COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Direct synthesis of ordered mesoporous materials constructed with polymer–silica hybrid frameworks†

Yoon-Sok Kang,[a] Hyung Ik Lee,[b] Ye Zhang,[b] Yong Jin Han,[a] Jae Eui Yie,[c] Galen D. Stucky*[a] and Ji Man Kim*[b]

[a] *Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106, USA. E-mail: stucky@chem.ucsb.edu; Fax: +1-805-893-4120; Tel: +1-805-893-4872*

[b] *Functional Materials Laboratory, Department of Molecular Science & Technology, Ajou University, Suwon 442-749, Korea. E-mail: jimankim@ajou.ac.kr; Fax: +82-31-219-2394; Tel: +82-31-219-1850*

[c] *Catalyst and Surface Laboratory, Department of Applied Chemistry, Ajou University, Suwon 442-749, Korea*

Received (in Columbia, MO, USA) 9th February 2004, Accepted 27th April 2004
First published as an Advance Article on the web 25th May 2004

Highly ordered mesoporous materials constructed with integrated polymer–silica hybrid frameworks can be obtained *via* a one-step synthetic strategy using a mixture of polymer and silicate as the framework sources in the presence of a structure-directing agent.

Mesoporous materials have generated considerable interest as a consequence of their high surface areas, unusual stability, processability, and well defined pores with narrow size distributions.[1–4] A wide variety of mesostructured inorganic compositions can be readily synthesized using cationic, anionic and neutral surfactants and amphiphilic block copolymers as the supramolecular templates.

The versatility of mesoporous materials can be greatly enhanced by the preparation of materials constructed with organic–inorganic hybrid frameworks.[5–10] The presence of organic groups within the frameworks has been found to give these materials a number of favorable properties: structural rigidity, functionality and a designed degree of hydrophobic character, all useful for many applications including catalysis, separations and the creation of advanced electro-optic materials. There are three general routes to obtain the organic–inorganic hybrid mesoporous materials. The post-synthesis procedure *via* grafting a suitable organosilane at the silanol groups of the mesoporous silica materials was the first to be used for pore surface modification.[5] Second is the one-pot synthesis of mesoporous materials with an organically modified pore surface by co-condensation of siloxane and organosiloxane precursors in the presence of organic templates.[6,7] More recently, the synthesis of periodic mesoporous organosilica has been reported, where the organic component is built in the frameworks, using bridged silsesquioxanes as the framework source.[8–10] However, there remain limitations for the preparation and applications of organic–inorganic hybrid mesoporous materials since all of these preparation methods use organosiloxane precursors to give functionality to the materials.

In this communication, we propose a direct synthesis method to create ordered organic–inorganic mesoporous materials constructed with polymer–silica frameworks. This new procedure involves a one-step synthetic strategy based on the blending of a polymer containing a desired functional group and the silica precursor, before adding the mixture to a template solution or initiating the silica polymerization. In particular, polyacrylic acid (PAA) is a good candidate because of its amphiphilic character, mesostructural ordering capability with cationic surfactants, low-cost commercial availability, acid functional group and good solubility in water.[11,12] This approach needs neither the use of an expensive organically modified ceramic precursor nor the additional post-synthetic reaction of silanol groups to create a functional group on the wall of mesoporous silica.

An aqueous solution of sodium silicate with Na/Si = 0.5 (20 wt% of SiO_2) was used as the silica source.[13] Typically, 10 g of myristyltrimethylammonium bromide (Aldrich, MTAB, $C_{14}H_{29}N(CH_3)_3Br$) was dissolved in 162 g of doubly distilled water. An aqueous solution of sodium polyacrylate (35 wt%, NaPAA, M_w = 100 000) was mixed with the sodium silicate solution. The weight fractions of PAA to total framework source were varied in the range of 0–60%. For the 20 wt% of PAA content, 3.18 g of NaPAA solution was mixed with 32.7 g of the sodium silicate solution. This polymer–silicate mixture was added drop by drop to the MTAB solution at room temperature while the solution was stirred vigorously. After continuously stirring for 1 h, the mixture was aged at 373 K for 24 h under static conditions. The mixture was cooled to room temperature and the pH of the mixture was adjusted to 10 with acetic acid.[14] The mixture was heated again for 24 h at 373 K. pH adjustment and subsequent heating were repeated once more before the precipitated product was finally filtered off. The product was washed with doubly distilled water and dried in an oven at 373 K overnight. The templates were removed from the as-made materials by washing with an acetic acid–methylene chloride mixture. These samples are denoted MCM-41-PAA-*x*, where the *x* means the weight fraction of PAA to total framework source.

Fig. 1 shows X-ray diffraction (XRD) patterns for the MCM-41-PAA-*x* materials before and after the template removal. All the materials give XRD patterns which exhibit the characteristics of 2D hexagonal symmetry (*P*6*mm*). Thus, the mesomorphic orders of the mesoporous materials are completely retained on inclusion of PAA. Most of the surfactant, but no detectable PAA, can be removed by washing with an acetic acid–methylene chloride mixture at room temperature, which is confirmed by IR spectra and thermogravimetric analysis (TGA) experiments made before and after washing.

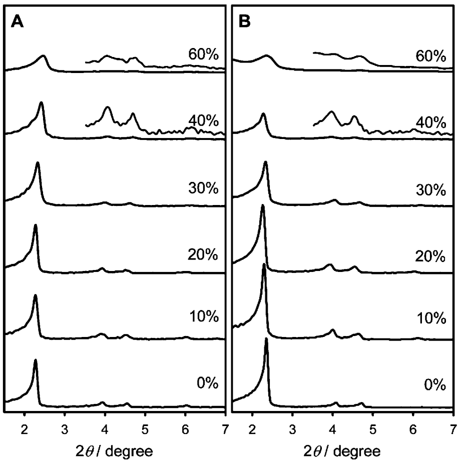

Fig. 1 XRD patterns for MCM-41-PAA-*x* materials: (A) as-made and (B) washed.

---

† Electronic supplementary information (ESI) available: Fig. S1. See http://www.rsc.org/suppdata/cc/b4/b402037e/

DOI: 10.1039/b402037e

There are no significant changes in XRD patterns (Fig. 1b) upon the removal of templates except for the expected change in XRD peak intensity. The XRD patterns show that four XRD peaks are still observed, confirming that the hexagonal structures are preserved during extraction procedures, until $x = 40$. However, when $x = 60$, the XRD intensity decreases, which suggests that the polymer–silica framework structures are not maintained without an adequate amount of the silica framework. This is a general phenomenon in polymer-surfactant mesostructured composites.

A transmission electron microscopy (TEM) image (see Fig. S1 of the ESI†) of the washed MCM-41-PAA-20 shows well ordered hexagonal arrays of mesopores (1D channels) and further confirms that the sample has the hexagonal structure. Nitrogen adsorption-desorption isotherms for the present materials are Type IV (see Fig. 2) with a sharp increase in the adsorption around $p/p_0 = 0.3$, which is typical of mesoporous solids.[1–7] All the samples exhibit narrow BJH pore size distribution curves around 2.5 nm, after the removal of template. The weight percentages and the acid capacities of the PAA within the framework of MCM-41-PAA-*x* materials (Table 1) were determined by TGA and titration. As shown in Table 1, the observed PAA contents and acid capacities are very close to the calculated values until $x = 20$. The results indicate that most of the PAA can be successfully incorporated within the polymer–silica hybrid frameworks. However, the observed amount is lower than that calculated above $x = 40$, which means that part of the PAA is washed out during the surfactant removal. Wall densities of the MCM-41-PAA-*x* materials, which are determined by helium pycnometer, gradually decrease from 2.2 to 1.3 g cc^{-1} upon the increase of polymer contents as shown in Table 1. This clearly shows the formation of polymer–silica hybrid frameworks *via* the present approach.

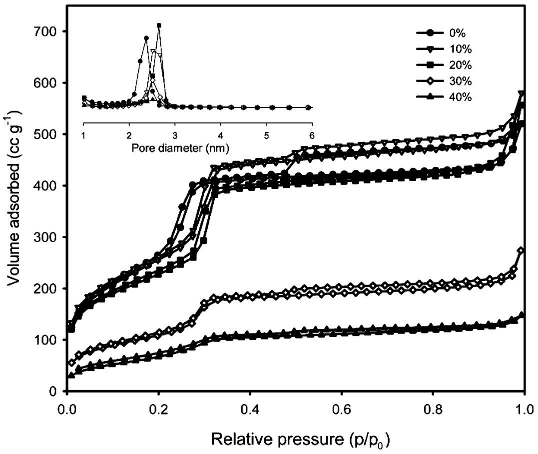

Fig. 2 N_2 sorption isotherms and the corresponding BJH pore size distribution curves for MCM-41-PAA-*x* materials.

Table 1 Physico-chemical properties of MCM-41-*x* materials

x	S_{BET}/m^2 g^{-1}	*D*[a]/nm	ρ[b]/g cc^{-1}	PAA content[c]/wt%	Calculated acid capacity/mmol g^{-1}	Observed acid capacity[d]/mmol g^{-1}
0	1153	2.3	2.23	0	0.00	0
10	1156	2.5	1.88	7	0.99	0.79
20	931	2.5	1.81	15	2.12	2.01
30	544	2.5	1.73	26	3.66	3.07
40	324	2.5	1.64	29	4.09	3.58
60	—	—	1.28	39	5.49	2.16

[a] Pore diameters obtained by BJH model. [b] Real density of framework determined by helium pycnometry. [c] Obtained polymer content from TGA after template removal. [d] Obtained by titration method.

The generality of the present approach for synthesis is further illustrated by the synthesis of SBA-15-PAA, which can be obtained using the triblock copolymer P123 as the template under acid conditions. Thus, the pore size of PAA containing silica can be extended up to 10 nm. MCM-48 type material constructed with silica–PAA composite can also be obtained by following the same procedure decribed elsewhere,[14] except that a silica–PAA mixture is used as the framework source. The synthesis of ordered hybrid mesoporous materials containing polystyrene sulfonate (PSS) is also possible by using the silica–PSS mixture as the framework source instead of the PAA–silicate mixture. One would expect that MCM-41-PSS thus obtained has stronger acid strength than that of the MCM-41-PAA.

The acid-functionalized products reported here have large uniform pore sizes, high surface areas, good mesoscopic order, and relatively high acid capacity, all of which are necessary properties for prospective catalytic applications. A key idea of the present work is that the polymer–silica precursor blend has a chance to approach chemical equilibrium, and from this vantage point both of these species can efficiently combine with the templating materials. Sodium cations in the reaction mixture may help the polymer to incorporate into the silica frameworks. As a result, these two parts can be mixed completely with each other although usual polymer and silica are immiscible. To the best of our knowledge, this work provides not only the easiest and cheapest way to introduce a functional polymer as part of the pore wall structure, but also the first synthesis of mesoporous materials whose frameworks consist of polymer–silica composites. Thus, by altering the polyelectrolyte (charge, cationic, anionic, hydrophobicity, glass transition temperature) and template (low molecular weight, polymeric), a wide spectrum of organic–inorganic hybrid materials could be generated. Our simple approach to this system, based on self-organization, uses cheap starting materials which are available in large quantities. The further development of this class of materials may therefore be expected.

This work was supported by the Korea Science and Engineering Foundation (KOSEF, R01-2002-000-00164-0(2003)). YSK also acknowledges the postdoctoral fellowship program from the KOSEF. GDS acknowledges the support of the National Science Foundation through NSF DMR-0233728.

Notes and references

1 C. T. Kresege, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
2 S. A. Bagshaw, E. Prouzet and T. J. Pinnavaia, *Science*, 1995, **269**, 1242.
3 D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548.
4 J. Y. Ying, C. P. Mehnert and M. S. Wong, *Angew. Chem., Int. Ed.*, 1999, **38**, 56.
5 J. H. Clark and D. J. Macquarrie, *Chem. Commun.*, 1998, 853.
6 Q. Huo, D. Margolese and G. D. Stucky, *Chem. Mater.*, 1996, **8**, 1147; D. Margolese, J. A. Melero, S. C. Christiansen, B. F. Chmelka and G. D. Stucky, *Chem. Mater.*, 2000, **12**, 2448; J. A. Melero, G. D. Stucky, R. van Grieken and G. Morales, *J. Mater. Chem.*, 2002, **12**, 1664.
7 S. L. Burkett, S. D. Sim and S. Mann, *Chem. Commun.*, 1996, 1367.
8 S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna and O. Terasaki, *J. Am. Chem. Soc.*, 1999, **121**, 9611; S. Inagaki, S. Guan, T. Ohsuna and O. Terasaki, *Nature*, 2002, **416**, 304.
9 Q. Yang, M. P. Kapoor and S. Inagaki, *J. Am. Chem. Soc.*, 2002, **124**, 9694.
10 T. Asefa, M. J. MacLachian, N. Coombs and G A Ozin, *Nature*, 1999, **402**, 867.
11 P. Ilekti, T. Martin, B. Cabane and L. Piculell, *J. Phys. Chem. B*, 1999, **103**, 9831.
12 M. Antonietti, C. Burger and A. Thunemann, *Trends Polym. Sci.*, 1997, **5**, 262.
13 R. Ryoo and J. M. Kim, *Chem. Commun.*, 1995, 711.
14 R. Ryoo, S. H. Joo and J. M. Kim, *J. Phys. Chem. B*, 1999, **103**, 7435.