Spontaneously Ordered Sol−Gel Composites with Submicrometer Periodicity

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Current interest in mesoperiodic materials is due to their potential in fields as diverse as catalysis,[1] chromatography,[2] filtration,[3] and lithography of mesostructured films[4,5] and as anisotropic hosts for photoactive species.[6,7] In the general synthetic route to these structures, liquid-crystalline phases of molecular[8,9] or polymeric[10−13] surfactants guide the growth of an inorganic network (typically through sol−gel processing of silicon and metal alkoxides) into ordered geometries. However, the thermal or chemical-extraction techniques used for template removal introduce macroscopic inhomogeneities in products, which are mostly isolated as white powders. Moreover, these structures are restricted to the mesoscale dimensions ($\leq$30 nm) of their templates.

A template-free, room-temperature sol−gel route to ordered composites with submicrometer periodicity is described here. We have found that sol−gel processing of simple silicon and transition metal alkoxides with acrylate substituents forms networks with long-range, microstructural organization with $\approx$250-nm periodicity. Photoinitiated free-radical polymerization of the olefin groups then "locks" this organization into mechanically robust, optically clear, but birefringent monoliths. Before organic polymerization, composites could be spin-cast as microstructured, bicontinuous thin films. These findings are surprising because previous studies have assumed that room-temperature sol−gel processing without templates leads to amorphous networks.

We applied this method to commercially available alkoxysilanes, including 3-methacryloxypropyltrimethoxysilane (MAPTMS), 3-methacryloxymethyltrimethoxysilane, 3-methacryloxypropylmethyldimethylsilane, 3-acryloxypropyltrimethoxysilane, and 3-acetoxytrimethoxysilane in combination with methacrylic acid: zirconium *n*-propoxide or titanium *iso*-propoxide complexes. Here, we describe the MAPTMS system, which consisted of 5 molar equiv of the alkoxysilane, an equimolar methacrylic acid:zirconium *n*-propoxide complex (2 molar equiv), and 0.05 M HCl (10.5 molar equiv). Acidified H_2O (3.75 molar equiv) was first added to the alkoxysilane. This phase-separated system cleared rapidly (2.5 min) after hydrolysis and condensation reactions of alkoxide groups were initiated by stirring. The solution now consisted of unreacted alkoxysilane, H_2O, and low-molecular-weight siloxanes. The latter were characterized by solution ^{29}Si NMR (spectra were dominated by T_1 (−52.0 ppm) and T_2 (−58.8 ppm) species, characteristic of weakly branched oligomers), FT-IR spectroscopy (where the ν_{as}(Si−O−Si) mode corresponding to siloxane chains was observed at 1080 cm^{-1}), and ES-mass spectrometry (which indicated they were predominantly linear oligomers with a maximum $m/z = 1079.80$ ionized with Na$^+$, corresponding to 5 Si centers). The solution was then mixed with the transition-metal alkoxide complex, followed by 6.75 molar equiv of H_2O. To form monoliths, the colloid was doped with a photoinitiator (5 wt % of bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide) and filtered through a 0.2-μm PTFE membrane before exposure to a broadband UV lamp (200−500 nm, with 5 mW cm^{-2} at 253.7 nm for 20 s) to initiate free-radical polymerization of methacrylate groups.

The solid monoliths ($\approx$1 cm^2 × 0.5 cm) obtained in this way were transparent but birefringent, when observed between crossed polarizers. Transmission electron microscopy of microtomed cross sections showed that optical anisotropy is due to their uniaxial organization, which consists of a close-packed, periodic array of 250-nm-wide domains (Figure 1a). We deliberately include a defect introduced during sample preparation in Figure 1b, to show how each domain is discrete and detachable from its neighbors; the "fuzzy" exposed edges reveal the interfacial layers that attach domains to each other. From birefringence measurements, we observed that structural coherence (i.e., "monocrystallinity") was maintained over macroscopic (thousands of micrometers) distances in the monoliths.

Prior to irradiation, thin films could also be solution spin-cast (5000 rpm for 10 s) from the colloids ($\approx$20 wt % in 2-propanol) onto planar Si substrates. Here, the domains organized into a bicontinuous arrangement, reminiscent of the organization in nanostructured films cast from the self-assembled block copolymer phases,[14] over areas greater than 2 cm^2. Because of the submi-

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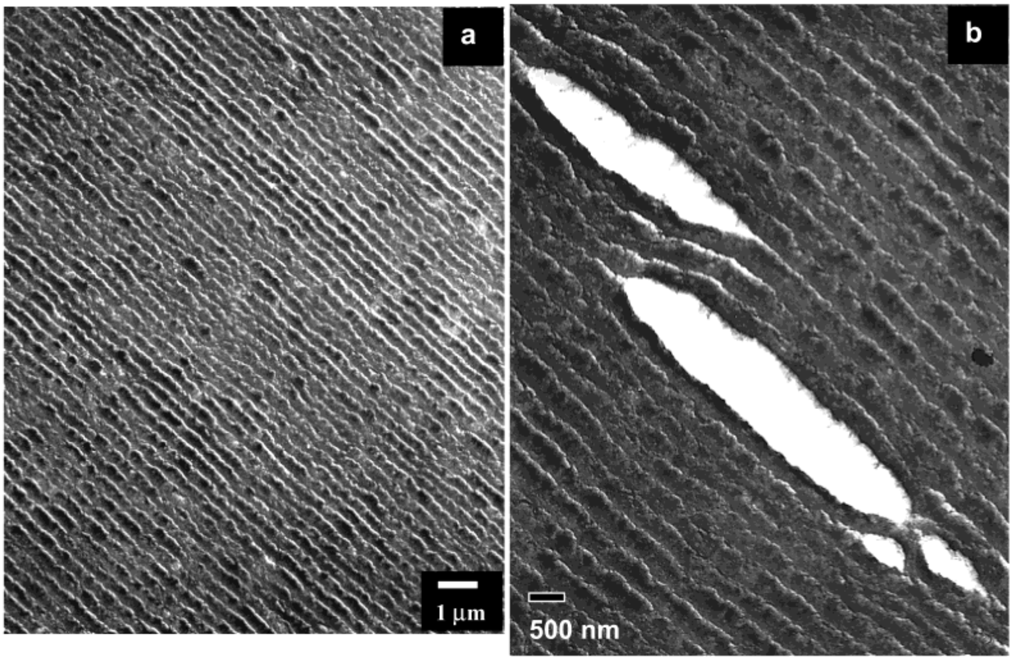

Figure 1. (a) Cross-sectional TEM of an ordered composite composed of (b) discrete 250-nm-wide domains.

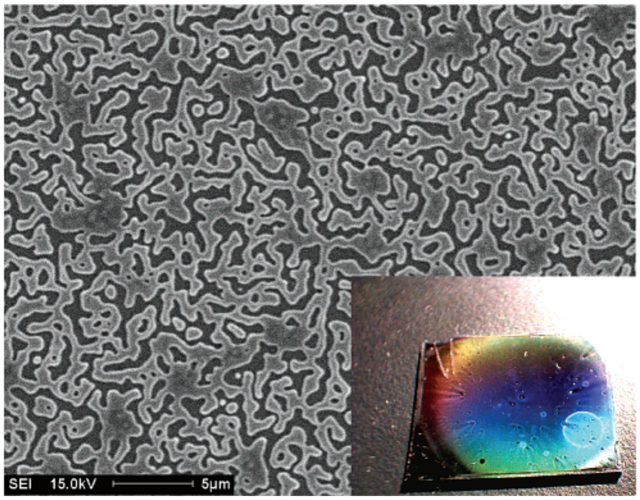

Figure 2. Scanning electron micrograph of microstructured composite films cast from 20 wt % solutions of the composite, which are iridescent (inset photograph) under ambient light.

crometer length scales of organization, the microstructured films were iridescent under ambient light (Figure 2, inset).

We propose a model based on bicontinuous microemulsions[15] to explain the unusual submicrometer periodicity and interdigitated geometry (vide infra) of the composites. Mesoscale liquid-crystal phases, employed in surfactant-templated reactions,[8-13] form above a critical concentration of amphiphiles in an aqueous medium. By contrast microemulsions are ternary systems, composed of organic (oil), H_2O, and surfactant phases. The first signature of microemulsification in our system is the rapid elimination of phase separation between MAPTMS and H_2O when oligosiloxanes formed in the reaction mixture.[16] This is because the oligomers, similar to silicone−polyether copolymer surfactants,[17] consist of a hydrophobic siloxane backbone with polar propyl methacrylate substituents and are therefore amphiphilic. Because of their relatively short organic chains ($n = 7$), steric hindrance of siloxane bonds, and nonionic headgroups, these oligomers cannot form highly curved micellar structures. Instead, they are likely to self-assemble into minimal-energy, amphiphilic monolayers[18] with low curvature and bending rigidity[15] that occupy the interfaces (and dramatically reduce surface tension) between immiscible organic (unreacted MAPTMS) and H_2O phases, as depicted in Figure 3. This leads

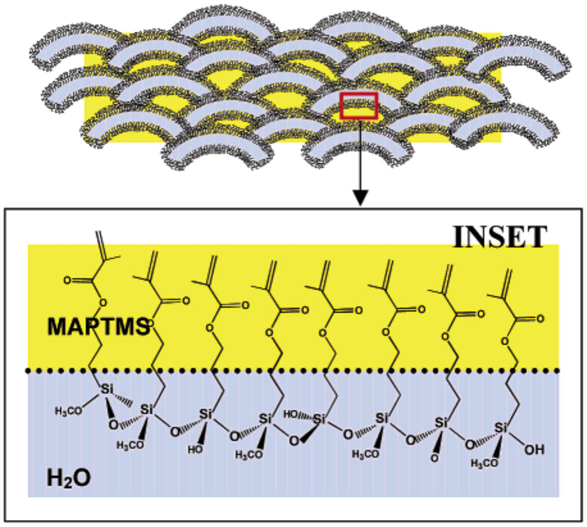

Figure 3. Proposed bicontinuous microemulsion formed when amphiphilic siloxane oligomers partition unreacted MAPTMS and H_2O regions (INSET).

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[18] Our assumption here of self-assembled oligosiloxane monolayers has been further strengthened by the recent observations of vesiculation (K. Saravanamuttu and R. G. Denning) in these reaction systems.

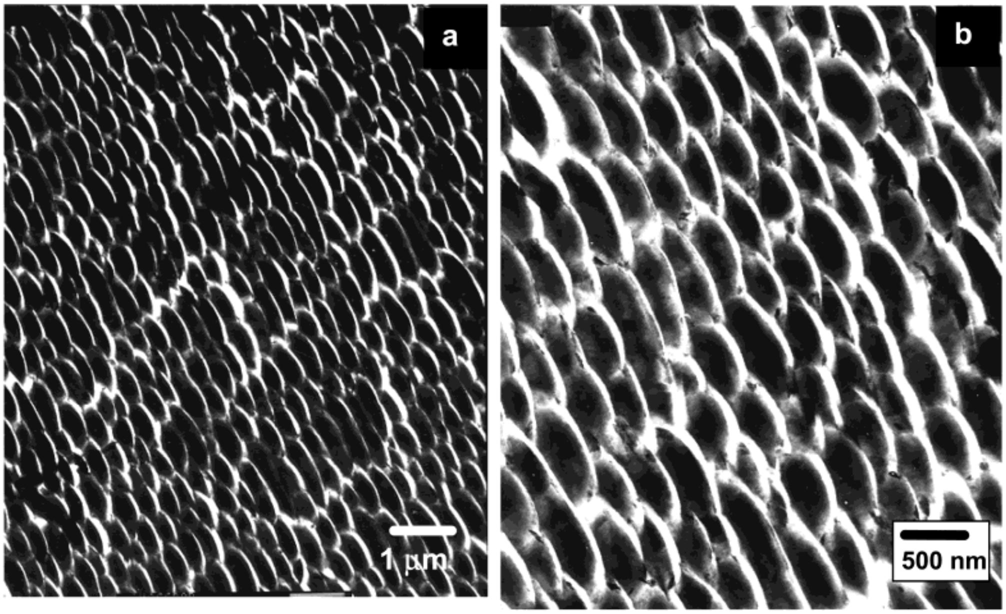

Figure 4. Interdigitated organization of the composite is brought into relief after heating in air at 700 °C for 10 h.

to a thermodynamically stable bicontinuous microemulsion in which the oligosiloxane monolayers partition organic and aqueous phases into discrete volumes. Although macroscopically the system becomes transparent, we can infer from the final structures of both the monoliths and thin films that it actually has a periodic and bicontinuous morphology composed of mutually interpenetrating water and organic channels (Figure 3).

Sol–gel reactions (of both remnant MAPTMS and newly added transition-metal alkoxides) will now be restricted to the aqueous regions and form domains that correspond to the shape of the H_2O channels. As alkoxides participate in network growth, the organic phase is gradually depleted until the hydrophilic domains remain separated only by their original amphiphilic boundaries. The initial transparency of the microemulsion shows that the length scale of its microstructure is $\ll$350 nm. However, the submicrometer dimensions in the final material (Figure 1) indicate a significant widening of hydrophilic domains as sol–gel growth of silica and zirconia (or titania) networks proceeds within them, although the (highly regular) structural anisotropy of the microemulsion phase is retained. In other words, the oligosiloxane monolayers serve as flexible *spatial boundaries* that control the *shape* but not the *size* (length scale) of domains in the evolving microstructure. Subsequent photoinitiated free-radical polymerization between interfacial methacrylate groups links domains to each other, creating the tightly packed array observed in Figure 1. (Networks formed in amphiphilic phases that retain the general morphology of their hosts but possess increased length scales also occur naturally—through amphiphilic boundary-mediated mineralization processes[19] and have been observed synthetically—as organic gels with submicrometer- and micrometer-scale microstructures formed through polymerization-induced "demixing" in lyotropic *meso*scale liquid crystals.[20])

To further demonstrate the role of the oligosiloxanes as amphiphilic boundaries in our systems, we selectively removed the organic component by heating monoliths at 700 °C in air for 10 h. The resulting inorganic skeleton (Figure 4), although denuded of its adhesive methacrylate layers, retains the periodicity and geometry originally defined by the amphiphilic walls. Shrinkage caused by further silica condensation amplifies interfacial curvature and brings into relief the unusual interdigitation of domains that could be attributed to the mutually interpenetrating H_2O and oil channels in bicontinuous morphologies.

Our findings show that stable, ordered phases are accessible through room-temperature sol–gel processing of commonly used alkoxides. The composites have potential in photonics due to their transparency, the ability to tune their index of refraction by judicious choice of transition-metal-oxide dopants, and their photosensitivity and ease of processing into ordered monoliths and microstructured films with large surface areas. Furthermore, the length scales of these composites correspond to optical wavelengths, the fundamental requirement for self-assembled photonic crystals.[21]

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