherm shows a hysteresis loop at higher relative pressures, a feature that is typically associated with capillary condensation within mesopores, indicating that textural mesoporosity exists within the wall structure. For the ordered RF materials, the average BJH pore diameter was ∼9 nm, giving rise to a BET surface area of ∼72 $m^2 g^{-1}$. The surface areas of the ordered macroporous CAs were typically lower (∼25 $m^2 g^{-1}$) than those of their uncarbonized counterparts. This difference may be due to the fact that carbonization of RF aerogels prepared under high catalyst conditions (low R/C ratios) leads to a significant decrease in the surface area of the CA relative to the pre-carbonized material. It has been shown previously that the small primary particles of the RF aerogel tend to fuse together during pyrolysis,
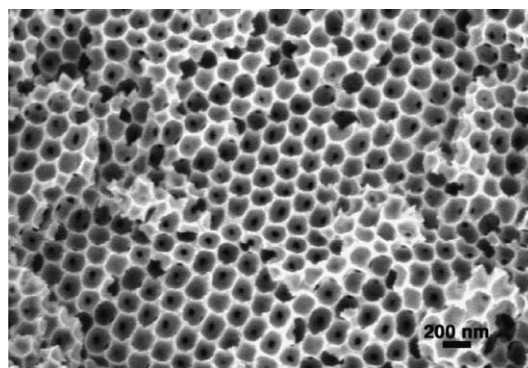

Fig. 5. Scanning electron micrograph of a macroporous carbon aerogel following thermal removal of the colloidal crystal template (450 nm PS spheres).

leading to larger particles in the carbonized state and the concomitant loss of surface area [50]. Since these macroporous aerogels was prepared under high catalyst conditions as well, this same effect may be responsible for the low surface area in the macroporous CA. Nevertheless, the procedure presented here is general and the sol–gel formulation used to prepare the macroporous solids can be changed to target materials with higher surface areas, as has been previously demonstrated [46].

4. Discussion

To demonstrate the feasibility of our approach, we selected a sol–gel formulation in the template-directed synthesis of the ordered macroporous organic aerogels that would generate a relatively dense RF matrix (600 mg cm^{-3}) so that the replicate structure would be robust enough to withstand the removal of the template. In addition, the resorcinol-to-catalyst ratio (R/C = 35) was adjusted so that the organic gel would set within 4 h without a heat cure cycle. We have since demonstrated that other sol–gel formulations can be used to prepare ordered macroporous aerogels [46]. Nevertheless, the formulation utilized in the work presented here indicated that organic sol–gel chemistry can indeed be used to create novel porous materials that exhibit hierarchical pore structures.

From the SEM examination, it is clear that preparation of macroporous aerogels by this method results in volume-templated structures [29], as opposed to surface-templated structures [10] that are obtained using inorganic sol–gel techniques or chemical vapor deposition. In volume-templated structures, the material grows both in the voids between the building blocks of the template as well as on the surfaces of the individual spheres. This motif is evident in the material prepared here due to the fact that the RF gel not only completely fills the template but also forms in the gaps and cracks of the colloidal crystal. By contrast, surface-templated structures mainly form on the surfaces of the template, forming shells around the spheres, but do not grow into the grain boundaries. The advantage of volume-templated structures is that a higher volume fraction of solid material is obtained compared to surface-templated structures. Since the solid material that comprises the walls in these ordered macroporous aerogels is inherently mesoporous, porous structure with extremely high surface areas can be prepared. As mentioned earlier, materials with hierarchical pore structures should exhibit enhanced properties over materials with single-sized pores due to increased mass transport through the larger ordered macropores while maintaining the high specific surface area of the meso- and microporous wall structure. In addition, these mesoporous channels can serve as interconnections between the larger voids and provide access to supported catalysts or binding sites within the wall structure. These features are important in the design of materials for sensors, separations, and catalysis applications.

5. Conclusions

The synthesis of periodic macroporous solids is currently an active area of research since materials of this type can impact a wide range of applications. In this report, we describe a general procedure for the synthesis of ordered macroporous resorcinol–formaldehyde (RF) and carbon aerogels in which colloidal crystals of polystyrene spheres were used as templates. With this approach, ordered arrays of latex spheres are infused with an organic sol–gel solution and, following chemical removal of the template and supercritical drying, periodic macroporous RF aerogels are obtained. These materials can then be carbonized under a nitrogen atmosphere to afford the corresponding macroporous CAs. SEM examination shows that both the organic and carbon materials consist of many hexagonally ordered domains of spherical cavities with different crystal orientations. One of the benefits of this technique is that it is general and a variety of organic sol–gel formulations can used to prepare ordered porous materials. We are currently applying this procedure to the preparation of new periodic macroporous aerogels that are doped with either organic or inorganic species. We anticipate that such materials should exhibit interesting new catalytic or transport properties.

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