NANOSTRUCTURED CERAMICS THROUGH SELF-ASSEMBLY

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Opportunity

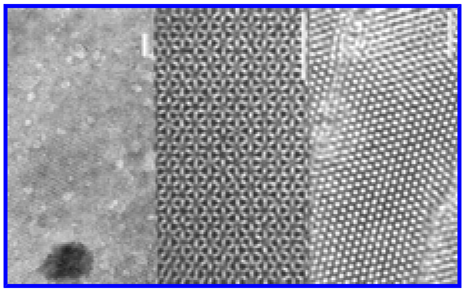
The length scales defining structure and organization determine the fundamental characteristics of a material. Traditional ceramic materials exhibit organization on two length scales: the atomic scale, e.g., the unit cell of the crystal or the local arrangement of amorphous materials, and the scale of the grain size within the composite, typically much longer length and on the order of micrometers or greater. In biogenic materials, however, we observe a much broader range of organizational length scales: (1) a hierarchical organization always starts at the nanometer length scale, in which case, nanostructural design is the building block of larger scale composite structures; and (2) the nested levels of structural hierarchy appear to yield improved properties for particular functions (Aksay et al. 1994; NAP 1994).

In biogenic systems, nanostructural design is accomplished through the self-assembly of organics. Inorganic structures form via template-assisted self-assembly, where self-assembled organic material (e.g., proteins and/or lipids) form the structural scaffolding for the deposition of inorganic material (Sarikaya and Aksay 1994; Sarikaya and Aksay 1992). Organic materials are organized on length scales of 1100 nm and used as frameworks for specifically oriented and shaped inorganic crystals (i.e., ceramics such as hydroxyapatite, $CaCO_3$, SiO_2, and Fe_3O_4) (Lowenstam and Weiner 1989; Mann 1993 a and b; Heywood and Mann 1992). In some cases, structurally organized organic surfaces catalytically or epitaxially induce growth of specifically oriented inorganic thin films. Further, nature's way of mineralization uses environmentally balanced aqueous solution chemistries at temperatures below 100°C. This approach provides an opportunity for the processing of inorganics with nanoscale patterns. Two examples are used to illustrate the potential of this approach.

Template Assisted Nanostructured Ceramic Thin Films

A new class of materials discovered by scientists at Mobil Corporation ideally illustrates the utility of self-assembly in materials design (Kresge et al. 1992; Beck et al. 1992). Silica precursors when mixed with surfactants result in polymerized silica "casts" or "templates" of commonly observed surfactant-water liquid crystals. Three different mesoporous geometries have been reported (Kresge et al. 1992; Beck et al. 1992; McGehee 1994; McGehee et al. 1994; Monnier et al. 1993), each mirroring an underlying surfactant-water mesophase (Figure 4.1). These mesoporous materials are constructed of walls of amorphous silica, only ten or so angstroms thick, organized about a repetitive arrangement of pores up to a hundred angstroms in diameter. The resulting materials are locally amorphous (on atomic length scales) and crystalline on larger (tens to hundreds of angstrom) length scales.

The availability of highly controlled pores on the 10 to 100 Å scale offers opportunities for creating unusual composites, with structures and properties unlike any that have been made to date. However, the effective use of mesoporous silicates requires two critical achievements: (1) controlling the mesophase pore structure and (2) synthesizing large monolithic and mesoporous "building blocks" for the construction of larger, viable composite materials. Although important information exists on some aspects of controlling the mesoporous structure (Kresge at a. 1992; Beck et al. 1992; Huo et al. 1993), large scale structures have not yet been constructed. However, the general outline for fabricating useful composites is known: First, rigid silica (or other ceramic) skeletons form at the surfactant-water interface. This is followed by the removal of the organic phase to yield a ceramic cellular solid containing periodic, 1-10 nm diameter pores. The porous structures may be used as a cellular solid or subsequently infiltrated with secondary phases.



(a) (b) (c)

Fig. 4.1. Transmission electron microscope images of (a) the lamellar morphology, (b) the cubic phase with Ia3d symmetry viewed along its [111] zone axis, and (c) the hexagonal phase viewed along its [001] zone axis of the silica/surfactant nanostructured composites by coassembly (McGehee 1994; McGehee et al. 1994) (bars = 30 nm).

The synthesis scheme of silica-based mesostructured materials (Kresge et al. 1992; Beck et al. 1992; Monnier et al. 1993; Huo et al. 1993) using supramolecular assemblies of surfactant molecules to template the condensation of inorganic species has now been extended to include a wide variety of transition metal oxides (Antonelli and Ying 1995) and recently, cadmium sulfide and selenide semiconductors (Braun, Osenar, and Strupp 1996). Although the exact mechanism for this type of mineralization is still controversial (Monnier et al. 1993), this technique holds great promise as a synthetic scheme to produce nanostructured materials with novel thermal, electronic, optical, mechanical, and selective molecular transport properties. For any of these applications to be realized, however, what is clearly required is a method by which these nanostructures can be formed into controlled shapes and patterns rather than the microscopic particulates (Aksay et al. 1996; Yang et al. 1996).

Our work (Aksay et al. 1996) has shown that continuous mesoporous silicate films can be grown onto a wide variety of substrates. Of primary concern here is the structure of the first layer of adsorbed surfactant at each of these interfaces. Although the molecular organization and self-assembly of surfactants at interfaces is a widely studied area, little is yet known about the precise structure of adsorbed surfactant layers. Recent work (Manne et al. 1994) has shown that three-dimensional surfactant structures such as cylindrical tubules and spheres can be formed at solid/liquid interfaces. Adsorbed hemi-micellar arrangements are observed on poorly orienting amorphous substrates such as silica, and aligned tubular structures are observed on more strongly orienting crystalline substrates such as mica and graphite. The latter substrates orient adsorbed surfactants via anisotropic attraction (either van der Waals or electrostatic) between the crystalline substrate and the surfactant molecule. The amorphous silica substrate has no preferential orientation for surfactant adsorption.

Figure 4.2 shows in-situ atomic force microscopy (AFM) images of the atomic lattice of mesoscopic films grown on mica and graphite interfaces. The structure of the respective substrates is shown in each insert, with the main image revealing the structure of the mesoscopic silica overlayer growing on each surface. All films are continuous and display distinctly different textures at length scales between 0.510 microns.

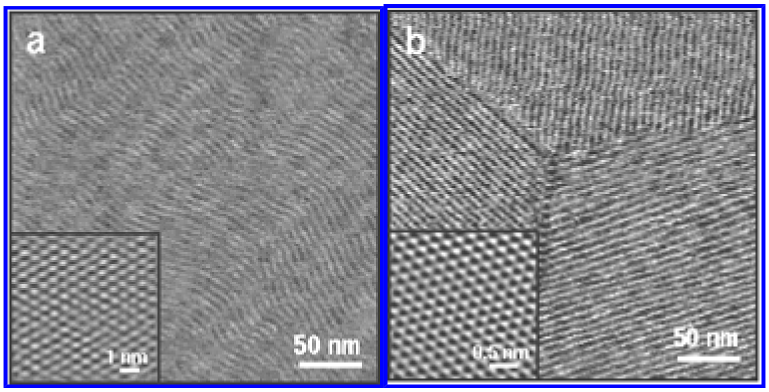


Fig. 4.2. In-situ AFM images of mesostructured films growing on (a) mica and (b) graphite substrates, respectively. AFM images of the substrates used to grow mesoscopic silica films are shown in the insets. (a) and (b) illustrate the periodic mica and graphite atomic lattice onto which CTAC adsorb and orient (Aksay et al. 1996).

Nanoscale Patterning With Block Copolymers

Towards the goal of forming nanostructured composites with periodic patterns, we have also successfully grown amorphous $BaTiO_3$ regio-selectively onto polybutadiene (PB) interdomains within a polystyrene (PS)-polybutadiene-polystyrene triblock copolymer, Kraton D1102® (Shell Chemical Company, Houston, TX) thin film (Figure 4.3). The structure of Kraton was preserved throughout the chemical reactions. $BaTiO_3$, a dielectric and a ferroelectric, was selected as the inorganic phase because it is used extensively in multilayer capacitors, thermistors, and electrooptic devices (Wakino, Mirai, and Tamura 1984; Maurice and Buchanan 1987). Its low temperature (< 100°C) synthesis, an essential requirement for coupling with polymers, is well understood (Slamovich and Aksay 1996).

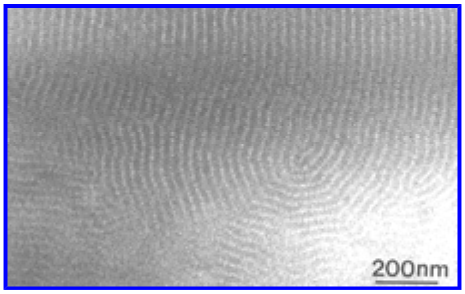


Fig. 4.3. A TEM bright field image of the amorphous barium titanated (dark lines) thin film of Kraton (Lee, Yao, and Aksay 1997).

Unlike the "solid-state micelle" method of Cohen and coworkers (Cummins et al. 1991; Yue and Cohen 1994), our approach allows: (1) the nanodomains in solid films to be chemically functionalized in situ, (2) the inorganic precursors to propagate along template macromolecules within the interdomains in solid films, and (3) the inorganic precursors to grow on the top of the polymerized ceramic precursors.

Conclusions

Similar to the processes observed in the processing of biogenic composites, the architectures generated through self-assembly of surfactants or macromolecules can serve as templates to process ceramics with nanostructural patterns. Two examples given in this summary illustrate the potential of this approach, especially in applications where substrates cannot be exposed to high temperatures. The method is ideal for processing organic/inorganic nanocomposites. However, the removal of the organic yields nanostructured ceramic scaffoldings that can be used to process ceramic/ceramic or ceramic/metal nanocomposites as well.

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