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Disordered mesoporous silicates formed by templation of a liquid crystal (L_3)

Abds-Sami Malik, Daniel M. Dabbs, Ilhan A. Aksay, Howard E. Katz[1]
Princeton University, Dept. of Chemical Engineering and Princeton Materials Institute, Princeton, NJ 08540
[1]Bell Laboratories, Lucent Technologies, Murray Hill, NJ 07974

ABSTRACT

For a wide range of technological applications the need for optically transparent, monolithic, mesoporous silicates is readily apparent. Potential areas of utility include filtration, catalysis, and optoelectronics among many others. This laboratory has previously reported on the synthesis of such materials that are formed through the addition of tetramethoxysilane to a liquid crystal solution of hexanol, cetylpyridinium chloride, and 0.2 M hydrochloric acid, and our investigation into the properties of these materials is a continuing process. We have achieved defect and fracture free material of suitable size (0.5 cm x 3 cm diameter disks) via supercritical drying of the silicate under ethanol or CO_2. The dried materials are remarkably similar to ordinary glass in strength, texture, and clarity. They possess pore volumes of *ca.* 1.0 cm^3/g, with BET surface areas >1000 m^2/g. We can re-infiltrate the dried monolith with hydroxyethylacrylate, a photo-polymerizable monomer, to create an inorganic/organic nanocomposite. There is fracturing upon re-infiltration, but preliminary tests show that the polymerization proceeds despite the mechanical failure. These findings suggest many possible applications for these unique nanocomposites.

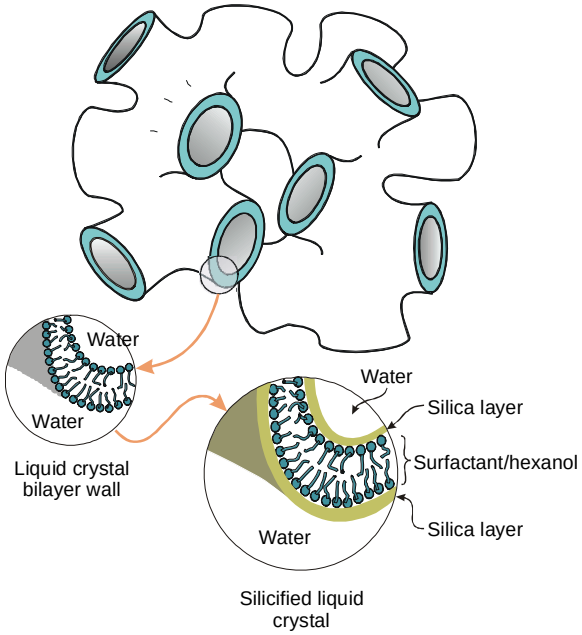

Figure 1: A sketch of the L_3 phase liquid crystal structure, derived from electron microscopy done on freeze fractured samples, as well as theoretical considerations. The pore diameters are uniform, but are randomly interconnected in all three dimensions resulting in short range order with long range disorder. The bilayer forming the liquid crystal can then be templated by a silica layer to capture the original liquid crystal structure as solid silica gel. (Source: McGrath *et al.*, *Langmuir*, vol. 16, **2000,** pp. 398-406)

INTRODUCTION

In recent years, there has been an explosion of interest in mesostructured and mesoporous materials, partly because they are seen to have high potential for applications over a wide range of technological needs. Possible areas of use include filtration, biological separation, catalysis, and patterned thin film formation for use in optoelectronics. The need for optically isotropic, transparent, monolithic material is apparent, especially for optoelectronic applications.

A liquid crystalline phase, termed the L_3 phase, has been explored for a quasiternary system formed from hexanol, cetylpyridinium chloride, and 1 wt % aqueous NaCl solution.[1] This phase, which is optically isotropic and transparent, can be described as a surfactant bilayer that is convoluted to form a sponge-like structure with randomly distributed mesopores interconnected in all three dimensions (Figure 1). This liquid crystal has also been referred to as the 'sponge phase.'[2] The addition of tetramethoxysilane to this template leads to the formation of optically isotropic, transparent silica, which possesses the original L_3 structure. These mesoporous silicas are large monoliths (several cubic centimeters) that conform to the shape of the reaction vessel.

Because of these properties, we propose that the silica L_3 could be used as a basis for constructing nanocomposite materials. It is possible to impregnate the mesopores with a photo–active monomer. Selective polymerization (with a laser) could then be used to 'write' patterns within the silica/monomer composite. Unique optoelectronic properties may be obtained.

In this paper we report on the synthesis, characterization, and processing of mesoporous silica formed by templation of an L_3 phase liquid crystal. We use supercritical ethanol or supercritical carbon dioxide to dry the silica. We then soak the dry silica in photopolymerizable monomers. Although some fracturing is observed in the test material, we can show that photopolymerization does take place within the pores of this material.

EXPERIMENTAL DETAILS

The synthesis procedure for templated silica has been reported before [3,4], and is briefly summarized here for completeness. An L_3 liquid crystal solution was made by first dissolving cetylpyridinium chloride and hexanol in 0.2 M hydrochloric acid (pH 0.7). The liquid crystal

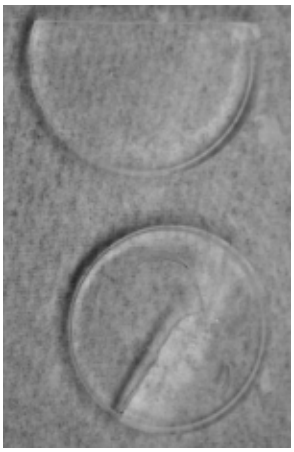

Figure 2: Samples of dried silica, (top) super-critical ethanol, (bottom) supercritical carbon dioxide.

was then silicified by adding tetramethoxysilane (TMOS), cast into a 1 inch diameter petri dish, and allowed to age one to two days to form a gel body.

After forming a gel, the silica disk was placed directly into a 50%/50% methanol/water solution (by volume). After several washings (one day each) with progressively higher concentrations of methanol, the gel disk underwent slight syneresis, which allowed it to be removed from the petri dish. Then the washings were continued with progressively higher concentration of ethanol until the disk was in (nominally) 100% ethanol.

Supercritical drying in ethanol was accomplished by heating (260°C) the silica disk in a stainless steel, sealed pressure vessel partially filled with ethanol. The supercritical ethanol was extracted from the chamber by slowly opening a valve and allowing the hot gas to escape. (**Caution:** Work with supercritical fluids is extremely dangerous, and adequate precautions must be taken to ensure worker safety.) The pressure was eventually brought to ambient, and then the chamber was allowed to cool slowly to room temperature. Supercritical carbon dioxide was also used to dry the silica disk, using an automatic, computer-controlled extraction apparatus. In both cases, dried silica disks were obtained (Figure 2).

Disks were re-infiltrated with solvent, such as ethanol, simply by placing into the infiltrating liquid. This uncontrolled reinfiltration usually caused the monolith to granulate, forming pieces less than a millimeter in dimension. But, sometimes, larger portions measuring as much as 1 cm^2 would survive reinfiltration with liquid. These pieces were recovered and placed into liquid monomer for further studies.

Pieces that had been soaked with the acrylate (hydroxyethyl acrylate) monomer were then placed into more monomer solution with photo-initiator. The piece was taken out of the solution, placed in a Schlenk flask under flowing nitrogen, and exposed to visible light from a strong reading lamp. Infrared spectroscopy done on these pieces and suggested that polymerization had indeed occurred (Figure 3).

Surface area and bulk porosity measurements were done on the dried silica. For materials dried with supercritical ethanol, results indicated that surface areas ranged from 1200

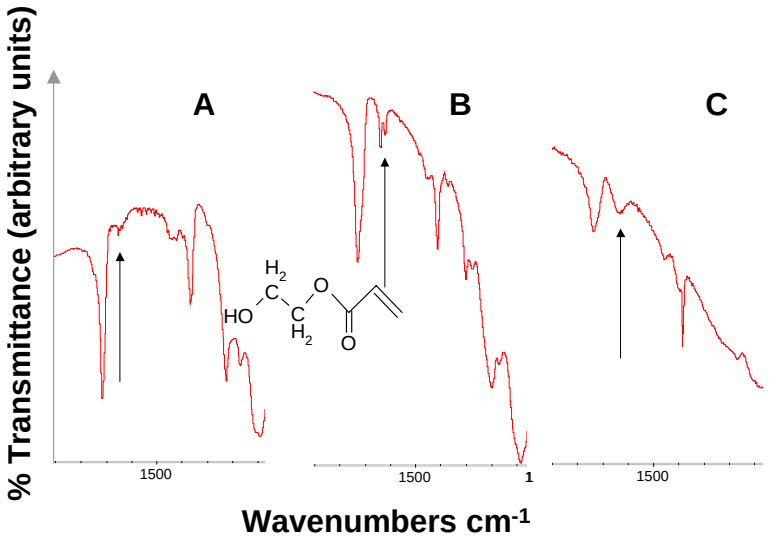

Figure 3: Infrared spectra of dried silica (A), the photomonomer (hydroxyethyl acrylate) in the porous silica (B), and the polymerized acrylate within porous silica. The change in the IR resonance around 1600 cm^{-1} indicates that polymerization has occurred. The silica did not appear to fracture during the polymerization.

cm^3/g to 1400 cm^3/g, and that approximately two thirds of the total volume was composed of pores. Silica dried using supercritical carbon dioxide had less surface area and less pore volume.

Thermogravimetric analysis (TGA) also showed that silica dried in supercritical ethanol did not exhibit weight loss until after 250°C, whereas samples dried in supercritical CO_2 exhibited weight loss starting from 50°C.

RESULTS AND DISCUSSION

Pores of uniform dimension formed by surfactant bilayers characterize the L_3 liquid crystal. The TMOS undergoes a series of acid catalyzed hydrolysis and condensation steps after being added to the liquid crystal. It is then templated by the surfactant to capture the liquid crystal structure in solid form (Figure 4). After gelation, the organic surfactant is trapped in the silica matrix. Therefore, supercritical ethanol is required not only to dry the silica, but also to extract the surfactant. We found that supercritical carbon dioxide treatment did not succeed in removing the surfactant. This was apparent in the TGA experiments as well as surface area measurements and could be attributed to the poor solvating power of supercritical carbon dioxide as compared to supercritical ethanol.

The dried silica monoliths could be impregnated with solvent and monomers, but they frequently cracked or pulverized. The loss of the monolithic structure is thought to be due to the capillary pressures that must exist within the nanopores of the silica when liquid infiltrates the sample. However, we were able to obtain some pieces that did not crack upon reinfiltration. Specifically, porous silica that had been soaked in monomers were subjected to polymerization. Upon polymerization, further cracking was observed in the monoliths but infrared spectroscopy revealed that polymerization did occur in these composites.

CONCLUSIONS

The porous silicates that have been impregnated with photopolymerizable monomers are a novel nanocomposite material. We believe that they are unique and could eventually find applications as novel opto-electronic materials. Furthermore, the demonstration that the porous silica can be impregnated with solvent opens up possibilities for constructing other nano-composite materials. The pores could be impregnated with metal-alkoxides, such as vanadium

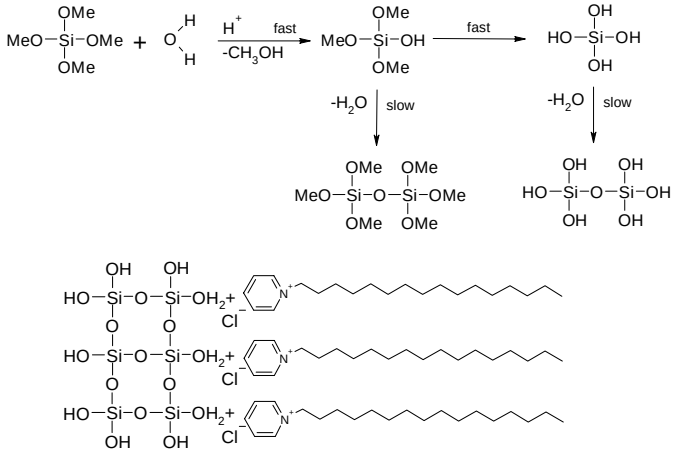

Figure 4: TMOS undergoes a series of acid catalyzed hydrolysis and condensations steps. Then, it is templated by the cetylpyridinium chloride as shown in the lower half of the figure. Only a small portion of the bilayer formed by the surfactant is shown.

alkoxide, to form a silica supported vanadium oxide for catalysis. Such a material has been reported before [5], but only in mesoporous silica powders. Our material offers the promise of fabricating larger monoliths. Metals could also be introduced through electroless deposition, which may have application as supercapacitors. Similarly the pores could be functionalized with proteins and other biomaterials for use as sensors. These and other applications for L_3 templated silica are being actively pursued in our laboratories.

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