Communication

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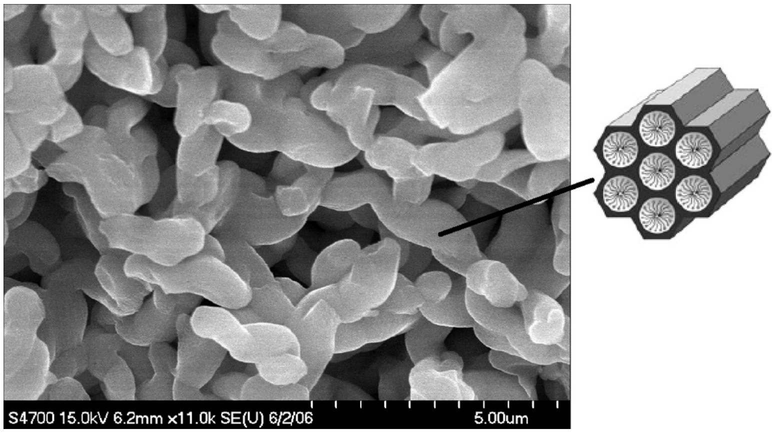

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Stresses at the Interface of Micro with Nano

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Bicontinuous materials consisting of an open interconnected macroporous system with mesoporous walls create a wide range of possibilities for sorption, catalysis, drug delivery, electrochemical energy storage, and separations (filtration, HPLC).[1,2] In monoliths, macropores provide low hydraulic resistance, hence easy access to the bulk by pressure-driven flow, whereas the large mesoporous surface area is always a very short distance away from everywhere and is accessed quickly by diffusion.[3] Here we report that in dry form those materials have innate stresses built in at the interface of the two size regimes. Relief and stabilization against collapse is possible by coating all internal surfaces with polymer.

Materials with ordered hexagonal mesopores can be made through a modified sol−gel process that involves a surfactant such as Pluronic P123 (a $PEO_{20}PPO_{70}PEO_{20}$ triblock copolymer) as a structure directing agent (template). That is, at the right concentration, Pluronic P123 self-assembles in closely packed hexagonal stacks of cylindrical pillars, and subsequently a sol−gel step adds silica filling the voids around them. Post-gelation removal of Pluronic P123 leaves behind a sol−gel material perforated by a hexagonal arrangement of tubes (SBA-15 type materials).[4] The diameter of the tubes can be increased by using a swelling agent such as 1,3,5-trimethylbenzene (TMB),[4,5] but if the concentration of TMB is increased above a certain threshold, the result is a mesoporous cellular foam (MCF), namely, a bicontinuous macroporous system with random mesoporous walls.[6] If the concentration of Pluronic P123 by itself or in combination with TMB is adjusted carefully, the result is a macroporous silica with walls consisting of regular (organized) mesopores.[7] For several applications, wet gels of these materials may need to be dried, and the question is *whether macro- and mesopores shrink the same*. If not, stresses are included at the interface of the two fractal levels, causing the inherent structural instability associated with a potential collapse or at the very least a dimensional change of the material upon drying. Addressing this question, however, is not trivial because it requires stabilization of the internal stresses in order to produce dry forms preserving the dimensions of wet gels. In other words, the bicontinuous porous system should become capable of resisting shrinkage during drying. This was accomplished by coating all internal surfaces with a diisocyanate-derived polymer. As it turns out, shrinkage is indeed different at the nano and the micro size regimes.

For our purposes, bicontinuous macro/mesoporous silica was prepared by Nakanishi's modification of Stucky's method where mesoporous gels rather than precipitates are obtained by reducing the volume of the sol.[7] Typically, Pluronic P123 (P, 4 g) was dissolved in 1.0 M aqueous HNO_3 (12 g), and TBA (T, 0.4 g) was added at room temperature. After stirring for 30 min, samples were cooled to 0 °C, TMOS (5.15 g) was added, and stirring continued for another 30 min. The mixture was poured into molds, which were kept at 60 °C for gelation (110 min). Samples were aged for 5× the gelation time. Following Nakanishi's notation,[7] the material is referred to as native MP4-T045. However, preparation of dry self-standing monoliths is not straightforward: Nakanishi's procedure that calls for drying at 60 °C under ambient pressure followed by burning Pluronic P123 off at 600 °C led to coarse powders. Structural collapse, with or without prior removal of Pluronic P123 (vide infra), occurs during drying rather than during calcination. Therefore, reasoning that surface tension forces on the skeletal framework by the residing vapor/liquid interface might be responsible for shrinkage,[8] we resorted to an aerogel-like workup strategy: after the template and swelling agent were removed from the wet gels by a Soxhlet extraction (CH_3CN), pore filling solvents were exchanged with liquid CO_2, which was taken out supercritically. This approach did produce monoliths which, as opposed to typical silica aerogels, still shrink significantly (29%) relative to the dimensions of their wet gels.

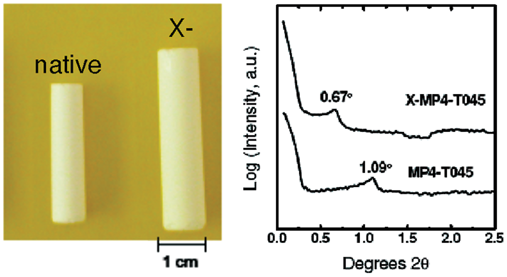

Figure 1. Left: Photographs of typical dry native (MP4-T045; $\rho_{\mathrm{bulk}} = 0.367 \pm 0.003$ g cm^{-3}; $\rho_{\mathrm{skeletal}} = 1.935 \pm 0.002$ g cm^{-3}) and diisocyanate-treated (X-MP4-T045; $\rho_{\mathrm{bulk}} = 0.755 \pm 0.017$ g cm^{-3}; $\rho_{\mathrm{skeletal}} = 1.279 \pm 0.001$ g cm^{-3}) bicontinuous meso/macroporous silica monoliths, made using Pluronic P123 as structure directing agent, 1,3,5-trimethylbenzene as swelling agent, and supercritical fluid removal of pore solvents. Both gels were prepared using 1.04 cm diameter molds, so size differences reflect different shrinkage upon drying. The diameter of the native samples is 0.743 ± 0.005 cm and of the X-samples it is 0.909 ± 0.007 cm. Right: Powder XRD patterns of samples as indicated. The X-sample shows a smaller diffraction angle, indicative of a larger spacing between ordered features.

In order to "lock" the skeletal framework at the wet gel stage, immediately after Soxhlet extraction, wet gels were exposed to an aliphatic diisocyanate solution (Desmodur N3200 from Bayer) that reacts both with the surface −OH groups forming urethane and with adsorbed water forming amines; in turn, amines react with more diisocyanate from the pores, yielding tethers of polyurea.[9] Thus, the bulk density of dry monoliths increases by a factor of 2.05, but now they shrink only by 13% relative to the molds versus 29% of native samples. The diisocyanate-treated material is referred to as X-MP4-T045 ("X" for cross-linked). Figure 1 compares native and X-monoliths at the two size extremes. The presence of the small-angle XRD pattern suggests that the mesoporous systems of

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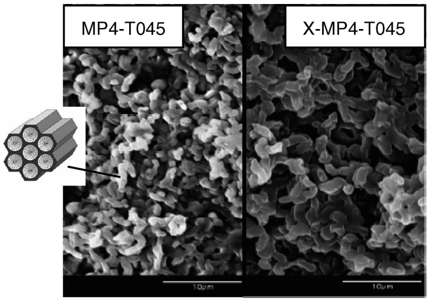

Figure 2. Low resolution (10 μm bar) SEMs of a native (MP4-T045) and of a diisocyanate-treated monolith (X-MP4-T045) similar to those of Figure 1. The worm-like objects consist of stereoregular tubes (Figure 3). Despite the massive polymer uptake (X-MP4-T045 sample consists of 70% w/w polymer), X-samples seem very similar to their native counterparts.

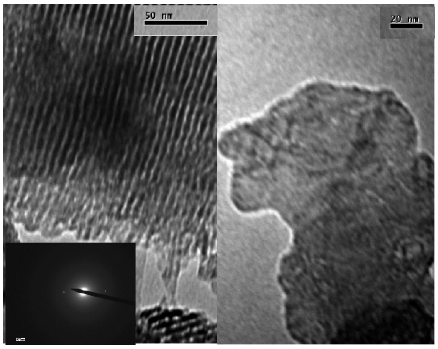

Figure 3. TEM of native MP4-T045 (left) and of X-MP4-T045 (right). The organized mesoporosity in the native sample is immediately obvious. After polymer uptake (X-sample), the ordered structure is barely visible (if at all) signifying that the tubes have been filled with polymer. Inset confirms the one-dimensional organization of the tubular structure in MP4-T045.

the two materials are stereoregular and indicates that the ordered features producing the diffraction pattern are spaced further apart in the X-samples, in agreement with the fact that they shrink less.

SEM in combination with TEM confirms the fractal structure of the MP4-T045 material, which consists of macropores (Figure 2, left) surrounded by stereoregular mesoporous walls (Figure 3, left). After treatment with diisocyanate, the macroporous structure appears more “open” (Figure 2, right) in agreement with the larger monolith size, and it still consists of entangled worm-like objects whose shape is maintained, but they look thicker, suggesting that new material (polymer) has been deposited on the macroporous surfaces conformally. Indeed, the porosity (calculated from bulk and skeletal density data) has been decreased, but not dramatically: from 81% empty space before polymer treatment to 50% after. By looking inside the worm-like objects, though, the picture is quite different. First, in TEM (Figure 3, right), the ordered tubular structure is barely visible, probably due to lack of Z-attenuation between the polymer and silica. Second, the BET surface area has decreased dramatically, from 612 $m^2\ g^{-1}$ for native samples to 2.96 $m^2\ g^{-1}$ for X-samples! Either mesopores have collapsed completely or access to them has been blocked at the mouth of the tubes or mesopores have been filled with polymer. XRD data (Figure 1) show that the tubular structure is still present. If polymer had simply clogged the entrance of the mesopores, the TEM contrast would have been preserved and the tube structure would still be clearly visible in Figure 3, right. All data suggest that the polymer has completely filled the mesopores, and the net result is that the composite material shrinks much less upon drying.

Now, shrinkage at the macroscopic level is quite different from shrinkage of the mesopores. This is inferred by comparing the ratio of a macroscopic linear dimension (e.g., the monolith diameter) with the ratio of a nanoscopic linear dimension (e.g., the spacing between the tubes in the worm-like objects). Thus, (diameter of X-MP4-T045)/(diameter of native MP4-T045) = 1.23 and (unit cell of X-MP4-T045)/(unit cell of MP4-T045) = 1.63. Since X-samples closely resemble the wet gels in size and shape, it is clear that upon drying the spacing between the tubes, and therefore the size of the worm-like objects, has been reduced more than the size of the monolith, which in turn reflects the average spacing between the worm-like objects. The reasons might not be difficult to reconcile.

All silica surfaces are terminated with silanols, and practically all BET surface area is in the tubes where an interesting situation arises: in the concave mesoporous surfaces, hydroxyls point inward, and owing to the small pore diameter, they are forced close to one another where they can interact strongly through hydrogen bonding.[10] The latter pulls the pore walls together; eventually new Si−O−Si bonds are formed in a process that resembles an extreme case of syneresis (shrinking during aging),[7] and the worm-like objects contract. In contrast, hydroxyls on top of the worm-like objects are about as close as on a flat surface. The fact that the worm-like objects tend to shrink introduces stresses at the interface of the two size regimes, pulling the worm-like objects apart, and the structure is expected to become weaker. The tendency of tubular stereoregular mesopores to constrict upon drying explains also the fact that native MP4-T045 monoliths do shrink significantly despite use of supercritical fluid CO_2 that eliminates surface tension forces. Being able to obtain any monoliths at all suggests that Si−O−Si bridges not only break but are also re-formed at different locations during processing. Nevertheless, the fact that the monolith diameter-to-unit cell size ratio is different for native and X-samples indicates that the former have residual stresses. Filling the mesoporous tubes with polymer stabilizes the structure, but by the same token, the X-materials may be thus more appropriate for filtration rather than chromatography. Furthermore, owing to exceptional mechanical properties, X-materials are also evaluated for ballistic applications.

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References

(1) Hoffman, F.; Cornelius, M.; Morell, J.; Fröba, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3216−3251.
(2) Sakamoto, J. S.; Dunn, B. *J. Mater. Chem.* **2002**, *12*, 2859−2861.
(3) Svec, F.; Huber, C. G. *Anal. Chem.* **2006**, *78*, 2100−2107.
(4) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B.; Stucky, G. D. *Science* **1998**, *279*, 548−552.
(5) Yang, C. M.; Zibrowius, B.; Schmidt, W.; Schüth, F. *Chem. Mater.* **2004**, *16*, 2918−2925.
(6) Schmidt-Winkel, P.; Lukens, W. W. J.; Zhao, D.; Yang, P.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1999**, *121*, 254−255.
(7) Amatani, T.; Nakanishi, K.; Hirao, K.; Kodaira, T. *Chem. Mater.* **2005**, *17*, 2114−2119.
(8) (a) Brinker, C. J.; Scherer, G. W. *Sol-Gel Science. The Physics and Chemistry of Sol-Gel Processing*; Academic Press: New York, 1990. (b) Scherer, G. W. *Langmuir* **1996**, *12*, 1109−1116.
(9) (a) Leventis, N.; Sotiriou-Leventis, C.; Zhang, G.; Rawashdeh, A.-M. M. *Nano Lett.* **2002**, *2*, 957−960. (b) Meador, M. A. B.; Capadona, L. A.; MacCorkle, L.; Papadopoulos, D. S.; Leventis, N. *Chem. Mater.* **2007**, *19*, 2247−2260. (c) Leventis, N. *Acc. Chem. Res.* **2007**, http://dx.doi.org/10.1021/ar600033s.
(10) Anedda, A.; Carbonaro, C. M.; Clemente, F.; Corpino, R.; Ricci, P. C. *J. Phys. Chem. B* **2003**, *107*, 13661−13665.

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