Fine-tuning the degree of organic functionalization of mesoporous silica nanosphere materials *via* an interfacially designed co-condensation method†

Daniela R. Radu, Cheng-Yu Lai, Jianguo Huang, Xu Shu and Victor S.-Y. Lin*

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A synthetic method that can fine tune the amount of chemically accessible organic functional groups on the pore surface of MCM-41 type mesoporous silica nanosphere (MSN) materials has been developed by electrostatically matching various anionic organoalkoxysilanes with the cationic cetyltrimethylammonium bromide micelles in a base-catalyzed condensation reaction of tetraethoxysilane.

Recent advancements in utilizing organic surfactants or block copolymers as structure-directing templates for the syntheses of structurally well-defined mesoporous silica materials, such as MCM-41/48,[1] SBA-15,[2] MSU-*n*,[3] and FSM-16,[4] has attracted much attention for their potential applications in sensing,[5] catalysis,[6] and drug delivery.[7] Obviously, the realization of these applications greatly depends on the ability of functionalization of the interior and exterior surfaces of the mesoporous silicas with various organic functional groups. Although a wide variety of synthetic approaches have been pursued and some significant progresses have been made, few would argue that the current state-of-the-art methods, such as post synthesis grafting[8] and organosiloxane/siloxane co-condensation[9] methods, need to be improved in terms of controlling the amount and location of the incorporated functional groups on the surface of the mesoporous silica materials. For example, functional groups incorporated *via* the post synthesis grafting method typically congregate at the opening parts of porous channels resulting in an inhomogeneous surface coverage,[10] whereas the amount of functional groups introduced by the organosiloxane/siloxane co-condensation method is yet to reach above 25% surface coverage without destroying the structural integrity and the long-range periodicity of the synthesized materials.[9,10] Herein, we report on a new co-condensation method that could generate organically functionalized, MCM-41 type of mesoporous silica nanosphere materials while controlling the surface concentration of organic functional groups.

As depicted in Fig. 1, our method involves the utilization of disulfide-containing organotrimethoxysilanes that have different anionic functional groups, such as 3-(3′-(trimethoxysilyl)propyldisulfanyl)propionic acid (CDSP-TMS), 2-[3-(trimethoxysilyl)propyldisulfanyl]ethanesulfonic acid sodium salt (SDSP-TMS), and mercaptopropyltrimethoxysilane (MP-TMS), to electrostatically match with cationic cetyltrimethylammonium bromide (CTAB) surfactant micelles in a NaOH-catalyzed condensation reaction of tetraethoxysilane (TEOS). We were inspired by the recent reports by Larsen and Magid,[11] where they observed the anionic lyotropic series (citrate $< CO_3^{2-} < SO_4^{2-} < CH_3CO_2^- < F^- < OH^- < HCO_2^- < Cl^- < NO_3^- < Br^- < CH_3C_6H_4SO_3^-$) for interaction with the CTAB surfactant micelle based on the enthalpy of transfer of the salt from water to solutions of 0.1 M CTAB. They concluded that anions less hydrated than Br^-, such as sulfonate, will be able to replace Br^- and bind tightly to the cetyltrimethylammonium head group of the CTAB molecule thereby effectively mitigating the repulsion between these cationic head groups and stabilizing the micelle structure. Also, several recent reports[12] have discovered that the long-range structure ordering of CTAB-templated mesoporous silicas could be improved by the additions of various anions. The tightly bound (less hydrated) anions, such as acetate and BF_4^-, became incorporated in the silicate matrix due to their ability to compete with the silicate anions in displacing Br^- from the CTAB micelle.

In the present communication, we investigated the different electrostatic matching effects of various anionic organoalkoxysilanes, such as thiolate-, carboxylate- and sulfonate-containing organoalkoxysilanes, to CTAB micelles in governing the degree of organic functionalization of the MCM-41 type mesoporous silica

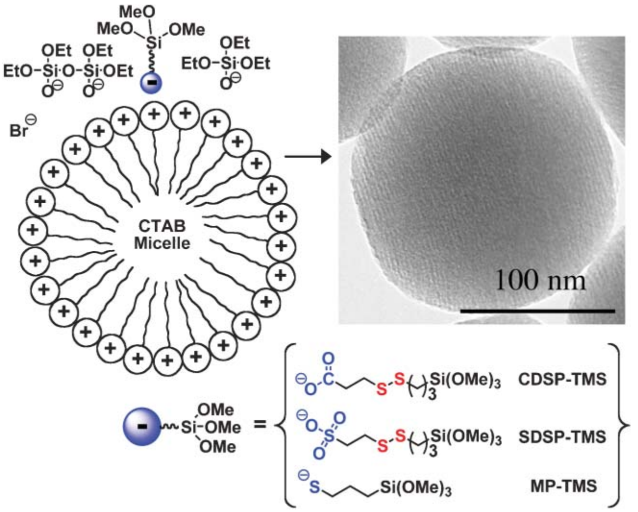

Fig. 1 Schematic representation of the utilization of anionic organoalkoxysilane for controlling the functionalization of the MSN materials. The MCM-41 type mesoporous channels are illustrated by the parallel stripes shown in the TEM micrograph of the MSN-SH material.

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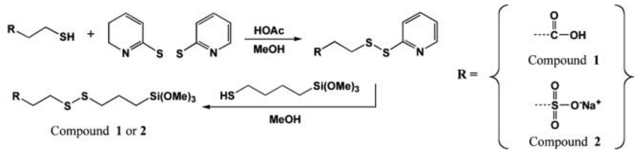
† Electronic supplementary information (ESI) available: Experimental details, SEM, N_2 adsorption isotherms, XRD, TGA, and solid state ^{13}C NMR spectra. See http://www.rsc.org/suppdata/cc/b4/b412618a/

*vsylin@iastate.edu



Scheme 1

materials. First, two disulfide-containing organotrimethoxysilanes (CDSP-TMS and SDSP-TMS) with carboxylic and sulfonic acid groups, respectively, were synthesized *via* a synthetic approach outlined in Scheme 1. As described in detail in the ESI,† these two compounds were synthesized *via* a simple thiol activation of 3-mercaptopropionic acid and 2-mercaptoethanesulfonic acid sodium salt with 2,2′-dipyridyl disulfide followed by a disulfide exchange reaction with mercaptopropyltrimethoxysilane.

Three organically functionalized mesoporous silica materials, MSN-COOH, MSN-SO_3H, and MSN-SH, were prepared by adding an ethanolic solution (2 mL, 2.24 mmol) of CDSP-TMS, SDSP-TMS, and the commercially available MP-TMS, respectively, to an aqueous solution (480 mL, 80 °C) of CTAB (2.74 mmol), NaOH (7.00 mmol), and TEOS (22.40 mmol, added at 80 °C prior to the addition of organoalkoxysilanes). The reaction mixture was stirred for 2 h. The solid products were isolated by filtration and washed thoroughly with methanol. Surfactant-removed materials were obtained with an acid extraction (see ESI†). All three materials exhibited spherical particle shape with an average particle diameter of 200 nm (Fig. 1).† The mesoporous structures of these organically functionalized MSN materials were determined by nitrogen adsorption–desorption surface analysis (BET isotherms and BJH pore size distributions), TEM, and powder X-ray diffraction (XRD) spectroscopy. All three MSN materials exhibited type IV BET isotherms with similar average BJH pore diameters (Table 1).† Hexagonally packed mesoporous channels were clearly observed in the TEM micrographs of these MSNs (Fig. 1). In addition, these materials exhibited diffraction patterns characteristic of hexagonal MCM-41 silicas, including (100), (110) and (200) peaks.† The existence of the organic functional groups was confirmed by ^{13}C solid state NMR spectroscopy.†

To quantify the amount of *chemically accessible* functional groups that are incorporated and oriented properly on the mesopore surfaces, we chemically converted the surface bound organic groups of the MSN-COOH and MSN-SO_3H materials to thiol (–SH) by treating them with a disulfide reducing agent, dithiothreitol (DTT) as depicted in Fig. 2. As shown in Scheme 2, reactions of the resulting free thiol-functionalized materials with the 2,2′-dipyridyl disulfide gave rise to 2-pyridyldithio-derivatized surface functional groups along with a 2-pyridothione compound as the side product. Given that every surface-bound thiol that reacted with the 2,2′-dipyridyl disulfide would yield one 2-pyridothione molecule in solution, the amount of chemically accessible surface thiol functionality of these three materials could be quantified by measuring the concentration (UV/Vis absorbance) of the 2-pyridothione (λ_{max} = 343 nm, ε = 8080 $M^{-1}cm^{-1}$)[13] in the supernatants of these reactions. The results showed that the solution concentrations of 2-pyridothione increased in the order of MSN-SH < MSN-COOH < MSN-SO_3H, indicating that the surface concentration of the chemically accessible thiol functional group increases from MSN-SH (0.56 ± 0.01 mmol g^{-1}), MSN-COOH (0.97 ± 0.01 mmol g^{-1}) to MSN-SO_3H (1.56 ± 0.01 mmol g^{-1}).

Table 1 N_2 Sorption analysis of the organically functionalized MSNs

Material	BET Surface area/m^2 g^{-1}	Pore volume/cm^3 g^{-1}	BJH Average pore diameter/Å
MSN-SH	999	0.793	25.8
MSN-COOH	920	0.657	27.3
MSN-SO_3H	863	0.755	28.1

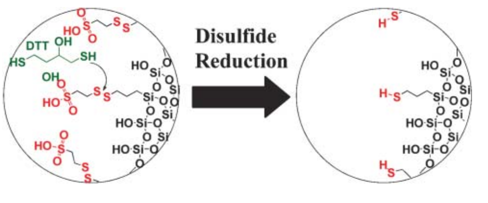
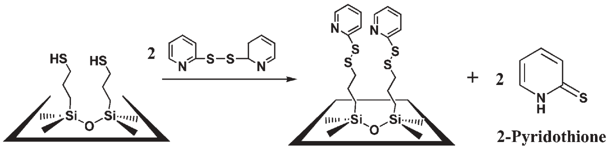


Fig. 2 Schematic representation of the formation of thiol-functionalized mesoporous silica material (MSN-SO_3H) *via* disulfide reduction with dithiothreitol (DTT).



Scheme 2

Table 2 Elemental analysis (%) of the organically functionalized MSNs

Material	C	H	S
MSN-SH	13.23 ± 0.01	2.74 ± 0.01	10.09 ± 0.01
MSN-COOH	8.60 ± 0.01	2.33 ± 0.01	5.98 ± 0.01
MSN-SO_3H	9.79 ± 0.01	2.60 ± 0.01	7.95 ± 0.01

Interestingly, the elemental analyses of these materials showed a decreasing trend in the wt% of sulfur and carbon among these materials (MSN-SH > MSN-SO_3H > MSN-COOH) as summarized in Table 2. In spite of a lower loading of organic functional groups in MSN-SO_3H, the results suggested that the amount of the chemically accessible organic functional groups in MSN-SO_3H is in fact higher than those of MSN-COOH and MSN-SH. Such a difference in the loading and spatial orientation of the organic functional groups could be attributed to the competition between the anionic species, *i.e.*, Br^-, silicates, and the anionic organoalkoxysilane precursors (CDSP-TMS, SDSP-TMS and MP-TMS), for the cationic surfactants (CTAB). Indeed, the least hydrated sulfonate group-containing SDSP-TMS gave rise to the highest loading of chemically accessible organic groups. Furthermore, relative to the carboxylate group, the thiolate offered less stabilization of the CTAB micelle aggregates, and therefore yielded the lowest loading.

In conclusion, our results have shown that the amount of chemically accessible organic functional groups of MCM-41 silicas can be fine-tuned by carefully designing the interfacial electrostatic matching between the surfactant head groups and the desired organic functional group precursors in co-condensation reaction.

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Daniela R. Radu, Cheng-Yu Lai, Jianguo Huang, Xu Shu and Victor S.-Y. Lin*
Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111, USA. E-mail: vsylin@iastate.edu; Fax: 515-294-0105; Tel: 515-294-3135

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