COMMUNICATION

ChemComm
www.rsc.org/chemcomm

A versatile pathway for the direct assembly of organo-functional mesostructures from sodium silicate

Jainisha Shah, Seong-Su Kim and Thomas J. Pinnavaia

Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lanisng, MI 48824, USA. E-mail: pinnavai@cem.msu.edu; Fax: 517-432-1225; Tel: 512-432-1222

Received (in Columbia, MO, USA) 20th November 2003, Accepted 5th January 2004
First published as an Advance Article on the web 6th February 2004

Silica mesostructures with well-expressed hexagonal and wormhole framework structures and up to 50% organo-functionalization of the framework silicon sites have been directly assembled from sodium silicate.

Organo-functionalized mesoporous molecular sieve silicas with the anhydrous composition $(SiO_2)_{1-x}(LSiO_{1.5})_x$, where L is a covalently bonded organo group, exhibit exceptional activity, selectivity and stability in a number of catalytic reactions and sorption processes.[1,2] Two general synthetic pathways have been developed for the synthesis of these materials, namely (i) the post-synthesis grafting of organosilane reagents onto the pore walls of a pre-assembled mesostructure through coupling reactions with surface silanol groups and (ii) the direct assembly of SiO_4 and $LSiO_3$ units, into a mesostructured framework in the presence of a structure-directing surfactant porogen. Both synthetic approaches have been used to prepare hexagonal MCM-41[3–5] and SBA-15 structure types[6,7] as well as HMS[8–10] and MSU-X derivatives with wormhole frameworks.[11,12] Organo groups incorporated into the mesostructures have included thiol groups for the trapping of mercury and other heavy metals,[13,8] amine groups for base-catalyzed reactions and the trapping of arsenate ions,[14] carboxylic acid groups for the immobilization of biological molecules,[15] among many others.[16,17]

In general, the direct assembly of organo-functional mesostructures is preferred over the grafting pathway, in part, because it minimizes processing steps and allows for a more uniform distribution of organo groups fully integrated into the framework walls.[18] In addition, direct assembly synthesis oftentimes provides a higher loading of organo groups without closing the framework mesopores.[19,20] As the materials applications of $(SiO_2)_{1-x}(LSiO_{1.5})_x$ materials becomes more widespread, it becomes important to develop cost effective direct assembly routes to these materials. However, almost all of the previously reported direct assembly routes to these compositions have used silicon alkoxides, most notably, tetraethylorthosilicate (TEOS), as the precursor to the SiO_4 framework subunits, along with organosilicon alkoxides as the source of the $LSiO_3$ units.

The use of tetraethylorthosilicate (TEOS) for the direct assembly of organo-functional mesostructures represents a materials cost disadvantage. Some progress has been made recently in replacing TEOS with sodium silicate for the assembly of $(SiO_2)_{1-x}(LSiO_{1.5})_x$ mesostructures,[21] but the degree of organo-functionalization was low ($x \sim 0.10$), the framework structure was highly disordered, and the range of organo groups L was limited to a few simple hydrocarbon moieties and only one functional group (*i.e.* a mercapto group). In the present work we report the use of sodium silicate as the silica source for the direct assembly of $(SiO_2)_{1-x}(SiLO_{1.5})_x$ mesostructures with a high degree of organo-functionalization ($x \leq 0.50$) and highly ordered hexagonal framework structures, as well as wormhole structures. Moreover, our assembly pathway is applicable to a range of organo functionalities, including those containing cyano, mercapto and amino groups.

Our approach is based on an electrically neutral S^oI^o assembly pathway, where S^o is a nonionic surfactant and I^o represents the electrically neutral silicic acid formed from sodium silicate and the hydrolysis product of an organosilane precursor of the type $LSi(OR)_3$, where L is the desired organo-functional group. The great advantage of the S^oI^o pathway,[22,23] is that it relies on H-bonding between S^o and I^o and circumvents charge matching constraints. Consequently, the pathway affords more fully cross-linked framework structures in comparison to mesostructures formed through electrostatic S^+I^- and $S^o(H^+X^-)I^o$ pathways.[24] Although S^oI^o assembly tends to provide mesoporous silicas with wormhole framework structures, we show here that even well ordered hexagonal framework structures are possible for certain organo-functional derivatives.

In order to achieve homogeneous mixing of the reagents, it was necessary to neutralize the sodium silicate with an appropriate acid (acetic acid) and to use a judicious addition sequence for mixing the reagents. In a typical synthesis the non-ionic surfactant Brij 56 ($C_{16}H_{33}(OCH_2CH_2)_{10}OH$) was dissolved in 16.7 M acetic acid and ethanol. The acid content of the solution equalled the sodium hydroxide content of the sodium silicate solution (27% SiO_2, 14% NaOH). An appropriate mole fraction of the organosilane reagent (x = 0.05–0.50) in the form of 3-mercaptopropyltrimethoxysilane (MP), phenyltrimethoxysilane (Ph), 3-aminopropyltrimethoxysilane (AP) or 3-triethoxysilylpropylnitrile (CN), was then added to the reaction mixture and stirred for 1 h to allow for the hydrolysis of the organosilane reagent. The silicate solution in deionized water was then added to the above reaction mixture and aged at 65 °C for 24 h. The overall molar composition of the reaction mixture was $1-x\,SiO_2$:0.140 Brij 56:x organosilane:0.80 acetic acid:3.4 EtOH:134 H_2O. The resulting precipitate was collected by filtration and air dried for 24 h. Surfactant removal was accomplished by solvent extraction with ethanol to yield the organo-functionalized mesoporous materials.

Fig. 1 shows the XRD powder patterns and TEM images for a representative $(SiO_2)_{1-x}(LSiO_{1.5})_x$ composition with a hexagonal framework structure (L = γ-cyanopropyl, x = 0.15). Table 1 provides the textural properties of four different organo-functional derivatives over a broad range of x values. ^{29}Si MAS NMR studies for thiol-, amino- and phenyl-functionalized derivatives with x = 0.30, showed that most of the organosilicon centers are integrated into the framework walls through T^2 and T^3 linkages, wherein two and three oxygen atoms of the $LSiO_3$ units are bridging to framework silicon centers in the walls.

These results show that well expressed hexagonal or wormhole mesostructures are assembled from sodium silicate at organo-

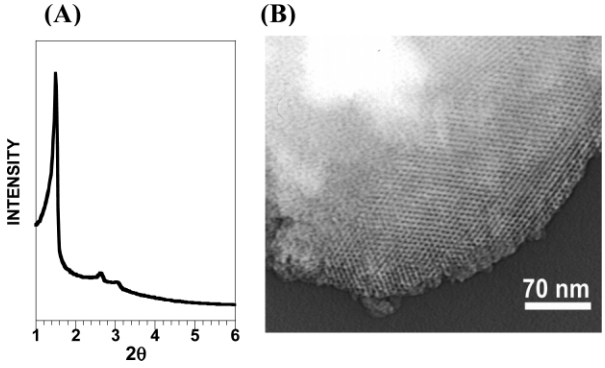

Fig. 1 (A) XRD pattern and (B) TEM image for a hexagonal $(SiO_2)_{1-x}(LSiO_{1.5})_x$ mesostructure with L = γ-cyanopropyl and x = 0.15.

DOI: 10.1039/b315032a

functionalization levels corresponding to x values of at least 0.25, regardless of the nature of the organo-functional group. Even higher levels of organo-functionalization are possible (x = 0.50) in the case of phenyl and γ-cyanopropyl moieties (see Table 1). In all cases the average framework pore size is at least 2.5 nm, with values up to 5.9 nm being possible for the smaller phenyl groups. In general, the pore size decreases with increasing levels of functionalization, but for L = phenyl, the pore size increases with increasing x up to a value of 0.30 and then decreases at x = 0.50. This suggests that the phenyl group acts as a pore expander during the assembly process by initially dissolving into the hydrophobic region of the surfactant micelle before being transferred to the wall of the mesostructure. The surface areas of the resulting mesostructures are in the range 500–1100 $m^2\ g^{-1}$, depending on L.

Amino functional mesostructures are perhaps the most difficult derivatives to assemble, even when TEOS is used as the silica source. The S^oI^o pathway based on sodium silicate as the silica source nevertheless provides well expressed wormhole structures even for γ-aminopropyl derivatives, with x values up to 0.30.

Table 1 Textural properties of $(SiO_2)_{1-x}(LSiO_{1.5})_x$ mesostructures prepared from sodium silicate

L	x	Framework structure	d_{100}/nm	S.A.[a]/ $m^2\ g^{-1}$	Pore vol.[b]/ $cm^3\ g^{-1}$	Pore size[c]/ nm
None	0.00	Hexagonal	5.8	858	0.98	3.7
$(CH_2)_3NH_2$	0.05	Wormhole	4.2	682	0.98	4.4
$(CH_2)_3NH_2$	0.10	Wormhole	4.3	656	0.92	3.9
$(CH_2)_3NH_2$	0.15	Wormhole	6.2	553	0.71	3.7
$(CH_2)_3NH_2$	0.20	Wormhole	4.5	660	0.87	3.6
$(CH_2)_3NH_2$	0.25	Wormhole	4.5	582	0.89	3.5
$(CH_2)_3NH_2$	0.30	Wormhole	–	515	0.87	3.4
$(CH_2)_3SH$	0.05	Hexagonal	5.7	1079	1.04	3.7
$(CH_2)_3SH$	0.10	Hexagonal	5.7	1118	1.02	3.5
$(CH_2)_3SH$	0.15	Hexagonal	5.8	1021	0.82	3.0
$(CH_2)_3SH$	0.20	Hex/Wrmhl	5.0	936	0.72	2.9
$(CH_2)_3SH$	0.25	Hex/Wrmhl	6.2	775	0.53	2.5
C_6H_5	0.05	Hexagonal	6.0	1084	1.14	4.0
C_6H_5	0.10	Wormhole	7.3	1190	1.15	4.8
C_6H_5	0.15	Wormhole	8.1	1145	1.07	5.6
C_6H_5	0.20	Wormhole	9.0	1066	1.11	5.7
C_6H_5	0.25	Wormhole	–	1020	1.05	5.9
C_6H_5	0.30	Wormhole	–	983	1.04	5.8
C_6H_5	0.50	Wormhole	–	860	0.59	3.6
$(CH_2)_2CN$	0.05	Hexagonal	5.8	992	1.05	3.7
$(CH_2)_2CN$	0.10	Hexagonal	5.8	1082	1.15	3.6
$(CH_2)_2CN$	0.15	Hexagonal	5.9	1041	1.06	3.5
$(CH_2)_2CN$	0.20	Hexagonal	5.9	1061	0.99	3.7
$(CH_2)_2CN$	0.25	Hexagonal	5.9	1043	1.02	3.6
$(CH_2)_2CN$	0.30	Hex./Wrmhl.	6.0	986	0.94	3.5
$(CH_2)_2CN$	0.50	Hex./Wrmhl.	–	590	0.67	3.5

[a] Surface area calculated by the Brunaeur–Emmett–Teller (BET) method. [b] Total pore volume determined at P/P_0 = 0.98. [c] Pore size determined by the Barrett–Joyner–Halenda (BJH) method. Out-gassing of the samples was carried out at 100 °C for 12 h under vacuum.

In summary, the S^oI^o pathway based on sodium silicate as the silica source is an efficient, low-cost route to the preparation of organo-functional silica mesostructures from sodium silicate. At least 30 mol%, and up to 50 mol%, of the framework silicon sites can be functionalized with retention of a hexagonal or wormhole framework structure with mesopores of 2.5–5.9 nm. This pathway should be useful for the production of mesostructure compositions for use in trapping and chemical catalysis.

The support of this research through assistantships to J. S. and S.-S. K. under NIEHS grant ESO4911 and NSF grant CHE-0211029, respectively, is gratefully acknowledged.

Notes and references

1 D. Brunel, A. C. Blanc, A. Galarneau and F. Fajula, *Catal. Today*, 2002, **73**, 139–152.
2 A. Stein, *Adv. Mater.*, 2003, **15**, 763–775.
3 S. L. Burkett, S. D. Sims and S. Mann, *Chem. Commun.*, 1996, 1367–1368.
4 X. Feng, G. E. Fryxell, L. Q. Wang, A. Y. Kim, J. Liu and K. M. Kemner, *Science*, 1997, **276**, 923–926.
5 S. B. Mann, S. L. Burkett, S. A. Davis, C. E. Fowler, N. H. Mendelson, S. D. Sims, D. Walsh and N. T. Whilton, *Chem. Mater.*, 1997, **9**, 2300–2310.
6 D. Margolese, J. A. Melero, S. C. Christiansen, B. F. Chmelka and G. D. Stucky, *Chem. Mater.*, 2000, **12**, 2448–2459.
7 M. A. Markowitz, J. Klaehn, R. A. Hendel, S. B. Qadriq, S. L. Golledge, D. G. Castner and B. P. Gaber, *J. Phys. Chem. B*, 2000, **104**, 10820–10826.
8 J. Brown, L. Mercier and T. J. Pinnavaia, *Chem. Commun.*, 1999, 69–70.
9 L. Mercier and T. J. Pinnavaia, *Chem. Mater.*, 2000, **12**, 188–196.
10 D. J. Macquarrie, *Chem. Commun.*, 1996, 1961–1962.
11 R. Richer and L. Mercier, *Chem. Commun.*, 1998, 1775–1776.
12 A. Stein, B. J. Melde and R. C. Schroden, *Adv. Mater.*, 2000, **12**, 1403–1419.
13 J. Brown, R. Richer and L. Mercier, *Microporous Mesoporous Mater.*, 2000, **37**, 41–48.
14 H. Yoshitake, T. Yokoi and T. Tatsumi, *Chem. Mater.*, 2002, **14**, 4603–4610.
15 H. H. P. Yiu, P. A. Wright and N. P. Botting, *J. Mol. Catal. B: Enzym.*, 2001, **15**, 81–92.
16 W. Van Rhijn, D. De Vos and P. A. Jacobs, *Fine Chemicals through Heterogeneous Catalysis*, ed. R. A. Sheldon and H. van Bekkum, Wiley–VCH, Weinheim, 2001, pp. 106–115.
17 R. J. P. Corriu, Y. Guari, A. Mehdi, C. Reye, C. Thieuleux and L. Datas, *Chem. Commun.*, 2001, 763–764.
18 A. Walcarius and C. Delacote, *Chem. Mater.*, 2003, **15**, 4181–4192.
19 Y. Mori and T. J. Pinnavaia, *Chem. Mater.*, 2001, **13**, 2173–2178.
20 M. Kruk, T. Asefa, M. Jaroniec and G. A. Ozin, *Stud. Surf. Sci. Catal.*, 2002, **141**, 197–204.
21 N. Yu, Y. Gong, S. Wang, D. Wu and Y. Sun, *J. Mater. Sci. Lett.*, 2003, **22**, 1229–1231.
22 P. T. Tanev and T. J. Pinnavaia, *Chem. Mater.*, 1996, **8**, 2068–2079.
23 T. R. Pauly and T. J. Pinnavaia, *Chem. Mater.*, 2001, **13**, 987–993.
24 Q. S. Hue, D. I. Margolese, U. Ciesla, P. Y. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schuth and G. D. Stucky, *Nature*, 1994, **368**, 317–321.