Surface-Functionalized Periodic Mesoporous Organosilica Hollow Spheres

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Surface-functionalized periodic mesoporous organosilica (PMO) hollow spheres are successfully synthesized by using a hybrid silica precursor, 1,2-bis(trimethoxysilyl)ethane (BTME), and five precursors with different functional groups ($-\text{SH}$, $-\text{NH}_2$, $-\text{CN}$, $-\text{C}=\text{C}$, $-\text{benzene}$) as well as surfactants, fluorocarbon and cetyltrimethylammonium bromide, combining a new vesicle and liquid crystal “dual templating” technique. Different disruption effects on the final mesostructure are observed following the order of $-\text{SH}$ from 3-mercaptopropyltrimethoxysilane (MPTMS) $>$ $-\text{benzene}$ from (trimethoxysilyl)benzene (TMSB) $\sim$ $-\text{C}=\text{C}$ from vinyltrimethoxysilane (VTMS) $>$ $-\text{NH}_2$ from 3-aminopropyltriethoxysilane (APTES) $>$ $-\text{CN}$ from 3-cyanopropyltriethoxysilane (CPTES). The particle size, cavity size, and wall thickness of these hollow spheres can be adjusted by changing the amount of precursors or surfactants applied. In terms of providing better control over surface properties of products and giving more uniform surface coverage of functional groups, this direct synthesis method may benefit future production of hollow particles by a combination of various bridged organic and terminal functional groups for more versatile applications in catalyst, separation, drug/gene delivery, microelectronics field, etc.

Introduction

A hollow sphere of silica with nanometer size and ordered mesoporous wall structure is very attractive because of its unique topology that offers low density, high surface area, high pore volume, narrow pore size distribution, and a permeable mesoporous matrix wall. The well-organized pores and hollow morphology can make it suitable for applications in confined nanocatalysts, biosensors, targeted drug and gene delivery, enzyme encapsulation, and nanoreactors.^{1–6} There have been reports about synthesis of silica hollow spheres by several methods such as sonochemical,⁷ solid particle templates,^{8–10} surfactant/vesicle templates,^{11–17} and emulsion templating technology.^{18,19} However, only several reports have occasionally involved the synthesis of hollow spheres with ordered porous wall structures.^{7,13,18} Moreover, their particle sizes are usually not uniform.

Since the first successful synthesis of periodic mesoporous organosilica (PMO),^{20–22} preparation of this kind of materials with different bridged organic groups,^{23–29} pore structure,^{30–33} and morphologies^{34–40} has been widely reported. Furthermore, the potential application of PMOs in catalysis,^{41–44} bioadsorption,^{45–47} microelectronics, chromatography, and sensors⁴⁸ has also attracted considerable attention. Unfortunately, it is impossible for any functional group to be incorporated into PMOs because of the lack of available organosilica precursors with desirable bridged organic groups. A feasible method to introduce some functional groups is the combination of organic bridged hybrid silane with terminally functionalized organosilanes.^{49–52}

Generally, there are two approaches on surface functionalization: one is by direct synthesis or co-condensation and the other by post-synthesis or grafting. Each of them may have their own advantages and disadvantages. Briefly said, the advantage of grafting is better preservation for the mesostructure after modification process.^{53,54} However, this method leads to a significant decrease of surface area, pore volume, and size since the space is occupied by functional groups.⁵⁵ Furthermore, there is no guarantee if the functional groups grafted may be uniformly distributed. In fact, the study indicates they are nonuniformly attached on the external surface of host materials.⁵⁴ The control over the amount and distribution of the functional groups to the host material can be restricted by the number of surface silanol and its accessibility; also, successful grafting process may depend on the precursor reactivity, steric factor, and diffusion limitation.⁵⁴ In contrast, the direct synthesis/co-condensation method may offer high loading and more homogeneous distribution of functional groups with shorter preparation time;⁵⁶ thus, it can bring better performance for adsorption of guest compounds.⁵⁵ It is also believed that stability of the material synthesized by co-condensation is better than that done by the post-grafting method.⁵⁷ However, the mesostructure of the final product may closely relate to the ratio of the functional group toward the silica precursor used; once they are not in the right proportion, the mesostructure cannot be well-maintained.^{54,58}

Although some reports have described the preparation of PMOs with well-defined morphologies, such as spheres,³⁵ rods,^{36,37} dodecahedron,³⁸ decaoctahedron,³⁹ and films,⁴⁰ there has been little report on the synthesis of PMO hollow spheres. Recently, highly ordered mesoporous hollow spheres of organosilica have been successfully synthesized in our research group.⁵⁹ Further studies on the synthesis of hollow spheres with

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functionalized surface, uniform nanoparticle sizes, and ordered mesoporous wall, as well as their formation mechanism, are highly desirable since various applications may demand different types of surface functional groups to accommodate their necessity. In this paper, we report a successful synthesis of thiol-, amine-, cyanide-, vinyl-, and phenyl-functionalized PMO hollow spheres with a highly ordered mesoporous structure and uniform particle size by direct synthesis using a vesicle and liquid-crystal “dual templating” technique. A fluorocarbon surfactant, $[\text{C}_3\text{F}_7\text{O}(\text{CF}_2\text{CF}_2\text{CF}_2\text{O})_2\text{CF}_2\text{CF}_3\text{CONH}(\text{CH}_2)_3\text{N}^+(\text{C}_2\text{H}_5)_2\text{CH}_3\text{I}^-]$ (FC4), is utilized as the vesicle template (VT) to form a hollow sphere structure, followed by a cationic surfactant, cetyltrimethylammonium bromide (CTAB), as the liquid-crystal template (LCT) to produce the mesoporous wall matrix around that vesicle. 1,2-Bis(trimethoxysilyl)ethane (BTME) is employed as the hybrid silica precursor, and 3-mercaptopropyltrimethoxysilane (MPTMS), 3-aminopropyltriethoxysilane (APTES), 3-cyanopropyltriethoxysilane (CPTES), vinyltrimethoxysilane (VTMS), or (trimethoxysilyl)benzene (TMSB) is used as the precursor of the functional group. Particle size and wall thickness of PMO hollow spheres can be adjusted by changing the amount of FC4 and precursors. Herein, we also investigate the co-condensation behavior of different precursors in the presence of dual templates under alkaline condition, which brings different levels of mesostructure disorder, as the consequence of interaction between different functional headgroups and organic silica precursors. Effects of FC4 as co-template, total molar amount of silica sources, and molar ratio of precursors on the final structure and geometry of materials also are studied.

Experimental Section

Chemicals. BTME (96%), MPTMS (95%), APTES (99%), CPTES (98%), VTMS (98%), TMSB (97%), and CTAB (>99%) were purchased from Sigma Aldrich. Sodium hydroxide (NaOH >97%) was obtained from Merck. Fluorocarbon surfactant, FC4, was bought from Yick Vic Chemicals (Hong Kong).

Preparation of Functionalized PMO Hollow Spheres. Surface modification of PMO hollow spheres with various functional groups was performed through three different sets of experiments to study the effect of the molar ratio of precursors (terminally functionalized organosilane/BTME), amount of fluorocarbon surfactant (FC4), and total molar amount of silica sources upon the morphology and structure of the final product. To investigate the effect of the molar ratio of precursors on final products, five terminally functionalized hybrid silica sources (X), each with different functional groups (—SH from MPTMS, —NH₂ from APTES, —CN from CPTES, —C=C from VTMS, and —benzene from TMSB), were employed together with organic bridged hybrid silane (BTME) at four different molar ratios of X/BTME = 1:10, 1:5, 1:2.5, and 1:1.5 to synthesize PMO hollow spheres while keeping the total molar amount of silica precursors (0.006 mol) and the amount of FC4 (0.3 g) constant. As a representative, we present the synthesis path of thiol-functionalized PMO hollow spheres (MPTMS/BTME = 1:5) here. In this typical synthesis, 0.3 g of FC4 was dissolved in 96.0 mL of water and stirred at room temperature for 1 h. Then, 0.2 g of CTAB and 0.7 mL of 2.0 M NaOH were added; meanwhile, the temperature was raised to 80 °C. A mixture of 0.768 g of BTME and 0.113 g of MPTMS was added to the solution under vigorous stirring. The final reactant molar composition is FC4/CTAB/Si/NaOH/H₂O = 0.053:0.092:1.0:0.233:888.8. After being stirred at 80 °C for 2 h, the whole reaction system was cooled down in static conditions for 2 h.

The solid precipitate was collected by the filtration through a 200 nm porous membrane, washed by deionized water and ethanol, then air-dried at room temperature. For template removal, the resulting powders were extracted by ethanol and HCl at 50–60 °C for 6 h.

To study the effect of varied surfactant FC4 amounts on final products, different amounts of FC4 (0.1, 0.3, and 0.5 g) were applied while keeping the total silica molar amount (0.006 mol) and molar ratio of MPTMS/BTME (1:5), APTES/BTME (1:2.5), and TMSB/BTME (1:5) constant. The experiments were carried out with the same conditions and details as described in the previous set of experiments, but the amount of FC4 was changed correspondingly. In the synthesis of thiol-functionalized PMO hollow spheres, four different total molar amounts of silica sources (MPTMS and BTME) were used (0.004, 0.006, 0.008, and 0.01 mol) to investigate their effect upon final products, in which the molar ratio of precursors (MPTMS/BTME = 1:5) and amount of surfactant FC4 (0.3 g) were kept constant.

Characterization. Powder X-ray diffraction (XRD) measurements were carried out on a Bruker D8 Advanced Diffractometer at 40 kV and 30 mA using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). Scanning electron microscopy (SEM) images were obtained with a JEOL JSM-6400F field emission microscope operated at 15 kV acceleration voltages on platinum coated samples. Transmission electron microscopy (TEM) characterization was performed on a JEOL JEM-2010 electron microscope operating at an acceleration voltage of 200 kV. Nitrogen sorption isotherms of samples were measured by a Quantachrome's Autosorb analyzer at 77 K, and samples were degassed at 120 °C overnight in a vacuum before measurements. The Brumauer–Emmet–Teller (BET) surface area was calculated using experimental points at a relative pressure of $P/P_0 = 0.05\text{--}0.25$. Total pore volume was calculated by the N₂ amount adsorbed at the highest P/P_0 ($P/P_0 \sim 0.99$). The pore size distribution was calculated by the Barrett–Joyner–Halenda (BJH) method. Elemental analysis of the prepared material was carried out by an Eager 300 CHNS Analyzer. Solid-state NMR spectra were acquired on a Varian/Chemagnetics InfinityPlus 400 WB spectrometer operating at a magnetic field strength of 9.4 T, and the Larmor frequencies of ¹H, ²⁹Si, and ¹³C were 399.9, 79.4, and 100.5 MHz, respectively. The chemical shifts of ¹H, ²⁹Si, and ¹³C were referenced to TMS. A Varian/Chemagnetics T3 7.5 mm triple-tuned probe was used to acquire all spectra with a spinning rate of 6 kHz. For ¹H → ¹³C CP experiments, the ¹H 90° pulse length was 6 μs , and the Hartmann–Hahn condition was determined using adamantane. A 5 s pulse delay and a 2 ms contact time were used. The proton decoupling field is 42 kHz. For ²⁹Si MAS experiments, a 30° pulse of 1.7 μs and a 120 s pulse delay were utilized.

Results and Discussion

Effect of the Molar Ratio of Terminally Functionalized Hybrid Silica to BTME. XRD patterns of surfactant-extracted functionalized PMO hollow spheres with various functional groups, (a) —SH from MPTMS, (b) —NH₂ from APTES, (c) —CN from CPTES, (d) —C=C from VTMS, and (e) —benzene from TMSB, synthesized using different molar ratios of X/BTME (1:10, 1:5, 1:2.5, and 1:1.5) are shown in Figure 1. In the synthesis of these samples, the total molar amount of silica precursors and amount of FC4 are kept at 0.006 mol and 0.3 g, respectively. The XRD peaks, assigned to the (100), (110), and (200) diffractions, reflect a two-dimensional hexagonal mesostructure with a space group of *P6mm*. The obvious high intensity and resolution of peaks can be attributed to the long-

Figure 1. XRD patterns of surfactant-removed samples (a–e) synthesized by different terminally functionalized hybrid silica precursors X = MPTMS, APTES, CPTES, VTMS, and TMSB, respectively, at various molar ratios of X/BTME (1:10, 1:5, 1:2.5, and 1:1.5).

range regularity of the wall mesostructure as presented by the molar ratio of X/BTME = 1:10 and 1:5. Even when the molar ratio increases to 1:2.5, there is still a highly ordered mesoporous structure in the wall matrix of most functionalized materials. However, further increasing the molar ratio to 1:1.5 results in broad XRD peaks, then less order in the pore wall structure. The gradual changing trend of XRD patterns may vary depending on each of the functional groups used, which clearly indicates the different interactions between each reactive site of the functional group and BTME as they served cooperatively in building the mesoporous wall of functionalized PMO hollow spheres. For samples synthesized using MPTMS as a precursor (Figure 1, graph a), three well-resolved peaks exist for a MPTMS/BTME ratio of 1:10, then the two secondary peaks become weakened by increasing the amount of MPTMS to a ratio of 1:5. The changing of the primary peak from a sharp to broad peak and disappearing of secondary peaks can be observed starting from a ratio of 1:2.5 and become more obvious by a ratio of 1:1.5. Thus, MPTMS's effect on disrupting the mesostructure assembly is quite significant once its concentration is over a certain limit. For samples synthesized using APTES as a precursor (graph b), the primary peaks keep constantly sharp for various molar ratios, but second and third peaks gradually become weakened by increasing the amount of APTES used. It can be found that APTES has a less disruptive effect than MPTMS in constructing the mesopore network under alkaline medium condition. It is interesting to note that APTES has been reported to be significantly disruptive in acidic medium, which is due to the protonation effect of APTES under strong acidic condition. This can lead to a potential cross-link with surface silanol groups, which, in turn, disturbs the mesostructure formation.⁵³ However, a similar phenomenon was not found in alkaline medium in this study. For samples synthesized using CPTES (graph c), both primary and secondary small peaks have very good resolution; apparently, not much difference for the

Figure 2. TEM and SEM images (a–f) of surfactant-removed samples synthesized by different terminally functionalized hybrid silica precursors X = MPTMS, APTES, CPTES, VTMS, and TMSB, respectively, at a molar ratio of X/BTME = 1:2.5.

samples with various molar ratios can be observed, except a very minor weakening pattern for the secondary peaks. Thus, the interaction between CPTES and BTME within the molar ratio and condition studied here is still compatible and mutually beneficial to form an ordered mesopore network. For samples synthesized with VTMS (graph d), the difference in their peaks' pattern can be obviously seen when the molar ratio of X/BTME is 1:2.5 or 1:1.5, in which the primary peak is broadened and the secondary peaks disappear. From the XRD patterns of samples synthesized by TMSB (graph e), it can be seen that the peaks gradually change by increasing the amount of TMSB: starting from a ratio of 1:5, the secondary peaks become weaker and gradually disappear for ratios of 1:2.5 and 1:1.5. This indicates a less ordered mesostructure of particles produced.

Figure 2a–f presents TEM and SEM images of the samples synthesized by MPTMS, APTES, CPTES, VTMS, and TMSB with a molar ratio of X/BTME = 1:2.5. SEM images in Figure 2b reveal a spherical morphology with the diameters of particles ranging from 250 to 350 nm (–SH functional group). Particle sizes of all other samples synthesized with various functional groups and molar ratios, derived from counting more than 60 particles in SEM images, are listed in Table 1, which indicates all hollow sphere particles are quite uniform with sizes from 200 to 350 nm. TEM images in Figure 2 show that all samples are hollow spheres with either spherical or hexagonal cavities, and their wall matrices maintain an ordered mesostructure with a hexagonal pore array (the inset in Figure 2d). Another interesting feature of these hollow spheres is the abnormal “shell” structure inside the cavities. It can be seen that a thin shell exists within the cavities (such as in Figure 2c,d), which display a sharp-edged feature. The wall thickness of hollow spheres can be approximately evaluated from TEM images (by counting more than 30 particles), and the results are also listed in Table 1. Further TEM image analysis for samples synthesized

TABLE 1: Physical Properties of PMO Hollow Spheres with Different Functional Groups^a

functional groups from (X)	molar ratio	<i>P</i> (nm)	<i>W</i> (nm)	<i>S</i> (m ² /g)	<i>V</i> (m ³ /g)	<i>D</i> (nm)
–SH (MPTMS)	1:10	250–350	60–80	717	0.82	2.5
	1:5			779	0.75	2.2
	1:2.5			645	0.59	2.2
	1:1.5			322	0.43	2.1
–NH ₂ (APTES)	1:10	200–350	45–70	645	0.76	2.7
	1:5			528	0.73	2.7
	1:2.5			526	0.71	2.7
	1:1.5			574	0.69	2.5
–CN (CPTES)	1:10	200–350	45–70	675	0.79	2.7
	1:5			750	0.82	2.7
	1:2.5			546	0.58	2.5
	1:1.5			487	0.51	2.5
–CH=CH ₂ (VTMS)	1:10	220–310	40–70	799	0.89	2.8
	1:5			658	0.77	2.7
	1:2.5			654	0.71	2.5
	1:1.5			516	0.53	2.5
–benzene (TMSB)	1:10	210–320	50–80	555	0.66	2.4
	1:5			879	0.88	2.3
	1:2.5			1064	0.72	1.9
	1:1.5			711	0.49	1.7

^a Where X is the terminally functionalized hybrid silica precursors (MPTMS, APTES, CPTES, VTMS, TMSB); molar ratio is X/BTME; *P* is particle size (from SEM observation for more than 60 particles); *W* is wall thickness (from TEM observation for more than 30 particles); *S* is BET surface area calculated using adsorption data in a relative pressure range of $P/P_0 = 0.05–0.25$; *V* is total pore volume estimated at $P/P_0 = 0.99$; and *D* is pore size calculated from adsorption branches by the BJH model. All samples were synthesized by keeping the total molar amount of silica precursors (0.006 mol) and the amount of FC4 (0.3 g) constant.

Figure 3. Nitrogen sorption isotherm of surfactant-removed samples (a–e) synthesized by different terminally functionalized hybrid silica precursors X = MPTMS, APTES, CPTES, VTMS, and TMSB, respectively, at various molar ratios of X/BTME (1:10, 1:5, 1:2.5, and 1:1.5). The isotherms for curves b–e are shifted by 200–1000 cm³ g^{−1} STP for clarity.

with different molar ratios of X/BTME (not shown here) reveals that they have similar wall thicknesses (around 40–80 nm, Table 1).

Nitrogen sorption analysis results, depicted by Figure 3, show a typical isotherm type of IV with type H4 hysteresis loop. Previous reports assigned the hysteresis loop with parallel and almost horizontal branches observed in the range of 0.5–1.0

P/P_0 to N₂ filling of the defect holes,⁶⁰ textural mesopores associated with vesicular (lamellar) morphology,^{15,61} or hollow caves.⁶² In our study, combined with TEM observations, this hysteresis loop can be attributed/ascribed to the contribution of hollow cavities. The remarkably sharp capillary condensation steps of isotherms at relative pressure of $P/P_0 = 0.25–0.35$ reveal that most of the materials have a highly ordered mesostructure. It is worthy to note that, for some materials with high molar ratio of MPTMS/BTME and TMSB/BTME (1:2.5 and 1:1.5), the capillary condensation steps of isotherms are fairly flat or cannot be significantly observed, which reveals their less ordered mesoporous wall structure. By combining with the XRD results, we may summarize different disruption effects of functional groups on the final mesostructure as MPTMS > TMSB ~ VTMS > APTES > CPTES. Apparently, CPTES, with its –CN reactive site, gives the most stable performance, which means it reacts compatibly with BTME on constructing a mesostructure network, whereas MPTMS and TMSB bring the highest disruption effect on the resulting samples.

The pore size distributions calculated by the BJH method using adsorption curve data are shown in Figure 4 (graphs a–e) for the samples synthesized with MPTMS, APTES, CPTES, VTMS, and TMSB, respectively. Physical properties of these samples are listed in Table 1. It can be seen from Figure 4 that, at the same molar ratio, samples synthesized with APTES, CPTES, and VTMS have larger pore sizes than these prepared by MPTMS and TMSB. For the latter, they have a wide pore size distribution, especially at molar ratios of X/BTME of 1:2.5 and 1:1.5, which further confirms the conclusion obtained from XRD and nitrogen adsorption isotherm data; that is, the high content of MPTMS or TMSB (high molar ratios of X/BTME of 1:2.5 and 1:1.5) significantly interferes with the formation of an ordered mesostructure and leads to nonuniform pore size. When we compared the pore sizes of materials synthesized by the same precursor but with a different molar ratio of X/BTME, we found (Table 1) that the pore size gradually decreases as the content of terminally functionalized organosilane increases, and for various functionalized materials studied here, the pores

Figure 4. Pore size distribution of surfactant-removed samples (a–e) synthesized with different terminally functionalized hybrid silica precursors X = MPTMS, APTES, CPTES, VTMS, and TMSB, respectively, at various molar ratios of X/BTME (1:10, 1:5, 1:2.5, and 1:1.5).

shrink by 0.20–0.70 nm with increasing molar ratio of X/BTME from 1:10 to 1:1.5. The most significant shrinkage of pore comes from the sample synthesized with TMSB (0.69 nm), followed by moderate shrinkage from samples synthesized with MPTMS and VTMS (0.35–0.39 nm). The samples synthesized with APTES and CPTES give the smallest pore shrinkage of around 0.2 nm. It is worthy to note that the trend of pore size shrinkage is similar to the disruption effect of functional groups on the final mesostructure, as concluded above. However, the only difference is that the effect of TMSB on pore shrinkage is much more significant than that of MPTMS, which is probably due to the strong hydrophobicity of TMSB and rigidity of the phenyl group as compared with other functional groups.

Figure 5A illustrates the ^{13}C CP MAS NMR spectrum of representative samples synthesized with (MPTMS, APTES, CPTES, VTMS, or TMSB)/BTME and corresponding molar ratios (X/BTME) of 1:5, 1:1.5, 1:1.5, 1:5, and 1:2.5, respectively. A predominant peak resonates at 5.4 ppm for all five samples, which can be assigned as carbons in the $-\text{Si}-\text{CH}_2-\text{CH}_2-\text{Si}-$ fragment of the wall framework from the BTME source.^{63,64} A shoulder peak at 12.7 and two weak peaks at 30.3 and 23.4 (or 19.8) ppm are attributed to C^1 , C^2 , and C^3 incorporated in the framework from $-\text{Si}-\text{C}^1-\text{C}^2-\text{C}^3-\text{R}$, where R is a reactive site SH from MPTMS, NH_2 from APTES, or CN from CPTES, respectively.^{53,65} Meanwhile, one small peak that resonates at 119 ppm for the sample synthesized with CPTES may be attributed to C^4 from a C–N bond. A small peak resonates at position of 130 ppm for the sample synthesized with VTES, which is probably contributed from a vinyl group ($-\text{C}=\text{C}-$). For the sample synthesized with TMSB, two significant peaks located at 127 and 134 ppm are from a benzene ring ($-\text{C}_6\text{H}_5$).⁵³ Another two weak peaks located at 16.2 and 58.5 ppm are due to the surface-bound ethoxy groups ($\text{SiOCH}_2\text{CH}_3$) formed during the solvent extraction.^{39,66} In the ^{29}Si MAS NMR spectrum (Figure 5B), three signals are observed at –47, –57.8, and

Figure 5. ^{13}C CP MAS NMR spectra (A) and ^{29}Si MAS NMR spectra (B) of samples (a–e) synthesized with different terminally functionalized hybrid silica precursors MPTMS, APTES, CPTES, VTMS, and TMSB, respectively.

–66.2 ppm, corresponding to the three unique Si environments of T^1 [$\text{Si}(\text{OH})_2(\text{OSi})$], T^2 [$\text{Si}(\text{OH})(\text{OSi})_2$], and T^3 [$\text{Si}(\text{OSi})_3$], respectively. The strong intensity of the peak due to the T^3 site indicates the formation of a highly condensed organosilicate framework. No signal due to Q^n [$\text{Si}(\text{OH})_{4-n}(\text{OSi})_n$] species is observed in the ^{29}Si spectrum, implying that all framework of Si atoms are bound to at least one C atom.

Quantitative determination of the organic group incorporated into the final samples was made with elemental analysis based on the C, H, N, and S element contents (Table 2). By comparison with the theoretical contents calculated from the initial molar amount of precursors (100% conversion), it was found that only 50–90% of the organic groups in the initial mixture was incorporated. This nonstoichiometric incorporation behavior was also observed in the previous reports. The primary reason is the different hydrolysis rates between the matrix precursor and the functional silanes.

In our previous study, a vesicle and liquid-crystal dual templating mechanism was proposed to explain the formation of periodic mesoporous organosilica hollow spheres, in which FC4 played a primary role in constructing vesicles to form a hollow cavity structure and CTAB played a templating role for building mesopores in the final products.⁵⁹ Different from common hydrocarbon surfactants that are hydrophobic and lipophilic, FC4 is a kind of hydrophobic and highly lipophobic surfactant,⁶⁷ with a strong positively charged $-\text{N}^+$. Thus, in the present work, it may interact with ethyl chains, functional

TABLE 2: Element Analysis Results of Functionalized PMO Hollow Spheres

sample	nitrogen % ^a		carbon % ^a		hydrogen % ^a		sulfur % ^a	
	<i>b</i>	<i>c</i>	<i>b</i>	<i>c</i>	<i>b</i>	<i>c</i>	<i>b</i>	<i>c</i>
(MPTMS/BTME) = 1:5	0	0.0	35.7	16.5	8.1	5.7	2.8	2.5
(APTES/BTME) = 1:1.5	2.5	1.5	40.9	20.2	9.0	5.9	0	0
(CPTES/BTME) = 1:1.5	2.4	1.4	40.0	20.5	8.5	5.2	0	0
(VTMS/BTME) = 1:5	0	0	36.3	18.2	8.1	5.2	0	0
(TMSB/BTME) = 1:2.5	0	0	40.9	25.9	7.8	4.7	0	0

^a Weight percentage (wt %). ^b By theoretical calculation. ^c From element analysis.

Figure 6. Small-angle XRD patterns (A), N₂ sorption isotherms (B), and pore size distributions (C) of surfactant-removed APTES/BTME = 1:2.5 samples (a–c) synthesized using different amounts of FC4 (0.1, 0.3, and 0.5 g), respectively, keeping the total molar amount of silica precursors constant (0.006 mol). The isotherms for curves a and b in panel B are shifted by 400 and 200 cm³ g^{−1} STP, respectively, for clarity.

groups, together with negatively charged silica species of organosilanes (terminally functionalized organosilane/BTME), generating composite vesicles as a “nucleus” through a vesicle templating process. Meanwhile, hybrid silica precursors interact with CTAB surfactants to produce co-assembly micelles by a liquid-crystal templating process that can further form a hexagonal mesostructured wall around the vesicle “nucleus” and contribute to the stabilization of this vesicle. When the wall with hexagonal mesostructured channels grows around the vesicle “nucleus”, the local curvature energy near the vesicle becomes very large. Thus, linear channels may reconcile with the closed surface of a sphere to relieve the curvature energy at the interface of the vesicles. As a result, the pores oriented to be parallel in the shell of hollow spheres are observed in TEM images (inset in Figure 2d).

The introduction of other terminal trialkoxysilylorganosilanes (MPTMS, APTES, CPTES, VTMS, and TMSB) results in the decrease of orderliness of the structure. This disruption effect of silica precursors on the final mesostructure may be summarized as MPTMS > TMSB ~ VTMS > APTES > CPTES, which can be explained by the polarity and hydrophobicity of functional groups. For these organoalkoxysilane precursors, the polarity order of their functional groups is $-\text{CH}=\text{CH}_2 < -\text{benzene} < -\text{SH} < -\text{NH}_2 < -\text{CN}$, indicating that their mutual interactions with cationic surfactant CTAB gradually increase with the increase of their polarity. APTES and CPTES have very strong interactions with the cationic CTAB micelles due to their electrostatic matching under alkaline condition. The tight binding of the silica precursor to the cetyltrimethylammonium headgroup of the CTAB molecule can effectively mitigate the repulsion between these cationic headgroups and stabilize the micelle structure, therefore, resulting in a highly ordered mesostructure.⁶⁸ In contrast, weak attraction and strong repulsion interactions between TMSB or VTMS and CTAB micelles lead to large shrinkage and instability of CTAB micelles, which results in a less ordered mesostructure and smaller pore size. This demonstrates that TMSB and VTMS exhibit notable disruption effects on the final mesostructure as compared with APTES and CPTES precursors. It is worthy to note that,

although MPTMS is a polar precursor, it has the same behaviors as TMSB or VTMS in pore size shrinkage and the disruptive effect on the mesostructure of final products. Element analysis shows that 90% of the thiol group is incorporated into the wall network, which is much higher than other organic groups and results in the formation of a disordered mesostructure. Moreover, it was found in our recent work that MPTMS was the same as TMSB and VTMS but different from APTES in the role of morphology transition from spheres to helical rods under alkaline condition,⁶⁹ which further demonstrated specific self-assembly phenomena of MPTMS and CTAB.

Effect of Varied Amount of FC4 as Vesicle Template. To study the effect of FC4 as a vesicle template on final products, functionalized PMO hollow spheres were synthesized by combining three individual terminally functionalized organosilanes, MPTMS, APTES, and TMSB with BTME, as precursors and using different added amounts of FC4 (0.1, 0.3, and 0.5 g) while keeping the total molar amount of silica sources constant (0.006 mol). Figure 6A shows XRD patterns of APTES/BTME (1:2.5) samples synthesized with 0.1, 0.3, and 0.5 g of FC4, which are depicted as curves a, b, and c, respectively (for samples MPTMS/BTME = 1:5 and TMSB/BTME = 1.5, see Figures S1 and S2 in the Supporting Information for their XRD patterns, nitrogen adsorption isotherms, and pore size distributions). The three diffraction peaks of samples synthesized with 0.1 and 0.3 g of FC4, assigned to the (100), (110), and (200) diffractions, reflect a highly ordered two-dimensional hexagonal mesostructure with a space group of *P6mm*. The results reveal that a small quantity of FC4 (0.1 and 0.3 g) incorporated in the synthesis brings less effect on the disruption of the mesostructure, whereas increasing the amount of FC4 to 0.5 g leads to a broader peak with lower intensity, which relates to a less ordered or disordered mesostructure of the wall matrix. Again, it can be seen from peak intensities and widths that these three different functional groups show different degrees of disruption effect, and MPTMS with an $-\text{SH}$ group brings the highest degree of disruption effect toward mesostructure geometry (see Figure S1 in the Supporting Information).

TABLE 3: Physical Properties of the Samples Synthesized with Different Amounts of Surfactant FC4^a

sample	FC4 (g)	<i>P</i> (nm)	<i>W</i> (nm)	<i>S</i> (m ² /g)	<i>V</i> (m ³ /g)	<i>D</i> (nm)
MPTMS/BTME = 1:5	0.1	350–500	100–150	1068	0.79	2.2
	0.3	250–350	60–80	779	0.75	2.2
	0.5	120–200	25–35	626	0.77	2.5
APTES/BTME = 1:2.5	0.1	300–450	90–150	497	0.55	2.5
	0.3	200–350	45–70	526	0.71	2.7
	0.5	140–250	25–50	572	0.73	2.7
TMSB/BTME = 1:5	0.1	310–500	95–115	1059	0.70	2.2
	0.3	210–320	50–85	879	0.88	2.3
	0.5	150–210	25–45	904	0.86	2.2

^a Where FC4 is the added amount of FC4 in the synthesis (g), *P* is particle size, *W* is wall thickness, *S* is BET surface area calculated using adsorption data in a relative pressure range of $P/P_0 = 0.05–0.25$, *V* is total pore volume estimated at $P/P_0 = 0.99$, and *D* is pore size calculated from adsorption branches by the BJH model. Samples were synthesized by keeping the total molar amount of silica precursors constant (0.006 mol).

Figure 7. TEM images of the APTES/BTME = 1:2.5 samples (a–c) synthesized using different amounts of FC4 (0.1, 0.3, and 0.5 g), respectively, keeping the total molar amount of silica precursors constant (0.006 mol).

Nitrogen sorption analysis results of APTES/BTME (1:2.5) samples synthesized with 0.1, 0.3, and 0.5 g of FC4 are shown in Figure 6B, indicating that isotherms of all samples are classified as a type of IV isotherm with a type H4 hysteresis loop, which is characteristic of hollow spheres with a mesoporous wall. However, the sizes of their loops are different, which are probably relative to the different sizes of existing hollow cavities. The smaller the cavity is inside the particle, the smaller the hysteresis loop is found from its nitrogen isotherm curve. It may be seen that, as a template of a hollow cavity, a small amount of FC4 (0.1 g) results in small cavity size, but the cavity size of the sample synthesized with 0.5 g of FC4 does not seem to be larger than that of the sample prepared with 0.3 g of FC4. It means that cavity size does not increase equally with the increasing amount of FC4 used. (For MPTMS/BTME = 1:5 and TMSB/BTME = 1.5 samples, see Figures S1 and S2 in the Supporting Information.)

Pore size distributions of APTES/BTME (1:2.5) samples synthesized with 0.1, 0.3, and 0.5 g of FC4 are depicted in Figure 6C (for other samples, see Figures S1 and S2 in the Supporting Information), indicating the sample synthesized with a small amount of FC4 (0.1 g) has a narrow pore size distribution peak (curve a), that is, uniform pore size, whereas a large amount of FC4 (0.5 g) leads to a slightly broad and low intensity peak (curve c), that is, less ordered mesostructure. This observation reveals that FC4 not only acts as a cavity template but also disrupts the self-assembly of surfactant CTAB to form ordered arrayed micelles. Detailed physical properties of samples discussed here are summarized in Table 3. When we compared the pore sizes, pore volumes, and surface areas of samples synthesized with different added amounts of FC4, we find that no consistent trend of FC4's effect on them can be found and concluded.

Figure 7a–c presents the TEM images of the samples synthesized with APTES with applying different amounts of FC4 (0.1, 0.3, and 0.5 g), respectively (see Figure S3 TEM images in the Supporting Information for samples synthesized

with MPTMS and TMSB). These images clearly confirm that the cavity size increases as the amount of FC4 increases from 0.1 to 0.3 g, but this trend does not maintain with increasing the FC4 amount from 0.3 to 0.5 g, which is consistent with the nitrogen adsorption observation. Further careful observation and analysis show that, for samples synthesized with various functional groups, the particle sizes and wall thicknesses of their hollow spheres reduce with the increasing amount of FC4 from 0.1 to 0.5 g (Table 3).

As concluded from the above observations, FC4 can act as both a template of the hollow sphere cavity⁵⁹ and an agent to limit particle growth.⁶⁷ This may explain the effect of the FC4 amount upon the resulting particle size and wall thickness of hollow spheres. FC4 surfactant has rigid and bulky C–F chains and usually creates loosely packed micelles to form a vesicle template. Increasing the amount of FC4 used may, consequently, increase the number of “nucleus” generated by FC4; hence, the quantity of hybrid silica precursors available to pack around each “nucleus” automatically reduces, leading to thinner wall thickness and small particle size. In contrast, a reduced amount of FC4 used will lead to a comparatively large quantity of co-assembly micelles of organosilanes/CTAB to interact with less amounts of vesicle “nucleus” to form a mesostructured wall matrix, which results in larger particle size and a thicker wall of hollow spheres. Except for acting as the template of the hollow sphere cavity, FC4 can also limit particle growth in silica particle synthesis. FC4 attached on the exterior surface of hollow spheres during the preparation/growth process probably blocks the cross-link of co-assembly micelles of CTAB/precursors, therefore, confining further growth of particles.⁶⁷

The effect of the FC4 template on the vesicle size and shape of hollow spheres may be explained as follows. With increasing the amount of FC4 added from 0.1 to 0.3 g, the size of the vesicle “nucleus” indeed increases due to the congregation and self-assembly of surfactant FC4. However, further increasing the amount of FC4 from 0.3 to 0.5 g may increase the number of “nucleus” but not the size of the vesicle “nucleus” due to

Figure 8. Small-angle XRD patterns (A), N₂ sorption isotherms (B), and pore size distributions (C) of MPTMS/BTME = 1:5 samples (a–d) synthesized using different total silica molar amounts of 0.004, 0.006, 0.008, and 0.01 mol, respectively, keeping the FC4 amount constant (0.3 g). The isotherms for curves a, b, and c in panel B are shifted by 700, 400, and 200 cm³ g^{−1} STP, respectively, for clarity.

TABLE 4: Physical Properties of the Samples Synthesized with Different Total Silica Molar Amounts^a

sample	total molar	<i>P</i> (nm)	<i>W</i> (nm)	<i>S</i> (m ² /g)	<i>V</i> (m ³ /g)	<i>D</i> (nm)
MPTMS/BTME = 1:5	0.004	250–350	30–50	566	0.61	2.4
	0.006		60–80	779	0.75	2.2
	0.008		70–80	759	0.64	2.2
	0.01		80–150	782	0.65	2.2

^a Where total molar is the total molar amount of silica precursors used in the synthesis (MPTMS and BTME), *P* is particle size, *W* is wall thickness, *S* is BET surface area (at $P/P_0 = 0.05–0.25$), *V* is total pore volume (at $P/P_0 = 0.99$), and *D* is pore size (calculated from adsorption branches by the BJH model). Samples were synthesized by keeping the amount of FC4 (0.3 g) constant.

strong mechanical stirring and loose packing of FC4 micelles, which leads to similar cavity size, as observed by nitrogen adsorption and TEM results. The different shapes of cavities and the shell structure inside the cavities are observed in TEM images (Figure 7). It is believed that the cationic FC4 may interact with the negatively charged silica species to generate composite vesicles through a vesicle templating process.⁵⁹ The composite vesicles are quite flexible in solution; hence, further growth of micelle-templated mesoporous materials surrounding them may influence the shape of cavities. On the removal of templates, various nucleus vesicles are left as a shell inside the cavities.

Effect of Total Molar Amount of Silica Sources. Four different total molar amounts (0.004, 0.006, 0.008, and 0.010 mol) of combined silica sources (MPTMS/ BTME = 1:5) were used in the synthesis to study its effect on the final morphology and mesostructure. Figure 8A depicts XRD patterns in which peaks basically can be assigned to (100), (110), and (200) diffractions with a two-dimensional hexagonal mesostructure. It reveals that a variation of total molar amount of silica sources in the range of 0.004–0.010 mol does not bring great effect on their pore geometry. Nitrogen sorption isotherms presented in Figure 8B show that they still follow a typical type IV with a hysteresis loop of type H4, and capillary condensation steps occur at relative pressure of $P/P_0 = 0.25–0.35$. No obvious difference in the hysteresis loop can be traced between each sample. Furthermore, the pore size distribution graphs as depicted by Figure 8C for the all samples also show similar narrow peaks, proving their uniform pore sizes. A detailed list of physical properties for all samples is summarized in Table 4.

Figure 9 show representative TEM images of the samples synthesized with different amounts of silica sources. It can be seen that all four samples are hollow spheres with highly ordered mesoporous wall matrixes. The particle sizes of all samples are in the range of 250 to 350 nm; however, their wall thicknesses are significantly different. The wall thickness of the sample synthesized with totally 0.004 mol of silica sources is 30–50 nm; however, it increases to 80–150 nm

Figure 9. TEM images of MPTMS/BTME = 1:5 samples (a–d) synthesized using different total silica molar amounts of 0.004, 0.006, 0.008, and 0.01 mol, respectively, keeping the FC4 amount constant (0.3 g).

for the sample synthesized with 0.010 mol of silica sources, indicating that the wall thickness increases with increasing total molar amount of silica sources. The effect of the total molar amount of precursors on the wall thickness may be explained by the formation mechanism mentioned in the section above. An increased total molar amount of precursors can indirectly lead to more silica sources available to interact with CTAB and form a mesostructured wall matrix around the similar amount of vesicle “nucleus” (if same amount of FC4), which results into a thicker wall of hollow spheres.

Conclusion

In summary, five functionalized PMO hollow spheres with different terminal groups of $-\text{SH}$, $-\text{NH}_2$, $-\text{CN}$, $-\text{C}=\text{C}$, and $-\text{benzene}$ and a highly ordered mesostructured wall were successfully synthesized by combining hybrid organosilica precursor BTME and terminally functionalized organosilane precursors and using fluorocarbon FC4 and cationic CTAB surfactants as vesicle and liquid-crystal templates, respectively. Different reactive sites of each functional group bring different disruptive effects on the mesopore geometry of particles synthesized, which follow the order of $\text{MPTMS} > \text{TMSB} \sim \text{VTMS} > \text{APTES} > \text{CPTES}$. CPTES, with its $-\text{CN}$ reactive site, presumably, is able to react compatibly with BTME on constructing a mesostructure network, which is proven by its most stable performance within four different molar ratios of CPTES/BTME (1:10, 1:5, 1:2.5, and 1:1.5). In contrast, MPTMS with an $-\text{SH}$ group has a great affect on the self-assembly of surfactant CTAB and organosilica precursors to form a mesostructure. Their particle size and wall thickness can be tailored by changing the amount of surfactant FC4 or silica precursors used. A larger amount of FC4 (0.5 g) can result in smaller particle size (120–250 nm) and thinner wall thickness (25–50 nm) of hollow spheres, but it also disturbs the formation of an ordered mesostructure. Different total molar amounts of silica precursors used in this study (0.004–0.01 mol) do not have a significant effect on the order of the mesostructure but has, indeed, a significant effect on wall thickness; that is, more silica precursors lead to an increase in the wall thickness of hollow spheres. This particular vesicle and liquid-crystal “dual templating” technique might be used to produce silica hollow spheres with a highly ordered mesostructured wall by the combination of various bridged organic and terminal functional groups for versatile applications in nanocatalysts, biosensors, microelectronics, targeted drug and gene delivery, enzyme encapsulation, and nanoreactors.

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Supporting Information Available: Small-angle XRD patterns, nitrogen sorption isotherms, pore size distributions, and TEM images of the surfactant-removed MPTMS/BTME = 1:5 and TMSB/BTME = 1:5 samples synthesized using different amounts of FC4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- Lin, H. P.; Mou, C. Y.; Liu, S. B.; Tang, C. Y. *Chem. Commun.* **2001**, 1970–1971.
- Zhu, Y. F.; Shi, J. L.; Shen, W. H.; Dong, X. P.; Feng, J. W.; Ruan, M. L.; Li, Y. S. *Angew. Chem., Int. Ed.* **2005**, *44*, 5083–5087.
- Yu, A. M.; Wang, Y. J.; Barlow, E.; Caruso, F. *Adv. Mater.* **2005**, *17*, 1737–1741.
- Wang, Y. J.; Caruso, F. *Chem. Commun.* **2004**, 1528–1529.
- Fornasieri, G.; Badaire, W.; Backov, R.; Mondain-Monval, O.; Zakri, U.; Poulin, P. *Adv. Mater.* **2004**, *16*, 1094–1097.
- Zhang, L.; Qiao, S. Z.; Jin, Y. G.; Chen, Z. G.; Gu, H. C.; Lu, G. Q. *Adv. Mater.* **2008**, *20*, 805–809.
- Rana, R. K.; Mastai, Y.; Gedanken, A. *Adv. Mater.* **2002**, *14*, 1414–1418.
- Wang, X. D.; Yang, W. L.; Tang, Y.; Wang, Y. J.; Fu, S. K.; Gao, Z. *Chem. Commun.* **2000**, 2161–2162.
- Caruso, F.; Caruso, R. A.; Mohwald, H. *Science* **1998**, *282*, 1111–1114.
- Chen, J. F.; Ding, H. M.; Wang, J. X.; Shao, L. *Biomaterials* **2004**, *25*, 723–727.
- Tan, B.; Lehmler, H. J.; Vyas, S. M.; Knutson, B. L.; Rankin, S. E. *Adv. Mater.* **2005**, *17*, 2368–2371.
- Hentze, H. P.; Raghavan, S. R.; McKelvey, C. A.; Kaler, E. W. *Langmuir* **2003**, *19*, 1069–1074.
- Li, Y. S.; Shi, J. L.; Hua, Z. L.; Chen, H. R.; Ruan, M. L.; Yan, D. S. *Nano Lett.* **2003**, *3*, 609–612.
- Lin, H. P.; Cheng, Y. R.; Mou, C. Y. *Chem. Mater.* **1998**, *10*, 3772–3776.
- Kim, S. S.; Zhang, W. Z.; Pinnavaia, T. J. *Science* **1998**, *282*, 1302.
- Yeh, Y. Q.; Chen, B. C.; Lin, H. P.; Tang, C. Y. *Langmuir* **2006**, *22*, 6–9.
- Liu, J.; Yang, Q. H.; Zhang, L.; Yang, H. Q.; Gao, J. S.; Li, C. *Chem. Mater.* **2008**, *20*, 4268–4275.
- Schacht, S.; Huo, Q.; Voigt-Martin, I. G.; Stucky, G. D.; Schuth, F. *Science* **1996**, *273*, 768–771.
- Sun, Q. Y.; Kooyman, P. J.; Grossmann, J. G.; Bomans, P. H. H.; Frederik, P. M.; Magusin, P.; Beelen, T. P. M.; van Santen, R. A.; Sommerdijk, N. *Adv. Mater.* **2003**, *15*, 1097–1100.
- Asefa, T.; MacLachlan, M. J.; Coombs, N.; Ozin, G. A. *Nature* **1999**, *402*, 867–871.
- Inagaki, S.; Guan, S.; Fukushima, Y.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **1999**, *121*, 9611–9614.
- Melde, B. J.; Holland, B. T.; Blanford, C. F.; Stein, A. *Chem. Mater.* **1999**, *11*, 3302–3308.
- Liang, Y. C.; Hanzlik, M.; Anwender, R. *J. Mater. Chem.* **2005**, *15*, 3919–3928.
- Hunks, W. J.; Ozin, G. A. *Adv. Funct. Mater.* **2005**, *15*, 259–266.
- Hunks, W. J.; Ozin, G. A. *J. Mater. Chem.* **2005**, *15*, 764–771.
- Landskron, K.; Ozin, G. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 2107–2109.
- Olkhoviyk, O.; Jaroniec, M. *J. Am. Chem. Soc.* **2005**, *127*, 60–61.
- Olkhoviyk, O.; Pikus, S.; Jaroniec, M. *J. Mater. Chem.* **2005**, *15*, 1517–1519.
- Morell, J.; Wolter, G.; Froba, M. *Chem. Mater.* **2005**, *17*, 804–808.
- Bao, X. Y.; Zhao, X. S.; Li, X.; Li, J. *Appl. Surf. Sci.* **2004**, *237*, 380–386.
- Zhang, Z. D.; Yan, X. X.; Tian, B. Z.; Shen, S. D.; Chen, D. H.; Zhu, G. S.; Qiu, S. L.; Zhao, D. Y. *Chem. Lett.* **2005**, *34*, 182–183.
- Zhao, L.; Zhu, G.; Zhang, D.; Di, Y.; Chen, Y.; Terasaki, O.; Qiu, S. *J. Phys. Chem. B* **2005**, *109*, 764–768.
- Liang, Y. C.; Hanzlik, M.; Anwender, R. *Chem. Commun.* **2005**, 525–527.
- Bao, X. Y.; Zhao, X. S. *J. Phys. Chem. B* **2005**, *109*, 10727–10736.
- Rebbin, V.; Jakubowski, M.; Potz, S.; Froba, M. *Microporous Mesoporous Mater.* **2004**, *72*, 99–104.
- Goto, Y.; Inagaki, S. *Chem. Commun.* **2002**, 2410–2411.
- Qiao, S. Z.; Yu, C. Z.; Hu, Q. H.; Jin, Y. G.; Zhou, X. F.; Zhao, X. S.; Lu, G. Q. *Microporous Mesoporous Mater.* **2006**, *91*, 59–69.
- Kapoor, M. P.; Inagaki, S. *Chem. Mater.* **2002**, *14*, 3509–3514.
- Guan, S.; Inagaki, S.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **2000**, *122*, 5660–5661.
- Dag, O.; Yoshina-Ishii, C.; Asefa, T.; MacLachlan, M. J.; Grondy, H.; Coombs, N.; Ozin, G. A. *Adv. Funct. Mater.* **2001**, *11*, 213–217.
- Liu, J.; Yang, Q. H.; Kapoor, M. P.; Setoyama, N.; Inagaki, S.; Yang, J.; Zhang, L. *J. Phys. Chem. B* **2005**, *109*, 12250–12256.
- Yang, Q. H.; Liu, J.; Yang, J.; Kapoor, M. P.; Inagaki, S.; Li, C. *J. Catal.* **2004**, *228*, 265–272.
- Baleizao, C.; Gigante, B.; Das, D.; Alvaro, M.; Garcia, H.; Corma, A. *Chem. Commun.* **2003**, 1860–1861.
- Wight, A. P.; Davis, M. E. *Chem. Rev.* **2002**, *102*, 3589–3613.
- Burleigh, M. C.; Markowitz, M. A.; Spector, M. S.; Gaber, B. P. *Environ. Sci. Technol.* **2002**, *36*, 2515–2518.
- Qiao, S. Z.; Yu, C. Z.; Xing, W.; Hu, Q. H.; Djojoputro, H.; Lu, G. Q. *Chem. Mater.* **2005**, *17*, 6172–6176.
- Qiao, S. Z.; Djojoputro, H.; Hu, Q. H.; Lu, G. Q. *Prog. Solid State Chem.* **2006**, *34*, 249–256.
- Hatton, B.; Landskron, K.; Whitnall, W.; Perovic, D.; Ozin, G. A. *Acc. Chem. Res.* **2005**, *38*, 305–312.
- Asefa, T.; Kruk, M.; MacLachlan, M. J.; Coombs, N.; Grondy, H.; Jaroniec, M.; Ozin, G. A. *J. Am. Chem. Soc.* **2001**, *123*, 8520–8530.
- Burleigh, M. C.; Markowitz, M. A.; Spector, M. S.; Gaber, B. P. *Chem. Mater.* **2001**, *13*, 4760–4766.
- Wahab, M. A.; Ha, C. S. *J. Mater. Chem.* **2005**, *15*, 508–516.
- Wahab, M. A.; Imae, I.; Kawakami, Y.; Ha, C. S. *Chem. Mater.* **2005**, *17*, 2165–2174.
- Chong, A. S. M.; Zhao, X. S.; Kustedjo, A. T.; Qiao, S. Z. *Microporous Mesoporous Mater.* **2004**, *72*, 33–42.
- Lim, M. H.; Stein, A. *Chem. Mater.* **1999**, *11*, 3285–3295.

- (55) Song, S. W.; Hidajat, K.; Kawi, S. *Langmuir* **2005**, *21*, 9568–9575.
- (56) Vinu, A.; Hossain, K. Z.; Ariga, K. *J. Nanosci. Nanotechnol.* **2005**, *5*, 347–371.
- (57) Macquarrie, D. J.; Jackson, D. B.; Mdoe, J. E. G.; Clark, J. H. *New J. Chem.* **1999**, *23*, 539–544.
- (58) Chong, A. S. M.; Zhao, X. S. *J. Phys. Chem. B* **2003**, *107*, 12650–12657.
- (59) Djojoputro, H.; Zhou, X. F.; Qiao, S. Z.; Wang, L. Z.; Yu, C. Z.; Lu, G. Q. *J. Am. Chem. Soc.* **2006**, *128*, 6320–6321.
- (60) Lin, H. P.; Wong, S. T.; Mou, C. Y.; Tang, C. Y. *J. Phys. Chem. B* **2000**, *104*, 8967–8975.
- (61) Tanev, P. T.; Liang, Y.; Pinnavaia, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 8616–8624.
- (62) Kooyman, P. J.; Verhoef, M. J.; Prouzet, E. *Stud. Surf. Sci. Catal.* **2000**, *129*, 535–542.
- (63) Hamoudi, S.; Yang, Y.; Moudrakovski, I. L.; Lang, S.; Sayari, A. *J. Phys. Chem. B* **2001**, *105*, 9118–9123.
- (64) Cho, E. B.; Kwon, K. W.; Char, K. *Chem. Mater.* **2001**, *13*, 3837–3839.
- (65) Feng, X.; Fryxell, G. E.; Wang, L. Q.; Kim, A. Y.; Liu, J.; Kemner, K. M. *Science* **1997**, *276*, 923–926.
- (66) Guo, W. P.; Park, J. Y.; Oh, M. O.; Jeong, H. W.; Cho, W. J.; Kim, I.; Ha, C. S. *Chem. Mater.* **2003**, *15*, 2295–2298.
- (67) Han, Y.; Ying, J. Y. *Angew. Chem., Int. Ed.* **2005**, *44*, 288–292.
- (68) Radu, D. R.; Lai, C. Y.; Huang, J. G.; Shu, X.; Lin, V. S. Y. *Chem. Commun.* **2005**, 1264–1266.
- (69) Zhang, L.; Qiao, S. Z.; Jin, Y. G.; Cheng, L.; Yan, Z. F.; Lu, G. Q. *Adv. Funct. Mater.* **2008**, *18*, 3834–3842.

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