

Rapid Communication

# Mesoporous hybrid organosilica containing urethane moieties

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## Abstract

Mesoporous hybrid material containing urethane moieties in functionalized long chain organic group have been synthesized by using bis[3-(triethoxysilyl) propyl urethane]ethane (BTESPUE) and tetraethoxysilane as structural ingredients. The incorporation of BTESPUE within the framework of mesoporous material was confirmed by Fourier transform-infrared, X-ray photoelectron spectroscopy, solid-state NMR spectroscopy and thermogravimetric analysis. This material had a thick wall and uniform pore, which may be attributed to the hydrogen bonding inside framework due to urethane moieties.

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**Keywords:** Urethane; Mesoporous hybrid organosilicas; Co-condensation method

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## 1. Introduction

Since ordered mesoporous silicas using self-assembled surfactants as supramolecular templates were synthesized by the Mobil group [1], the modification of channel structure, surface property and structural ingredient was carried out by many other groups. The syntheses of periodic mesoporous organosilicas (PMOs) with organic groups covalently linked to Si inside the silica frame-work [2,3] and SBA-15 using triblock copolymer as a templating agent for the enlargement of mesopore [4] are very important development in the field of mesoporous material. It is expected that the distribution of functional organic group within the framework of mesoporous hybrid materials through co-condensation and grafting makes it possible to opening of the possibility for applications such as sensing, separation, enzyme immobilization, chromatographic supports and so on. The property of the framework of PMO could be modified by incorporating the functional organic group such as short aliphatic chains and aromatic moieties [2,3,5,6,7]. It was investigated that mechanical, hydrothermal stability of methylene, ethylene and phenylene bridged PMO's is better than pure PMO's [7]. In order to be applied as hosting materials more widely,

PMO's have to have various surface polarities with short or long organic group inside silica framework. However the syntheses of PMO's incorporateing long chain functional organic groups were reported in limited literatures [8–10] because of the difficulty of formation of regular pores resulted from the lack of structural rigidity in the long organic portion of silsesquioxanes.

In this communication, we report for the first time the synthesis of PMO containing the urethane moieties in relatively long organic group within framework using bis[3-(triethoxysilyl) propyl urethane]ethane (BTESPUE) and tetraethoxysilane (TEOS) as structural ingredients.

## 2. Experimental

In order to prepare the silsesquioxane with two urethane moieties named by BTESPUE, ethylene glycol (1.00 mL) and 3-(triethoxysilyl) propyl isocyanate (8.88 mL) were refluxed in tetrahydrofuran (40 mL) at 60 °C for 48 h. The liquid product was separated by the evaporation of tetrahydrofuran, purified by silica-packed column chromatography using the mixture of ethyl acetate and *n*-hexane of 1:10 volume ratio as an eluent and characterized by infrared (IR) and NMR spectroscopy.

Mesoporous hybrid material containing urethane moiety within framework was synthesized from the reaction mixture of BTESPUE, TEOS, ethanol, triblock copolymer

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Pluronic P<sub>123</sub> (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>), HCl and water by the following procedure. A mixture of Pluronic P<sub>123</sub> (1.00 g), HCl (1.5 M, 40 mL) was vigorously stirred in a Teflon bottle at room temperature. And then the solution consisting of BTESPUE (0.35 mL) and TEOS (2.09 mL) in a mixed solvent (10 mL) of ethanol and water (1:1 weight ratio) was added to Teflon bottle with stirring. The ratio of TEOS to BTESPUE was 15. After stirring for 2 h, the reaction mixture was aged in an oven at 60 °C for 24 h, and reacted at 100 °C for 24 h. The white solid product was filtered and washed with deionized water and dried at 60 °C for 24 h. The templating agent was removed thrice by stirring at room temperature for 2 h in HCl ethanol solution and filtering. The solid product was named by urethane functionalized periodic mesoporous organosilica (UFPMO).

The Brunauer, Emmett and Teller (BET) measurement was performed with Micromeritics Instrument Corporation ASAP 2400. Small angle X-ray scattering (SAXS) pattern was recorded using a RIGAKU D/MAX-2500 Image Plate system with Cu K $\alpha$  radiation (50 kV, 100 mA) for counting time of 2 h. The X-ray photoelectron spectroscopy (XPS) was recorded using a VG-Scientific ESCA-LAB 250 spectrometer with monochromatized Al K $\alpha$  X-ray source (1486.6 eV). Scanning electron microscope (SEM) images were obtained using a HITACHI S-2400 with an acceleration voltage of 20 kV by tungsten filament electron gun. Transmission electron microscope (TEM) images were obtained using a JEOL JEM-2010 microscope operating at 200 kV by LaB<sub>6</sub> filament electron gun. IR spectra were recorded on Fourier transform-infrared (FT-IR) spectrometer (Shimadzu Corp., FTIR-8210PC) with 2 cm<sup>-1</sup> resolution and 100 scan times using the KBr pellet technique. <sup>29</sup>Si CP-MAS and <sup>13</sup>C CP-MAS NMR was performed with DSX 400 MHz solid state FT-NMR

spectrometer at 6 kHz power. Thermogravimetric analysis (TGA) data were obtained with PERKIN-ELMER TGA 7 thermobalance under N<sub>2</sub> atmosphere at the temperature range of 50–800 °C. The heating rate was 10 °C/min.

### 3. Results and discussion

The characteristic peaks in IR and NMR of BTESPUE prepared in our laboratory are listed in Ref. [12].

The incorporation of BTESPUE within the framework of UFPMO was confirmed by FT-IR, XPS, solid-state NMR and TGA. Fig. 1 shows (a) FT-IR, (b) XPS, (c) <sup>13</sup>C CP-MAS NMR and (d) <sup>29</sup>Si MAS NMR spectrum of P<sub>123</sub> surfactant-extracted UFPMO. As shown in Fig. 1(a), the peaks at 1700, 1540, 3400 and 1450–1470 cm<sup>-1</sup> can be assigned to C=O stretching, N–H bending, N–H stretching, CH<sub>2</sub> bending and C–N stretching. Fig. 1(b) shows the XPS survey scan spectrum of UFPMO. The several peaks at ca. 99.15, 282.69, 399.91 and 529.52 eV are due to Si 2p, C 1s, N 1s and O 1s, respectively [11]. The atomic ratio of silicon to nitrogen obtained from the XPS peaks was 9.65, which is comparable with the Si/N ratio of 8.5 calculated from the composition of reaction mixture. The <sup>13</sup>C CP-MAS NMR spectrum exhibits the several peaks corresponding to organic moiety and residual surfactant, as shown in Fig. 1(c). The peaks at chemical shift of 10.15, 21.87, 43.33, 62.03 and 158.62 ppm were attributed to different chemical environment of C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub> and C<sub>5</sub> numbered in Scheme 1, respectively. The peaks in the range of 67–77 ppm and a peak at 16.48 ppm are due to the residual surfactant, which resulted from the incomplete removal of surfactant by solvent extraction. The <sup>29</sup>Si MAS NMR in Fig. 1(d) exhibits the silica bands (Q<sup>2</sup>, Si(OSi)<sub>2</sub>(OH)<sub>2</sub>; Q<sup>3</sup>, Si(OSi)<sub>3</sub>(OH); Q<sup>4</sup>, Si(OSi)<sub>4</sub>) in the chemical shift range of 90–110 ppm and organosilane

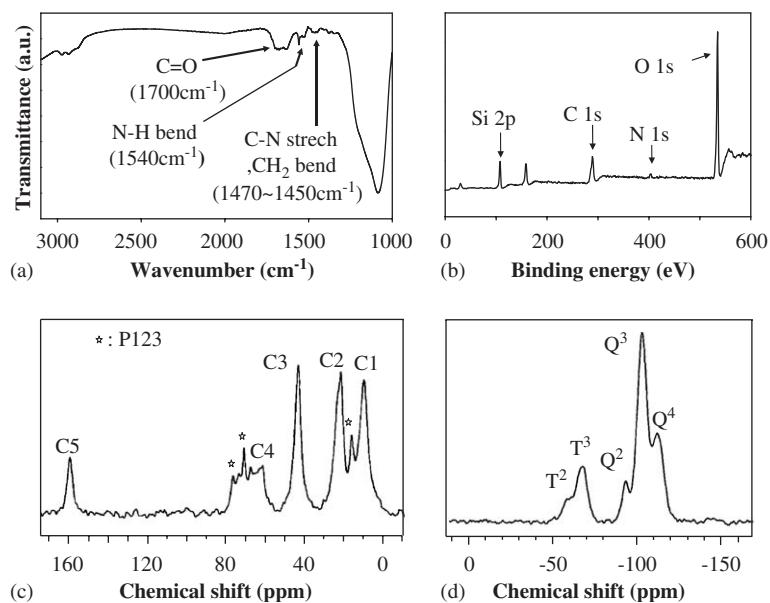
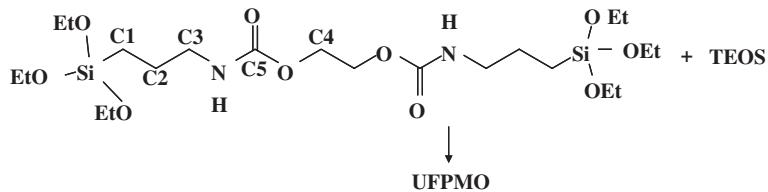


Fig. 1. (a) FT-IR, (b) X-ray photoelectron, (c) <sup>13</sup>C-CP MAS NMR and (d) <sup>29</sup>Si-MAS NMR spectrum of surfactant-extracted UFPMO.



Scheme 1. Syntheses of UFPMO with urethane moieties.

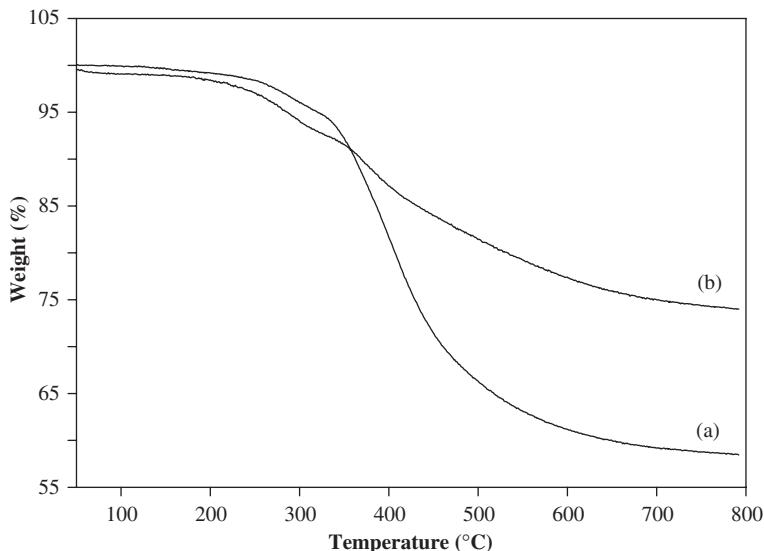


Fig. 2. TGA curves of (a) as-prepared and (b) surfactant-extracted UFPMO.

bands ( $T^2$ ,  $CSi(OSi)_2(OH)$ ;  $T^3$ ,  $CSi(OSi)_3$ ) of 50–70 ppm. The calculated area ratio of silica to organosilane bands from the mole ratio of TEOS to BTESPUE in a reaction mixture is 7.5:1. These results in Fig. 1 indicate that the urethane functionalized organic moieties incorporated within the framework of UFPMO.

And the external morphology of UFPMO in SEM is homogeneously in a short-rod shape without any other morphology, indicating that the BTESPUE is dispersed homogeneously inside the framework of UFPMO (not shown).

Fig. 2 show TGA curves of (a) as-prepared and (b) surfactant-extracted UFPMO. The weight loss can be divided into two step. The first step at 50–350 °C can be attributed to the loss of water and the second at 350–800 °C, the organic moiety of framework and residual templating agent. The total weight loss of as-prepared and surfactant-extracted UFPMO was 42% and 26%, respectively. Considering that the weight % of organic moiety within framework of UFPMO calculated from TEOS/BTESPUE of 15 is 18% and the weight loss of water is 6%, the weight % of residual templating agent is ca. 2%. Comparing with TGA of as-prepared UFPMO, it indicates that ca. 90% of the templating agent was removed.

The pore array, pore size distribution, surface area and wall thickness of surfactant-extracted UFPMO were confirmed by SAXS, TEM and  $N_2$  adsorption–desorption

isotherm measurement. The SAXS pattern of UFPMO in Fig. 3(a) exhibits hexagonal symmetry ( $p6mm$ ), which is identified by (100) and (110) Bragg reflections at 0.94° and 1.70° of  $2\theta$  value, respectively. The interplanar spacing,  $d_{100}$ , and unit cell parameter,  $a_0$  ( $2d_{100}/\sqrt{3}$ ), calculated from  $2\theta$  value of (100) reflection were 93.9 Å and 108.4 Å, respectively. The TEM image in Fig. 3(b) shows clearly the hexagonally arranged pore arrays of UFPMO. Low temperature nitrogen adsorption–desorption isotherm of UFPMO gives a type IV isotherm, typical of mesoporous solids, as shown in Fig. 3(c). The pore diameter of UFPMO obtained from the desorption branch of isotherm by Barret–Joyner–Halenda (BJH) formula was 42.0 Å. The half-width-at-half-maximum (HWHM) of pore size distribution curve shown in the inset in Fig. 3(c) is ca. 2 Å, indicating that the pore of UFPMO is nearly uniform. The BET surface area was 587 m<sup>2</sup>/g and pore volume, 0.62 cm<sup>3</sup>/g. The wall thickness calculated by subtracting the pore diameter from the unit cell parameter was 66.5 Å. Lower surface area and pore volume of UFPMO than those typical of SBA-15 can be attributed to thick wall and the incomplete removal of templating agent. Thickening of wall may be ascribed to hydrogen bonding between N–H in urethane moiety and oxygen of siloxane or silanol. Moreau et al. [13] reported that the hydrogen bonding plays an important role in the formation of self-organized hybrid silica from silsesquioxane containing of urea groups in long

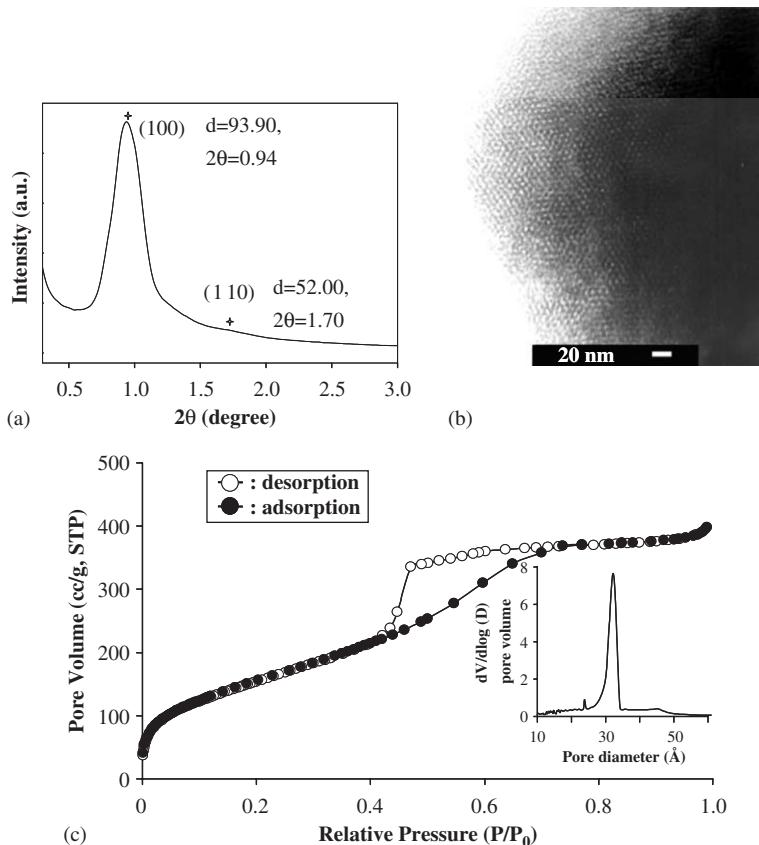


Fig. 3. (a) SAXS pattern, (b) TEM image and (c)  $N_2$  adsorption–desorption isotherm of surfactant-extracted UPMO. Inset shows the pore-size distribution.

organic group. And it seems that the hydrogen bonding plays a role also in remaining intact without the collapse or disordering of framework containing long organic groups after the removal of surfactant.

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### References

- [1] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* 359 (2002) 710.
- [2] S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna, O. Terasaki, *J. Am. Chem. Soc.* 121 (1999) 9611.
- [3] T. Asefa, M.J. MacLachlan, N. Ohsuna, G.A. Ozin, *Nature* 402 (1999) 867.
- [4] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, *J. Am. Chem. Soc.* 120 (1998) 6024.
- [5] J. Morell, G. Wolter, M. Froba, *Chem. Mater.* 17 (2005) 804.
- [6] S.R. Hall, C.E. Fowler, B. Lebeau, S. Mann, *Chem. Commun.* 201 (1999).
- [7] M.C. Burleigh, M.A. Markowitz, M.S. Spector, B.P. Gaber, *J. Phys. Chem. B* 105 (2001) 9935.
- [8] A.M. Wahab, I. Kim, C.-S. Ha, *J. Solid State Chem.* 177 (2004) 3439.
- [9] R.J.P. Corriu, A. Mehdi, C. Reye, C. Thieuleux, *Chem. Commun.* 1382 (2002).
- [10] O. Olkhovik, M. Jaroniec, *J. Am. Chem. Soc.* 127 (2005) 60.
- [11] M.A. Markowitz, J. Klaehn, R.A. Hendel, S.B. Qadriq, S.L. Golledge, D.G. Castner, B.A. Gaber, *J. Phys. Chem. B* 104 (2000) 10820.
- [12] [IR-spectrum: N–H stretching ( $3335\text{ cm}^{-1}$ ), aliphatic C–H ( $2976\text{--}2885\text{ cm}^{-1}$ ), N–H bending ( $1540\text{ cm}^{-1}$ ), C=O stretching ( $1700\text{ cm}^{-1}$ ), C–N stretching ( $1470\text{--}1450\text{ cm}^{-1}$ ), N–H OOP ( $775\text{ cm}^{-1}$ ), C–O stretching ( $1008\text{--}1242\text{ cm}^{-1}$ ).  $^1\text{H}$  NMR spectrum ( $300\text{MHz}$ ,  $\text{CDCl}_3$ ) NH ( $\delta$  5.3 ppm, singlet),  $\text{COOCH}_2$  (4.2 ppm, singlet),  $\text{SiOCH}_2\text{CH}_3$  (3.6–3.9 ppm, quartet),  $\text{SiOCH}_2\text{CH}_3$  (1.2–1.3 ppm, triplet),  $\text{SiCH}_2\text{--CH}_2\text{NH}$  (3.1 ppm, quartet),  $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}$  (1.5–1.7 ppm, quintet),  $\text{SiCH}_2\text{CH}_2\text{CH}_2$  (0.6 ppm, triplet)].
- [13] J.J.E. Moreau, L. Vellutini, M.W.C. Man, C. Bied, J.-L. Bantignies, *J. Am. Chem. Soc.* 123 (2001) 7957.