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# Formation of Novel Oriented Transparent Films of Layered Silica–Surfactant Nanocomposites

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Self-organization of molecules into a highly ordered architecture has attracted increasing attention from a wide range of scientific interests.[1–3] Polymerization of organic or inorganic monomers in an environment with ordered structure is a method by which polymers or composites with unique structures and properties can be prepared.[4–12] Recently, alkyltrimethylammonium salts have been used as templates for the preparation of mesoporous silicates[8–12] and other metal oxides.[10] In this communication, the synthesis of novel transparent thin films of layered silica–surfactant nanocomposites by polymerization of tetramethoxysilane in aqueous solutions of alkyltrimethylammonium salts is reported. This is the first report of the successful imparting of highly ordered nanostructure to the practically important alkoxysilane-derived materials.[13,14] Since the composites are obtained as oriented transparent films in which microscopic anisotropy can be directly converted into macroscopic anisotropy, they can be a new class of materials for molecularly designed self-assembly.

The silica–surfactant nanocomposites were prepared as follows: tetramethoxysilane (abbreviated as TMOS) was partially hydrolyzed by a substoichiometric amount of water (the molar ratio of TMOS:$H_2O$ was 1:2) under acidic conditions (pH = 3) for 2 h at room temperature. Initially the mixture was an emulsion, but it became homogeneous as the hydrolysis proceeded. Then an aqueous solution of alkyltrimethylammonium bromide ($C_nH_{2n+1}N(CH_3)_3^+$; C*n*TAB, where *n* denotes the carbon number in the alkyl chain) was added, and the mixture was stirred at room temperature. The concentrations of C*n*TAB in the solutions were 1 M for C6–12TAB, 0.8 M for C14TAB, and 0.3 M for C16TAB. Then the solution was spin coated on a glass substrate and dried in air at 100 °C to remove solvent and to complete condensation of the silica. Thus, transparent thin films formed on the substrates.[15] Powdered samples were prepared by drying solutions of TMOS and C*n*TAB at an elevated temperature (around 70 °C).

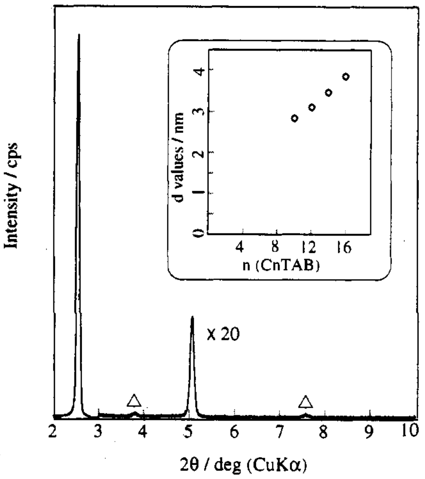

**Figure 1.** X-ray diffraction pattern of the silica–C14TAB composite film (at a TMOS:C14TAB ratio of 2.5:1). △: C14TAB crystal. Inset: The variation of the *d* values of the layered silica–C*n*TAB nanocomposites as a function of alkyl chain length.

Figure 1 shows the X-ray diffraction pattern of the silica–C14TAB composite film (the molar ratio of TMOS:C14TAB is 2.5:1) with a thickness of ca. 1 μm. A very sharp diffraction peak with a *d* value of 3.5 nm, which accompanied second-order reflection (*d* value of ca 1.8 nm), was observed in the XRD pattern. Transparent thin films were obtained for the composites with C6-, C8-, C10-, C12-, and C16TABs. However, the diffraction peaks were very weak and broad when C6- and C8TABs were used. The *d* values for the compounds obtained for C10–C16TABs are shown in the Figure 1 inset. The *d* values changed linearly as a function of the alkyl chain length of C*n*TAB. Considering the fact that the shorter alkyltrimethylammonium bromides (C6TAB and C8TAB) did not give highly ordered structures, the aggregation of C*n*TAB seems to be essential for this layered organization of silica and C*n*TAB.

The infrared spectrum of the layered silica–C14TAB composite showed absorption bands characteristic of C14TAB (such as a C–H stretching vibration of the $CH_2$ group at 2925 and 2853 $cm^{-1}$, which can be assigned to aggregated C14TAB[16]) and silica (such as a Si–O–Si symmetric stretching vibration at around 1230 and 1080 $cm^{-1}$ and a Si–O–Si bending vibration at around 460 $cm^{-1}$). This shows that the composites are composed of siloxane polymer and aggregated C14TAB. Thermogravimetric analysis of the composites showed a weight loss corresponding to the amount of C14TAB starting from 200 °C, The DTA curve showed an exothermic peak around 300 °C due to oxidative decomposition of C14TAB, and the behavior is similar to that of C*n*TAB intercalated in a layered aluminosilicate (montmorillonite).[17] The DTA curve of C14TAB shows a sharp endothermic peak at around 100 °C due to melting. The absence of the endothermic peak at 100 °C in the DTA curve of the silica–C14TAB composite indicates that most of C14TAB was complexed with silica. These results on XRD, IR, and thermal analysis confirmed the formation of the silica–C14TAB nanocomposites. Similar results were obtained for the silica–C10–16TAB systems.

Rapid evaporation of solvent before gelation is essential for the formation of the highly ordered layered composites. Thinner films gave more intense X-ray diffractions, and the X-ray diffraction peaks of the powdered sample are broad compared with those of the films. Moreover, no layered composite was obtained when the reaction mixture was allowed to react until

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(15) The thickness of the film can be varied by changing the spinning ratio on coating or the period of mixing. Films with a thickness of ca. 1 μm were used for the present study because thicker films may be peeled off from the substrate.

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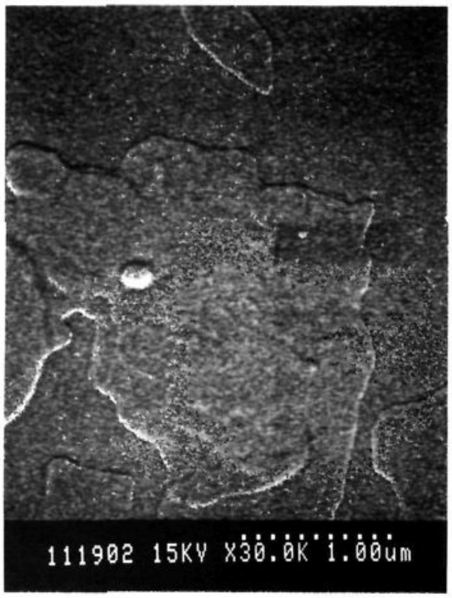

**Figure 2.** Scanning electron micrograph of the surface of the layered silica–C16TAB composite film. This micrograph was obtained on a Hitachi S-900 scanning electron microscope.

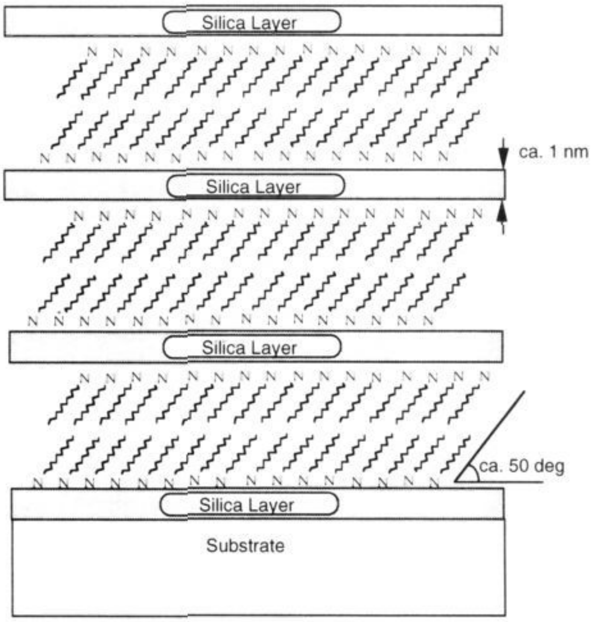

**Figure 3.** A proposed schematic structure of the layered silica–C*n*TAB nanocomposite films.

gelation. Thus, the present system is apparently different from the so-called sol–gel processes.[13] From these observations, the following reaction mechanism is proposed for the formation of the layered composites. During evaporation of solvents, C*n*TAB form lamellar aggregates and the hydrophilic silica oligomers interact with the hydrophilic head groups of the surfactants that are located at the external surface of the lamellar aggregates. Being surrounded by the silica layer, the lamellar aggregates solidify upon evaporation of solvents to form the layered silica–C*n*TAB nanocomposites without crystallization of C*n*TAB.

A scanning electron micrograph (SEM, Figure 2) of the surface of the silica–C16TAB film shows that the platelet aggregates piled up on the surface. This observation also indicates that the film is composed of a regular multilayered structure in which molecular orientation can be directly converted into macroscopic anisotropy. From these observations, a schematic structure is proposed for the present composites (Figure 3).

The films are thought to be composed of lamellar aggregates of C*n*TAB being sandwiched by thin silica layers. Since the silica polymers are hydrophilic after the hydrolysis, they tend to interact with hydrophilic head groups. The *d* value (ca. 1.2 ± 0.1 nm) extrapolated to $n = 0$ in a plot of *d* spacings versus the alkyl chain length corresponds to the thickness of the layers of silica and head groups (trimethylammonium bromide). It may be supposed that the C*n*TAB aggregate as bilayers with their alkyl chains fully extended, the alkyl chains of C*n*TAB inclined to the lamellae at ca. 50°. There may be other possible structures that satisfy the observed results on the layered silica–C*n*TAB organization. In order to determine the exact structure of the composites, further study is now underway and will be reported subsequently.

The relative ratio of TMOS:C14TAB was changed to determine the composition of the layered composites. When the relative ratio of TMOS:C14TAB was 1:1, the diffraction peaks due to the C14TAB crystal were clearly detected by XRD (the most intense diffraction peak due to the C14TAB crystal was observed at $2\theta = 3.7°$, corresponding to a *d* value of 2.4 nm) together with those of the layered composite. An endothermic peak was observed at around 100 °C in the DTA curve of the sample, showing the existence of the C14TAB crystal in the sample. Very weak diffraction peaks due to the C14TAB crystal were also detected in the XRD pattern of the film prepared at the relative TMOS:C14TAB ratio of 2.5:1 (Figure 1). In contrast, the XRD pattern of the product prepared at a relative TMOS:C14TAB ratio of 10:1 showed no diffraction peaks due to the C14TAB crystal and a broadened diffraction peak (*d* value of ca. 4.0 nm) due to the composite. The DTA curve supported the absence of the C14TAB crystal in the sample (TMOS:C14TAB = 10:1). An excess amount of C14TAB was isolated and crystallized, as is evidenced by XRD and DTA results. There is a general tendency that the *d* value increases slightly with the increase in the relative ratio of TMOS to C*n*TAB. This change in the *d* values is assumed to be due to the change in the thickness of the silica layer. Thus, the composition of $SiO_2$:C14TAB in the layered composites can be varied around 2.5:1 to some extent.

Preparation of siloxane polymers in the hydrophobic[5,6] or hydrophilic[7] part of bilayer membranes has been reported. Since the amphiphiles used in those studies form bilayers by themselves, the organization and the interactions are different from those of the present system. Crystalline layered silicate–surfactant composites have been obtained by crystallization of silicate[9,10] or intercalation of surfactants into a crystalline layered silicate.[18] Although they have been used as a precursor of mesoporous silicates, the mechanism of their transformation into mesoporous silicates has been controversial. The layered composites reported here formed by a different mechanism, because they formed at room temperature under an acidic condition where silicates do not crystallize.

It should be noted that the composites have been obtained as highly transparent films in a wavelength region from 220 to 2000 nm. Additionally, poorly water soluble organic compounds such as pyrene can be introduced into the layered composites. Surfactant aggregates in solutions[19,20] and their transformation into solids such as LB films[21] and synthetic bilayer membranes[22] have widely been investigated for constructing molecularly ordered architecture. The composites reported in this paper represent a novel state of surfactant aggregates, and their application is promising because of the simple preparation, the micro- and macroscopic anisotropy, and transparency.

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