Using Carbazole as a Structural Modifier of CTAB-Templated Silicate Sol−Gel Thin Films

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We report the use of organic additive carbazole as a structural modifier to change the mesophase of the mesostructured silicate cetyl trimethyl ammonium bromide (CTAB)-templated sol−gel thin films. The films were made by a dip-coating method on glass slides, which results in optical transparency. The films were characterized by X-ray diffraction patterns. For the small molar concentrations of carbazole (0.1−0.41) to CTAB, the films exhibit a two-dimensional hexagonal structure, which is also obtained for the films that do not have carbazole. As the molar concentration increases from 0.43 to 1.2, surprisingly the films acquire a lamellar structure with an extremely long-range order. This is an unusual result for the films prepared with CTAB, which always gives a hexagonal structure. We study the solvent effect to understand the cause of such a dramatic transformation in the films.

Introduction

There have been numerous reports on the surfactant-templated sol−gel silica thin films formed by the dip-coating method. They exhibit a highly ordered hexagonal, cubic, or lamellar structure.[1,2] Molecules can be incorporated either in the surfactant region or in the inorganic silicate framework in the mesostructured silica films.[3] The possibility of tailoring the functionality of the mesostructured silica films allows for the incorporation of a charge-transporting molecule (carbazole) and a second-order chromophore (Disperse Red 1; DR1) in the sodium dodecyl sulfate templated films. It is interesting to study the charge-transport mechanism in them by corona discharge and photoconductivity techniques[4] and their nonlinear optical properties.[5]

Surfactant molecules form micelles, vesicles, or related aggregates when they are solubilized in aqueous media beyond a certain concentration. The presence of both nonpolar (hydrophobic) and polar (hydrophilic) groups in the same molecule gives these molecules their amphiphilic character. The surfactant packing parameter P, introduced by Israelachvili et al.[6] provides an empirical criterion for predicting the shape that the aggregates of a given surfactant will adopt in aqueous solutions. The packing parameter P is defined by $P = v/(al)$, where v is the volume occupied by the hydrophobic moiety of the amphiphilic molecule, l is the critical length in the fully extended conformation, and a is the optimal cross-sectional surface area occupied by an amphiphilic headgroup at the water−aggregate interface. Specific values of P are associated with spherical micelles ($P < 0.33$), wormlike micelles ($0.33 < P < 0.5$), vesicles ($0.5 < P < 1$), flat bilayers ($P = 1$), and inverted micelles ($P > 1$).

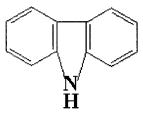

Figure 1. Molecular structure of carbazole.

Table 1. Molar Ratios of CTAB/THF

vol EtOH (mL)	vol THF (mL)	CTAB/THF molar ratio	*d* spacing (H[a]; Å)	*d* spacing (L[a]; Å)	mesophase	r (%)
19.7	5	1:25	33.6		hexagonal	18
17	7.7	1:41	31.3	25.4	mixed	28
7.7	17	1:84	31.9	26.0	mixed	60
3	21.7	1:109	35.6	25.2	mixed	75

[a] H = hexagonal; L = lamellar.

Table 2. Molar Ratios of CTAB/Benzene

CTAB/benzene molar ratio	*d* spacing (Å)	*d* spacing[a] (Å)	mesophase	*r* (%)
1:0	37.8		hexagonal	0
1:4	34.8	28	hexagonal	3
1:10	35.6	31.8	hexagonal	7
1:20	35.1	30.1	hexagonal	13

[a] After calcination at 400 °C for 4 h.

Cetyl trimethyl ammonium bromide (CTAB)-templated hexagonal-phase silica films were also prepared to investigate the same charge-transport mechanism and compare with the results those of the lamellar-mesostructured films. But a structural modification was observed, and we decided to study it. It is well-known that the carbazole molecule is planar and has mirror symmetry.[7−9] Figure 1 shows the molecular structure of carbazole.

The solvent tetrahydrofuran (THF) was used to dissolve the carbazole and DR1. The solvent THF can form a well-

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(1) Huang, M. H.; Dunn, B. S.; Zink, J. I. *J. Am. Chem. Soc.* **2000**, *122*, 3739−3745.

(2) Lu, Y.; et al. *Nature* **1997**, *389*, 364−368.

(3) Hernandez, R.; Franville, A.-C.; Minoofar, P.; Dunn, B.; Zink, J. I. *J. Am. Chem. Soc.* **2001**, *123*, 1248−1249.

(4) Valverde, G.; García, J.; Cruz, D.; Zink, J. I.; Hernández, R. *J. Sol.-Gel Sci. Technol.* **2003**, *26*, 605−608.

(5) Chaput, F.; et al. *Chem. Mater.* **1996**, *8*, 312−314.

(6) Israelachvili, J. N.; Marcelja, S.; Horn, R. G. *Rev. Biophys.* **1980**, *13*, 121.

(7) Robinson, P.; Scott, H. *Mol. Cryst. Liq. Cryst.* **1969**, *5* (4), 405−411.

(8) Kurahashi, M.; Fuyuko, M.; Shimada, A.; Furusaki, A.; Nitta, I. *Bull. Chem. Soc. Jpn.* **1969**, *42* (8), 2174−2179.

(9) Bhattacharya, S.; Haldar, J. J. *Colloid Surf., A* **2002**, in press.

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Table 3. Molar Ratios of CTAB/Carbazole from Thin Films with 3.5 wt % CTAB

additive	additive wt (g)	CTAB/additive molar ratio	vol THF (mL)	*d* spacing (H[a]; Å)	*d* spacing (L[a]; Å)	mesophase
carbazole	0.05	0.1	17	29.6		hexagonal
	0.08	0.2	17	30.3		hexagonal
	0.17	0.41	17	35.3		hexagonal
	0.18	0.43	17	34.0	32.4	mixed
	0.2	0.5	17		30.46	lamellar
	0.5	1.2	17		32.6	lamellar
	0.3	0.62	20 (benzene)		29.7	lamellar

[a] H = hexagonal; L = lamellar.

defined lamellar phase from $r = 20-30\%$ (r ratio is defined as the cosolvent weight percent in the micellar solution) in powders.[10]

Experimental Section

The sol was prepared by refluxing tetraethoxysilane (TEOS; Aldrich), ethanol, water, and HCl (molar ratio of 1:3.8:1:0.022) at 60 °C for 90 min. This forms the stock solution,[1,11] designed to minimize the siloxane condensation rate. The hydrolysis was performed under acidic conditions with THF as the solvent. A total of 0.1 mL of water, 0.4 mL of HCl (0.07 N), 7.7 mL of ethanol, and 17 mL of THF were added to 3.3 mL of the stock solution. The sol was stirred for 24 h at room temperature. Afterward, the carbazole and 3.5 wt % CTAB were added. The final molar proportions of the constituents were 1:22.5:5:0.011:29.6:0.019:0.0022−0.022 TEOS/EtOH/H_2O/HCl/THF/CTAB/carbazole.

The glass substrates were boiled in a solution of 4:1 H_2SO_4/H_2O_2 for 0.5 h. They were then placed in deionized water and boiled for 0.5 h. They were then rinsed three times with deionized water and stored in deionized water at room temperature prior to use. The films were dip-coated on the glass substrates (9 cm × 1 cm × 1 mm) at a rate of 5.3 cm/min. The films were drawn with the equipment described previously that uses hydraulic motion to produce a steady and vibration-free withdrawal of the substrate from the sol.[11] Convection-free drying was critical to obtaining high-optical-quality films.

The structure of the final films was characterized with X-ray diffraction (XRD) patterns at low and high angles. XRD was recorded on a Siemens D500 diffractometer using Ni-filtered Cu Kα radiation with an integration time of 1 s at the low angle and 5 s at the high angle.

To examine the effect of the THF solvent on the formation of the mesostructure in the sol−gel thin films, several molar ratios of CTAB/THF (1:25−109) were made. Table 1 shows the molar ratios used.

Benzene was also used instead of THF to test the change on the mesostructure of the CTAB-templated sol−gel films (Table 2). Carbazole was then added to the sol at different molar ratios (1:0.1−1.2 CTAB/SiK). The films exhibit a dramatic change from the hexagonal phase to the lamellar phase. Table 3 shows the molar ratios of CTAB/carbazole. There are four molecules of carbazole per unit cell, and the cell volume is 825.3 Å^3.[12] The volume of the micelles formed in the films is 350.2 Å^3 (this value corresponds to the films with a lamellar phase), and the number of carbazole molecules per micelle is approximately 1.7.

Results

This study was divided in two sections. First, we wanted to determine the effect of the solvent (THF and benzene) without organic additives. And second, we wanted to determinate the effect when carbazole was added.

1. Effect of THF as the Solvent. Figure 2a shows a typical XRD pattern for a CTAB-templated sol−gel silica film. A hexagonal phase is present with a *d* spacing of 39.8 Å.

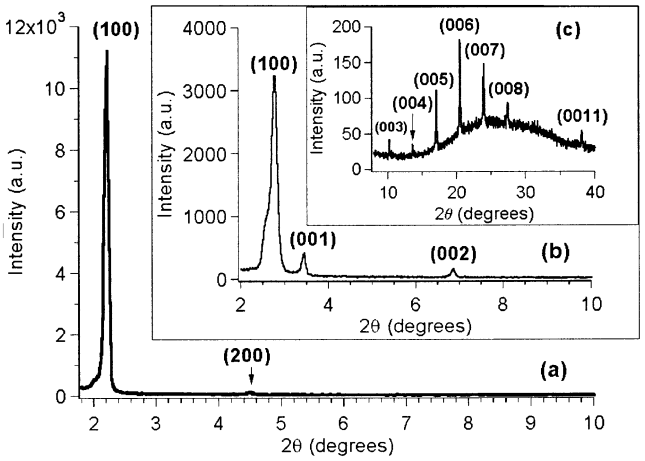

Figure 2. (a) XRD pattern of a 3.5 wt % CTAB sol−gel silica film that shows a hexagonal phase. (b) XRD patterns at a low angle of the mesostructured silica thin films with a CTAB/THF molar ratio of 1:84. (c) XRD patterns at a high angle from the same film as that in part b.

It was noticed that THF can modify the hexagonal phase (Figure 2a) to a mixed phase (Figure 2b,c). Table 1 lists the relative volumes of ethanol to those of THF in the sol and the resulting mesostructure formed in the films. Parts b and c of Figure 2 show the effect of a molar concentration of 1:84 CTAB/THF, or 60 wt % THF of the final sol. The peak at $2\theta = 2.77°$, or a *d* spacing of 31.9 Å, corresponds to the (100) peak of the hexagonal-mesophase structure. The (200) peak is not present in this sample, but it shows up in the films prepared with a CTAB/THF molar ratio of 1:109 (or $r = 75\%$). The lamellar phase is identified with the presence of several diffraction peaks with an average 2θ spacing of 3.44° between adjacent peaks, which can be indexed as (001), (002), ..., (008). The XRD patterns from other concentrations of CTAB/THF look very similar. The peak at $2\theta = 38.13°$ is likely due to molecular-level ordering.

2. Effect of Benzene as the Solvent. Benzene is another solvent that is used to study the effect of the cosolvent on the mesostructure of the sol−gel films because it mixes well with the sol. Table 2 show the molar ratio of CTAB/benzene used.

Figure 3a shows the effect of benzene. The films possess a hexagonal phase with $r = 13\%$ (dashed line). The films were calcined at 400 °C for 4 h to eliminate the surfactant and reduce the pore size. The (100) and (200) peaks were shifted, and this indicates that the films possess an excellent hexagonal phase (solid line). When carbazole is added to the sol containing benzene, the XRD patterns reveal that the films also exhibit a pure lamellar mesostructure. Figure 3b shows the XRD pattern of a 3.5 wt % CTAB sol−gel film with a CTAB/carbazole molar ratio of 1:0.62. The *d* spacing is 29.7 Å, and the average spacing between adjacent peaks is 2.75°. Benzene does not change the mesophase as THF does.

(10) Anderson, M. T.; Martin, J. E.; Odinek, J. G.; Newcomer, P. P. *Chem. Mater.* **1998**, *10*, 311−321.
(11) Nishida, F. et al. *J Am. Cer. Soc.* **1995**, *78*, 1640−1648.
(12) Clarke, P. T.; Spink, J. M. *Acta Crystallogr., Sect. B* **1969**, *25*, 162.

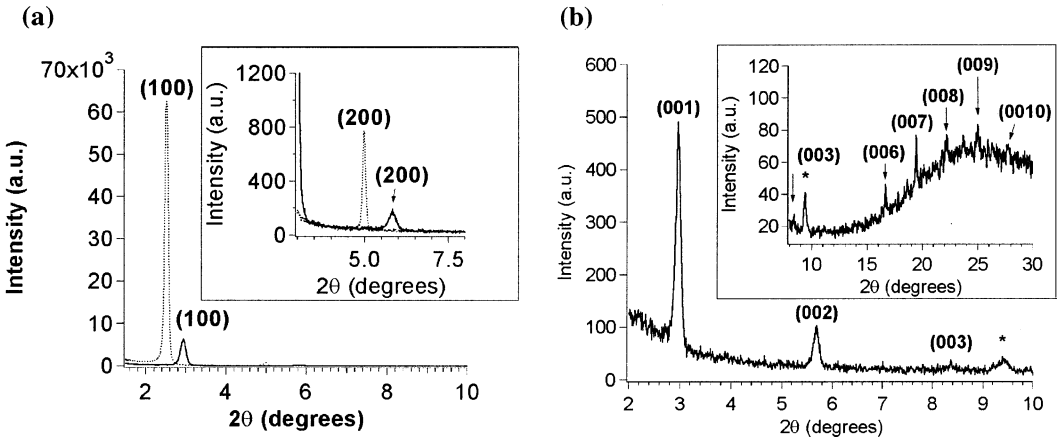

Figure 3. (a) XRD pattern of a 3.5 wt % CTAB sol−gel silica thin film with 1:20 CTAB/benzene (Table 2) before calcination (dashed line) and after calcination (solid line). The inset shows the (200) peaks. (b) XRD pattern of a 3.5 wt % CTAB sol−gel silica thin film with 1:0.62 CTAB/carbazole (Table 3) using benzene as the solvent. It shows a lamellar phase.

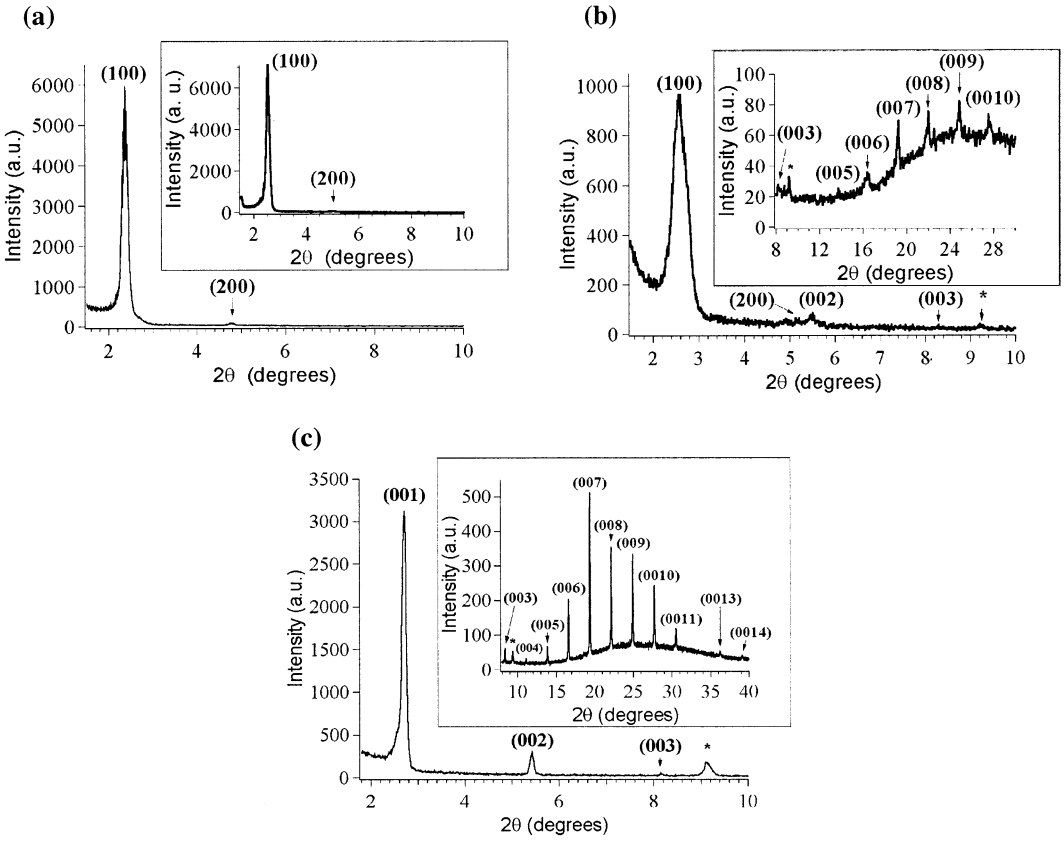

Figure 4. XRD patterns of the thin films with carbazole and a 3.5 wt % CTAB sol−gel silica film. (a) Thin film deposited on a glass substrate with 1:0.1 CTAB/carbazole. The inset corresponds to 1:0.41 CTAB/carbazole. Both have a hexagonal mesophase. (b) Thin film with 1:0.43 CTAB/carbazole; it has a mixed phase. (c) Lamellar phase for 1:1.2 CTAB/carbazole.

3. Effect of Carbazole/THF as the Solvent. THF, carbazole, DR1, and 3.5 wt % CTAB were added to the sol. Table 3 shows the molar concentrations used.

Figure 4 shows the XRD patterns of the transformation from a hexagonal to a lamellar phase in the thin films containing carbazole. Figure 4a shows the hexagonal phase in the case of low concentrations of carbazole (1:0.1 CTAB/carbazole) with a *d* spacing of 37.4 Å. The inset shows the diffraction pattern from 1:0.41 CTAB/carbazole. It also shows a hexagonal phase with a *d* spacing of 30.3 Å. When the molar concentration changes from 0.41 to 0.43, the transformation from hexagonal to lamellar occurs (see Figure 4b), the film exhibits a mixed phase, the hexagonal phase is present with the (100) and (200) peaks, and the lamellar phase appears with the successive (002), (003), ..., (0010) peaks. All the films with the lamellar phase have a peak at $2\theta = 9.33°$ that corresponds to the carbazole powder.

Figure 4c shows a pure lamellar phase for the highest concentration of carbazole, 1:1.2 CTAB/carbazole. Strong highly ordered peaks indicate an extremely long-range-ordered lamellar-phase structure in the film. The *d* spacing is 32.6 Å, and the average spacing between peaks is 2.75°. Therefore, the most important factor is the amount of carbazole added to the solution. But the THF plays an important role; it helps in some way to define the phase that the film will finally have. A possible explanation about this mesophase transformation is based on the change of

the micellar curvature due to the incorporation of solvent molecules into the hydrophobic interior of the micellar structure during the film-formation process. The literature reports that liquid crystals with a lamellar phase were produced by using larger quantities of benzene, for example, molar ratios of benzene/CTAB greater than 3.5.[13] But in this study, the hexagonal mesophase was not modified in the films prepared with a molar ratio of CTAB/benzene of 1:20 (see Table 2).

On the other hand, the polarity of the cosolvent affects the existence of the region of ordered hexagonally packed silica, which is much larger for polar than for nonpolar cosolvents. In our case, THF and benzene are nonpolar cosolvents, but THF possesses a larger polarity than benzene, and THF has a larger effect than benzene on the overall formation kinetics of the hexagonal mesophase.

The success of using carbazole as an effective film-mesophase modifier agent suggests that we examine other organic additives with similar structures. XRD shows that the mesophase changes satisfactorily. But complementary studies of differential scanning calorimetry will reveal the presence of different phases in the films. Also, experiments of transmission electron microscopy (TEM) will help to study these mesophase changes. Some of these studies are underway.

(13) Firouzi, A.; Schaefer, D. J.; Tolbert, S. H.; Stucky, G. D.; Chmelka, B. F. *J. Am. Chem. Soc.* **1998**, *119*, 9466−9477.

Conclusions

The major discovery of this study is the ability to change the structure of the CTAB-templated silica thin films from two-dimensional hexagonal to lamellar by adding a solvent, THF, and carbazole. When a great amount of carbazole is incorporated, the films show a pure lamellar phase. This transformation may be the result of the change from a spherical micelle ($P < 0.33$) to a more elongated planar micelle ($0.33 < P < 0.5$) when the carbazole is added to the sol by the incorporation of the organic solvent molecules into the hydrophobic interior of the micelle.

In the sol−gel silica thin films, we found that THF alone forms a mixed hexagonal-lamellar phase ($r = 28-75\%$), and benzene does not have an important role.

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