Mesostructured Silica-Based Hybrids

Direct Formation of Mesostructured Silica-Based Hybrids from Novel Siloxane Oligomers with Long Alkyl Chains**

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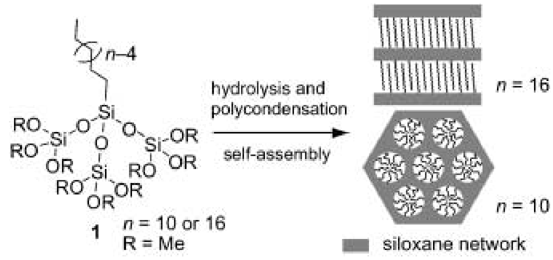
Silica-based hybrids derived from organoalkoxysilanes have been extensively studied because of their potential for novel nanomaterials as well as their scientific significance. Although a wide variety of hybrids can be designed at a molecular scale by the modification of the precursors, the control of their nanostructures is still an important subject of research.[1,2] Recently, intensive efforts have been made in the synthesis of mesostructured (lamellar, hexagonal, or cubic) hybrids by using surfactant assemblies as structure directors.[3–7] However, their formations are governed by weak interactions between surfactant molecules and silicate or organosiloxane species. The control of the hybrid nanostructures without the use of surfactants is a great challenge, and the preparation of a novel building block with self-organizing ability should be important. The design of such a single precursor would open up the possibility of creating nanohybrid materials that are not accessible through surfactant-directed processes.

Herein we report an innovative method for the formation of ordered silica-based hybrids by using newly designed siloxane-based oligomers **1**, consisting of an alkylsilane core and three branched trimethoxysilyl groups ($C_nH_{2n+1}Si(OSi(OMe)_3)_3$, $n = 10$ or 16), as single precursors. The self-assembly of **1** during the hydrolysis and polycondensation leads to the formation of lamellar or hexagonal-like mesostructures that are controlled by changing the length of the alkyl chain (Scheme 1).



Scheme 1. Formation of mesostructured hybrids from siloxane-based oligomers **1** with two different chain lengths.

The ability of organoalkoxysilanes to self-organize during hydrolysis and polycondensation was recently explored.[8–14] This is an attractive feature based on the weak interactions of the organic groups and the hydrophilic nature of the silanol groups. However, all attempts to prepare ordered hybrids through self-assembly have resulted in layered structures, except for the specific case in which a precursor bearing a surfactant molecule with a Si–C bond was employed.[12] We have reported the formation of multilayered hybrids from alkyltrialkoxysilanes.[13] Although the morphological control of the transparent films was attained by cocondensation of alkyltrialkoxysilane with tetraalkoxysilane, oligomeric species with well-defined structures have never been formed in precursor solutions,[14] which implies that highly organized nanoarchitectures are formed with difficulty.

The precursors **1** ($n = 10$ and 16) were synthesized by the reaction of corresponding *n*-alkylsilanetriols and tetrachlorosilane, followed by methanolysis of Si–Cl groups. Hydrolysis and polycondensation reactions of **1** were performed in the solutions with a molar composition of **1**/THF/H_2O/HCl = 1:50:18:0.002. The mixtures were stirred at 25 °C for 12 h, and water (H_2O:**1** = 32) was then added. The resulting

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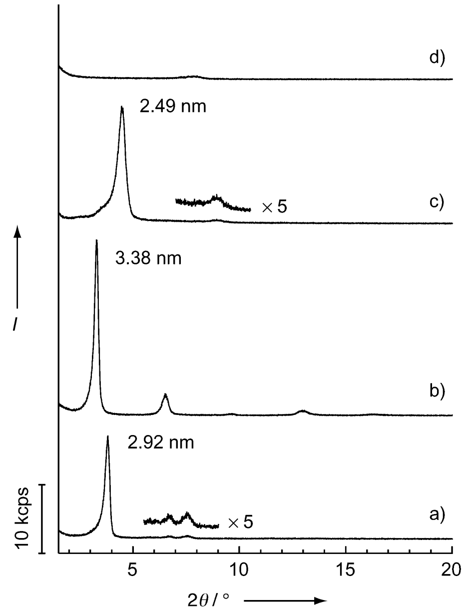

Figure 1. Powder XRD patterns of the products derived from **1**: a) $n=10$ (as-synthesized), b) $n=16$ (as-synthesized), c) $n=10$ (calcined), and d) $n=16$ (calcined). The patterns were recorded on a Mac Science M03XHF^{22} diffractometer with Mn-filtered $Fe_{K\alpha}$ radiation.

precursor solutions were cast on glass substrates, and air-dried at room temperature for 2 days. The resulting platelike solids were pulverized before characterization.

The powder X-ray diffraction (XRD) patterns of the hybrids ($n=10$ and 16) exhibit low-angle diffraction peaks corresponding to the d spacings of 2.92 and 3.38 nm, respectively (Figure 1 a, b). In the case of $n=16$, all the peaks observed at higher angles ($2\theta = 6$–$17°$) are attributed to higher order diffractions, thus indicating the well-ordered layered structure of the product. This ordering was revealed by the increase of the d value to about 4.7 nm upon adsorption of n-decyl alcohol. The interlayer chains appear to take a monolayer arrangement, because the d value (3.38 nm) is much smaller than that for lamellar alkylsiloxanes with a bilayer structure ($d = 4.80$ nm).[13] On the other hand, the pattern for $n=10$ (Figure 1 a) shows quite a different profile with several small peaks at the higher region, and the structure of the product can tentatively be assigned as 2D hexagonal.

Figure 2 shows the transmission electron microscopic (TEM) images of the products. The hybrid with $n=16$ exhibits exclusively well-defined striped patterns whose periodicity is close to the d spacing. In contrast, a hexagonal-like structure is observed for the hybrid with $n=10$, in agreement with the XRD data. The structure is slightly distorted, possibly due to the anisotropic shrinkage of the siloxane frameworks during the polycondensation process. Although a future detailed structural study is needed, the present results evidently show that the precursors have the ability to form both lamellar and hexagonal mesophases through self-assembly.

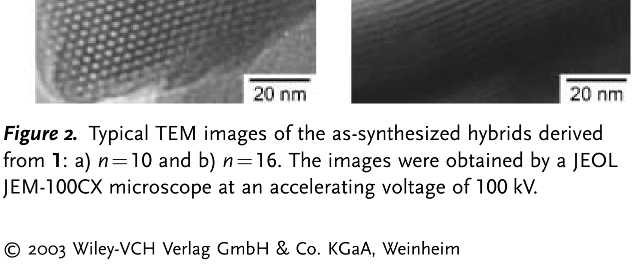

Figure 2. Typical TEM images of the as-synthesized hybrids derived from **1**: a) $n=10$ and b) $n=16$. The images were obtained by a JEOL JEM-100CX microscope at an accelerating voltage of 100 kV.

The formation of the siloxane networks was confirmed by ^{29}Si MAS NMR spectroscopy of the hybrids (Figure 3). The spectra for $n=10$ and 16 are similar and display signals corresponding to the T^1, T^2, and T^3 units (T^x, $CSi(OSi)_x(OH)_{3-x}$), and also to the Q^2, Q^3, and Q^4 units (Q^x, $Si(OSi)_x(OH)_{4-x}$). The presence of the T^1 and T^2 units suggests the partial cleavage and the rearrangement of the original Si–O–Si bonds in the precursor **1** during hydrolysis and polycondensation. We confirmed that the signals arising from the Q^0 species did not appear in the ^{29}Si NMR spectra of the solution during the reaction, thus suggesting a very slow rate of the hydrolysis of Si–O–Si bonds in **1** to form smaller species. Further work to investigate the detailed reaction process is underway and will be reported subsequently.

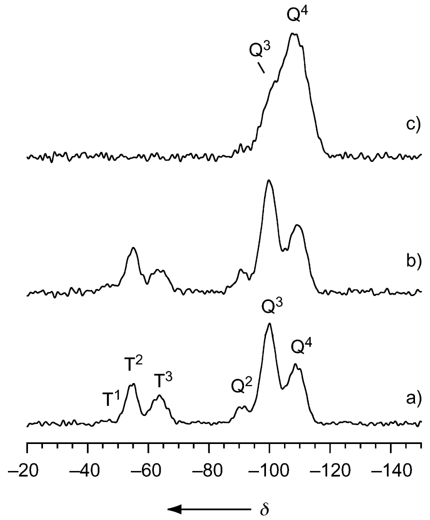

Figure 3. Solid-state ^{29}Si MAS NMR spectra of the products derived from **1**: a) $n=10$ (as-synthesized), b) $n=16$ (as-synthesized), and c) $n=10$ (calcined). The spectra were recorded on a JEOL JNM-CMX-400 spectrometer at a resonance frequency of 79.42 MHz with a 45° pulse and a recycle delay of 100 s. The relative intensity ratios of the signals are listed in the Supporting Information.

These results prove the formation of two types of nanostructured hybrids as depicted in Scheme 1. The products are structurally unique because organic regions are filled with alkyl chains covalently attached to nanostructured-silica frameworks. The formation of these products depends on the self-assembly of the single precursor, and is quite different from conventional methods, including cocondensation of organotrialkoxysilane and tetraalkoxysilane in the presence of surfactants, or postmodification of mesoporous silica or layered silicates with organosilanes.[4,5]

The difference in the nanostructures was further confirmed by the calcination of the hybrids at 500 °C for 8 h to remove organic components. The ^{29}Si NMR spectra of the calcined samples mainly showed the Q^3 and Q^4 signals (Figure 3c), which suggests the conversion of the T units to Q units by thermal degradation of the organic moieties. While the layered structure ($n = 16$) collapsed upon calcination (Figure 1d), the ordered structure was retained in the case of $n = 10$ with a decrease in the *d* spacing (Figure 1c), which was also supported by TEM (see Supporting Information). The nitrogen adsorption measurement revealed that the calcined hybrid ($n = 10$) was a microporous solid with a Brunauer–Emmett–Teller (BET) surface area of 1070 $m^2 g^{-1}$, the average Barrett–Joyner–Halenda (BJH) pore diameter of about 1.7 nm, and pore volume of 0.41 $cm^3 g^{-1}$, while the as-synthesized hybrid was nonporous (see Supporting Information). Although several researchers have proposed the idea of using organoalkoxysilanes as organic templates to prepare microporous silica,[15–18] this work is truly the first synthesis of the hexagonally ordered porous silica. Such a method has the advantage of producing relatively small pores compared to those obtained by using surfactants with the corresponding chain length.[19]

The siloxane oligomers formed by the hydrolysis and polycondensation of **1** can be regarded as a polyhydroxy amphiphile containing a hydrophobic alkyl chain and hydrophilic silanol groups.[20] It is plausible that the nanostructured hybrids are formed by the self-assembly of the alkylsiloxane species upon evaporation of the solvents, followed by siloxane formation. The difference in the nanostructures of the hybrids depending on the alkyl chain length can be explained in terms of the geometrical packing of alkylsiloxane oligomers.[21] In contrast to the several reports on the formation of lamellar hybrids from organoalkoxysilanes with the general formula of $RSi(OR')_3$ or $(R'O)_3Si{-}R{-}Si(OR')_3$ (R, R′ = organic groups),[9–11,13] this example is the first self-assembly of organosilane molecules into a hexagonal structure, which is apparently due to the large occupying volume of the hydrophilic headgroup in the precursor **1** compared to that of a single $Si(OH)_3$ group. It should be noted that such mesostructures cannot be obtained by the random cocondensation of alkylalkoxysilane-tetraalkoxysilane mixtures,[14] thus suggesting the importance of well-designed molecular structure of the precursor.

Furthermore, the control of the macroscopic morphology of the hybrids was achieved because of the high cross-linking ability of **1**. Transparent thin films with the thickness of about 450–600 nm were obtained by spin coating (3000 rpm, 10 s) the precursor solutions on glass substrates. The XRD patterns of the films ($n = 10$ and 16) are shown in Figure 4. Both patterns show the smaller *d* spacings than those of powdered samples, which may in part be ascribed to the difference in the degree of polycondensation. It is noteworthy that the film for $n = 10$ exhibits a very sharp and intense peak with only second and third order diffractions, which is typical for the well-ordered 2D hexagonal structures in which cylindrical assemblies are oriented parallel to the substrate.[22,23] Evidence for the hexagonal structure of the film was obtained from the cross-sectional TEM image (Figure 4 inset).

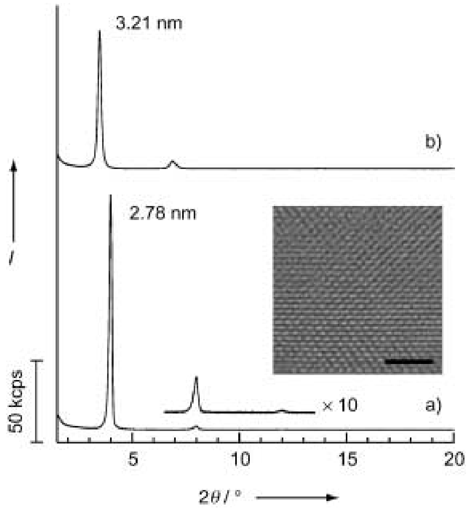

Figure 4. XRD patterns of the as-synthesized hybrid films derived from **1**: a) $n = 10$ and b) $n = 16$. Inset shows the cross-sectional TEM image of the film with $n = 10$ (scale bar; 20 nm). The image was obtained by a JEOL JEM-2010 microscope at an accelerating voltage of 200 kV.

In conclusion, we have demonstrated the successful formation of silica-based hybrids with highly ordered lamellar and 2D hexagonal nanostructures by using novel alkylsiloxane oligomers as single precursors. Such a method proves to lead to the better control of composition, mesostucture, and morphology of silica-based hybrids. It is of great interest that a hexagonally ordered hybrid is prepared for the first time without the use of surfactants and any other silica source, thus providing a novel pathway to ordered porous silica. The further design of precursors based on the organic group and/or the siloxane part will allow functionalization as well as variations of the architecture at molecular and nanometer scales.

Experimental Section

n-Alkylsilanetriols ($n = 10$ and 16) were synthesized by the hydrolysis of decyltrichlorosilane ($C_{10}H_{21}SiCl_3$) and hexadecyltriethoxysilane ($C_{16}H_{33}Si(OEt)_3$). Detailed procedures are described in the Supporting Information. In a typical synthesis of **1**, 12.0 g of alkylsilanetriol dissolved in THF (600 mL) was added to a vigorously stirred mixture of $SiCl_4$ (100 mL) and hexane (240 mL) at room temperature. Removal of the solvents and unreacted $SiCl_4$ under reduced pressure afforded a slightly turbid liquid which contained mainly $RSi(OSiCl_3)_3$ (R = alkyl) and a small amount of $RSiCl(OSiCl_3)_2$. $RSi(OSiCl_3)_3$ was isolated by vacuum distillation, and the conversion of Si–Cl groups to Si–OMe groups was performed by the addition of methanol with degassed HCl under reduced pressure. The precursor **1** was obtained as a clear and colorless liquid. The spectroscopic data are contained in the Supporting Information.

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