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Growth of Mesoporous Silica Film with Vertical Channels on Substrate Using Gemini Surfactants

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S Supporting Information

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The mesoporous silica thin films have attracted extreme interests in recent years because of their potential applications as sensors, optoelectronic devices, and functional membranes.[1] Such films with lamellar, hexagonal, and cubic mesostructures can be formed at solid/liquid/vapor interfaces[2] by spin-/dip-coating methods.[3] In general, these films are expected to have a three-dimensional (3D) or two-dimensional (2D) mesostructure with mesochannels normal to the substrate. It then makes great sense to fabricate films that have highly ordered structures and high porosity, yet are mechanically strong and allow selective but free transportation of materials through the films. Mesoporous silica films with 3D structures were synthesized under the direction of gemini surfactants in acidic conditions.[4] However, most prevailing 2D-hexagonal mesostructures are usually composed of parallel-oriented channels.[2a,4b,5] For obtaining films with 2D vertical mesochannels, some complicated strategies and special conditions were applied in previous works, which included nanophase separation of eutectic materials,[6] microphase separation of block copolymers,[7] surface modification for confinement effects,[8] employment of electric and magnetic fields,[9] electrochemical assistance,[10] introduction of ternary surfactant systems,[11] and $\pi-\pi$ interaction of template molecules.[12] However, the synthesis of mesoporous silica films with macroscopic 2D vertical channels is still full of challenges.

Gemini surfactants are a class of amphiphilic molecules with two polar head groups, which have a high charge density and a large headgroup area. The high hydrophilic/hydrophobic ratio makes gemini surfactants suitable supramolecular templates for the construction of mesostructures with a high organic/inorganic interface curvature.[13] To create 2D vertical mesochannels directly from the substrate—solution interface, the surfactants must self-assemble along the vertical direction rather than parallel to the substrate surface. In this work, we found that mesoporous silica films with vertical channels on silicon wafers can be easily grown by the self-assembly of gemini surfactants, costructure directing agents (CSDAs), and silica precursors in the presence of cosurfactant ethanol. Anionic gemini surfactants, *N*-acyl-L-glutamic acid with different chain length (C_n-GluA, $n = 12-18$), and cationic gemini surfactants, $C_{18}H_{37}N(CH_3)_2\text{-}(CH_2)_3N(CH_3)_3]Br_2$ (C_{18-3-1}), were used as directing agents of the mesopores. 3—aminopropyltrimethoxysilane (APS) and 3-carboxyethylsilanetriol sodium (CES) were used as CSDAs in the anionic and cationic surfactant templating routes, respectively. Tetraethyl orthosilicate (TEOS) was used as the silica source. The effect of ethanol on the mesostructure and homogeneity of the film was studied from the aspect of surfactant packing parameter and polymerization rate of the silica source. The growth process of thin films was studied, and a possible mechanism is proposed.

Silica films with 2D vertical mesochannels were typically prepared as follows: gemini surfactant was dissolved in a mixed solvent (ethanol/deionized water = 1:1, mass ratio), and then CSDA, TEOS and 0.10 M sodium hydroxide were added subsequently. After 10 min stirring, a silicon wafer was immersed horizontally in the solution and the reaction continued at 0 °C under stable conditions for a desired period of time. The mesoporous silica film was then formed on the substrate. The silicon wafer was then taken out, washed by deionized water ultrasonically, and dried at room temperature for about 2 h. Finally, the wafer was treated at 550 °C for 6 h or refluxed in an ethanolamine/ethanol (3:7, v/v) solvent mixture for 12 h to remove the surfactant. The synthesis molar composition is listed in Supporting Information 1.

Figure 1 shows the morphology and structure of a silica film synthesized with anionic surfactant C_{16}-GluA and APS in the presence of ethanol. The scanning electron microscopy (SEM) images illustrate that the silica film is macroscopically uniform and smooth (Figure 1A and C). For TEM, the sample was prepared by mechanically removing (scraping) some pieces of the mesoporous films from the substrate, which were then dispersed in ethanol and collected on a carbon-coated copper grid. The top view transmission electron microscopy (TEM) image and the corresponding Fourier transform diffracttogram (FD) of the mesoporous film are shown in Figure 1B, where hexagonally arranged mesochannels (plane group p6mm) with domain structures can be clearly observed. From the FD, the (10) plane spacing $d_{(10)} = 4.44$ nm is found (see also Supporting Information 2). The film was then sectioned on an ultramicrotome for cross-sectional TEM. Figure 1D suggests the cylindrical channels are perpendicular to the substrate. The thickness of the film is measured about 50 nm.

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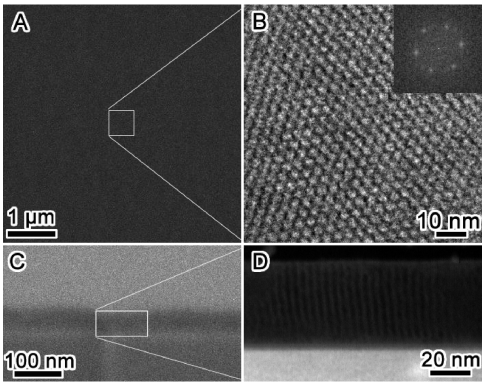

Figure 1. Top view (A) SEM and (B) TEM images, and cross-sectional view (C) SEM and (D) TEM images of a calcined mesoporous silica film synthesized with anionic gemini surfactant C_{16}-GluA. The synthesis molar composition is shown in Table 1 as sample 1 (Supporting Information 1). D is the dark-field image taken under scanning transmission (STEM) mode.

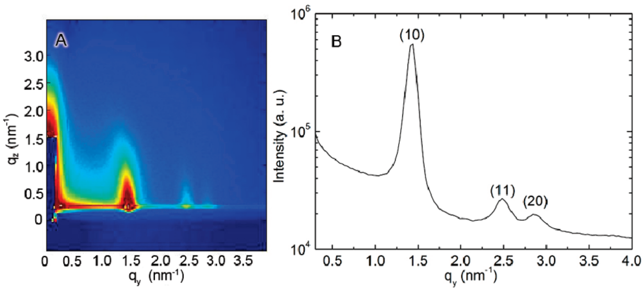

Figure 2. (A) GI-SAXS pattern. (B) Horizontal linecut along the in-plane wave vector transfer qy at the Yoneda wing. The three peaks positions, 1.411, 2.481, and 2.481 nm^{-1}, correspond to (10), (11), and (20) planes of a 2D hexagonal packing.

The mesostructure of the silica film was further characterized by grazing-incidence small-angle X-ray scattering (GI-SAXS) analysis. The 2D GI-SAXS pattern showed in Figure 2A illustrates that the channels in the silica film are perpendicular to the substrate.[14] The peak positions in its horizontal linecut (see Figure 2B) scale as $1{:}\sqrt{3}{:}2$, corresponding to the (10), (11) and (20) planes of a 2D hexagonal packing (plane group *p6mm*) in the film. The $d_{(10)}$ value was found to be 4.45 nm, which agrees very well the TEM analysis.

The other anionic gemini surfactants with different chain length of C_{12}-GluA, C_{14}-GluA, and C_{18}-GluA have also been used as directing agent. All of them create mesoporous silica films with vertical channels. Moreover, the cationic gemini surfactant C_{18-3-1}, can also direct the formation of vertical cannels with or without the help of CSDA. As shown in the Supporting Information 3, the film is homogeneous and smooth with a thickness of about 120 nm, and it contains the hexagonally aligned mesochannels with 2D *p6mm* plane group symmetry. The $d_{(10)}$ is measured 3.30 nm.

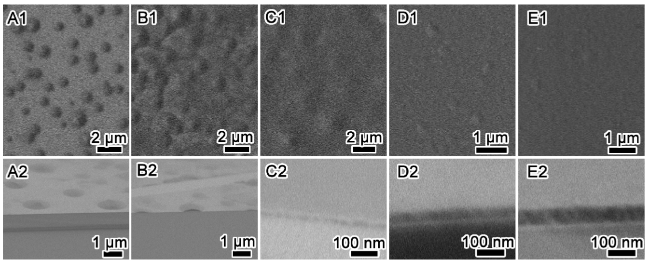

Figure 3. Top view (A1−E1) and cross-sectional view (A2−E2) SEM images of as-synthesized film products sampled at different reaction time. (A) 25, (B) 30, (C) 35, (D) 45, and (E) 60 min. The synthesis molar composition was the same to the sample 1 shown in Table 1 (Supporting Information 1).

To investigate the morphological and structural evolution of the mesochannels during synthesis, SEM images (Figure 3) of the products were observed as a function of reaction time. Several substrates were synchronously put into a beaker filled with precursor solution, and each one was taken out from the solution at different reaction times. The SEM images indicate that the condensation of the silica occurred at some "seed points" in the beginning (Figure 3A, 25 min). The seed points then grew to merge (Figure 3B, 30 min). Thirty-five minutes later, the film with about 10 nm thickness was formed preliminarily, but the film surface was still uneven (image 3C). The film became thicker with the reaction time and the surface of the film turned flat gradually (image 3D, 45 min). Finally, a smooth, flat film with about 70 nm thickness was obtained at 60 min (image 3E).

The formation of the silica film coincides with the nucleation-extend growth theory of thin films and the cooperative assembly mechanism.[15] First, the surfactant molecules were absorbed and accumulated at some active points on the substrate, then the surfactant molecules and the hydrolytic silica source molecules were synergistically assembled on the liquid/substrate interface to form initial nucleus with ordered channels at the active points. The nucleus absorbed surfactants and hydrolytic silica source molecules to grow continuously, and they combined to form a thin film finally. Hence the film was composed of many micro-domains, as shown in image 1B and Supporting Information 2.

The formation of the film mesostructure, its thickness, as well as the quality, were dependent on ethanol amount, ionization degree of the surfactant (controlled by the acid and alkali amount in the anionic surfactant system), CSDA/surfactant, and TEOS/CSDA molar ratios, temperature, and synthesis time. Among them, the ethanol amount was found to be the key parameter. For example, we found that the film surface became smooth with an increasing ethanol/water molar ratio from 0.07 to 2.35 (Figure 4A1−D1). It can be considered that the homogenization of film depends on the film growth rate. The presence

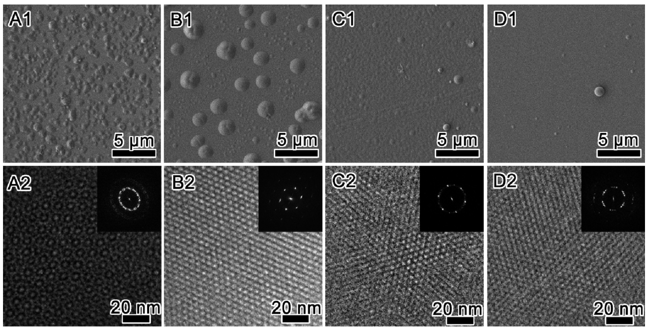

Figure 4. Top view SEM images (upper line with suffix '1') and TEM images (under line with suffix '2') of mesoporous silica films obtained with different ethanol amounts. Ethanol/H_2O mole ratios are (A) 0.07, (B) 0.16, (C) 0.22, and (D) 2.35, respectively. The synthesis molar composition is corresponding to sample 1−4 in Table 2 (Supporting Information 1), respectively.

of ethanol slows down the growth process, i.e., the hydrolysis reaction of TEOS and the condensation of silicate on the substrate. With a lower ethanol concentration, the particle aggregation is too fast for the homogenization growth of the film (Figure 4A1, B1). With a fairly higher ethanol concentration, the slower hydrolysis of TEOS and condensation of the silica—surfactant aggregates cause the homogenization of the film with vertical mesochannels (images C1 and D1). However, excessive ethanol significantly slows down the silicate hydrolysis and condensation, which may decrease the regularity of the cooperative surfactant self-assembly and thus induce disordering in the mesostructures (see the Supporting Information 4).

The effect of ethanol amount on the film mesostructure formation is shown in panels 4A2—D2. The TEM image taken from the film surface of a mole ratio of 0.07, with corresponding Fourier transform diffractogram shown in the inset, shows the [001] direction of cage-type cubic $Pm\bar{3}n$ mesostructure with defects and modulation (Figure A2). Films obtained from ethanol/water mole ratios in the range of 0.16—2.35 proved to have 2D hexagonal *p6mm* mesostructures at both bumps and flat surfaces (images B2—D2). The ethanol effect can be explained in terms of the packing parameter g of the surfactant micelles. According to the classical surfactant self-assembly theory,[16] it is well-known that the structure of the mesoporous materials depends on the $g = v/al$ (where v is the chain volume, a is the effective hydrophobic/hydrophilic interfacial area, and l is the chain length) value. The addition of ethanol increases v because ethanol molecules are more lipophilic than water; and the a value is decreased in virtue of the depressed polarity of the solution. It is well-known that, for lyotropic liquid crystals, the g parameter of a cubic $Pm\bar{3}n$ mesostructure is smaller than that of a 2D hexagonal *p6mm*.[17] Thus, large amount of ethanol facilitates the formation of the 2D hexagonal *p6mm* mesostructure rather than a 3D structure.

In conclusion, a series of gemini surfactants were successfully used to prepare silica films with perpendicular *p6mm* channels. In contrast, hexadecyltrimethylammonium bromide (CTAB) with a single polar head, a very widely used surfactant, can only form channels parallel to the substrates.[1a,3,4a] In our work, it was found that mesoporous silica films with perpendicular channel structures can be synthesized on both hydrophilic and hydrophobic substrate surfaces in a very wide water contacting angle range of 30—100° (Supporting Information 5). The assembly of the surfactants depends on the hydrophilic/hydrophilic properties of the surfactants, which imposes different interactions at the solution-substrate interface. Although the significantly high hydrophilicity of the gemini surfactants used in this work easily leads to the formation of vertical rodlike micelles on the substrate, how these micelles develop into vertical *p6mm* channels is still not completely understood in detail yet, and requires further investigations both experimentally and theoretically.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** (1) Experimental, (2) macroscopic observation of silica film, (3) mesoporous silica films synthesized with C_{18-3-1}, (4) effect of ethanol addition amount and (5) films grew on different surfaces. This material is available free of charge via the Internet at http://pubs.acs.org.

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