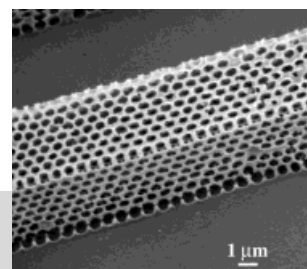


Patterning Porous Oxides within Microchannel Networks**

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A continuing challenge for materials chemists and engineers is the ability to create multifunctional composite structures with well-defined superimposed structural order from nanometer to micrometer length scales. Materials with three-dimensional structures ordered over multiple length scales can be prepared by carrying out colloidal crystallization and inorganic/organic cooperative self-assembly within microchannel networks. The resulting materials show hierarchical ordering over several discrete and tunable length scales ranging from several nanometers to micrometers. These patterned porous materials hold promise for use as advanced catalysts, sensors, low- k dielectrics, optoelectronic and integrated photonic crystal devices.

1. Introduction

Nature abounds in hierarchical structures that are formed through highly coupled and often concurrent synthesis and assembly processes over both molecular and long-range length scales.^[1] The existence of these structures such as abalones and diatoms has both biological and evolutionary significance. It has been a long-sought goal to mimic the natural processes responsible for these exquisite architectures using so-called biomimetic strategies to control the structural organization.

Several approaches are currently available for the preparation of ordered structures at different length scales. For example, organic molecular templates can be used to form zeolitic structures with ordering lengths less than 3 nm,^[2] mesoporous

materials with ordering lengths of 3–30 nm can be obtained through inorganic/organic cooperative assembly using surfactants or amphiphilic block copolymers as the structure-directing agents,^[3–6] the use of latex spheres affords macroporous materials with ordering lengths of 100 nm–1 μm ,^[7–19] and soft lithography can be used to make high-quality patterns and structures with lateral dimensions of about 30 nm to 500 μm .^[20–22] Recently, we demonstrated that by carrying out specific self-assembly processes within a microchannel network, it is possible to create porous structures that are ordered over multiple length scales (Fig. 1).^[23,24] These self-assembly processes include colloidal crystallization and surfactant templating. As a result, microporous, mesoporous, and macroporous materials can be directly patterned on the substrates. This article reviews recent progress in the synthesis, characterization, and potential applications of these patterned porous materials.

2. Patterned Mesoporous Oxides

Previously, micromolding has been used to form patterned mesoporous materials.^[25,26] These studies, however, used acidic aqueous conditions to carry out the cooperative self-assembly,^[27] which is disadvantageous because of the poor processibility of the aqueous solutions. Either non-continuous films were formed or an electric field was needed to guide the mesophase growth.^[26]

Scheme A in Figure 1 illustrates the procedure that we used to fabricate patterned mesoporous materials. Here, the gelation of a self-assembling sol–gel precursor solution was carried

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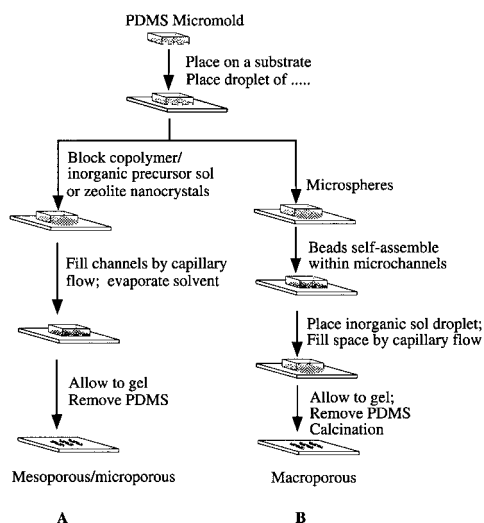


Fig. 1. Schematic diagrams of the fabrication process for patterning A) mesoporous/microporous and B) macroporous oxides on a substrate.

out in the microchannels formed between a poly(dimethylsiloxane) (PDMS) mold and a substrate.^[20] The precursor solution has the same composition as used in the preparation of mesoporous silica films,^[4,28] and is a homogeneous mixture of poly(ethyleneoxide)-*b*-poly(propyleneoxide)-*b*-poly(ethyleneoxide) (EO_nPO_mEO_n), tetraethylorthoxysilicane, ethanol, HCl, and H₂O. When the block copolymer Pluronic F-127 (EO₁₀₆PO₇₀EO₁₀₆) is used as the structure-directing species, a cubic mesophase results, while a hexagonal mesophase is obtained when Pluronic P-123 (EO₂₀PO₇₀EO₂₀) is used.^[28] The area of the patterned surface was typically 1–5 cm² with molded feature sizes in the micrometer size range. After removing the mold, the patterned material was calcined at 400 °C in air for 5 h to remove the amphiphilic block copolymer species and thereby produce patterned mesoscopically ordered porous solids.^[23] Recently, zeolite nanocrystals were used to fill the microchannels and to form patterned microporous solids.^[29]

Figure 2 shows several representative scanning electron microscopy (SEM) images of the patterned mesoporous materials. The structural ordering observed at the micrometer level is imparted by the microchannel network, while the mesoscopic ordering results from the self-assembly of the sol-gel block copolymer/inorganic solution. Both continuous (Fig. 2A) and isolated (Fig. 2B, formed by micromolding process^[23]) features can be produced. Mesoscopic ordering in these materials is characterized by low-angle X-ray diffraction and transmission electron microscopy (TEM) studies.^[28] The material shown in Figure 2A is hexagonal mesoporous silica (cell parameter *a* ~ 10.5 nm), while that in Figure 2B is cubic mesoporous silica (cell parameter *a* ~ 11 nm). The smallest line feature we have obtained with this process is about 100 nm. This hierarchical ordering process can be further extended to the preparation of other patterned mesoporous metal oxides, such as TiO₂, using sol-gel mesophase self-assembly chemistry.^[5]

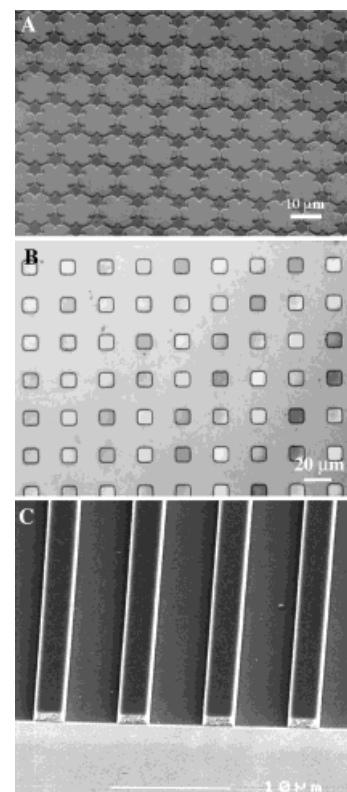


Fig. 2. A) SEM image of patterned continuous mesoporous silica, B) optical image of patterned isolated mesoporous silica, C) SEM image of patterned mesostructured silica waveguides. Reprinted with permission from Science, Copyright 1998, American Association for the Advancement of Science.

Combining the patterning capabilities of and the high porosities achievable (~70 %)^[28] for such mesoporous silica structures, they are extremely promising for use in low-dielectric materials related to the miniaturization of electronic circuits and devices. In addition, these patterned mesoporous silica can be potentially used as waveguides and sensor arrays.^[24,30] For example, when mesostructured silica (Fig. 2C, hexagonal mesophase without calcination) was patterned on a mesoporous silica thin film, waveguiding can be enabled due to the low-refractive-index mesoporous SiO₂ thin film support. Figure 3A shows a typical input and output beam profile for a half-millimeter-long waveguide array. No scattering is visible along the waveguides, indicating high smoothness of the surfaces.

When doped with rhodamine 6G, these waveguides exhibited an amplified spontaneous emission, with low thresholds of 10–25 kW cm⁻². These thresholds are an order of magnitude lower than has been reported for sol-gel glass waveguides.^[31] This is attributed to the ability to incorporate the luminescing species within the high surface area ordered mesopores of the waveguides, which results in a homogeneous dye distribution that maintains high dispersion and isolation of the individual dye molecules at relatively high dye concentrations. The gain-narrowed emission (577 nm) is from the end of the waveguides and directed parallel to their axes. Figure 3B shows an optical image of the axial output beams

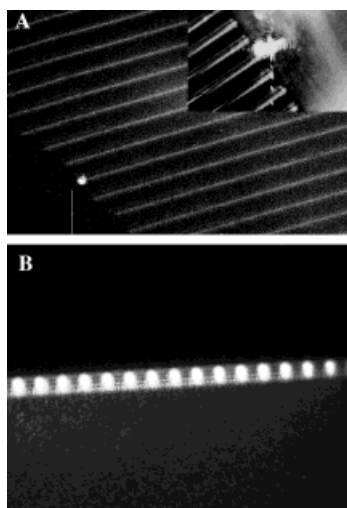


Fig. 3. A) Optical image demonstrating the waveguiding capability of the patterned mesostructured silica composite arrays. The inset shows the single-mode optical fiber used to couple light into an individual waveguide. Each waveguide has a width of 2.4 μm . B) Optical image of the axial output beams (amplified spontaneous emission) recorded using a CCD camera. Reprinted with permission from Science, Copyright 2000, American Association for the Advancement of Science.

recorded using a charge coupled device (CCD) camera when the patterned mesostructured lines (Fig. 2C) were pumped with a Nd:YAG laser (532 nm) above the threshold power density.^[24] These highly processible, self-assembling mesostructured hosts offer great potential for the one-step fabrication of microlaser arrays and components for integrated optical circuits and microanalytical applications.

More recently, researchers at Sandia National Laboratories successfully combined silica-surfactant self-assembly with three rapid printing procedures—pen lithography, ink-jet printing, and dip-coating of patterned self-assembled monolayers—to form functional, hierarchically organized structures in seconds.^[32] This high speed fabrication process may prove useful for directly writing sensor arrays and fluidic or photonic systems.

3. Patterned Macroporous Oxides

Ordered macroporous materials with pore sizes in the sub-micrometer range have attracted much interest recently because of their potential application in fields such as catalysis, separation, and photonics. Macroporous oxides,^[7–11] semiconductors,^[12] metals,^[13–15] as well as polymers^[16–19] with well-defined pore sizes in the sub-micrometer regime have been successfully synthesized. In order to fabricate these macroporous materials into useful photonic devices, such as waveguide channels for microscopic light-manipulating purposes, it is important to be able to pattern these photonic crystals into two-dimensional arrays/circuits on the substrate.^[33] Current methodologies for patterning photonic crystals involve electron-beam lithography/anisotropic etching,^[34–37] two-photon polymerization,^[38] or holographic lithography,^[39] all of which

require elaborate equipment and complex procedures. Patterning macroporous photonic crystals within microchannel networks apparently represents a simple alternative approach.

The fabrication process is similar to that used for patterning mesoporous oxides except that colloidal crystallization within the microchannel networks is involved (Scheme B in Fig. 1). Generally, polymer or silica spheres with diameters of 200–2000 nm can be readily assembled and packed into a close-packed lattice within microchannels with depths and widths of 4–10 μm . Figure 4A shows an SEM image of such patterned polystyrene sphere arrays on a silicon substrate. A drop of inorganic precursor solution was then placed at the same end

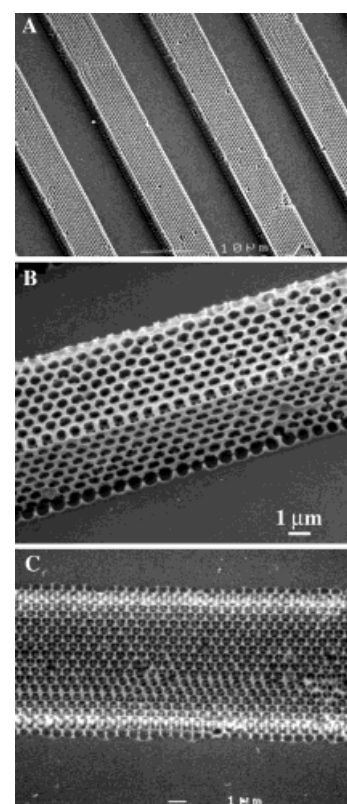


Fig. 4. A) SEM image of a 0.6 μm polystyrene sphere lattice, self-assembled within microchannel arrays. The channels have a width of 8 μm and a depth of 4.5 μm . B) SEM images of patterned macroporous silica, templated by 0.92 μm polystyrene spheres within microchannels. The channels have a depth of 6.5 μm and a width of 6 μm . The samples are tilted by 50°. C) SEM image of patterned macroporous titania, templated by 0.67 μm polystyrene spheres.

of the mold and imbibed into the latex-sphere-filled microchannels by capillary actions. Various precursors have been tested in our experiments, including tetraethoxysilane in ethanol, titanium(diisopropoxide) bis(2,4-pentanedianate) in isopropanol, and a prepolymer solution for PbTiO_3 . Upon calcination, patterned macroporous structures with condensed silica, anatase TiO_2 and PbTiO_3 framework are obtained. With the recent synthesis of macroporous Si and Ge using chemical vapor deposition,^[13,14] it will soon be possible to pattern them on substrates using patterned silica-sphere lattices as templates.

This capability of patterning macroporous materials with high refractive indexes (e.g., TiO_2 , PbTiO_3 , Si, Ge) may represent a viable way to fabricating single domain photonic crystals, three-dimensional photonic crystal devices or even circuits. Figures 4B and C show SEM images for patterned macroporous silica and titania structures. Overall, the orientation and large area single domain crystallinity of the template were replicated with high fidelity. The process can be readily applied to micromolds with depth profiles up to 10 μm . High depth profile is necessary in order to pack a sufficient number of macropore unit cells within the channel to enable multiple photon scattering at the interface. It is further possible to control the orientation of the patterned macroporous oxides^[40] by exploring different edge and confinement effects during the colloidal organization within a confined geometry.^[41–44] This orientation control is critical for the eventual realization of the macroporous photonic crystal devices on substrates.

When a block copolymer/inorganic precursor sol was used in Scheme B of Figure 1, mesoporosity could be introduced into the framework of the macroporous structure. The final materials exhibited a hierarchical ordering with discrete characteristic length scales of 10, 100, and 1000 nm. Figures 5A and B show typical SEM images for these ordered structures. Microchannel templating results in high-quality surface patterns with micron size dimensions (Fig. 5A); the patterned

features themselves are made of inorganic oxide solids, organized to form highly ordered macropores that have been templated by close-packed arrays of the polystyrene spheres (Fig. 5B). The different packing sequences observed in the larger triangular and the smaller bridge areas are direct results of the confinement effect during the geometrically confined colloidal crystallization.^[21,45] In addition, the inorganic oxide (silica, in this case) framework of the macroporous structure itself is made up of mesoscopically ordered cubic arrays of cages with characteristic dimensions of ~ 11 nm as established by the Pluronic F-127 block copolymer. Figure 5C shows a typical TEM image recorded for the same hierarchically ordered silica. The ordered macroporous structure (~ 100 nm) can be seen in these images, along with the silica framework consisting of ordered cubic arrays of mesopores (~ 11 nm). This structural ordering at multiple length scales within one material is reminiscent of those in living systems.^[1]

4. Conclusions

Microchannel networks have been used as confined space for patterning microporous, mesoporous, and macroporous materials of various compositions. The respective ordering structures and functionalities can be independently modified by choosing different mold patterns, microspheres, dopants, block copolymers, and inorganic precursors, although the defect control of the obtained structures is yet to be demonstrated. These patterned porous materials hold promises for their use as advanced catalysts, sensors, low- k dielectrics, optoelectronic, and integrated photonic-crystal devices.

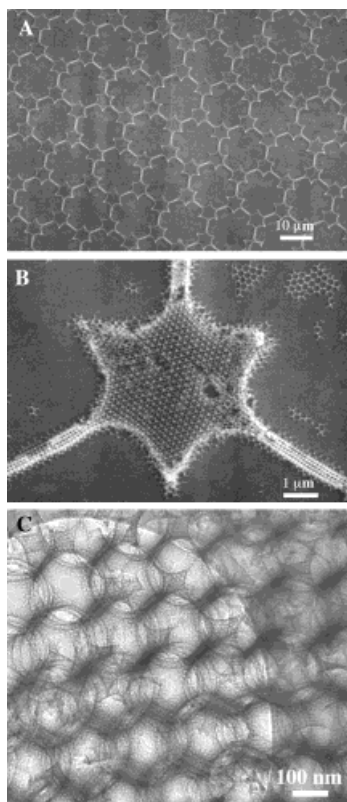


Fig. 5. A,B) SEM images, at different magnifications, of hierarchically ordered mesoporous silica possessing organization over three discrete, characteristic dimensions. C) TEM image of the same sample, showing that the framework of the macroporous skeleton is made up of ordered cubic mesoporous silica with an ordering length of ~ 11 nm. Reprinted with permission from Science, Copyright 1998, American Association for the Advancement of Science.

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