Preparation of Supported Mesoporous Silica Layers in a Continuous Flow Cell

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Since their introduction by Mobil researchers,[1] mesoporous oxides formed in the presence of surfactants have attracted considerable interest for applications including catalytic materials, filters, sensors, and optoelectronic devices.[2] Recently, film formation of M41S type materials has been introduced.[2−4] In these reports it was demonstrated that films with a preferred orientation can be prepared if an appropriate substrate such as graphite[2] or mica[3] is used. However, films grown on other substrates, such as glass, exhibit a rather disordered texture.[2] In this report it is demonstrated that mesoporous silica films can be prepared in a continuous-flow reactor and that an external flow field can induce a preferred orientation in the film.

The use of an applied flow field to manipulate the microstructure of complex fluids has been extensively applied to liquid-crystalline polymeric[5] and micellar solutions.[6] Applied shear flow causes preferential alignment of polymer or micelle directors in the bulk and at the boundaries in these systems. With no externally applied field, the microstructure of liquid-crystalline systems is characterized by orientational order; however, defects or boundary effects may cause substantial gradients in orientation resulting in a polydomain structure. Within domains, orientational order is preserved. However, on length scales greater than the domain size, orientational order is lost, thus rendering the material macroscopically isotropic. Recently, small-angle light-scattering experiments have demonstrated that shear flow generally elongates domains along the flow direction, and at the same time shear aligns the micelles or polymers within the domains[5,6] so as to render the sample macroscopically anisotropic.

M41S type material synthesis proceeds through condensation−polymerization of assembled silicate−surfactant mesostructures.[1,7,8] The existence of these mesostructures during synthesis provides an opportu-

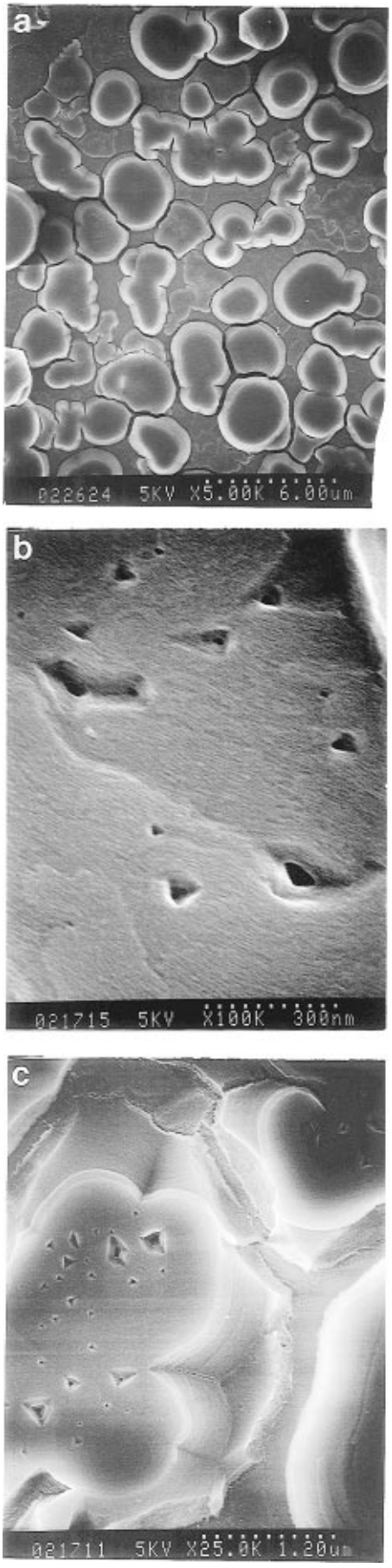

Figure 1. FE-SEM top views of films supported on glass deposited under static conditions for 1 h at 80 °C: (a) 5000× magnification of noncalcined film. (b) 100 000× magnification of calcined film. (c) 25 000× magnification of calcined film.

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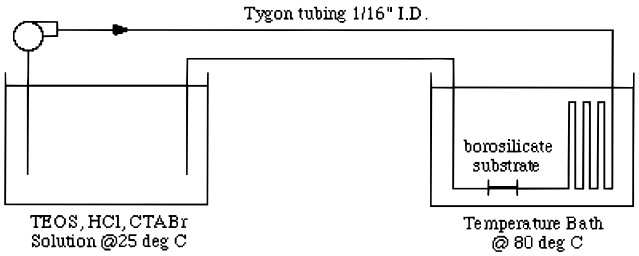

Figure 2. Schematic of continuous flow cell.

nity for the development of processing schemes to induce macroscopic order by external fields through mechanisms similar to those encountered in polymeric and micellar liquid crystals. In M41S materials, the surfactant−silicate assembly induces the primary structure of the nanotubes as well as the secondary structural arrangement, which varies from hexagonal to lamellar and cubic.[9] However, the tertiary structure due to the flexibility inherent in the surfactant−silicate assemblies consists of misaligned domains of the order of 100 nm. For film applications of M41S type materials, an additional orienting force is needed to direct the tertiary structures toward macroscopic perfection. For sufficiently thin films such orienting effects have been demonstrated to exist to some degree at the air−water and substrate−water interface for certain substrates. Such effects are usually lost when film thickness exceeds several microns.[2] If external fields can be shown to have an orienting effect on the tertiary structure of these systems, then additional flexibility will be provided for manipulating the microstructure of these materials which will be decoupled from or in addition to interfacial orientation effects.

We have prepared hexagonal mesoporous silica films on glass substrates (Fisher Scientific borosilicate glass Pasteur pipets) under quiescent and continuous-flow conditions. For the static experiments the glass capillaries are filled with and submerged in a solution with a molar composition of 1 TEOS:41.1 HCl:0.61 C_{16}TABr: 555 H_2O. The films are grown at 80 °C for periods of time ranging from 1 h to 1 day. These conditions have been reported to result in oriented films at the air−water and the mica−water interface.[3,4] In addition to growth on the substrate, substantial growth in solution proceeds under these conditions.

Figure 1 shows a collection of top-view field-emission scanning electron micrographs (FE-SEM) from a film grown under static conditions acquired using a Hitachi S-900 FE-SEM after coating the samples with Pt, using an ion sputter system equipped with a magnetron electrode (Hitachi E-1030). Disklike particles are dominant, as is evident in the low-resolution FE-SEM images such as that shown in Figure 1a. Along with the dominant disklike particles, tapelike features are observed. With increasing time of deposition, intergrown domains span the surface of the substrate. The origin of the dominant disklike morphology is evident from high-resolution images, such as that shown in Figure 1b. The surface texture from the tubule arrangement

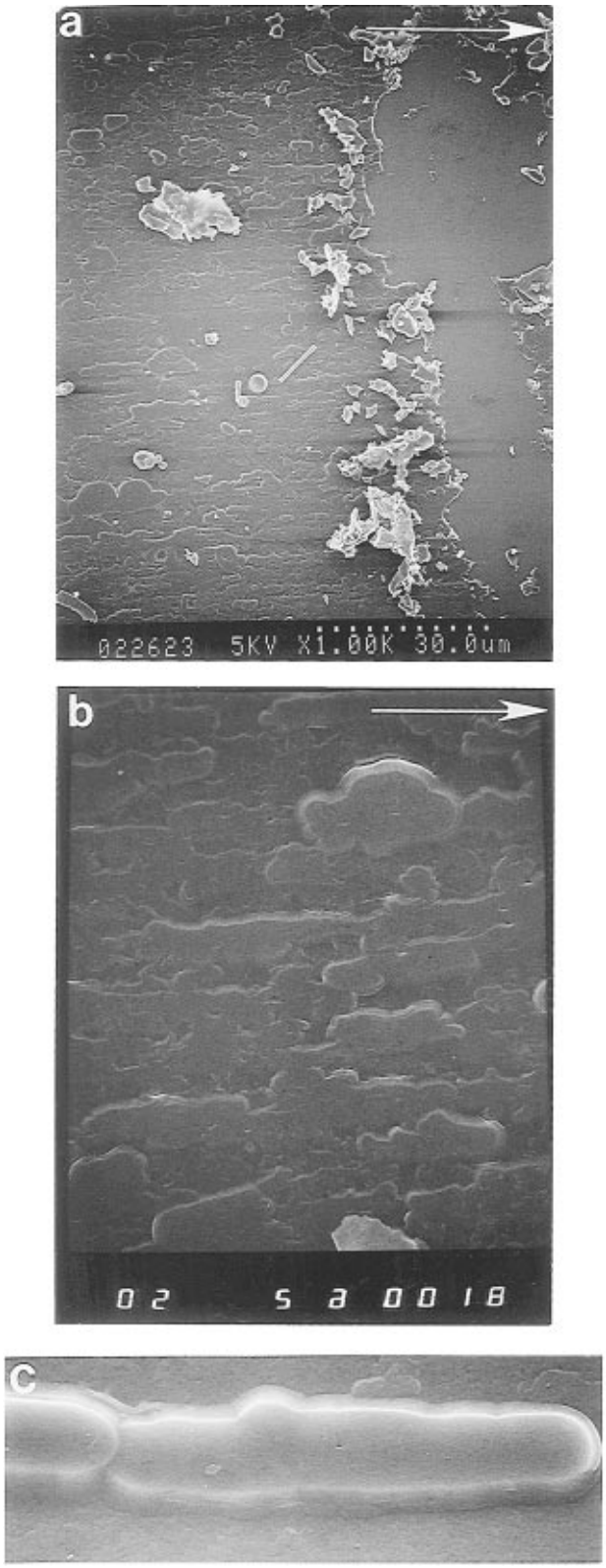

Figure 3. FE-SEM top views of films deposited under flow for 1 h at 80 °C. The arrows indicate the flow direction. (a) Low-magnification image (1000×). The film surface is marked by a scratch perpendicular to the flow direction. (b) 5000× magnification. (c) 20 000× magnification.

is resolved in the form of striations running along the imaging plane, suggesting that the tubules are oriented parallel to the substrate surface. The tubules apparently grow from the water−substrate interface; the growth continues toward the solution with further polymerization and assembly of surfactant−silicate

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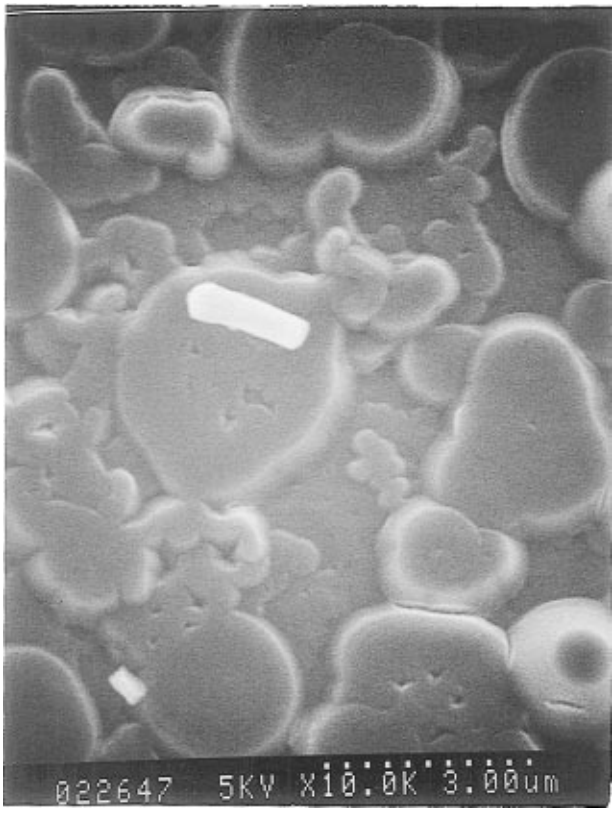

Figure 4. FE-SEM top view of film deposited under flow for 4 h at 80 °C. 10000× magnification.

species. This is further corroborated from the observation that the disks are wider at the bottom and narrow gradually as they grow away from the interface. This morphology suggests growth that proceeds through layer-by-layer deposition rather than deposition of preformed particles.

The growing mesostructures can bend in many directions resulting in disklike tertiary structures. Indentations, seen in Figure 1b,c, of the otherwise smooth surface of the disks occur where domains of differing orientation meet. Growth cannot proceed since the tubules would have to acquire large curvatures in order to further fill these gaps. Less often, under static conditions we observed features due to growth of the tubules pointing away from the substrate.

X-ray diffraction shows one low-angle reflection corresponding to a d_{100} spacing of approximately 33 Å, which is typical for hexagonal mesoporous silica formed from the synthesis mixture. After calcination at 500 °C examination by FE-SEM reveals no changes in the film texture; however, cracks develop that interrupt the film continuity as shown in Figure 1c.

For growth under a continuous-flow field a similarly prepared solution was pumped at 2.6 cm^3/min through a 1 mm i.d. glass capillary, which was kept in a temperature bath at 80 °C as illustrated in Figure 2. Films grown under shear flow for 1 h are shown in Figure 3; the flow direction is indicated by the arrows in the FE-SEM micrographs. The aligning shear rate at the surface was approximately 450 s^{-1}, and the resulting film was 200 nm in thickness. It is evident that flow has an effect on the tertiary structure of the films. Tapelike features running along the flow direction dominate the film morphology. In high-resolution images we observe less frequent indentations due to grain boundaries. Again, there was substantial particle growth in solution in the continuous-flow system; however, these large particles flowed through the system without depositing on the substrate.

The tapelike morphology is similar to that observed for films grown on mica,[3] where a preferred orientation was induced by the substrate lattice. Here the preferred orientation is induced by the flow field by hindering bending of the growing mesostructures in directions normal to the direction of the flow field. Therefore, endcap formation, although not eliminated, is reduced, and growth proceeds, on average, more along the flow direction and less in the transverse directions. However, for the conditions employed here this effect is observed only during the early stages of growth. Thicker films deposited for longer times (greater than 2 h) under flow do not show evidence of preferred orientation as shown in Figure 4 for a deposit formed after 4 h at 80 °C. A possible explanation is that the flow field in the vicinity of the growing film becomes disturbed as growth proceeds due to changes in the surface roughness. Also, depletion of the silica−surfactant species in solution may contribute to the dependence of the morphology on the reaction time.

In conclusion, we have demonstrated that intergrown layers of hexagonal mesoporous silica can be deposited under continuous flow and provided evidence that the flow field can induce a preferred orientation by mechanism(s) that are independent of or in addition to substrate−solution interfacial effects. To our knowledge this is the first time that orientation induced by an external flow field is reported for M41S type materials and may open new processing routes for film formation.

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