

# Mesocrystal engineering using non-bonded interaction to obtain optically transparent mesoporous silica films and plates with uniform orientation

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## Abstract

A sol–gel process which achieves self-organization between surfactant and silicate through van der Waals type, weak, multiple, non-bonded interaction has been developed in order to synthesize mesoporous silica in the form of optically transparent films, fibers and plates. The synthesis process consists of the following two steps: an organic silica precursor such as tetraethylorthosilicate is hydrolyzed and simultaneously condensed to a suitable degree of polymerization in non-aqueous solutions containing substoichiometric amounts of water, hydrochloric acid and surfactants. The solvent is subsequently evaporated so that the surfactant–silicate organization is achieved by the weak enthalpy effect without the interference of the mixing entropy effect. The synthesis can be controlled so that mesoporous channels with uniform diameter are either hexagonally packed, parallel to the flat external surface or randomly oriented, depending on the reactant ratios and degree of the silicate polymerization in the first step. The optically transparent mesoporous silica plates, which are crack-free up to centimeters in size and 0.5 mm in thickness, exhibit uniform birefringence throughout the entire plate like a single crystal. The mesoporous silica materials show possibilities of the application as advanced materials, direct measurement of transport properties through channels, investigation of the order–disorder effects, and spectroscopic investigation of adsorbed species without using the diffuse reflectance. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Zeolite; Molecular sieve; Mesoporous silica; Birefringence; Second harmonic generation

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## 1. Introduction

Zeolites can act as a solid solvent to control the size and the topology of various guest species of nanometer size such as semiconductor particles, conducting wires, and photosensitizers, inside the periodic array of their uniform micropores. The capability of hosting the nanometer size objects

shows many possibilities of the zeolites and other similar molecular sieves for advanced applications such as optoelectronics, sensors, laser sources and second harmonic generators of lasers [1]. Recently, the possibilities were highlighted by the discovery of mesoporous molecular sieves [2,3], of which the pore diameter could be controlled precisely in the range 2–10 nm by the synthesis conditions or the post-synthesis treatments [3–5]. Due to the large and tailorable channel diameters, the meso-

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porous molecular sieves have attracted much attention as hosts for advanced materials which are too large to enter conventional zeolite channels. However, the applications were still hindered by the availability of the mesoporous molecular sieves being limited mostly to the powder forms.

Recently, Ozin and coworkers synthesized the mesoporous molecular sieves in the form of thin films [6], both self-supporting and supported on mica [7]. Ogawa [8] used a sol-gel process in which the surfactant was directly dissolved into partially hydrolyzed tetramethylorthosilicate without solvent. Attard et al. [9] reported the formation of a monolithic surfactant-silicate mesostructure using aqueous solutions under high concentration of the surfactant. However, their monoliths suffered from cracks upon calcination. McGrath et al. [10] used an amphiphilic  $L_3$  phase as a template for nanoporous monolithic silicate and they did not remove surfactant. Very recently, we have reported [11] a brief outline of the synthesis of optically transparent, crack-free, mesoporous silica materials in the form of thin films, fibers, and plates as large as centimeters in size and 0.5 mm in thickness using the self-organization between surfactant and silicate through van der Waals type, weak, non-bonded interactions of long range forces in non-aqueous solvents.

Here, we describe details of the synthesis method to obtain the optically transparent, crack-free, mesoporous silicate materials. We also demonstrate the possibility of the mesoporous silica plate for advanced applications using the second harmonic generation (SHG) of the 1064 nm Nd-YAG laser after the adsorption of p-nitroaniline within the mesoporous channels.

## 2. Experimental

### 2.1. Synthesis of mesoporous silica plate

Tetraethylorthosilicate (TEOS, Acros, 98%) was used as the silica source. Concentrated hydrochloric acid (J.T. Baker, 36.5–38% HCl) was used as a catalyst to hydrolyze TEOS with doubly-distilled water. Binary azeotropes between ethanol and

various organic solvents such as acetonitrile, heptane, toluene, and chloroform were used as solvent. Alkylpyridinium chloride [ $C_nH_{2n+1}N(C_5H_5)Cl$ ,  $n=12, 16$ ] and alkyltrimethylammonium bromide [ $C_nH_{2n+1}N(CH_3)_3Br$ ,  $n=12-18$ ] were received from Aldrich. Alkyltriethylammonium bromide [ $C_nH_{2n+1}N(C_2H_5)_3Br$ ,  $n=12-18$ ], dihexadecyldimethylammonium bromide [ $(C_{16}H_{33})_2N(CH_3)_2Br$ ], hydroxy-functionalized surfactants [ $C_{16}H_{33}N(C_2H_5OH)_x(CH_3)_{3-x}Br$  ( $x=1, 2$ )] and  $C_{16-6-16}$  gemini surfactant [ $C_{16}H_{33}N(CH_3)_2(CH_2)_6(CH_3)_2NC_{16}H_{33}Br_2$ ] were synthesized following procedures in the literature [12–14]. [Dihexadecyldimethylammonium bromide was synthesized by the reaction of hexadecyldimethylamine (TCI, 85%) with 1-bromohexadecane (Acros, 97%) in ethanol under refluxing condition for 12 h. The product was recrystallized three times from ethylacetate in order to purify.]

In a typical synthesis experiment, 2.9 g of TEOS and 0.74 g of 0.1 M hydrochloric acid were added to a round-bottomed flask containing a mixture of 1.0 g of cetylpyridium chloride (CPCl, Aldrich, 98%), 5.2 g of ethanol and 6.6 g of acetonitrile with magnetic stirring at room temperature. The resulting reaction mixture in the flask had a molar composition of 1 CPCl:5 TEOS:15  $H_2O$ :0.027 HCl:41 ethanol:59 acetonitrile. The TEOS in the solution was partially hydrolyzed by substoichiometric amount of water ( $H_2O/TEOS < 4$ ), and the resulting silicate species was oligomerized while the solution was refluxed in the presence of the HCl catalyst. The refluxing time was 6 h for the synthesis of ordered silica plates, and 20 h for disordered plates. The reaction mixture after the silicate oligomerization was concentrated by the quick evaporation of the solvent using a rotary evaporator in a vacuum at 333 K. The resulting liquid with a high viscosity was coated on slide glass to form thin films, cast on a Petri dish, or pulled to a fiber through a nozzle equipped with a drying air flow. Solid films, plates and fibers were obtained upon complete evaporation of the solvent in a drying oven at 313 K. The material thus obtained was reinforced with additional silica by alternating the adsorption of TEOS vapor and evacuation repeatedly at 423 K. The material was then calcined in  $N_2$  flow while increasing the

temperature to 523 K, and subsequently in O<sub>2</sub> flow while increasing the temperature linearly to 823 K over 10 h. The calcined material was optically transparent and crack-free over centimeters in size.

## 2.2. Characterization and application of mesoporous silica plate

The mesoporous silica materials were characterized with X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). XRD patterns were obtained from a Rigaku D/MAX-III instrument using Cu K $\alpha$  radiation. SEM images were recorded on a Philips 535M apparatus operating at 20 kV. TEM images were obtained with a Philips CM 20 apparatus operating at 100 kV from thin edges of microparticles, which were obtained by grinding the sample using a porcelain mortar. The surface area was determined by the Brunauer–Emmett–Teller (BET) method with N<sub>2</sub> adsorption isotherms at 77 K. Pore size was analyzed following the Barrett–Joyner–Halenda (BJH) method, using argon adsorption–desorption isotherms measured with a Micromeritics ASAP 2010 apparatus at 87 K.

## 3. Results and discussion

### 3.1. The synthesis of mesoporous silica

Fig. 1 shows a photograph, SEM and TEM images of a mesoporous silica plate obtained by the typical synthesis procedure described in Section 2.1. The calcined silica plate is 0.5 mm thick, crack-free over a centimeter scale, and optically transparent. The BET surface area of the plate is 1250 m<sup>2</sup> g<sup>-1</sup>. As shown in Fig. 2, the silica plate exhibits a narrow pore size distribution centered at 1.6 nm.

Fig. 3 shows XRD patterns obtained for the silica materials as both the transparent plate form and the powder form ground in a porcelain mortar. The as-synthesized powder pattern displays four peaks, which can be indexed to the (100), (110), (200) and (210) Bragg reflections characteristic of the hexagonal structure similar to that of MCM-41

{2,3}. Thus, the XRD pattern indicates that the structure of the material is hexagonal packing of the uniform mesoporous channels. The XRD pattern taken as the transparent plate shows only the (100) and (200) reflections. The absence of the (110) and (210) reflections for the silica plate indicates that the mesoporous channel axis was oriented parallel to the flat external surface of the materials. XRD patterns very similar to that shown in Fig. 3 were obtained from ordered silica films coated on slide glass. The XRD patterns obtained after the calcination of the plate at 823 K indicate the same hexagonal structure, except that the calcination caused the  $d_{100}$  spacing to contract from 3.51 to 2.90 nm due to the calcination. The hexagonal structure is confirmed by the TEM image shown in Fig. 1(d).

In Fig. 4, optical properties of the ordered silica plate are compared with those of a disordered plate which was synthesized as described in Section 3.2. The disordered plate shows no significant differences from the ordered plate in the optical transparency, the BET area and the pore size distribution. However, the XRD pattern of the disordered plate shows only a broad peak centered in the region of  $2\theta = 2\text{--}3^\circ$ . The local structure of the channel connectivity of the disordered plate has been investigated using the TEM image after incorporating nanosize Pt wires within the mesoporous channels [15]. The result shows that the mesoporous channels have about the same diameter as that of the ordered plate, but the channels in the disordered plate are interconnected in a three-dimensional disordered way, similar to mesoporous silica materials reported recently in the powder form [16,17].

As appeared in Fig. 4, the ordered plate and the disordered plate show a remarkable difference when they are placed between two Polaroid plates with their optical polarizations oriented perpendicular to each other. Since each of the Polaroid plates is a plane-polarizer, light does not penetrate when the second polarization is oriented perpendicularly. The disordered plate placed between the two Polaroid plates does not affect the polarization of light, similar to amorphous glass. The disordered silica plate in Fig. 4(b) is invisible when the polarization of the Polaroid plates is perpendicu-

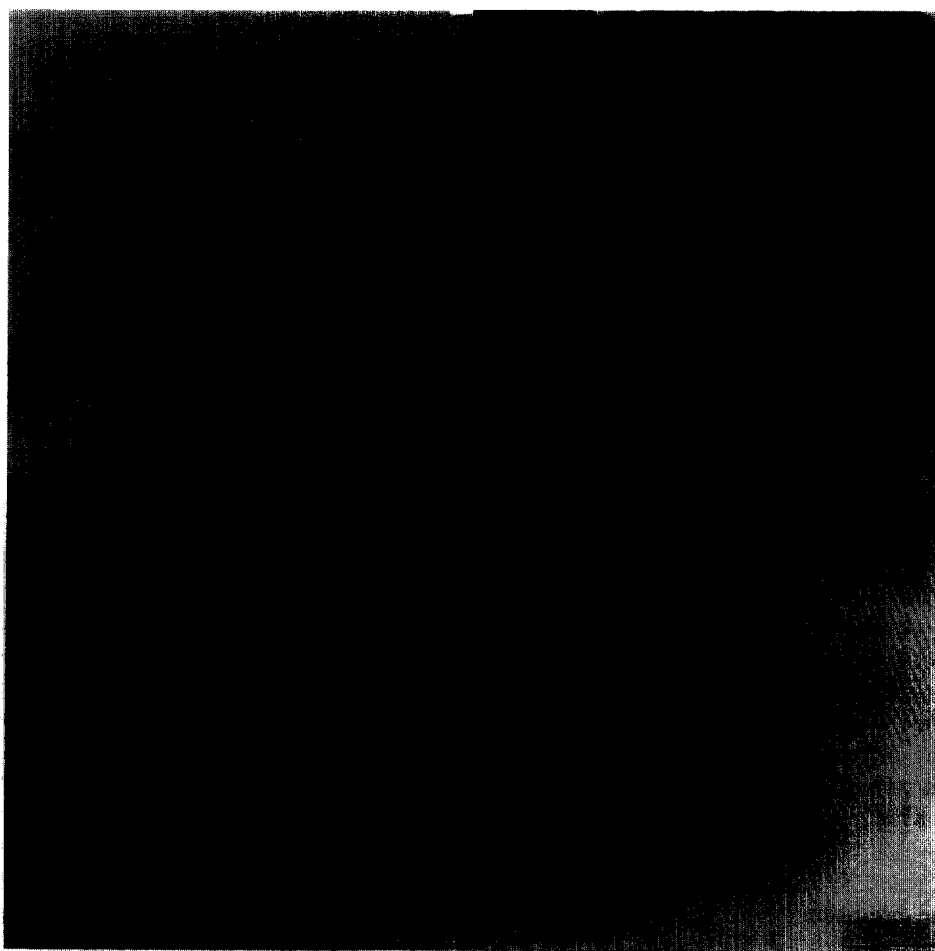


Fig. 1. Photograph (a), scanning electron micrographs (b, c) and transmission electron micrograph (d) for ordered silica plate after calcination at 823 K. The single free-standing plate shown in (a) is 0.5 mm thick.

lar. However, the ordered plate in Fig. 4(b) is visible, independent of the orientation of the Polaroid plates. Furthermore, the image is homogeneous. In contrast to the homogeneous image of the ordered plate, marble-like and mosaic-like images are obtained by the same experiment with silica plates consisting of heterogeneous domains. The results shown in Fig. 4 for the ordered silica plate would appear if the plate changed the plane-polarized light to circular-polarized light due to its birefringence property similar to single-crystalline substances with anisotropic optical axes. Although the exact cause of the unique optical property of the ordered plate should be investigated further,

the results in Fig. 4 indicate that the structure of the present ordered silica plate consists of uniform orientation of mesoporous channels.

### *3.2. Synthesis conditions controlling the structural order in the mesoporous silica*

Typical synthesis conditions to obtain the ordered silica plates are given in Table 1. The various conditions show that the synthesis depends on various experimental factors such as the nature of the surfactants, TEOS/surfactant, H<sub>2</sub>O/TEOS, TEOS/HCl molar ratios, and refluxing time for the silicate hydrolysis. It has been found that the

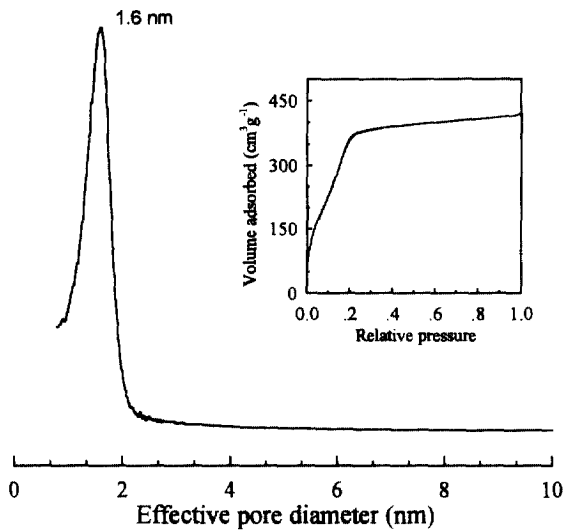


Fig. 2. Pore size distribution curve for the ordered mesoporous silica plate after calcination, obtained by the BJH analysis. The inset shows the corresponding argon adsorption-desorption isotherms obtained at liquid argon temperature (87 K).

synthesis also depends on the nature of the solvents, drying temperature, drying time, convection conditions in the oven, the sample size, surface roughness of the sample container, etc. Since all the experimental factors are inter-related, it is difficult to specify optimum conditions to obtain the ordered silica plates. One of the synthesis conditions is specified in Section 2.1.

Surfactants are separated from silicates during the solvent evaporation process if the synthesis is performed with lower TEOS/surfactant, H<sub>2</sub>O/TEOS, HCl/TEOS ratios and shorter refluxing times than the optimum conditions. The resulting surfactant-silicate mixtures in these cases are opaque. On the other hand, the mixtures are optically transparent under the opposite conditions. However, the porous silica resulting from calcination of the transparent mixtures has disordered pores. Our results with various refluxing times indicate that the ordered surfactant-silicate mesostructures can only be obtained when a certain optimum degree of the silicate oligomerization is achieved before the solvent is evaporated. The higher the TEOS/HCl ratios, the longer the refluxing time required for the silicate oligomerization. The surfactants and the silicates are separated at

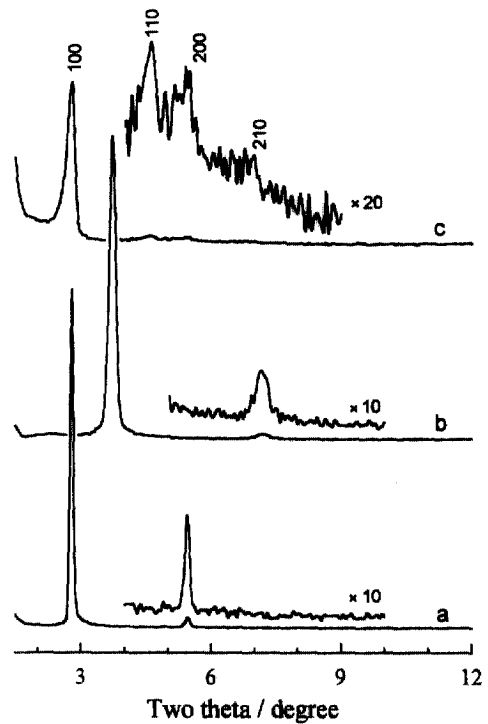


Fig. 3. X-ray diffraction patterns for ordered silica samples: (a) single free-standing plate (0.5 mm thick) as-synthesized; (b) after calcination at 823 K; and (c) after grinding the as-synthesized plate in an agate mortar.

a low degree of the silicate oligomerization. The structures are disordered if the degree of the silicate polymerization exceeds the optimum conditions before the solvent evaporation. Long heating time in the oven at high temperature results in structural disorder, probably due to the continuous silicate polymerization. These results indicate that the silicate polymerization decreases after the solvent is evaporated. Under inadequate conditions, the resulting silicate plates are disordered, cracks appear during the drying process, and XRD patterns show a difference between the top and bottom surfaces.

Table 2 shows that the selection of the solvent is important for the preparation of the ordered silica plate. We have tried the synthesis of the ordered silica plates using various solvents. Ethanol is a good solvent for both TEOS and surfactants used in the present synthesis. However, the use of the ethanol as a single solvent resulted

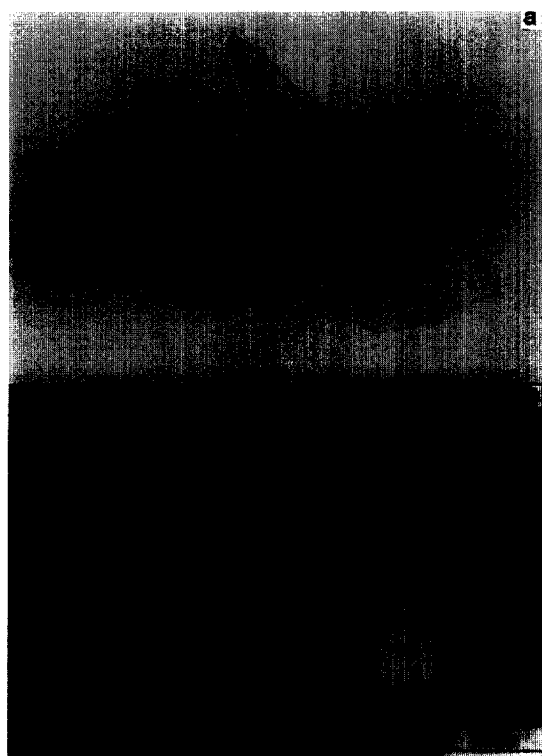


Fig. 4. Photographs of ordered (right) and disordered (left) mesoporous silica plates placed between two parallel Polaroid plates: (a) with polarization of the Polaroid plates oriented in the same direction, and (b) perpendicular.

in the formation of cracks. It is reasonable that the cracking problem depends on the hydrophilicity of the solvent, the surface tension of the solvent, and the solubility of the surfactants and the silica source. Bearing this in mind, we have tried the synthesis using binary azeotropes between ethanol and various other organic solvents. Boiling point is also a major point of concern in selecting the solvent since the boiling point determines the rate of silicate polymerization. The ethanol content in the solvent can affect the total solvent polarity, surface tension and surfactant solubility. The solvent refluxing time should be specified depending on the individual solvent, considering all these factors. We have obtained good results using ethanol–acetonitrile as the solvent, with a TEOS/HCl ratio of 185 and other conditions as given in the first row of Table 2.

We obtained the surfactant–silicate mesostructures in crack-free and optically transparent forms before calcination. However, the as-synthesized materials cracked and turned to tiny chips during the direct calcination in air flow. The size of the resulting chips was no more than 1–2 mm. After various attempts, we have discovered that the treatment with TEOS vapor at 423 K is useful to prevent the microcrack formation. It is reasonable that the surfactant–silicate mesostructure in the plate before calcination is a living silicate polymer so that TEOS vapor is added to the silicate frame-

Table 1  
Optimized synthesis conditions to obtain ordered silica plates<sup>a</sup>

Surfactant	TEOS/HCl <sup>b</sup>	TEOS/surfactant <sup>b</sup>	H <sub>2</sub> O/TEOS <sup>b</sup>	Refluxing time (h)
C <sub>16</sub> H <sub>33</sub> NC <sub>5</sub> H <sub>5</sub> Br	9.3	5.0	3.0	0.5
C <sub>16</sub> H <sub>33</sub> NC <sub>5</sub> H <sub>5</sub> Cl	18.5	5.0	3.0	1
C <sub>16</sub> H <sub>33</sub> NC <sub>5</sub> H <sub>5</sub> Cl	185	5.0	3.0	6
C <sub>16</sub> H <sub>33</sub> NC <sub>5</sub> H <sub>5</sub> Cl	1850	5.0	3.0	18
C <sub>14</sub> H <sub>29</sub> N(CH <sub>3</sub> ) <sub>3</sub> Br	18.5	4.5	3.5	1
C <sub>16</sub> H <sub>33</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Br	18.5	4.0	3.5	1
C <sub>16</sub> H <sub>33</sub> N(CH <sub>3</sub> ) <sub>3</sub> Br	18.5	4.5	3.5	1
(C <sub>16</sub> H <sub>33</sub> ) <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub> Br	18.5	4.0	3.0	3
C <sub>16</sub> H <sub>33</sub> N(C <sub>2</sub> H <sub>4</sub> OH)(CH <sub>3</sub> ) <sub>2</sub> Br	18.5	5.0	3.5	1
C <sub>16</sub> H <sub>33</sub> N(C <sub>2</sub> H <sub>4</sub> OH) <sub>2</sub> (CH <sub>3</sub> )Br	18.5	5.0	3.5	1
C <sub>16-6-16</sub> gemini surfactant <sup>c</sup>	18.5	4.0	3.0	1

<sup>a</sup> Binary azeotrope of ethanol and acetonitrile used as solvent.

<sup>b</sup> Molar ratio.

<sup>c</sup> [C<sub>16</sub>H<sub>33</sub>N(CH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>(CH<sub>3</sub>)<sub>2</sub>NC<sub>16</sub>H<sub>33</sub>]Br<sub>2</sub>.

Table 2  
Binary azeotropes and the refluxing time used for the synthesis of ordered silica plates

Azeotrope	Boiling point (°C)	Composition (wt%)		Refluxing time <sup>a</sup> (h)
		Ethanol	Other components	
Acetonitrile	72.5	44	56	6
Heptane	70.9	49	51	1
Benzene	67.9	32	68	1
Toluene	76.7	68	32	1
Chloroform	59.3	7	93	1

<sup>a</sup> The synthesis was performed with a molar composition of 1 CPCI:5 TEOS:15 H<sub>2</sub>O:0.027 HCl:100 (ethanol + other solvents).

works through the silicate condensation polymerization. The ethanol coming from the silicate condensation, as well as excessive TEOS, is removed by subsequent evacuation. It is believed that the repetition of the TEOS adsorption and the evacuation leads to the framework reinforcement until the space between the surfactant micelle and silicate framework is completely filled.

As mentioned above, disordered silica materials are obtained by increasing the refluxing time in the ethanol–acetonitrile solvent. Fig. 5 shows the structural change as a function of the refluxing time. The result was obtained with a molar composition of 1 CPCI:5 TEOS:15 H<sub>2</sub>O:0.27 HCl:41 ethanol:59 acetonitrile. As shown in Fig. 5, the (100) reflection peak decreased in intensity and increased in width with increasing the refluxing time. This result is due to gradual decreases in the structural order. At a certain refluxing time, the structure of the silica plate becomes very similar to that of the disordered mesoporous silica materials designated KIT-1 [16] and MSU-1 [17]. It may be reasonable that the arrangement of the surfactant micelles is disordered due to some disturbance from the excessive degree of the silicate polymerization.

### 3.3. Synthesis mechanism

The use of surfactant micelles [2–7,17–20] is a currently popular route to template nanostructured materials. Ordered mesoporous silicas can be synthesized in micrometer size powder forms [2,3] and thin films or monoliths [7–10] by templating silicates with surfactant micelles in aqueous solu-

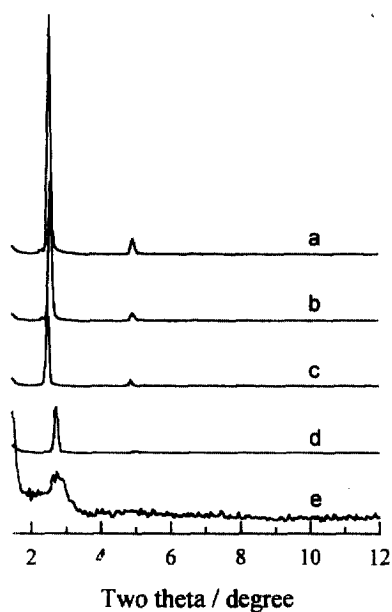


Fig. 5. X-ray diffraction patterns of the resulting plate samples displayed against the refluxing time: (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h, and (e) 10 h. The synthesis was performed with a molar composition of 1 CPCI:5 TEOS:15 H<sub>2</sub>O:0.27 HCl:41 ethanol:59 acetonitrile.

tions. The templating mechanism is based on the ionic interaction [2,7,19,20] and the hydrogen bonding [17,18] between surfactant micelles and silicates which lead to self-organization into an ordered array of mesostructures. The self-organization of the surfactant–silicate mesostructures in the aqueous solution is a thermodynamic process which occurs due to strong enthalpy-driven effects of the ionic interaction between surfactant micelles and silicates.

CPCl, CPBr and hexadecyltrimethylammonium bromide used in the present synthesis are cationic surfactants which can template mesoporous silicas following the ionic templating route in the aqueous solution. The direct interaction between surfactant cation ( $S^+$ ) and silicate anion ( $I^-$ ) contributes to the formation of surfactant–silicate mesostructures in basic aqueous solutions, following a  $S^+I^-$  type ionic mechanism [19]. On the other hand, the silicate surface can be positively charged in strongly acidic aqueous media with pH lower than the isoelectric point, due to a high concentration of  $H^+$ . The formation of the mesostructures in the acidic solution is known to occur via a  $S^+X^-I^+$  type ionic mechanism where  $X^-$  is a counter-anion of  $S^+$  [19]. However, the ordered mesostructures have been obtained in the present study even when the HCl/TEOS molar ratio is decreased to  $1 \times 10^{-4}$ . Under the present synthesis conditions, the concentration of the positively charged silicate species is too low to follow the ionic templating route. The smaller the amount of HCl used as a catalyst, the longer the reaction time required for the TEOS hydrolysis and oligomerization. It is evident that the molecular weight of the silicate is an important factor to control the self-organization. Ordered structures are not obtained at low degrees of the silicate polymerization. These results lead us to conclude that the formation of the surfactant–silica mesostructure in the present case occurs due to weak, multiple, non-bonded interactions between surfactants and silicates such as ion–dipole, dipole–dipole, etc., as well as weak hydrogen bonding between  $Cl^-$  ions and HO–Si groups. It is also reasonable that an ordered mesostructure is difficult to form if the size of the silicate species increases beyond the preferred silicate wall thickness.

Recently, a disordered mesostructure has been reported to form between non-ionic surfactants and silicates, following a hydrogen bonding route (i.e. the  $S^0I^0$  route) [17,18]. Although the non-bonded interaction between silicates and surfactant micelles is not strong enough for the formation of the ordered mesostructures in solutions, due to the naturally disordering effects of entropy, we have found that the formation of the mesostructures can be performed by using the weak interaction if

the solvent is removed. In situ X-ray diffraction indicates that ordered mesostructures are not formed in the viscous liquid which was used to cast plates and coat films, but obtained during complete evaporation of the solvent in the oven.

The preparation of ordered mesoporous silica in the form of continuous film and monolith has also been attempted in other recent reports [8–10]. In one study, tetramethylorthosilicate (TMOS) was added to a concentrated aqueous solution of surfactant to form a uniform and continuous liquid crystalline phase [9]. In the other study, surfactant was added to a partially hydrolyzed TMOS without solvents [8]. The XRD patterns of the resulting materials showed the (100), (110) and (200) reflections similar to powder XRD patterns for the hexagonal phase. However, the monolith suffered from microcracks upon calcination. The synthesis conditions were difficult to control since the silicate polymerization and the self-organization with surfactant occurred simultaneously. In a third report an amphiphilic  $L_3$  phase was used to template the corresponding silica with TMOS, and surfactant was not removed [10]. Our results show that precise control of the degree of silicate polymerization is very important for the self-organization with surfactant. The reinforcement of the silicate framework using the concept of living silicate polymer is also very useful in preventing the microcracks, as described in Section 3.2.

### 3.4. The second harmonic generation (SHG)

The SHG experiment has been performed using the 1064 nm Nd-YAG laser as a source of incident beam, after p-nitroaniline is adsorbed within the mesoporous channels of the ordered silica plate by sublimation in vacuum at 423 K. Fig. 6 shows the resulting SHG intensity as a function of the polarization angle. The non-linear optical effect shown in Fig. 6 indicates that adsorbed molecules are aligned, perhaps, in a statistically preferred orientation.

## 4. Conclusion

Our results indicate that optically transparent mesoporous silica plates can be synthesized, with



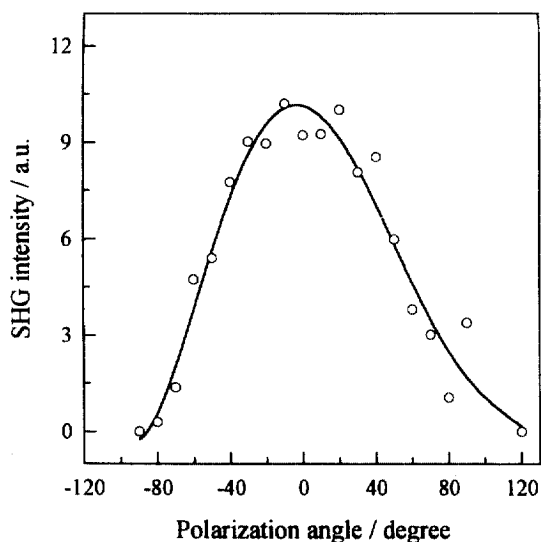


Fig. 6. Second harmonic generation effects of the ordered mesoporous silica plate after the adsorption of p-nitroaniline, plotted against the polarization angle with respect to the channel direction.

the mesoporous channels oriented in the same direction like a single crystal, or can be randomly oriented. The synthetic mechanism is based on the self-organization between surfactants and silicates through van der Waals type, weak, multiple, non-bonded interaction. The preparation of such silica plates is so far limited to a few centimeters in size and a few millimeters in thickness. Nevertheless, the plates of this size show possibilities of application for advanced materials, direct measurement of transport properties through channels, investigation of the order–disorder effects, and spectroscopic investigation of adsorbed species without using the diffuse reflectance.

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