

Functionalized Mesoporous Materials Obtained via Interfacial Reactions in Self-Assembled Silica–Surfactant Systems

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A unique interfacial reactivity of self-assembled mesostructured silica–surfactant systems toward organosilanes was utilized to obtain ordered mesoporous materials such as MCM-41 with different surface functionality. The idea of this process is based on a direct replacement of electrostatic interactions between negatively charged silica species and surfactant cations by strong siloxane bonds. The current study shows that any suitable organosilane, having at least one reactive group (Cl–Si≡, EtO–Si≡, MeO–Si≡) in the structure, is able to displace template from self-assembled silica–surfactant mesostructures and form a covalent bonding with the silica surface. The aforementioned displacement process allows for the synthesis of mesoporous materials with high degree of structural ordering, desired surface functionality and high coverage of bonded ligands. Also, a proper choice of silane and templating surfactant provides an opportunity to tune the pore size of the resulting materials. In addition, this process improves the stability of self-assembled mesoporous materials and preserves their structural ordering, which is not always achieved when the surfactant template is removed via calcination.

Introduction

One of the major achievements in materials chemistry in the early 1990s was the synthesis of ordered mesoporous silicas (OMS) via supramolecular self-assembly of silica species and cationic surfactants followed by removal of the surfactant template via extraction and/or calcination.¹ This synthetic route affords OMS with pore sizes in the range between 2 and 10 nm when proper surfactants and synthesis conditions are used.² Another important achievement in this area includes the self-assembly of silica and other inorganic species around neutral amines³ and polymers,⁴ as well as the self-assembly of the bonded inorganic–surfactant pairs.⁵ The use of block copolymers as structure-directing agents afforded OMS with large pore sizes (up to 30

nm)^{4a} and thus opened new opportunities for self-assembling various inorganic and organic species including macromolecules.^{4–6}

The growing interest in the synthesis of novel self-assembled mesostructures is stimulated by potential applications of these materials in various areas such as adsorption, catalysis, and nanotechnology. In particular, the tendency for miniaturization of displays, electronic circuits, and microchips could benefit from utilization of mesostructures as templating and encapsulating matrices. Fabrication of nanodevices and nanosensors will require the preparation of self-assembled systems not only with desired structures but also with tailored pore chemistry.

The postsynthesis modification of calcined materials⁷ and one-pot synthesis,⁸ which involves co-condensation of tetraethoxysilane and proper organosilanes in the presence of the structure directing surfactant,⁸ are commonly used methods to alter surface chemistry of mesoporous silicas. Neither procedure is universal in terms of the structure ordering and surfactant recovery. Although the one-pot synthesis opened new avenues in

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this field, its initial procedure gave materials of average quality.^{8a} It was recently shown that the structural ordering of the aforementioned materials can be significantly improved by using proper silane molecules such as bis-silyl precursors.⁹ The latter approach allows for the synthesis of OMS with organic segments uniformly distributed inside of inorganic framework. However, the one-pot synthesis procedure still requires the extraction of the surfactant template and is less flexible for introduction of more sophisticated surface functionalities. On the other hand, conventional organosilane modification of the template-free OMS is limited to some extent by the necessity of employing the calcination and/or extraction procedures for the surfactant template removal. The high-temperature calcination ensures an effective removal of the template but simultaneously destroys potentially recoverable surfactant, and sometimes deteriorates the structural ordering and decreases the hydrothermal stability of OMS.

Unlike conventional modification⁷ and one-pot synthesis,^{8,9} a direct delivery of ligands to self-assembled (uncalcined) mesostructured systems¹⁰ represents an attractive and promising approach for surface functionalization of OMS. The previous attempts to manipulate with uncalcined OMS¹¹ were limited to some peripheral aspects and did not address the interfacial reactivity of these systems. In contrast, recent communications¹⁰ demonstrated that the surfactant template can be displaced via an ion-exchange process^{10a,b} or via reaction with alkylchlorosilanes.^{10c} In the ion-exchange procedure either metal cations^{10a} were employed as carriers to deliver some specific ligands to the pore walls or a free-base porphyrin^{10b} was used. In both cases a postsynthesis step was required to remove either the metal cations^{10a} or residual surfactant.^{10b} However, the reaction of self-assembled silica-surfactant systems with alkylchlorosilanes^{10c} allows one not only to attach the desired surface ligands but also to remove effectively the surfactant template, thus opening a new way for synthesis of functionalized materials.

The current work shows a general approach for preparation of mesoporous silicas of desired surface functionality by template displacement with organosilanes (TDS) containing at least one chloro (Cl⁻) or alkoxy (RO⁻) group. The main advantages of TDS are (i) removal of the surfactant template, which could be recovered, (ii) elimination of the calcination and/or extraction steps, (iii) attachment of desired surface ligands, and (iv) relatively short reaction time (about 8–10 h). In addition, the current study provides valuable information about reactivity of self-assembled mesostructured systems toward organosilanes, which

opens new opportunities for effective surface functionalization of these systems with simultaneous structure stabilization, thus providing OMS for specific applications in adsorption, catalysis, and nanotechnology.

Methods and Materials

Materials. Mesoporous MCM-41 silica with a low content of aluminum was provided by Mobil Technology Company (Paulsboro, NJ). The cerium-substituted MCM-41 material was obtained and characterized elsewhere.¹² The (3-aminopropyl)triethoxysilane, *n*-octyltriethoxysilane, and *n*-octyldimethylchlorosilane were from Aldrich Chemical Co. (Milwaukee, WI). (3-mercaptopropyl)trimethoxysilane was from Fluka Chemical Corp. (Milwaukee, WI). Hexane and isopropyl alcohol solvents (HPLC grade, water content below 0.02%) were from Fisher Scientific (Pittsburgh, PA). Toluene (water content below 0.001%) was from Aldrich Chemical Co. (Milwaukee, WI). All materials were used without additional purification.

Synthesis. All bonded phases were synthesized by reaction of the appropriate silane with the uncalcined mesoporous MCM-41 material without its initial pretreatment. Incorporation of silanes was performed without solvent. In a typical synthesis procedure 15 mL of silane was added to about 0.3 g of “as-synthesized” silica–surfactant material (containing surfactant inside mesopores), and the mixture was refluxed for 10 h. The resulting white solid was filtered out, washed with benzene and isopropyl alcohol and dried under vacuum for 6 h at 90 °C. No samples showed any change in color, but samples modified with octylsilyl groups were of light-gray tint. Additional modification was performed from *n*-heptane to investigate the influence of solvent on the grafting process.

The “as-synthesized” silica–surfactant mesostructured material and calcined sample were designated as MCM-U and MCM-C, correspondingly. The samples functionalized in the one-step procedure with octyldimethyl-, octyldiethoxy-, aminopropyl diethoxy-, and mercaptopropyl dimethoxysilyl groups were designated as MCM-UO, MCM-UEO, MCM-UENH₂, and MCM-UMSH, correspondingly.

Characterization Methods. The content of carbon, nitrogen, hydrogen, and sulfur in all samples was determined using a LECO model CHNS-932 elemental analyzer (St. Joseph, MI) with the relative error of less than 0.1%.

TA Instruments model TA 2950 (New Castle, DE) analyzer was used to carry out high-resolution thermogravimetric analysis. All thermogravimetric measurements were performed in nitrogen atmosphere over a temperature range from 25 to 1000 °C using the maximum heating rate 5 °C/min.

Nitrogen adsorption measurements were carried out using a Micromeritics model ASAP 2010 adsorption analyzer (Norcross, GA). Adsorption isotherms were measured at –196 °C over the interval of relative pressures from 10⁻⁶ to 0.995 using nitrogen of 99.998% purity. Before each analysis each sample was degassed for 2 h at 120 °C under vacuum of about 10⁻³ Torr in the degas port of the adsorption apparatus. Adsorption data in the range of relative pressures $p/p_0 = 0.05–0.15$ were used to calculate the BET specific surface area (S_{BET} , m² g⁻¹) of the materials studied.¹³ Pore size distributions were calculated from adsorption branches of nitrogen isotherms using the BJH method with corrected form of the Kelvin equation for capillary condensation in cylindrical pores.¹⁴ The position of the peak maximum is referred as the pore width (d_{BJH} , nm).

The BET specific surface area as well as carbon and hydrogen contents from elemental analysis were used to

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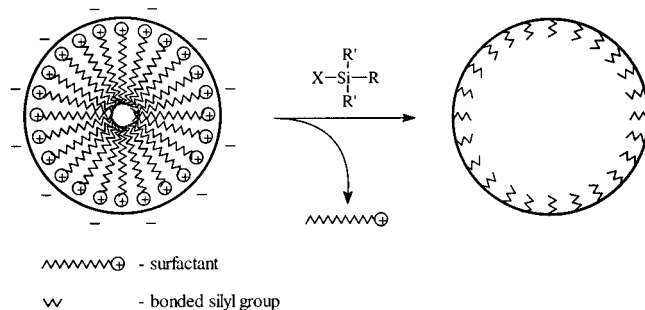


Figure 1. Scheme of template displacement with organosilanes (TDS process) in the self-assembled mesostructured systems. The left-side circle represents an inorganic silica framework with partial negative charge and the micelle-forming surfactant cations located inside this structure, whereas the right-side circle refers to the silica framework with bonded organic ligands.

estimate the concentrations of attached ligands. Their concentrations were related to 1 g of unmodified material (C_{lig} , mmol g^{-1}).

X-ray powder diffraction data were collected on a Siemens D5005 diffractometer using Cu $K\alpha$ radiation ($\lambda = 0.154056$ nm). The interplanar spacing (XRD d_{100} , nm) was calculated from the position of the first low-angle peak.

Results and Discussion

The current study shows that the self-assembled mesostructured silica-surfactant systems are stable during the TDS process of the pore opening (i.e., removal of the surfactant template). The TDS process (Figure 1) consists of a direct displacement of quaternary alkylammonium surfactant cation by desired silyl group, which in fact is the replacement of electrostatic interactions at the organic-inorganic interface by covalent bonds. More specifically, the interacting pairs $\equiv\text{Si}-\text{O}\cdots\text{S}^+$ ($\equiv\text{Si}-\text{O}^-$ is a unit of silicate oligomer and S^+ is the surfactant cation) are replaced by covalent bonds $\equiv\text{Si}-\text{O}-\text{SiR}'_2\text{R}$. Therefore, by selecting an appropriate silane molecule ($\text{X}-\text{SiR}'_2\text{R}$, where $\text{X} = \text{Cl}$ or AlkO ; $\text{R}' = \text{Alk}$ or AlkO ; and R denotes the functional group to be introduced) it is possible to attach almost any type of functionality to the silica surface. Also, "mild" synthetic conditions preserve the structural ordering of the self-assembled mesostructured systems. A detailed study of the TDS process showed that it requires about 8–10 h, much less than the time reported previously.^{10c} About 4 h are sufficient to remove over 70% of the surfactant template. It should be noted that the TDS process can be performed with or without solvent, which gives additional options for recovery of the surfactant and makes this process attractive from the viewpoint of green chemistry.

The XRD spectra for the MCM-41 materials before and after TDS process are shown in Figure 2. The starting self-assembled silica-surfactant system has the interplanar d_{100} spacing slightly above 5.0 nm (see Table 1). The d_{100} spacing decreased upon calcination due to the well-known effect of the structure shrinkage.¹⁵ In contrast, uncalcined samples subjected to the direct surfactant replacement by silyl groups (TDS process) do not shrink. In some cases, e.g., for aminopropyl

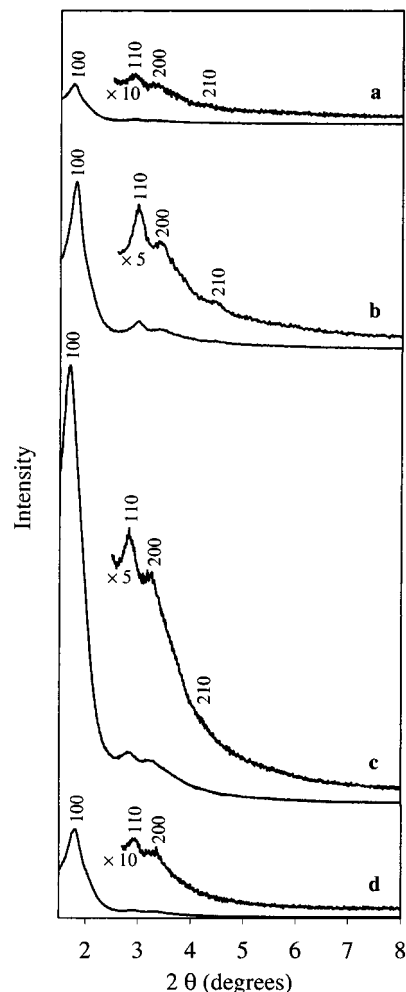


Figure 2. X-ray powder diffraction patterns for the materials studied: uncalcined (a), calcined (b), modified with aminopropylsilyl (c), and mercaptopropylsilyl (d) ligands. Inserts show enlarged area of the 110, 200, and 210 peaks.

silane, even a small increase in the d spacing was obtained (Figure 2c), which could be attributed to the structure expansion analogous to that observed during the postsynthesis restructuring with amines.¹⁶ Also, an increase in the XRD peak intensities was observed for the samples with attached aminopropyl groups, which indicates a noticeable improvement of the mesostructure ordering in comparison to that in the calcined samples.

The structural parameters evaluated on the basis of elemental analysis, high-resolution thermogravimetry (TGA), and nitrogen adsorption data for the self-assembled mesoporous materials studied are summarized in Table 1. The displacement of templating quaternary ammonium cations by silyl groups was monitored by high-resolution TGA (data not shown). The TGA data indicate that the surfactant template is removed around 180–230 °C, whereas non-hydrolyzed ethoxy or methoxy side groups of the silyl tether and its main chain decompose in the range from 350 to 550 °C. It should be noted that a small amount of surfactant,

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Table 1. Structural Parameters of the Self-assembled Materials Studied

sample	surface area S_{BET} ($\text{m}^2 \text{g}^{-1}$)	XRD spacing d_{100} (nm)	pore width d_{BJH} (nm)	pore volume V_{mes} ($\text{cm}^3 \text{g}^{-1}$)	ligand loading $C_{\text{Lig.}}$ ($\text{mmol g}^{-1} \text{SiO}_2$)
MCM-U	29	5.04	<i>b</i>	<i>b</i>	
MCM-C	800	4.93	4.9	0.96	
MCM-UO	410	<i>a</i>	3.3	0.42	2.10
MCM-UEO	500	<i>a</i>	3.5	0.53	1.45
MCM-UENH ₂	540	5.29	4.3	0.69	1.25
MCM-UMSH	455	5.04	3.8	0.50	2.45

^a XRD measurements were not carried out. ^b Mesopores filled with surfactant and nonaccessible for nitrogen molecules.

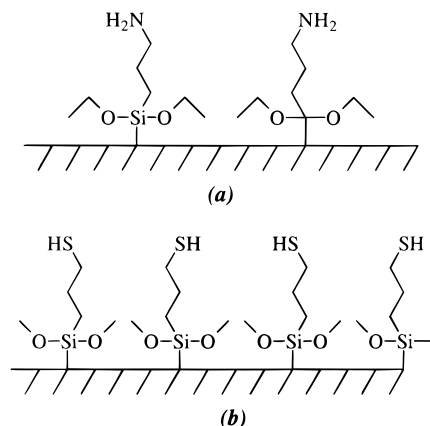


Figure 3. Schematic illustration of the side group effect on the bonding density for the MCM-UENH₂ (a) and MCM-UMSH (b) materials.

below 6% of its total amount present in “as-synthesized” samples, remains in the resulting materials (this amount did not depend on the type or amount of silanes used). Apparently, this finding suggests that the self-assembled silica-surfactant sample could possess some inaccessible parts of the pore structure. Such voids in the structure could be probably open only upon calcination.

The ligand coverages (from 1.25 to 2.7 mmol/g SiO₂) were determined from the elemental analysis data, i.e., the carbon content as well as nitrogen and sulfur contents in the case of ligands containing N and S atoms. The theoretical and experimental C:N or C:S ratios (for MCM-UENH₂ and MCM-UMSH, correspondingly) as well as ligand concentrations calculated from the carbon and nitrogen (sulfur) percentages were in a good agreement for the monomeric-type attachment of organosilane with unhydrolyzed alkoxy side groups (Tables 1S and 2S in the Supporting Information). However, a large discrepancy observed for the model with hydrolyzed side groups led us to the conclusion that alkoxy groups did not hydrolyze during the TDS process. This conclusion is also in agreement with the TGA data. The amount of attached groups was corrected for a small residue of the surfactant in the structure. A significant difference in the amount of grafted groups of the similar structure (MCM-UENH₂ vs MCM-UMSH and MCM-UO vs MCM-UEO) emphasizes the importance of the size of side chains in the anchoring ligands on their surface coverage (see Figure 3).

Nitrogen adsorption studies (Figures 4, 1S, and 2S) showed the opening of pores in uncalcined mesostructured samples upon treatment with organosilanes. A typical self-assembled mesostructured system with cationic surfactant inside of the silica framework has very low surface area (a few square meters per gram) and

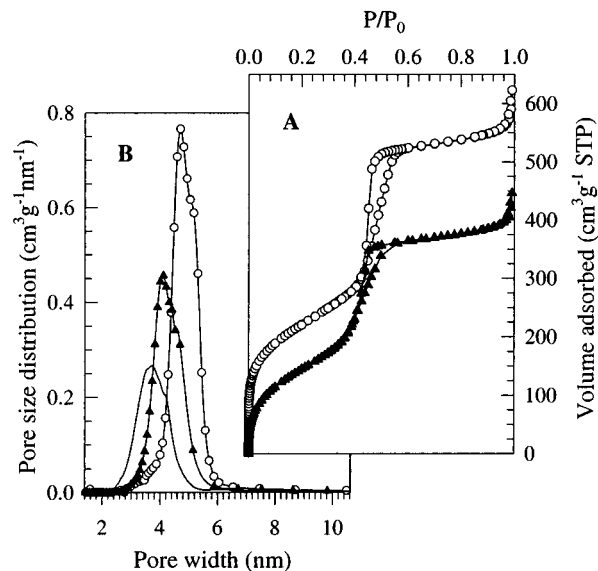


Figure 4. Nitrogen adsorption isotherms (A) for the MCM-41 sample after calcination (open circles) and the sample with aminopropylsilyl groups prepared by TDS process (closed triangles). Differential pore size distributions (B) calculated from nitrogen adsorption isotherms. The MCM-41 samples after calcination (open circles with solid line), after TDS process involving aminopropylsilane (closed triangles with solid line) and mercaptopropylsilane (solid line).

does not exhibit porosity. After the surfactant template was replaced by organosilane, the resulting material exhibits a very high specific surface area and well-ordered system of nanopores. A systematic decrease in the BET surface area and mesopore volume as well as a noticeable shift in the position of the capillary condensation step toward low relative pressures (Figures 4A and 1S) were observed for all silane-treated samples in comparison to the calcined material. The aforementioned changes correlate with the silane’s size (the smallest change was observed for mercaptopropyltrimethoxysilane, which is the smallest silane studied; see Table 1). The relatively high surface area and pore volume of the samples after TDS process indicate a full accessibility of pores for nitrogen molecules.

As can be seen from the differential pore size distributions (Figures 4B and 2S) a gradual decrease in the mesopore width is observed with increasing size of the functional group grafted. A smaller difference (only ~0.6 nm) between the pore size of the calcined sample and the uncalcined sample prepared with aminopropylsilane by the TDS process emphasizes both the absence of structure shrinkage during TDS process and smaller surface coverage of grafted groups. Adsorption and XRD studies of this sample as well as somewhat lower coverage of aminopropylsilyl ligands, in comparison to the other ligands of the similar size (MCM-UMSH) or

similar spacer group (MCM-UEO), suggest that the origin of such effect could be related to the specificity of interactions between the silica surface and amino species. Previous studies of chromatographic bonded phases indicate a two-step attachment of aminopropylsilyl ligands to the silica surface.¹⁷ In the first step, amino groups interact with surface silanols and next facilitate the attachment of the silane anchoring group to the silica surface. If such two-step mechanism is valid, it would require more space on the silica surface.

An important factor, which should be taken into account in the comparison of pore sizes of the samples functionalized via conventional and TDS methods, is the structure shrinkage effect. A typical calcination process is carried out at elevated temperatures (about 550 °C). At these conditions, the neighboring surface silanols condense with release of water and form siloxane bonds, which lead to the structure shrinkage.¹⁵ This "undesirable" condensation can be eliminated during the low-temperature TDS process because surface hydroxyls are eliminated by attaching silyl groups. It is not necessary to involve each silanol group in the silanization reaction. Elimination of one silanol out of two/three makes the condensation process more difficult and prevents the structure collapse, i.e., breakage of the strained siloxane bonds in the structure, which are formed during the high-temperature calcination.¹⁸ Thus, TDS process is gentler to the self-assembled mesostructured systems than high-temperature calcination because it gradually removes the source of the "future" structure collapse. Therefore, the step-by-step replacement of electrostatic surfactant-silanol interactions by covalent Si-O-Si bonds results in the structure stabilization.

The quality of the resulting materials prepared via TDS procedure is better than those usually prepared by one-pot synthesis. A direct incorporation of functionality via one-pot synthesis gives often the lower quality materials because of the complexity of interactions in multicomponent systems.^{8c,d} Also, the postsynthesis extraction of the surfactant can be a challenging problem. In contrast, the TDS process ensures the structure preservation during the attachment of organosilyl ligands. Also, this process shows several advantages over conventional modification of calcined samples because it requires little time, makes surfactant recoverable, reduces risk of destroying nanostructure during thermal treatment, simultaneously introduces useful functionality, and gives flexibility in attaching desirable ligands. The loading of ligands by the TDS procedure is higher than that achieved by conventional modification of calcined samples.^{10c} A similar trend was observed for the samples that underwent extraction¹⁹ instead of calcination prior organosilane functionalization. Note that in the case of calcined samples the condensation of silanols results in the lower ligand loading.¹⁹

In addition, the effect of structure stabilization and improvement is illustrated by using a mesoporous silicate with incorporated cerium (Si:Ce ratio 50) (Figure 5a). Upon calcination this sample had an average pore

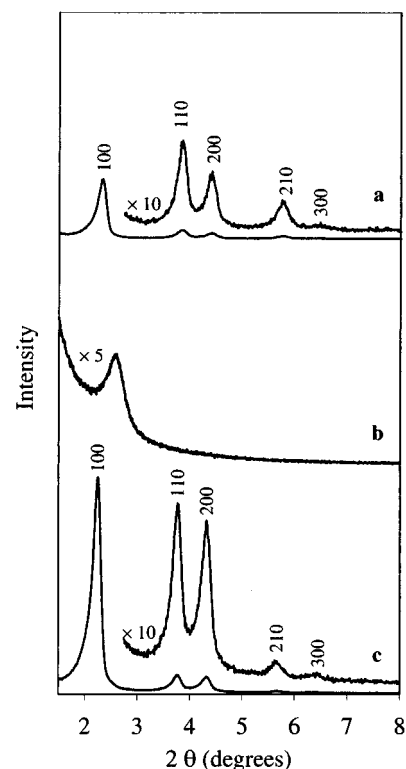


Figure 5. X-ray powder diffraction patterns for the cerium-incorporated mesostructured materials: uncalcined (a), calcined (b), and with attached aminopropylsilyl functionality (c). Inserts show enlarged area of the 110, 200, 210, and 300 peaks.

size about ~ 3.75 nm. After a few months of storage this sample disintegrated as evident by the XRD spectrum (Figure 5b). On the other hand, the uncalcined sample did not lose the structure ordering and after displacement of the surfactant template by silyl ligands showed several peaks on the XRD spectra and gave the interplanar spacing larger than initial material (d_{100} is 3.93 vs 3.80 nm). Probably, the key factors of such stabilization are the surface hydrophobization^{19,20} and a controlled elimination of silanols, which are responsible for condensation and subsequent structure collapse. This example demonstrates for the first time that the mesostructures showing a tendency for disintegration after calcination procedure can be successfully stabilized via TDS process proposed in the current work.

Conclusions

The current work addresses the issue of interfacial reactions in self-assembled silica-surfactant mesostructures. The proposed one-step opening of nanochannels through template displacement with organosilanes (TDS) allowed for preparation of mesoporous materials with tunable pores and surface functionality without necessity of their calcination. The simplicity of the TDS process and flexibility in the choice of functionality (almost any silane can be used) give a valuable tool for preparation of stable self-assembled nanostructures. Moreover this process eliminates the origin of the structure shrinkage/collapse via controlled removal of surface silanols by attached ligands. Additional benefits

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of the TDS process lie in allowing high bonding density of attached ligands and recovery of the surfactant template.

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Supporting Information Available: Tables 1S and 2S containing the CHNS analysis data for the samples studied, and figures showing nitrogen adsorption isotherms (Figure 1S) and differential pore size distributions (Figure 2S) for the samples prepared by the TDS procedure with octyltriethoxysilane and octyldimethylchlorosilane. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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