Thiol-functionalized mesostructured silica vesicles

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The direct supramolecular assembly of organofunctional mesostructures with a vesicular hierarchical morphology is reported for the first time for $(SiO_2)_{1-x}(LSiO_{1.5})_x$ compositions, where L is a mercaptopropyl group and x = 0.10–0.30.

Vesicular[1–8] and hollow sphere[6,9–14] hierarchical structures by now have been reported for several mesostructured forms of silica having a wormhole-like disordered or ordered hexagonal framework topology. The vesicular morphology, in particular, can provide certain advantages over monolithic forms of the same framework structure for catalytic applications in condensed phase media. When the framework structure is three-dimensional, as in wormhole framework structures, the thin walls of the vesicles define the path length for diffusion of reagents into the framework, thereby facilitating access to reaction sites on the framework walls.[15] Despite the advances in providing for vesicular forms of mesostructured silicas, there appear to be no examples of vesicular forms of organofunctional mesostructures prepared by direct assembly pathways. The present work reports the first examples of a thiol-functionalized wormhole framework structure in vesicular hierarchical form. Among the numerous organofunctional mesostructures that have been reported to date[16,17] thiol-active forms have been distinguished as trapping agents for the removal of mercury ions from aqueous solution[18,19] and as precursors to sulfonated derivatives for use in heterogeneous acid catalysts. The vesicular forms of these derivatives are expected to minimize the diffusion limitations for trapping and catalytic applications.

A series of mercaptopropyl-functionalized mesostructures were assembled from sodium silicate, (3-mercaptopropyl)trimethoxysilane (MPTS), and the triblock surfactant $(EO)_{20}(PO)_{70}(EO)_{20}$ (Pluronic 123) as the structure-directing porogen. In order to achieve a reaction pH of 6.5–7.0, concentrated acetic acid was mixed with the surfactant and MPTS in ethanol and then subsequently combined with the aqueous sodium silicate reagent. The overall reaction stoichiometry was $(1 - x)$ SiO$_2$: 0.78$(1 - x)$ NaOH : 0.0160 P123 : x MPTS : 0.8 acetic acid : 3.4 ethanol : 134 + 7.3$(1 - x)$ water. After a reaction time of 24 h at 60 °C, the as-made mesostructure was dried at 25 °C and then subjected to three extractions in refluxing ethanol to remove the surfactant. The relative integral intensities of the ^{29}Si NMR resonances corresponding to the Q and T centers in the framework were equal to the ratio of sodium silicate and MPTS initially present in the reaction mixture. Thus, the compositions of the mesostructures can be represented in anhydrous form as $(SiO_2)_{1-x}(LSiO_{1.5})_x$, where L is the mercaptopropyl group and x is the fraction of organosilicon centers in the framework.

Fig. 1 provides the N_2 adsorption–desorption isotherms for representative $(SiO_2)_{1-x}(LSiO_{1.5})_x$ compositions with x = 0.02, 0.10, and 0.30. An important feature to note is the dependence of the shapes of the adsorption and desorption branches on the loading x of thiol groups in the framework. As is reflected in the hysteresis loops, substantial changes in mesoporosity occur as the fraction of thiol groups in the framework is increased. Table 1 provides the textural properties and XRD basal spacings of the mesostructures as the level of thiol functionalization is increased from x = 0 to 0.30. The wide variations in the framework pore size (8.4–11 nm), surface areas (300–540 m^2 g^{-1}) and pore volumes (0.30–1.3 cm^3 g^{-1}) signal dramatic changes in structure over this composition range.

TEM images and X-ray powder diffraction patterns elucidate the changes that occur in both the framework structure and the hierarchical particle structure with increasing levels of thiol incorporation. Fig. 2 presents the TEM images for representative $(SiO_2)_{1-x}(LSiO_{1.5})_x$ compositions with x = 0.02, 0.10 and 0.30. The predominance of a hexagonal framework structure over the composition range x = 0.0 to 0.05 is verified by both the TEM images and by the presence of 100, 110 and 200 reflections in the XRD powder patterns. At x = 0.10, the hexagonal framework structure is replaced by a wormhole framework structure characterized by a single low angle XRD line.

The changes in framework structure are accompanied by dramatic changes in hierarchical structure. At x = 0.00 to 0.05 (*cf.*, Fig. 2) a hyperbranched hierarchical structure is observed. This hyperbranched motif is reminiscent of the morphology observed for hexagonal SBA-15 silicas assembled under metal ion-mediated assembly conditions.[21] At x = 0.10 the particle morphology is predominately vesicular, accompanied by a minor fraction of sponge-like particles. Increasing the thiol functionalization to x = 0.30 results in the nearly exclusive presence of a well-expressed vesicular hierarchical structure. Most of the vesicles have diameters in the 100–200 nm range and wall thicknesses of 15–25 nm.

A wide variety of organofunctional silica mesostructures have been assembled in the presence of different structure-directing porogens, including cationic,[22] anionic[23] and electrically neutral diblock[24] and triblock surfactants.[25] Even thiol-functionalized hexagonal structures have been prepared from sodium silicate and P123 surfactant,[26] the same silica source and porogen used in the present work. However, our chemistry provides the only known example of a vesicular hierarchical structure. The distinguishing feature of our assembly system is the silicate : MPTS : P123 ratio and the presence of sodium acetate at near-neutral pH which promotes the formation of a MPTS–P123 microemulsion in aqueous sodium silicate. It is quite clear from the observed morphology that the hierarchical structure forms around the

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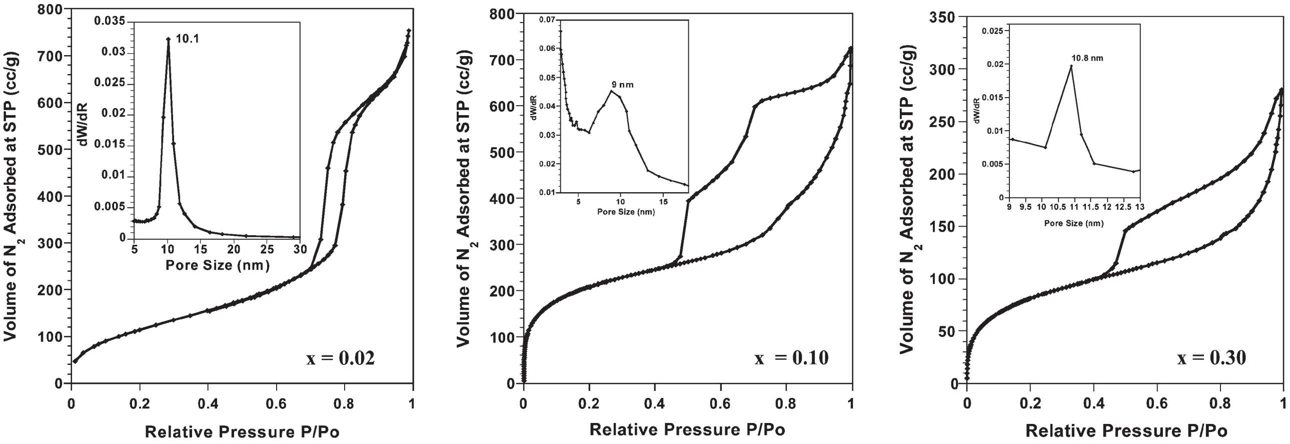

Fig. 1 N_2 adsorption–desorption isotherms and BJH pore size distributions (inserts) for $(SiO_2)_{1-x}(LSiO_{1.5})_x$ mesostructures, L = mercaptopropyl.

Table 1 Textural properties of $(SiO_2)_{1-x}(LSiO_{1.5})_x$ mesostructures, L = mercaptopropyl

x	d_{100}/nm	Surface area[a]/$m^2\ g^{-1}$	Pore volume[b]/$cm^3\ g^{-1}$	Pore size[c]/nm	Framework morphology[d]	Hierarchical structure
0.00	11.6	415	1.31	10.2	Hex	Hyperbranched
0.02	11.1	440	1.08	10.2	Hex	Hyperbranched
0.05	11.3	473	0.984	9.4	Hex/Wmhl	Hyperbranched/vesicles
0.10	12.6	510	0.938	8.4	Wmhl	Vesicles
0.20	>13	543	0.60	9.0	Wmhl	Vesicles
0.30	>13	303	0.34	11	Wmhl	Vesicels

[a] Calculated by the Bruanaeur–Emmett–Teller (BET) method. [b] Total pore volume determined at $P/Po = 0.98$. [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. [d] Hex = hexagonal, Wmhl = wormhole

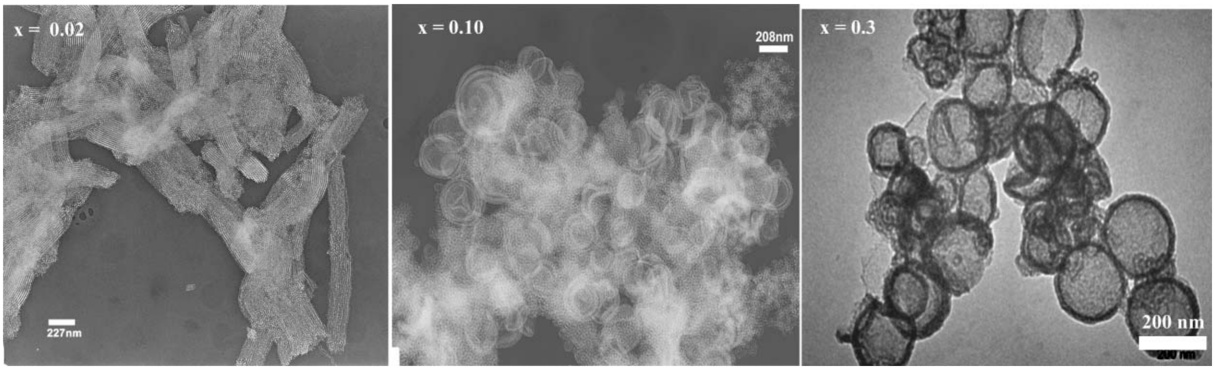

Fig. 2 TEM images for $(SiO_2)_{1-x}(LSiO_{1.5})_x$ mesostructures, L = mercaptopropyl.

microemulsion droplets at the initial stages of the assembly process and then the surfactant and MPTS is transported out of the droplets in forming the wormhole framework structure at the droplet–aqueous sodium silicate interface. As in the case of pure silica vesicles,[3,5–7] microemulsion formation is the key to forming organofunctional silicas with a vesicular hierarchical structure.

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