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Preparation of Transparent Silica-Surfactant Nanocomposite Films with Controlled Microstructures

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Novel silica-alkyltrimethylammonium (with the alkyl groups of decyl, dodecyl, tetradecyl, hexadecyl, and octadecyl) bromide nanocomposite films were synthesized by coating the precursor solutions containing prehydrolyzed tetramethoxysilane and alkyltrimethylammonium bromide. The composites are thought to be composed of aggregates of alkyltrimethylammonium bromides and thin silica layers. The *d* values of the products varied depending on the relative ratios of tetramethoxysilane and surfactants, suggesting that the microstructures of the products can be controlled by simply changing the compositions. Since the present composites are obtained as transparent films, they have potential applicability as a new class of functional materials, especially for photofunctional purposes.

Inorganic–organic nanocomposites with ordered structures have been investigated due to their well-defined structure, and stability. Recently, the preparation of inorganic–organic nanocomposites by using supramolecular assemblies of surfactants to template the reactions of inorganic species has attracted increasing interest as a biomimetic approach to the fabrication of inorganic/surfactant biphase array.[1)] The preparation of silica-based mesoporous materials by using surfactant aggregates as structure-directing agents is a successful example of this synthetic strategy.[2—9)] Although these solids may have potential applicability as adsorbents, catalysis and hosts for inclusion compounds, the mechanism for the formation and the detailed structure of the resulting composites are still controversial.[10—16)] The transformation of layered silicate, kanemite, during the intercalation of cationic surfactants and the cooperative assembly of soluble silicate and surfactants have been proposed to be two typical reactions for the formation of the mesostructured silica-surfactant composites. Many efforts are being made to elucidate the reaction mechanisms and the structures of the products further and to apply theses solids practically.

The morphology of the resulting mesostructured materials is another key feature in the formation of mesostructured inorganic–organic nanocomposite materials as a biomimetic process.[17—26)] Among them, the processing of the silica-surfactant mesostructured materials as thin films is one subject of current interest, since the films might be applied to sensors, optical or electronic materials, to which powder samples do not have any access. Very recently, thin films of silica-surfactant mesostructured materials have been prepared on solid substrates such as mica.[20,21,23)]

The preparation of the transparent thin films of periodic silica-alkyltrimethylammonium salt nanocomposites by simply depositing the solutions containing prehydrolyzed tetramethoxysilane and alkyltrimethylammonium salts has been reported by Ogawa.[27—30)] Since the resulting composites are obtained as oriented transparent films in which microscopic anisotropy can be directly converted into macroscopic one, they can be a new class of materials for constructing molecularly-designed self assembly. The transformation of surfactant aggregates into solids such as LB films, so called "self-assembly",[31)] and synthetic bilayer membranes [32)] have been widely investigated for constructing molecularly ordered architecture. The preparations of thin films of inorganic–organic nanocomposite materials have also been investigated as novel supramolecular systems.[33—35)] The composites reported in this paper are novel states of surfactant aggregates and their application is promising because of the simple operation for the preparation, the micro- and macroscopic anisotropy, transparency and so on. In this study, the preparation of the silica–surfactant nanocomposite films at variable compositions has been conducted to obtain composites with controlled microstructures.

Experimental

Materials. Tetramethoxysilane (abbreviated as TMOS) and alkyltrimethylammonium bromides [$(C_nH_{2n+1})(CH_3)_3NBr$; abbreviated as C_nTAB, where *n* denote the carbon number in the alkyl chain] were obtained from Tokyo Kasei Industries Co., and used without further purification.

Sample Preparation. The silica-surfactant nanocomposites were prepared as follows: TMOS was partially hydrolyzed by substoichiometric amounts of deionized and distilled water (the molar

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ratio of TMOS : H_2O was 1 : 2) under an acidic condition (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 C_nTAB was added and the mixture was stirred at room temperature. The concentrations of C_nTAB in the solutions were 1 M for C6-12TAB, 0.8 M for C14TAB, and 0.25 M for C16TAB (1 M = 1 mol dm^{-3}). When two kinds of surfactants with different ratios were mixed, the total concentration of the surfactants was fixed at 0.3 M. The solution was spin coated on a Pyrex glass substrate and dried in air at room temperature to remove solvent and to complete condensation of the silica. Thus, transparent thin films formed on the substrates.

For the solid-state NMR spectroscopy, powdered samples were prepared by drying the solutions of TMOS and C_nTAB at an elevated temperature (around 70 °C).

Characterization. X-Ray powder diffraction was performed on a RINT 1100 diffractometer (Rigaku) using Mn-filtered Fe $K\alpha$ radiation. The thicknesses of the films were determined with a surface profilometer (Kosaka Laboratory Co., SE 1700). ^{29}Si magic angle spinning nuclear magnetic resonance spectra were recorded on a JEOL GSX-400 spectrometer with the spinning ratio of 5000 rpm and the repetition time of 60 s.

Results and Discussion

By spin coating the mixture containing the prehydrolyzed TMOS and C_nTAB (at the molar ratio of TMOS : C_nTAB = 5 : 1), transparent thin films formed on the substrates. Very sharp diffraction peaks, which accompanied 2nd order reflections, were observed in the XRD patterns of the products when C10, C12, C14, C16, and C18TAB were used. However the diffraction peaks were very weak and broad when C6 and C8TABs were used. The *d* values increased with the increase in the alkyl chain length of C_nTAB. Considering the fact that the shorter alkyltrimethylammonium bromides (C6TAB and C8TAB) did not give highly ordered structures, the aggregation of C_nTAB seems to be essential for this organization of silica and C_nTAB. The *d* values observed here are similar to those reported for the silica–C_nTAB composite films at the molar ratio of TMOS : C_nTAB = 4 : 1,[27] suggesting that similar mesostructures were present in this system.

For the following NMR experiment, a powder sample was prepared from the mixture of TMOS and C16TAB (at the molar ratio of 5 : 1). The X-ray diffraction pattern of the powder sample showed a diffraction peak with the *d* value of 4.1 nm, although the diffraction peak was broad compared with that observed for the corresponding spin coated sample. The observed single diffraction peak with a similar *d* value implied that the powder sample possesses an ordered microstructure similar to that of the spin coated film. The ^{29}Si MAS-NMR spectrum of the powder sample is shown in Fig. 1. The spectrum showed three signals ascribable to Q2, Q3, and Q4 environments of silicon at around −90, −100, and −120 ppm relative to TMS, respectively. This spectrum showed that the TMOS polymerized to form siloxane network in the product. Additionally, the broadness of the signals indicated the non-crystalline nature of the siloxane network, as has previously been proposed for the silica-surfactant mesostructured materials.[5,13]

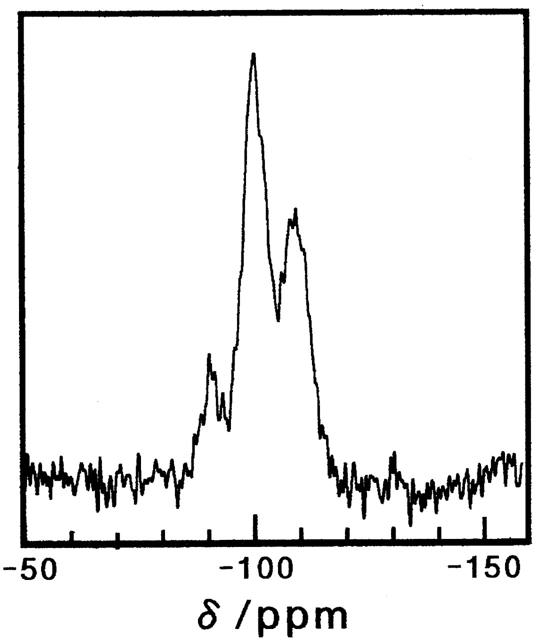

Fig. 1. The ^{29}Si-MAS NMR spectrum of the powder product prepared from the mixture of TMOS and C16TAB at the molar ratio of 5 : 1.

Different reaction conditions were employed for the preparation of the thin films, to understand the reaction further. The X-ray diffraction patterns of the silica–C16TAB films (TMOS : C16TAB ratio of 4 : 1) prepared at different spinning ratios (2000, 3000, and 4000 rpm) were recorded. The increased spinning ratios resulted in thinner films (The thicknesses of the films were determined by a surface profilometer to be ca. 2.0, 1.5, and 1.3 μm for the spinning ratios of 2000, 3000, and 4000, respectively) and the thinner films gave more intense X-ray diffractions with the same *d* values. As mentioned earlier, the X-ray diffraction peaks of the powdered sample are broad compared with those of the films. When the mixture was allowed to react for a longer period before the coating, the X-ray diffraction pattern of the resulting film became broader. Moreover, no ordered composite was obtained when the reaction mixture was allowed to react until gelation.

These observations suggest that the key requirement for the formation of the highly ordered composites is the rapid evaporation of solvent before gelation.[27] During the evaporation of solvents, C_nTAB form aggregates and the hydrophilic silica oligomers dissolved in the reaction mixture interact with the hydrophilic head groups of the surfactants that are located at the external surface of the C_nTAB aggregates. Being surrounded by the silica layer, the aggregates solidified upon evaporation of solvents to form the silica–C_nTAB nanocomposites without crystallization of C_nTAB. This reaction mechanism is apparently different from those proposed for the silica-based mesostructured materials which have been obtained as precipitates[2—16,20—26,36,37] and so-called "sol–gel processes" which have been used for the preparation of the functional silica-organic composites materials.[38]

It is worth noting as a merit of the present system that the composition of the products can be controlled by simply changing the relative ratios of TMOS to C_nTAB in the starting mixture. The molar ratio of TMOS to C_nTAB has been changed (from 50 : 1 to 1 : 1 for TMOS : C_nTAB) in order to vary the microstructures of the composites. The variation in the XRD patterns of the products obtained when C16TAB was used is shown in Fig. 2. The diffraction peak shifted toward lower 2θ region with the increase in the relative ratios of TMOS to C16TAB. When the amounts of TMOS were over 20, the diffraction peak became very broad. The changes in the XRD pattern again indicate the surfactant aggregation is a key factor for the formation of the highly ordered architecture.

Figure 3 represents the relationship between *d* values obtained from the XRD diffraction patterns shown in Fig. 2 as a function of the relative ratios of TMOS : C16TAB. There is a general tendency toward the larger *d* values with the increase in the relative ratio of the TMOS to C16TAB. This change in the *d* values is assumed to be due to the change in the thickness of the silica layer. The silica layer in the composite became thicker with the increase in the relative ratios of TMOS to C_nTAB, as is schematically shown in Fig. 4. Since the silica layer is composed of an amorphous siloxane network where SiO_4 tetrahedra are linked randomly, as revealed by the ^{29}Si-MAS-NMR result (Fig. 1), the detailed microstructures of the composites are difficult to elucidate. From the molar ratio of TMOS to C16TAB and their densities, the thickness of the silica layer can roughly be estimated. The thickness of silica layer is estimated to be ca. 1.0 nm when the TMOS : C16TAB was 5 : 1. This calculated value verified the proposed structures.

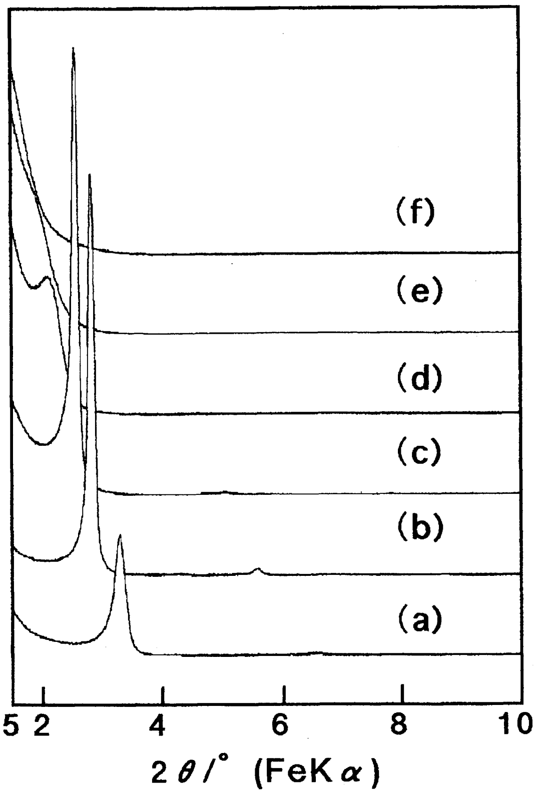

Fig. 2. The X-ray diffraction patterns of the silica–C16TAB composite films (prepared at the TMOS : C16TAB ratio of 2.5 : 1 (a), 5 : 1 (b), 10 : 1 (c), 15 : 1 (d), 20 : 1 (e), and 50 : 1 (f)).

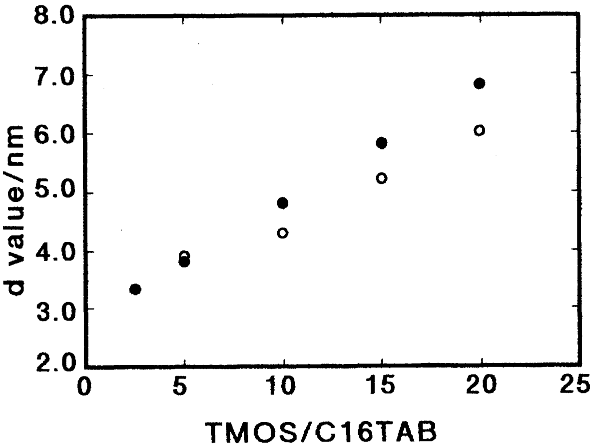

Fig. 3. The variation of the *d* values of the silica–C16TAB nanocomposite films as a function of the TMOS : C16TAB ratio. Open circle: experimental value closed circles: value calculated supposing that the lamellae aggregates.

Supposing that the composites are fully lamellar where the thin silica layer and surfactant bilayer piled up alternatively, the change in the *d* values must be larger. (The calculated change in the *d* values is also shown in Fig. 3.) Thus, the origin of the observed change in the *d* values is not so simple. The transition from the lamellar phase to the hexagonally packed cylindrical aggregate phase may be involved in the observed change in the *d* values, since a larger amount of silica is required to cover the cylindrical micelles than that required for the lamellar phase.

In the aqueous surfactant systems, the states of the surfactant aggregates depend on the concentration of the surfactant. Therefore, the ratio of surfactant to silica is thought to be an important factor to control the mesostructures in the present silica-surfactant composite systems. Besides the silica/surfactant ratios, the amounts of solvent and acid also affected the X-ray diffraction patterns of the products. The silica-surfactant mesostructured materials in which the hexagonally packed cylindrical surfactant micelles surrounded by a thin silica layer have been prepared by using surfactant powder instead of aqueous solutions of surfactants.[29] The surface properties of the silica in the reaction mixture during the formation of the composites are assumed to be related to the formation of the present mesostructured materials.

Similar experiments were conducted for the TMOS/C14TAB system. The change in the XRD pattern showed a similar tendency toward larger *d* spacings and broader X-ray diffraction patterns with the increase in the relative ratio of TMOS to C14TAB. The *d* value varied from 3.5 to 5.2 nm for the relative ratios of 2.5 : 1 to 15 : 1 (TMOS : C14TAB), suggesting the change in the thickness of silica layer.

Although the mesostructures need to be elucidated further,

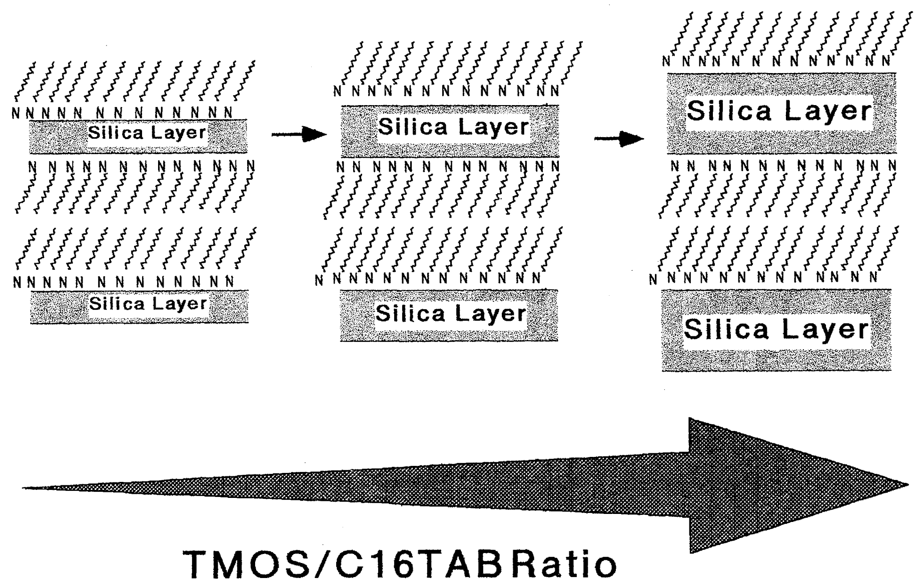

Fig. 4. Schematic drawing for the change in the microstructure of the silica–C_nTAB nanocomposite films.

the present results indicate that the microstructures of the silica-surfactant nanocomposites can be controlled by simply changing the composition of the starting mixture. This is a very important characteristic of the present synthetic approach because it is not so straightforward to control the microstructure of the products by other reported procedures and the thickness of the silica layer must affect the thermal and mechanical properties of the products, especially in practical applications.

Surfactant mixtures have been used as structure-directing agents in order to vary the microstructures of the products. In this series of experiments, C_nTABs with different alkyl chain lengths were mixed together before the reaction with TMOS and the molar ratio of TMOS : surfactants (total) was kept constant (4 : 1). The *d* values of the products obtained for the C16TAB/C12TAB mixture (C16TAB : C12TAB ratios were 5 : 1, 1 : 1, and 1 : 5) systems are shown in Fig. 5 as a function of the C16TAB/C12TAB ratios. The *d* values decreased with the decrease in the relative ratio of C16TAB to C12TAB. The C16TAB/C10TAB system gave similar results. Since the molar ratio of the TMOS : surfactant (total) was kept constant (4 : 1), the variation of the *d* values is thought to reflect the change in the microstructure, probably the thickness, of the surfactant aggregates in the composites. These observations suggest that the surfactants with different alkyl chain lengths were mixed to form aggregates in the composite film. The results described above for the mixed surfactant system open up a new opportunity to construct more sophisticated supramolecular systems.

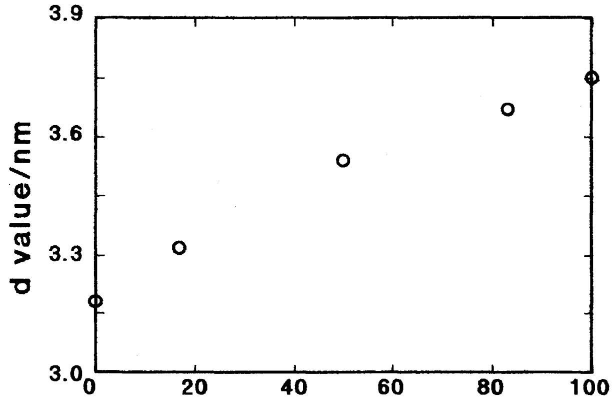

Fig. 5. The variation of the *d* values of the silica–C16TAB/C12TAB nanocomposite films as a function of the C16TAB : C12TAB ratio.

Conclusions

The silica-surfactant composite films with well-ordered mesostructures have been successfully synthesized by the reaction between TMOS and alkyltrimethylammonium salts under acidic conditions. In comparison with the other reported reactions for the preparation of silica-surfactant mesostructured materials, the present reaction offers some distinct advantages:

1) The products can be obtained as transparent films.

2) The composition of the product can be controlled easily by simply changing the ratio of the reaction mixture to influence the microstructure of the products.

3) The process occurs relatively quickly under ambient reaction conditions.

Thus, the newly developed reaction is a promising way for the preparation of functional inorganic–organic nanocomposite materials.

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References

1) J. H. Fendler, "Membrane-Mimetic Approach to Advanced Materials," Springer-Verlag, Berlin (1994).

2) T. Yanagisawa, T. Shimizu, K. Kuroda, and C. Kato, *Bull. Chem. Soc. Jpn.*, **63**, 988 (1990).

3) S. Inagaki, Y. Fukushima, and K. Kuroda, *J. Chem. Soc., Chem. Commun.*, **1993**, 680.

4) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature*, **359**, 710 (1992).

5) J. S. Beck, J. C. Vartuli, W. L. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmidt, C. T-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, and J. L. Schlenker, *J. Am. Chem. Soc.*, **114**, 10834 (1992).

6) A. Monnier, F. Schüth, Q. Huo, D. Kumar, D. Margolese, R. S. Maxwell, G. D. Stucky, M. Krishnamurty, P. Petroff, A. Firouzi, M. Janicke, and B. F. Chmelka, *Science*, **261**, 1299 (1993).

7) Q. Huo, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schüth, and G. D. Stucky, *Nature*, **368**, 317 (1994).

8) P. T. Tanev, M. Chibwe, and T. J. Pinnavaia, *Nature*, **368**, 321 (1994).

9) Q. Huo, D. I. Margolese, U. Ciesla, D. G. Demuth, P. Feng, T. E. Gier, P. Sieger, A. Firouzi, B. F. Chmelka, F. Schüth, and G. D. Stucky, *Chem. Mater.*, **6**, 1176 (1994).

10) C-Y. Chen, H-X. Li, and M. E. Davis, *Microporous Mater.*, **2**, 17 (1993).

11) C-Y. Chen, S. L. Burkett, H-X. Li, and M. E. Davis, *Microporous Mater.*, **2**, 27 (1993).

12) C-Y. Chen, S.-Q. Xiao, and M. E. Davis, *Microporous Mater.*, **4**, 1 (1995).

13) S. Inagaki, A. Koiwai, N. Suzuki, Y. Fukushima, and K. Kuroda, *Bull. Chem. Soc. Jpn.*, **69**, 1449 (1996).

14) S. Inagaki, Y. Sakamoto, Y. Fukushima, and O. Terasaki, *Chem. Mater.*, **8**, 2089 (1996).

15) A. Firouzi, D. Kumar, L. M. Bull, T. Besier, P. Sleger, Q. Huo, S. A. Walker, J. A. Zasadznsky, C. Glinka, J. Nicol, D. Margolese, G. D. Stucky, and B. F. Chmelka, *Science*, **267**, 1138 (1995).

16) J. C. Vartuli, C. T. Kresge, M. E. Leonowicz, A. S. Chu, I. D. Johnson, and E. W. Sheppard, *Chem. Mater.*, **6**, 2070 (1994).

17) S. Mann and G. Ozin, *Nature*, **382**, 313 (1996).

18) S. Baral and P. Schoen, *Chem. Mater.*, **5**, 145 (1993).

19) a) S. Oliver, A. Kuperman, N. Coombs, A. Lough, and G. A. Ozin, *Nature*, **378**, 47 (1995); b) D. Walsh and S. Mann, *Nature*, **377**, 320 (1995).

20) H. Yang, A. Kuperman, N. Coombs, S. Mamiche- Afara, and G. A. Ozin, *Nature*, **379**, 703 (1996).

21) H. Yang, N. Coombs, I. Sokolov, and G. A. Ozin, *Nature*, **381**, 589 (1996).

22) P. T. Tanev and T. J. Pinnavaia, *Science*, **271**, 1267 (1996).

23) I. A. Aksay, M. Trau, S. Manne, I. Honma, N. Yao, L. Zhou, P. Fenter, P. M. Eisenberger, and S. M. Gruner, *Science*, **273**, 892 (1996).

24) H-P. Lin and C-Y. Mou, *Science*, **273**, 765 (1996).

25) S. Schacht, Q. Huo, I. G. Voigt-Martin, G. D. Stucky, and F. Schüth, *Science*, **273**, 768 (1996).

26) A. Ayral, C. Balzer, T. Dabadie, C. Guizard, and A. Julbe, *Catal. Today*, **25**, 219 (1995).

27) M. Ogawa, *J. Am. Chem. Soc.*, **116**, 7941 (1994).

28) M. Ogawa, *Langmuir*, **11**, 4639 (1995).

29) M. Ogawa, *Chem. Commun.*, **1996**, 1149.

30) M. Ogawa, *Langmuir*, **13**, 1853 (1997).

31) A. Ulman, "An Introduction to Ultrathin Organic Films from Langmuir Blodgett to Self-Assembly," Academic Press Inc., San Diego (1991).

32) T. Kunitake, *Angew. Chem., Int. Ed. Engl.*, **39**, 709 (1992).

33) a) G. Cao, H.-G. Hong, and T. E. Mallouk, *Acc. Chem. Res.*, **25**, 420 (1992); b) T. E. Mallouk, H-N. Kim, P. J. Ollivier, and S. W. Keller, in "Comprehensive Supramolecular Chemistry," ed by G. Albelti and T. Bein, Pergamon, Oxford (1996), Vol. 7, pp. 189—217.

34) M. Ogawa, T. Handa, K. Kuroda, C. Kato, and T. Tani, *J. Phys. Chem.*, **96**, 8116 (1992); M. Ogawa, M. Takahashi, C. Kato, and K. Kuroda, *J. Mater. Chem.*, **4**, 519 (1994); M. Ogawa, M. Takahashi, and K. Kuroda, *Chem. Mater.*, **6**, 715 (1994).

35) B. Dunn and J. I. Zink, *J. Mater. Chem.*, **1**, 903 (1991).

36) a) K. Sakata and T. Kunitake, *J. Chem. Soc., Chem. Commun.*, **1990**, 504; b) K. Sakata and T. Kunitake, *Chem. Lett.*, **1989**, 2159.

37) a) M. Dubois, Th. Guik-Krzywicki, and B. Cabane, *Langmuir*, **9**, 673 (1993); b) M. Dubois and B. Cabane, *Langmuir*, **10**, 1615 (1994).

38) C. J. Brinker and G. W. Scherer, "Sol–Gel Science; The Physics and Chemistry of Sol–Gel Processing," Academic Press Inc., San Diego (1990).