Mesoporous Materials

Preparation of Mesoporous Silica Monoliths with Ordered Arrays of Macrochannels Templated from Electric-Field-Oriented Hydrogels**

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The fabrication of ordered inorganic arrays of varying length scales and with multimodal porosities is of practical importance owing to their potential application in many areas of materials chemistry, including catalysis and separations science.[1,2] A common approach to the controlled synthesis of this class of materials, first exploited in the synthesis of the MCM-41 family of molecular sieves, is to polymerize the inorganic phase around an organic template by using a sol–gel process.[3] The organic phase is then removed by calcination leaving a void space that is a replica of the size, orientation, and arrangement in space of the template. By using multiple templates of different length scales, hierarchically porous inorganic structures containing various combinations of micro-, meso-, and macropores have been realized.[4–9] We report herein the creation of a mesoporous silica monolith that contains oriented macroporous channels, which is achieved by the application of an electric field to a hydrogel template during polymerization and cross-linking.[8,9] To the best of our knowledge, this is first time an external electric field has been used to create ordered, hierarchical meso-/macroporous silicate materials.

The template matrix is created through the electrical alignment of a polyacrylamide hydrogel, which is accomplished by copolymerizing a mixture of acrylamide functionalized with immobiline and bisacrylamide in the presence of an electric field (60 $V\,cm^{-1}$). The presence of this field creates interstitial voids of approximately 10 μm in diameter. The channel structure, which can be imaged through confocal microscopy, is present in the field-oriented hydrogel (Figure 1a), but is replaced by a disordered structure (Figure 1b) when no field is applied.

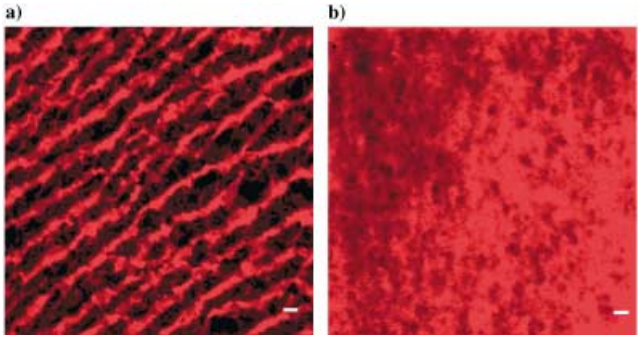

Figure 1. Fluorescence images of rhodamine-stained polyacrylamide hydrogels obtained by confocal laser scanning microscopy. The samples were polymerized in the presence (a) and the absence (b) of an externally applied electric field. Field of view: 210×210 μm^2; bar = 10 μm.

The silicate phase is introduced through the immersion of a freestanding hydrogel monolith in neat tetramethylorthosilicate (TMOS). Hydrolysis and condensation occurs as the TMOS infuses the hydrogel and reacts with water trapped in the voids. After a period of 24 h a hard solid white monolith, close in size to the hydrogel template, is formed. Calcination under O_2 at 500 °C removes the organic phase leaving a porous silica monolith.

Scanning electron micrographs of this material, imaged parallel to the electric field direction (Figure 2a), show striations oriented in the field direction. No such features are observed when the disordered template is used, which suggests that the channel/hydrogel interface is replicated

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[**] This work was supported by the NSF (CHE-20023105) and the American Chemical Society Petroleum Research Fund (37278-G5). We thank Kim Riddle and John Ekman for technical assistance with microscopy.

 DOI: 10.1002/ange.200352813

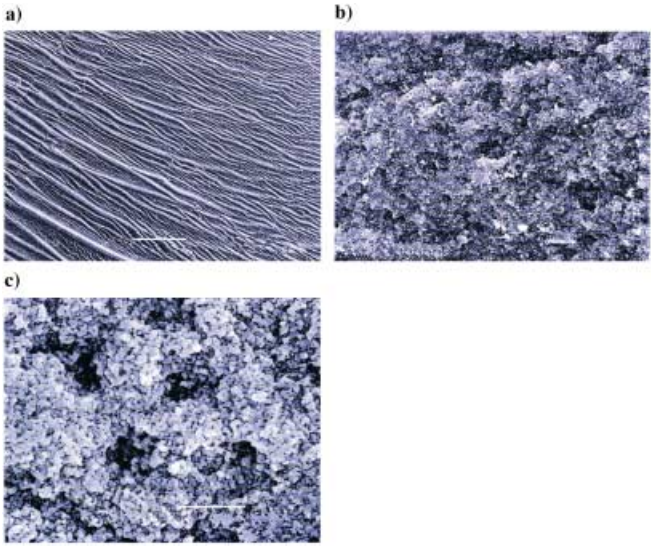

Figure 2. Scanning electron micrographs of calcinated silica monoliths created in electric-field-aligned polyacrylamide gels. The "striped" surfaces in (a) have a parallel orientation to the original electric field, whereas the "dotted" surface in (b,c) is perpendicular to the field vector. Field of view: a) $580\times435\ \mu m^2$; bar = 100 μm b) $110\times85\ \mu m^2$; bar = 10 μm, and c) $48\times37\ \mu m^2$; bar = 10 μm.

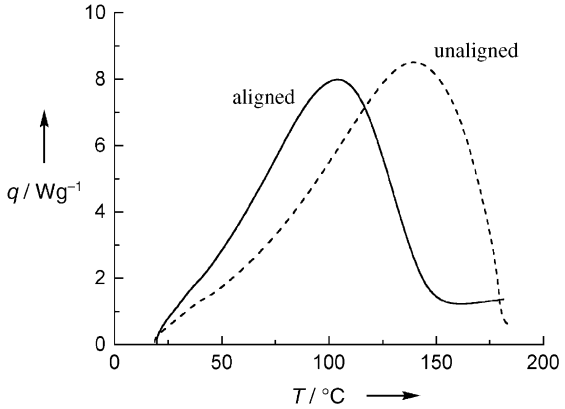

Figure 3. DSC measurements, collected at 20 K min^{-1}, of water desorption from templated silica. The solid and dashed lines correspond to material created in electric-field-aligned and unaligned hydrogels, respectively; q = heat flow.

during silicate formation. In general, hierarchical meso-/macroporous solids are made by using dual templates with the macropore region defined by a range of organized media at that scale length, including colloidal crystals of polymer spheres and even bacterial threads.[10–13] In the electric field oriented hydrogels the channels are empty and, potentially, can be filled with silica. However, prior to hydrolysis, TMOS has much greater solubility in the hydrogel itself and, as such, silicate formation preferentially occurs in this region during the initial stages of the reaction. This process defines an interface, as seen in the SEM image, and restricts the amount of silicate that reaches the channels, thus resulting in low-density silicate structures in the macrovoids. These structures are related to the difficult problem of achieving stable replicas of large voids (< 100 nm) in inorganic mineralization that was discussed by Mann and co-workers.[7] Evidence for these low-density regions can be seen in the bulk density, which is 0.806 g mL^{-1} for materials made from the field-oriented template and 0.960 g mL^{-1} for those made from a disordered hydrogels.

Figure 2b shows an SEM image of a field-oriented sample cut perpendicular to the field direction. In this orientation, the columns of low-density silica should appear as orifices of about 10 μm in diameter. The channel openings are vaguely discernible in the image but are occluded. However, after brief exposure to etching conditions (5 s immersion in 47% HF followed by neutralization in base), the openings of the channels (Figure 2c) are clearly evident, indicating that silica has been selectively removed from the low-density regions in the channels.

The effect of these channels on the physiochemical properties of the bulk materials can be demonstrated in a relatively straightforward fashion. Figure 3 shows differential scanning calorimetry (DSC) traces for water desorption from porous silica made from disordered and field-oriented templates. The field-oriented materials have an endotherm associated with desorption over a narrower temperature range with a maximum at 115 °C, close to the boiling point of pure water. Conversely, the disordered, purely mesoporous materials, have a broad desorption endotherm with a maximum at 150 °C. These differences are attributable to water acting as a pure liquid because of the large voids in which it is sequestered in the ordered material. Water trapped only in the mesoporous voids, which has a significant amount of interaction with the silica surface, desorbs over a wider temperature range and at a high average energy.

Information about the micro- and mesoporous regions of a hierarchically ordered material can be obtained through nitrogen-physisorption measurements. Isotherms collected on silica monoliths fabricated from both disordered and field-oriented hydrogels show a distinct hysteresis loop and are unambiguously of type IV which is characteristic of a mesoporous solid.[14] A BET (Brunauer, Emmett, and Teller) surface area of 314 and 337 m^2 g^{-1} for the disordered and oriented materials, respectively, is obtained from the isotherms.[15] The specific hysteresis loop displayed by the materials is one in which the desorption isotherm gradually diverges from the adsorption isotherm at high values of p/p^0 (p is the pressure of the gas, p^0 is the saturation pressure of the adsorbate) and then abruptly closes when the pores empty (type H3 in IUPAC notation). This is characteristic of slit-type pores found in adsorbents composed of plate-like particles in which the mechanisms of filling and emptying are completely different.[14] Such structures are directly evident in the SEM images of these materials (Figure 2b,c), which show that the walls between the channels, where the TMOS has penetrated the hydrogel network, consist of flat particles of ≈1 μm dimension. The single-point pore volumes were determined from the isotherms to be 0.52 and 0.73 cm^3 g^{-1}, with an average pore diameter 66.2 and 86.3 Å for the disordered and field-oriented matrices, respectively.

In summary, we have shown that ordered micrometer-scale arrays within organic templates are recovered in silica monoliths upon treatment with tetramethylorthosilicate and

subsequent calcination. The underlying idea exploits the self-organization of periodic density patterns within the organic gel that we induce by using an externally applied electric field during polymerization. This approach allows the indirect, internal patterning of silica yielding hierarchical arrays of large aspect ratio in a highly efficient way. The anisotropic features of the silica monoliths fabricated could make them interesting materials for separation science and related applications.

Experimental Section

Preparation of polyacrylamide gels: Aligned and unaligned polyacrylamide gels were synthesized in a FisherBiotech vertical electrophoresis unit (FB-VE10-1) that was connected to a Bio-Rad power supply (Powerpac 3000). The electric-field-induced alignment was achieved by applying a constant voltage of 600 V to the polymerizing system. This procedure is similar to one reported by Charlionet et al. for the synthesis of oriented polyacrylamide gels for quick analysis of proteins and DNA.[16]

In a typical preparation, 0.70 g acrylamide (Fluka), 90 mg, *N*,*N*′-methylenebisacrylamide (Fluka), 0.25 mL of immobiline (0.20 M stock solution of *N*-acryloyl glycine; Pharmacia) and 0.25 g polyethylene glycol (Fluka) were added to 9.75 mL of distilled water. The freshly prepared solution was deoxygenated by purging with nitrogen. After the addition of 12.5 μL of ammonium persulfate (10% w/v; Fluka) and 20 μL of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.002 M; Aldrich), the stirred solution was transferred between two, previously silanized, glass plates spaced at 3 mm. A 1.5% agarose gel was used to prevent leakage within the vertical electrophoresis unit. The upper buffer solution of the electrophoresis unit contained 200 mM Tris (Pharmacia), 50 mM glycine (USB), and 2 mM ammonium persulfate, whereas the lower buffer contained 200 mM Tris and 50 mM glycine.

Preparation of silica gels: Tetramethylorthosilicate (98%; Aldrich) is vacuum distilled directly before use. A section of hydrogel is added to neat TMOS and is allowed to react overnight. The silica-loaded sample is removed and allowed to dry in air. The samples were then calcined at 500 °C under oxygen.

Received: September 8, 2003 [Z52813]

Keywords: gels · materials science · mesoporous materials · polymerization · silicon

[1] P. T. Tanev, M. Chibwe, T. J. Pinnavaia, *Nature* **1994**, *368*, 321.
[2] Y.-N. Jun, D. M. Dabbs, I. A. Aksay, S. Erramilli, *Langmuir* **1994**, *10*, 3377.
[3] N. K. Raman, M. T. Anderson, C. J. Brinker, *Chem. Mater.* **1996**, *8*, 1682.
[4] B. Lebeau, C. E. Fowler, S. Mann, C. Farcet, B. Charleux, C. Sanchez, *J. Mater. Chem.* **2000**, *10*, 2105.
[5] B. J. Zhang, S. A. Davis, S. Mann, *Chem. Mater.* **2002**, *14*, 1369.
[6] S. D. Sims, D. Walsh, S. Mann, *Adv. Mater.* **1998**, *10*, 151.
[7] M. Breulmann, S. A. Davis, S. Mann, H. P. Hentze, M. Antonietti, *Adv. Mater.* **2000**, *12*, 502.
[8] R. A. Caruso, J. H. Schattka, *Adv. Mater.* **2000**, *12*, 1921.
[9] R. A. Caruso, M. Antonietti, *Adv. Funct. Mater.* **2002**, *12*, 307.
[10] O. D. Velev, P. M. Tessier, A. M. Lenhoff, E. W. Kaler, *Nature* **1999**, *401*, 548.
[11] Y. J. Lee, J. S. Lee, Y. S. Park, K. B. Yoon, *Adv. Mater.* **2001**, *13*, 1259.
[12] S. A. Davis, S. L. Burkett, N. H. Mendelson, S. Mann, *Nature* **1997**, *385*, 420.
[13] D. Y. Zhao, P. D. Yang, B. F. Chmelka, G. D. Stucky, *Chem. Mater.* **1999**, *11*, 1174.
[14] S. J. Gregg, K. S. W. Sing, *Adsorption, Surface Area and Porosity*, 2nd ed., Academic Press, London, **1982**, p. 131.
[15] S. Brunauer, P. H. Emmett, E. Taller, *J. Am. Chem. Soc.* **1938**, *60*, 309.
[16] R. Charlionet, N. MachourMerlet, S. Leclerc, J. J. Malandain, *Electrophoresis* **1997**, *18*, 1133.

