Bull. Chem. Soc. Jpn., ***78***, 932–936 (2005)

The Formation of Periodicity within the Pore Walls of Mesoporous Organosilica by Post-Synthesis Treatment

Yasutomo Goto, Kentaro Okamoto, and Shinji Inagaki*

Toyota Central R&D Labs. Inc., 41-1 Yokomichi, Nagakute, Aichi 480-1192

Received October 14, 2004; E-mail: inagaki@mosk.tytlabs.co.jp

The molecular scale periodicity within the pore walls of amorphous mesoporous phenylene-silicas, derived using triblock copolymers under acidic conditions, was generated by the post-synthesis treatment with alkaline solution. Usually, acid conditions are not favorable for the formation of periodic arrangement of phenylene-silica moieties. The treatment with alkaline solution at 363–373 K facilitated the restructuring of phenylene-silica moieties and resulted in the formation of periodic structure within the pore walls. The treatment also enlarged the pore size of mesoporous phenylene-silica from 5.4 to 12.4 nm. Such a material with large pore size and molecular periodicity should have several advantages in potential applications, particularly in the catalysis for relatively large molecules.

Since the discovery of the novel organic functionalized mesoporous materials synthesized from bridged organosilica precursor $(R'O)_3Si–R–Si(OR')_3$, an extension of variety of bridging organic group has been investigated for diverse applications as catalysts, templates for nano-clusters synthesis and selective adsorptions.[1–5] Among them, the phenylene ($–C_6H_4–$; Ph-HMM) and biphenylylene ($–C_6H_4–C_6H_4–$; Bp-HMM)-bridged mesoporous materials derived using cationic alkyltrimethylammonium surfactant in basic media have attracted particular attention due to a novel crystal-like periodic structure inside their pore walls.[6–10] The crystal-like pore walls are composed of hydrophobic organic layers and hydrophilic silicate layers arranged alternately in the channel direction at intervals of 0.76 and 1.19 nm for Ph-HMM and Bp-HMM, respectively. The formation of such an unique periodic structure inside the pore walls has been observed only in the mesoporous phenylene-silicas prepared under the basic conditions. The mesoporous phenylene-silicas synthesized in the acidic condition using alkyltrimethylammonium and block copolymers as surfactants showed almost no periodicity in the pore walls.[11–13] This implies that the acidic conditions are not favorable for the formation of periodic arrangement in the organosilane precursors. In a recent report, Wang et al. have pointed out the existence of periodicity in the pore walls of mesoporous phenylene-silicas derived under the acidic conditions using non-ionic surfactants.[14] TEM measurements showed very weak electron diffraction patterns due to the periodicity. However, the researchers failed to observe the periodicity using X-ray diffraction, which indicates the absence of the obvious molecular scale arrangement of phenylene.

Triblock copolymer surfactants usually act as a template in an acidic media. The uses of triblock coploymers have various advantages in the formation of mesostructures with large pores, thick pore walls, and microporosity in the walls. The formation of periodicity under acidic conditions is important due to their potential applications in diverse fields. In addition, the synthesis in acidic condition has also an advantage in the formation of mesoporous thin film.

In this report, we describe an alternative method for the development of molecular-scale periodicity in the pore walls of mesoporous phenylene-silicas synthesized using triblock copolymers under acidic conditions. And we demonstrate that the post-synthesis treatment of the as-made phenylene-silicas containing surfactant in basic solution could develop periodicity in the pore walls while preserving the large pore size, thick pore walls and some microporosity.

1. Experimental

1.1 Chemicals. 1,4-Bis(triethoxysilyl)benzene (BTEB) was purchased from Azmax Japan. Triblock copolymer P123 $[(EO)_{20}–(PO)_{70}–(EO)_{20}]$ ($M_{av} = 5800$) and 25 wt % solution of tetramethylammonium hydroxide (TMAOH) were obtained from Aldrich. Hydrochloric acid (36 wt %), sodium hydroxide (NaOH), and 28 wt % aqueous ammonia (aq NH_3) were purchased from Wako Chemicals Co., Ltd. All chemicals were used without further purification.

1.2 Syntheses. Phenylene-bridged mesoporous material with large pores was synthesized from a BTEB precursor in the presence of triblock copolymer template (P123) under acidic condition according to the previous report.[12] P123 (0.99 g) was dissolved in 36 mL of distilled water containing 200 µL of 36 wt % hydrochloric acid solution. BTEB (1.01 g) was then added to the solution and the mixture was stirred at 273 K for 1 h. The mixture was further stirred at 312 K for 20 h and finally kept at 373 K for 24 h in a closed vessel. The white precipitate obtained was recovered by filtration and repeatedly washed with water to yield as-made mesoporous materials containing surfactant. In a subsequent step, the as-made material was hydrothermally treated in an alkaline solution of NaOH, aq NH_3, or TMAOH. 0.5 g of as-made material was dispersed in alkaline solution and heated in a closed vessel at 373 K or 363 K for desired reaction time (see details in Table 1). Finally, the solids were filtered, washed with water and dried. Surfactants were removed by extraction with ethanol, followed by calcination at 623 K in air.

1.3 Characterization. X-ray powder diffraction (XRD) measurements were carried out on the Rigaku RINT-2200 using Cu Kα radiation (40 kV, 30 mA). Nitrogen adsorption isotherms

Published on the web May 6, 2005; DOI 10.1246/bcsj.78.932

Table 1. The Conditions of Post-Synthesis Treatments and Physical Properties of Products

Sample	Hydrothermal treatment				d_{10} value /nm	Pore diameter (BJH) /nm	Pore wall thickness[a] /nm	Pore volume (t-plot)		Surface area (BET) /$\text{m}^2\cdot\text{g}^{-1}$
	Alkaline additive	Concentration /mM	Tempareture /K	Time /h				Micropore /$\text{mL}\cdot\text{g}^{-1}$	Mesopore /$\text{mL}\cdot\text{g}^{-1}$	
PMML-1	—	—	—	—	8.7	5.4	4.6	0.12	0.59	862
PMML-2	NaOH	2.7	373	72	9.6	7.3	3.8	0.17	1.23	1072
PMML-3	NaOH	8.0	373	72	9.5	7.7	3.3	0.05	0.8	724
PMML-4	NaOH	12.0	373	72	—	—	—	—	0.98	989
PMML-5	aq NH_3	13.3	363	120	8.7	6.1	3.9	0.16	0.7	909
PMML-6	TMAOH	8.0	363	120	9.4	7.3	3.6	0.05	1.01	876
PMML-7	TMAOH	13.3	363	120	—	12.4	—	—	2.15	1207

a) Wall thickness $= d_{10} \times 2/\sqrt{3} -$ Pore diameter.

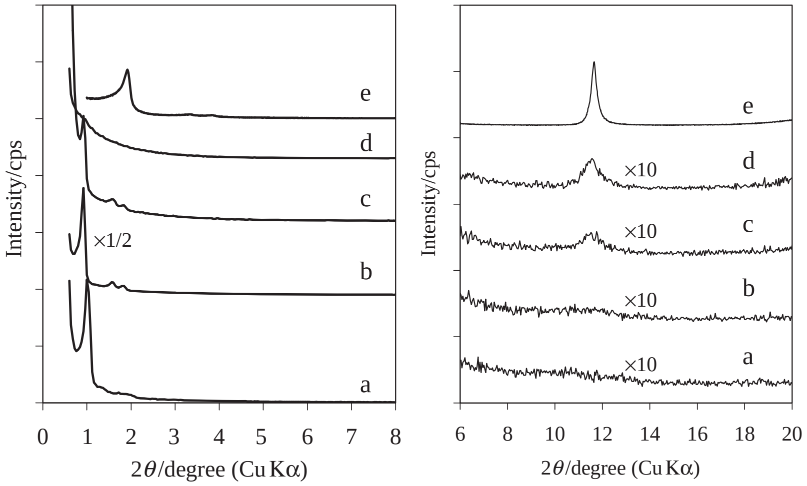

Fig. 1. X-ray diffraction patterns of mesoporous phenylene-silicas treated with various concentration of NaOH solution. (a) PMML-1 (no treat), (b) PMML-2 (2.7 mM), (c) PMML-3 (8.0 mM), (d) PMML-4 (12.0 mM), and (e) Ph-HMM synthesized using C_{18}TMACl in basic condition.[6]

at 77 K were obtained on the Quantachrome Autosorb-1 system. Prior to the measurement, the samples were degassed at 383 K for over 1 h. The surface areas were calculated using the BET method in the relative pressure (P/P_0) range between 0.05 and 0.2. The t-plot analyses were applied to determine the micropore and mesopore volumes. The pore sizes were calculated by the BJH method from adsorption isotherms. Transmission electron microscopic (TEM) images were taken with a JEOL JEM-200CX at an accelerating voltage of 200 kV. The ^{29}Si MAS NMR and ^{13}C CP MAS NMR spectra were recorded on a Bruker MSL-300WB spectrometer at 59.62 MHz and 75.47 MHz for ^{29}Si and ^{13}C, respectively. Their chemical shifts were referenced to tetramethylsilane and glycine respectively.

2. Results

X-ray diffraction patterns of mesoporous materials are shown in Fig. 1. The mesoporous phenylene-silica without the treatment of alkaline solution (PMML-1) showed three peaks in low angle diffraction region assignable to (10), (11), and (20) of two-dimensional (2D) hexagonal mesostructure. No peak at around $2\theta = 12°$ due to the 0.76 nm periodicity in the walls was observed. The mesoporous materials treated with NaOH solution (PMML-2, PMML-3, and PMML-4), however, exhibited a weak diffraction peak at $2\theta = 12°$, clearly indicating the development of periodicity in the walls similar to those reported for Ph-HMM and Bp-HMM materials.[6–10] The intensity of this peak increased with increasing amount of NaOH. This result confirmed that the periodicity of pore walls was generated by post-synthesis treatment with alkaline solution. The regular 2D-hexagonal mesostructures of the materials were retained up to 8.0 mM concentration of NaOH solution (PMML-3). The hexagonal arrangements of channels are shown in TEM images (Figs. 2a, b, and c), indicating the preservation of ordered mesostructure after NaOH treatment. Nitrogen adsorption isotherms of PMML-1, 2, 3, and 4 are shown in Fig. 3. The sharp increases in adsorption at $P/P_0 = 0.6$–0.8 indicate the very narrow pore size distributions. The pore size increased gradually from 5.4 to 7.4 nm with increasing amounts of NaOH. And, the pore wall thickness and microporosity decreased with increasing amount of NaOH. These results suggest that the alkaline treatment facilitated the restructuring of framework of mesoporous phenylene-silica. However, the treatment with excess amount of NaOH solution (13.3 mM NaOH, PMML-4) lowered the mesostructural ordering. Similar restructuring of framework by post-synthesis hydrothermal treatment has also been observed for conventional mesoporous silica.[15,16]

Figure 4 shows the XRD patterns of the mesoporous phen-

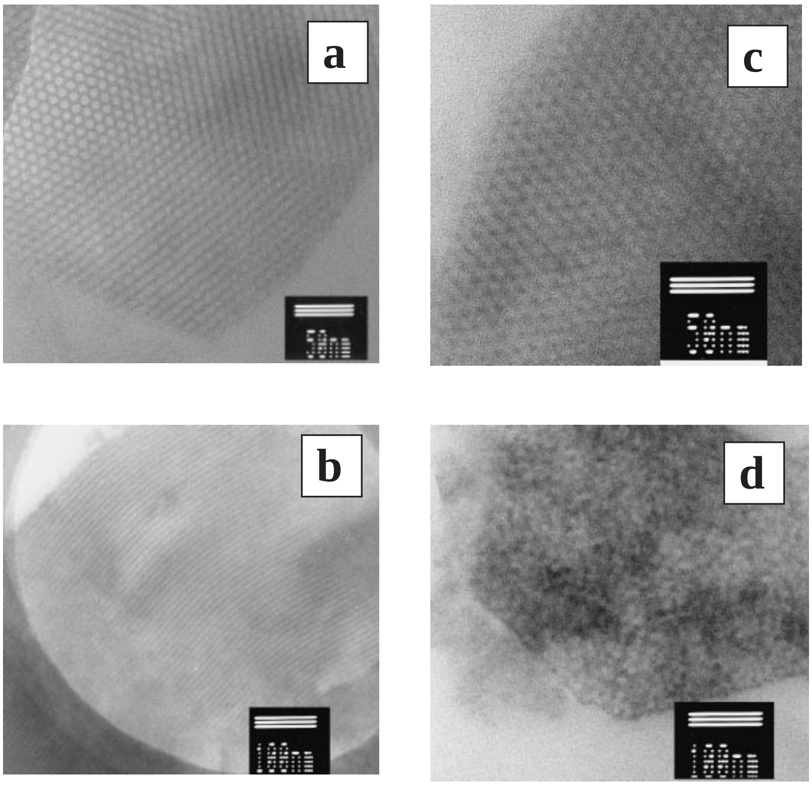

Fig. 2. TEM images of (a) PMML-2 (2.7 mM NaOH), (b) parallel and (c) cross section images of PMML-3 (8.0 mM NaOH), and (d) PMML-7 (13.3 mM TMAOH).

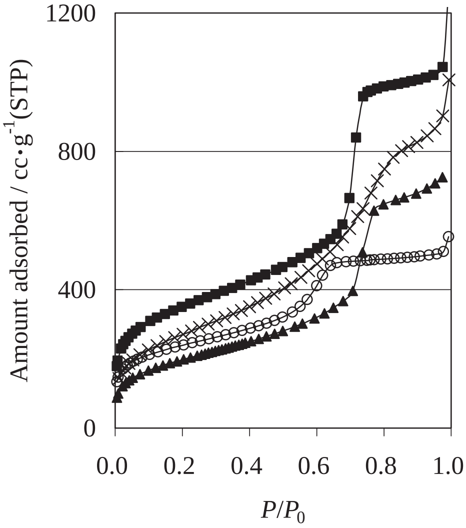

Fig. 3. N_2 adsorption isotherms of PMML-1 (no treat): ○, PMML-2 (2.7 mM NaOH): ■, PMML-3 (8.0 mM NaOH): ▲, and PMML-4 (12.0 mM NaOH): ×.

ylene-silicas treated with aq NH_3 and TMAOH solution. The diffraction peaks at $2\theta = 12°$ due to the 0.76 nm of periodicity in the pore walls were observed for TMAOH-treated samples (PMML-6 and PMML-7). The intensity of the peak increased with increasing amount of TMAOH, as in the case of NaOH treatment. Regular 2D-hexagonal mesostructure was observed for PMML-6 (8.0 mM TMAOH). However, the ordered mesostructure disappeared after treatment with higher concentration of TMAOH solution (13.3 mM, PMML-7). The nitrogen adsorption isotherm (Fig. 5) showed a sharp increase at $P/P_0 = 0.7$–0.8 for both PMML-6 and PMML-7, confirming the existence of uniform mesopores. And, the pore size was significantly increased from 5.4 to 12.4 nm. The large mesopores were clearly observed in TEM of PMML-7 (Fig. 2d). The significant enlargement of pore size is due to the binding of neighboring mesopores, which was reported for conventional mesoporous materials.[17] On the other hand, the product treated with 13.3 mM aq NH_3 solution (PMML-5) showed only a small structural change, due to the weakness of alkaline solution.

The ^{29}Si MAS NMR analysis revealed that carbon–silicon bonds in all phenylene-silicas were completely intact after post-synthesis treatment (Fig. 6). Three signals at −62, −71, and −78 ppm in NMR spectra were assigned to Si species covalently bonded to carbon atoms of T^1 [$\mathit{Si}C(OH)_2(OSi)$], T^2 [$\mathit{Si}C(OH)(OSi)_2$], and T^3 [$\mathit{Si}C(OSi)_3$]. This indicates that the pore walls of mesoporous phenylene-silica are made of a covalently bonded network composed of $O_{1.5}Si$–C_6H_4–$SiO_{1.5}$ units. The absence of SiO_4 species such as Q^3 [$\mathit{Si}(OH)(OSi)_3$] and Q^4 [$\mathit{Si}(OSi)_4$], whose signals are usually observed between −90 and −120 ppm, confirms that no cleavage of Si–C bond occurs during post-synthesis treatments. The ^{13}C CP MAS NMR spectra show signals at 133.1 ppm with side bands due to phenylene carbon (spectra not provided), also suggesting the preservation of Si–C bond in pore walls after post-synthesis treatment. The peak intensity ratio of T^3/T^2 at ^{29}Si MAS NMR was increased with increasing

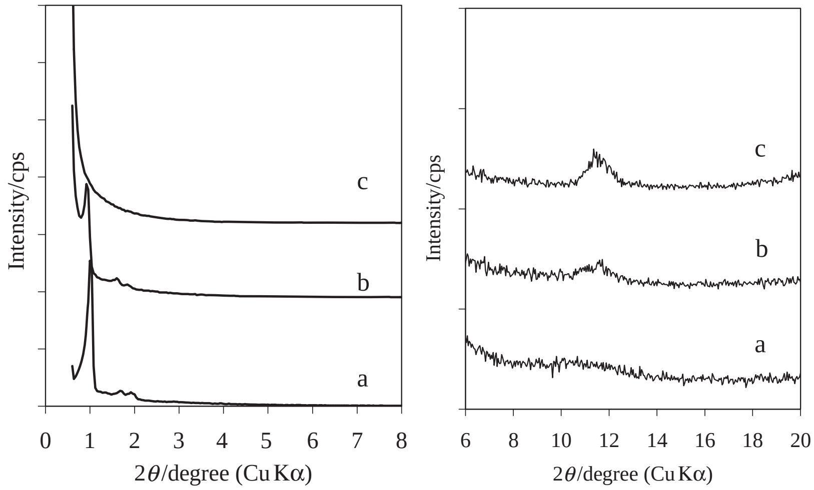

Fig. 4. X-ray diffraction patterns of mesoporous phenylene-silicas treated with aq NH_3 and TMAOH solution. (a) 13.3 mM aq NH_3 (PMML-5), (b) 8.0 mM TMAOH (PMML-6), and (c) 13.3 mM TMAOH (PMML-7).

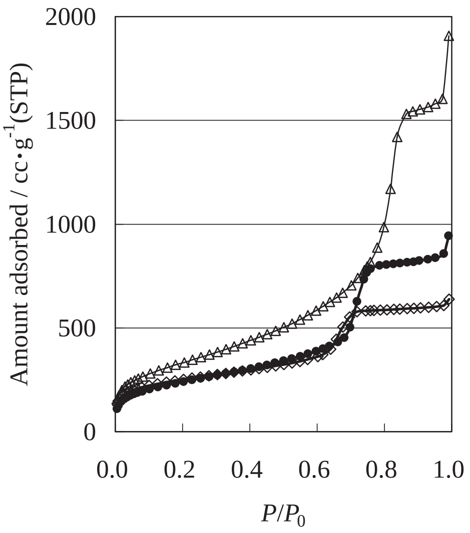

Fig. 5. N_2 adsorption isotherms of PMML-5 (13.3 mM aq NH_3): ◇, PMML-6 (8.0 mM TMAOH): ●, and PMML-7 (13.3 mM TMAOH): △.

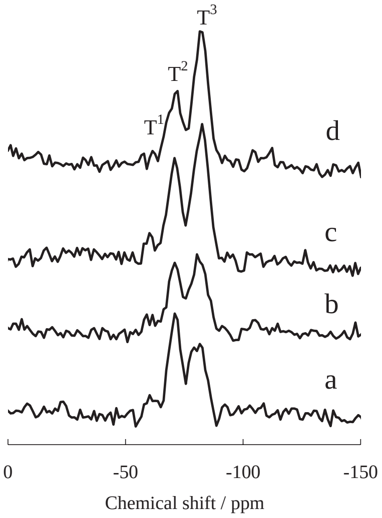

Fig. 6. ^{29}Si MAS NMR spectra of (a) PMML-2 (2.7 mM NaOH), (b) PMML-3 (8.0 mM NaOH), (c) PMML-4 (12.0 mM NaOH), and (d) PMML-7 (13.3 mM TMAOH). All materials are surfactant free.

amount of alkaline additive, indicating that the subsequent hydrothermal treatment accelerated the condensation of Si–OH within the pore walls. The accelerated condensation of Si–O–Si network also results in a decrease of the microporosities of the materials.

3. Discussion

The molecular-scale periodicity in the mesoporous aromatic-silica materials could be formed by self-assembly of hydrolyzed precursor species $[(HO)_3Si–(C_6H_4)_n–Si(OH)_3, n = 1, 2]$ due to their strong hydrophobic–hydrophilic interactions.[6] Hydrolysis of three alkoxides of the silyl group $–Si(OC_2H_5)_3$ completely occurred in basic condition, although the hydrolysis rate is slow. In acidic condition, one alkoxide group is easily hydrolyzed, but the remaining alkoxide groups are difficult to hydrolyze.[18,19] Therefore, the hydrophilicity of silyl groups of hydrolyzed precursor molecules is weaker in acidic condition than that in the basic condition. This is the reason why the molecular-scale periodicity in pore walls was not observed in the mesoporous materials prepared in acidic condition.

The post-synthesis treatment of the amorphous as-made material with a basic solution accelerates the complete hydrolysis of alkoxy groups and partial cleavage of siloxane bonds.[19] It induced the restructuring of framework structure and the formation of molecular-scale periodicity in the pore walls. The condensation degree of siloxane in material prepared in acidic condition is quite low (the T^3/T^2 ratio in ^{29}Si NMR is under 0.64); this low degree is favorable for the restructuring of framework structure. The post-synthesis treatment should be useful for formation of molecular-scale periodicity in the pore walls of other amorphous hybrid materials synthesized in acidic condition and the technique could also be applied for mesoporous thin films.

4. Summary

We have successfully demonstrated the development of the molecular-scale periodicity in the pore walls of mesoporous phenylene-silicas with large pores derived under acidic conditions via subsequent hydrothermal treatment under basic condition. The crystallinity of the pore wall was improved with increasing amount of alkaline additive. This basic treatment facilitated the restructuring of the phenylene moieties and resulted in the formation of crystal-like periodic structure in the pore walls. The enlargement of mesopore was also achieved up to 12.4 nm upon this treatment. Such large pore mesoporous phenylene-silicas with crystal-like pore walls could have several advantages in potential applications like catalysis for relatively large molecules.

The authors thank Y. Akimoto and N. Suzuki (TCRDL, Japan) for TEM observations. This work was partially supported by a Grant-in-Aid for the Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology (No. 16310094) and CREST, Japan Science and Technology Agency.

References

1 S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna, and O. Terasaki, *J. Am. Chem. Soc.*, **121**, 9611 (1999).

2 B. J. Melde, B. T. Holland, C. F. Blanford, and A. Stein, *Chem. Mater.*, **11**, 3302 (1999).

3 C. Y. Ishii, T. Asefa, N. Coombs, M. J. MacLachlan, and G. A. Ozin, *Chem. Commun.*, **1999**, 2539.

4 T. Asefa, M. J. MacLachlan, N. Coombs, and G. A. Ozin, *Nature*, **402**, 867 (1999).

5 S. Guan, S. Inagaki, T. Ohsuna, and O. Terasaki, *J. Am. Chem. Soc.*, **122**, 5660 (2000).

6 S. Inagaki, S. Quan, T. Ohsuna, and O. Terasaki, *Nature*, **416**, 304 (2002).

7 M. P. Kapoor, Q. Yang, and S. Inagaki, *J. Am. Chem. Soc.*, **124**, 15176 (2002).

8 M. P. Kapoor, Q. Yang, Y. Goto, and S. Inagaki, *Chem. Lett.*, **32**, 914 (2003).

9 N. Bion, P. Ferreira, A. Valente, I. S. Goncalves, and J. Rocha, *J. Mater. Chem.*, **13**, 1910 (2003).

10 M. P. Kapoor, Q. Yang, and S. Inagaki, *Chem. Mater.*, **16**, 1209 (2004).

11 Y. Goto and S. Inagaki, *Chem. Commun.*, **2002**, 2410.

12 M. P. Kapoor and S. Inagaki, *Chem. Lett.*, **33**, 88 (2004).

13 M. P. Kapoor, N. Setoyama, Q. H. Yang, M. Ohashi, and S. Inagaki, *Langmuir*, **21**, 443 (2005).

14 W. Wang, W. Zhou, and A. Sayari, *Chem. Mater.*, **15**, 4886 (2003).

15 L. Chen, T. Horiuchi, T. Mori, and K. Maeda, *J. Phys. Chem. B*, **103**, 1216 (1999).

16 M. Kruk, M. Jaroniec, and A. Sayari, *J. Phys. Chem. B*, **103**, 4590 (1999).

17 J. Fan, C. Yu, L. Wang, B. Tu, D. Zhao, Y. Sakamoto, and O. Terasaki, *J. Am. Chem. Soc.*, **121**, 12113 (2001).

18 S. Sakka and H. Kozuka, "The Third International Conference on Ultrastructure Proceeding of Ceramics, Glasses and Composites," San Diego, Feb., 24 (1987).

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