

Hierarchically Ordered Nanoporous-Macroporous Materials NSF Functional Nanostructures Grant CTS-9871970

Principal Investigators: David J. Pine, Bradley F. Chmelka
Dept. of Chemical Engineering
University of California, Santa Barbara, CA 93106

Research and Education Activities:

The objectives of this research project are to develop new classes of nanoscopically and macroscopically ordered materials with improved adsorption/reaction, structural, and/or optical properties. This is being achieved by combining methods of amphiphilic block copolymer self-assembly, emulsion/latex sphere templating, sol-gel chemistry, and soft lithography to develop new classes of porous materials that have ordered pore structures and/or patterns on multiple and vastly different length scales. Using strategies being developed with support from NSF grant CTS-9871970, we are able to control independently the dimensions and periodicities of mesoscopically and macroscopically ordered structures over a wide range of material compositions, surface functionalities, and/or morphologies. The resulting materials are being characterized to benchmark and optimize their properties for different target applications, particularly in catalysis and optics, where hierarchically ordered structures impart useful properties.

We have made substantial progress in developing and demonstrating nanoscopic/macroscopic processing strategies for novel optical materials and devices. In particular, processing methods have been developed for preparing transparent macroscopically patterned, mesostructured films and monoliths with included dye species that are efficient waveguides and display promising amplified spontaneous emission or optical limiting properties. Materials with high degrees of mesoscopic ordering were obtained using amphiphilic poly(ethyleneoxide)-poly(propyleneoxide)-poly(ethyleneoxide) triblock copolymers to organize polymerizing silica networks, while macroscopic ordering was produced by using soft lithography methods (micromolding), annealing, or shear flow. Low thresholds for achieving amplified spontaneous emission were achieved that are approximately two orders of magnitude below those published for dye-doped sol-gel glass systems, representing a significant improvement. Highly oriented transparent mesostructured silica/block-copolymer monoliths (Figure 1 below) have been prepared with the largest ordering domains yet observed, 1.5 cm x 1 mm x 1 mm, into which optical limiting dye species have been included. These have been characterized by two-dimensional X-ray diffraction analyses conducted in collaboration with Dr. Patrick Davidson at the Université de Paris-Sud, Orsay, France; this scientific exchange has been partially supported by a travel grant from the NSF Division of International Programs INT-9726744.

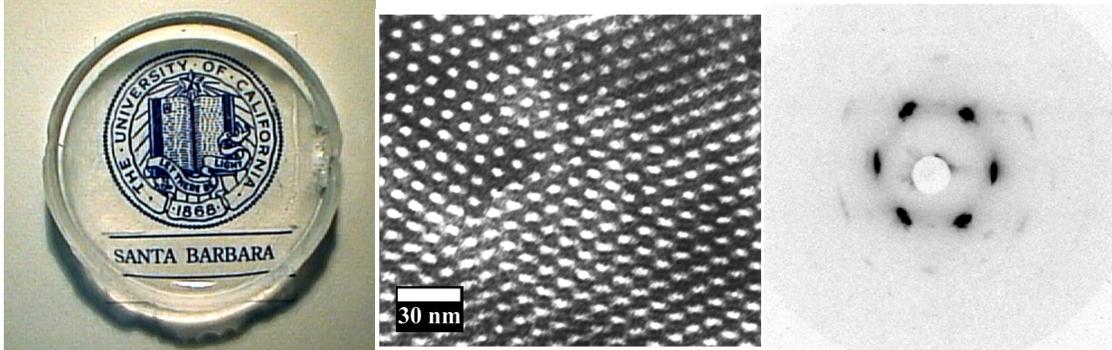
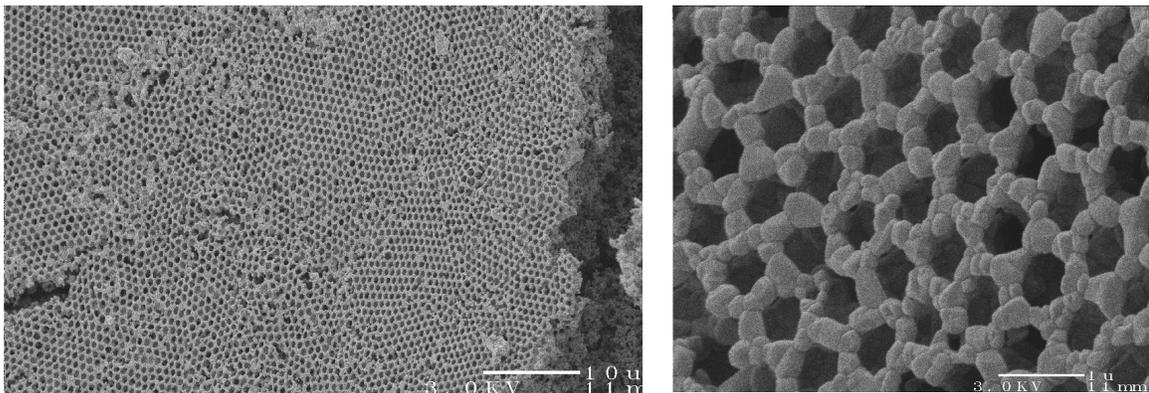


Figure 1: A 3-cm diameter x 3-mm thick mesostructurally ordered transparent block copolymer/silica monolith prepared with a composition of 60 wt% EO₁₀₆-PO₇₀-EO₁₀₆. TEM and XRD diffraction results demonstrate the high degrees of mesoscopic and macroscopic orientational ordering in the sample.

Closely related to these pursuits are our efforts to produce macroscopically ordered porous solids with high dielectric contrast and thus photonic bandgap properties. We have done so by using an emulsion templating technique to make inverse opals for photonic crystals. A primary motivation and advantage with this approach is that the colloidal crystalline template is made of deformable emulsion droplets rather than rigid solid particles. The deformability allows the materials to minimize stresses during shrinkage and thus avoids the cracking inherent in other methods. Thus, we have been able to make samples as large as 10 mm, an order of magnitude larger than sizes achieved using other procedures. An unanticipated benefit of our emulsion templating method is that it yields titania in the high refractive index rutile phase rather than the low index anatase phase characteristic of all other colloidal templating methods currently available. This is advantageous for producing optical stop bands over a greater fraction of the total solid angle, more than 60%, within the photonic crystal. Figure 2 below shows SEM micrographs of rutile titania photonic crystals.



Syntheses of related materials with bimodally ordered meso/macroscale pores have been demonstrated to improve reaction/diffusion properties for heterogeneous catalysis and separation processes involving large macromolecules. Materials that are currently available tend to have various combinations of small pore sizes, broad distributions of pore dimensions, and/or low surface areas that impart severe diffusional or reaction rate limitations to the processing of large molecular species. Specifically, a combination of block-copolymer self-assembly and emulsion templating strategies have been used to prepare meso/macroporous metal oxide materials with two independently adjustable characteristic length scales, one in the macroporous regime having an average pore diameter of 50 nm to several microns and the other in the mesoporous regime from 5 nm to 30 nm. In such systems, the interstices between the macropores are comprised of ordered mesoporous inorganic oxide frameworks. Catalysts or catalyst supports possessing independently adjustable meso/macropore sizes combine high surface areas for active sites in the mesopores with facile transport of diffusing guest species in the macropores.

Various approaches are being pursued to balance the conditions required for amphiphilic block copolymer self-assembly, while preserving the formation of stable emulsion droplets. The resulting hydrophobic regions, organized mesoscopically around the macroscopic (~1-10 μm) droplets, direct the structure of the polymerizing oxide (e.g., SiO_x) species. One particularly successful procedure uses block-copolymer templating to organize the mesopores and oil-in-water emulsion templating for macropores. Another approach uses a macroporous polystyrene foam (prepared by separate emulsion polymerization) as a precursor scaffold to organize an imbibed silica/block-copolymer mesophase that can be solidified and calcined to form meso/macroporous silica monoliths. This latter work is being conducted in collaboration with the group of Dr. Conxita Solans from the Centro de Investigación y Desarrollo in Barcelona, Spain. Currently, the primary metal oxides under study thus far are silica and silica/alumina with Si/Al mole ratios ranging from 8 to 50, which are being functionalized initially with sulfonic acid groups and/or dispersed platinum clusters. We are targeting particularly solution-phase reaction applications involving soluble macromolecular reagents, such as the hydrogenation of polystyrene, to benchmark improvements in diffusion and overall activity. Efforts are currently underway to functionalize the nano/macroporous materials with immobilized enzymes and metallocene moieties to enhance reaction/purification of biomolecule mixtures and polymers, respectively. Development of enabling materials synthesis chemistry continues, as catalytic reaction evaluation efforts expand to provide additional macroscopic property feedback.

Publications describing these results and acknowledging NSF grant CTS-9871970 have appeared in the journals *Science* (2), the *Journal of the American Chemical Society* (3), the *Journal of Physical Chemistry*, *Advanced Materials*, and *Chemistry of Materials* (2), with a number of additional manuscripts submitted or in preparation. Three patent applications have been filed based on these discoveries.