Hydrophobic Core/Hydrophilic Shell Structured Mesoporous Silica Nanospheres: Enhanced Adsorption of Organic Compounds from Water

Shuru Li, Xuan Jiao, and Hengquan Yang*

School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, P. R. China

ABSTRACT: Inspired by the structure features of micelle, we attempt to synthesize a novel functionalized mesoporous silica nanosphere consisting of a hydrophobic core and a hydrophilic shell. The obtained solid materials were structurally confirmed by N\textsubscript{2} sorption, X-ray diffraction (XRD), and transmission electron microscopy (TEM). Their compositions were characterized by Fourier transfer infrared spectroscopy (FT-IR), solid state NMR, X-ray photoelectron spectroscopy (XPS), and elemental analysis. Its fundamental properties such as dispersibility in water or organic phase, wettability, and adsorption ability toward hydrophobic organics in water were investigated. It was revealed that these important properties could be facilely adjusted through varying structure and composition. In particular, these materials showed much better adsorption ability toward hydrophobic organic molecules in water than conventional monofunctionalized mesoporous materials, owing to possessing the hydrophobic/hydrophilic domain-segregated and hierarchically functionalized mesoporous structures. The intriguing properties would make mesoporous materials more accessible to many important applications, especially in aqueous systems.

INTRODUCTION

Organic functionalization of mesoporous materials attracts extensive attentions in the areas of catalysis, sorption, biomedicine, and sensors because the introduction of functionality enables many key properties to be adjusted in light of application requirements.\textsuperscript{1−16} Within this field, the hydrophobization of mesoporous materials via replacing surface hydrophilic Si–OHs with hydrophobic functionalities is of particular interest since hydrophobization of mesoporous materials can significantly improve hydrothermal stability,\textsuperscript{17−19} adsorption efficiency toward organic molecules,\textsuperscript{20−26} and catalytic reaction rate.\textsuperscript{27−34} For example, our previous findings revealed that the hydrothermal stability of mesoporous silica MCM-41 was dramatically enhanced after modification with hydrophobic groups owing to preventing the hydrolysis of Si–O–Si linkages.\textsuperscript{17} Yang and co-workers also found that organically functionalized mesoporous materials exhibited significantly improved hydrothermal stability against structure collapses even under the basic conditions.\textsuperscript{18} The Zhao and Stucky groups demonstrated that hydrophobic mesoporous materials could considerably improve the adsorption ability toward hydrophobic pollutants in water.\textsuperscript{22,23} Xiao’s studies revealed that silylation of mesoporous materials with a hydrophobic group positively affected the reactivity of aqueous catalysis.\textsuperscript{27} Inumaru et al. reported that H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} polyoxometalate molecules confined in the hydrophobic nanospace of mesoporous materials exhibited a significantly enhanced activity in water.\textsuperscript{35} These samples clearly indicate that the hydrophobization can provide new possibility for the effective utilization of mesoporous materials in aqueous systems. However, the hydrophobization of mesoporous materials unavoidably leads to a decrease in the dispersion in water, to such an extent that mesoporous materials float on water and fail to disperse in water due to the surface energy incompatibility with water. The inherent performances of hydrophobic mesoporous materials are thus suppressed because of the decreased accessibility to the compounds dissolved in water. Moreover, the aqueous phase and oil/water biphases are prevailing in nature as well as artificial systems. The mesoporous material dispersion behavior in water and the partition behavior in biphasic oil/water systems directly govern their applications.\textsuperscript{35−37} In this context, how to tune the dispersion and distribution of the hydrophobic functional mesoporous materials in aqueous systems is of paramount importance for practical applications.

The features of micelles may bring an inspiration to design a new type of functional mesoporous materials to address these fundamental issues (Scheme 1). Micelle is an assembly of surfactant molecules in which the polar headgroup points outward and the hydrophobic tail points inward, forming a hydrophobic core/hydrophilic shell structure.\textsuperscript{38−40} Such a hydrophobic/hydrophilic domain-compartmentalized structure...
endows micelles with unique functions and interesting properties. The hydrophilic shell ensures a good "dispersion" of each micelle in water and high compatibility with a water system, while the hydrophobic core can trap hydrophobic organic compounds from water, which is often called as solubilization effects. On the basis of these functions and properties, micelle gains many important applications. For example, it is widely used in the aqueous-phase catalysis to improve the reaction rate owing to the solubilization effects and supplying large reaction interfaces. \(^41\-44\) Micelle and its analogues are also exploited to encapsulate hydrophobic drugs and deliver drugs in biological systems (water). \(^45,46\)

We envision that if mesoporous silicas own a "micelle-like" structure, i.e., hydrophobic core/hydrophilic shell (as shown in Scheme 1), the micelle functions would be built in mesoporous materials. The hydrophobic domains of the mesoporous materials would more efficiently trap (or adsorb) hydrophobic molecules and provide an organic microenvironment for catalysis and molecule cargoes. Meanwhile, they could be well dispersed in water without negative effects of hydrophobization. Such an encapsulation of a hydrophobic core with a hydrophilic shell might address the limitations of hydrophobic mesoporous materials. In spite of the possible intriguing properties and promising applications of the "micelle-like" solid materials, it lacks systematical investigations on the synthesis, tuning their properties and exploiting their applications.

Herein, we attempt to synthesize novel mesoporous silica nanospheres featuring a hydrophobic core and a hydrophilic shell and investigate their fundamental properties including dispersibility in water, wettability, and adsorption ability toward hydrophobic compounds in water. Our synthesis protocol in combination with particular organosilanes allows these properties to be tuned in a controllable fashion. Impressively, significant enhancement effects in adsorption of organic compounds in water are achieved, which may lay foundations for more efficient utilization of mesoporous materials in the aqueous systems.

**EXPERIMENTAL SECTION**

**Reagents.** Cetyltrimethylammonium chloride (CTAC) was purchased from Nanjing Robiot Co. Ltd. Methyl orthosilicate (TMOS) was purchased from the Aladdin Company (China). 1,3-Propane sultone and 4-heptylphenol were purchased from J&K. \(n\)-Octyltrimethoxysilane and 3-amino propyltrimethoxysilane were obtained from Gelest. All solvents were of analytical quality.

** Synthesis of Zwitterionic Organosilane.** 0.9 g of 3-amino propyltrimethoxysilane was added dropwise to 5 mL of acetonitrile containing 0.6 g of 1,3-propane sultone. The system was evacuated and purged with \(N_2\) four times. The mixture was stirred at room temperature for 24 h. The precipitated solid was isolated by centrifugation, washed with ethyl acetate and ether, and then dried under vacuum. Zwitterionic organosilane 3-[3-(trimethoxysilyl)-propylammonio]propane-1-sulfonate was eventually obtained. Elemental analysis calculated: C wt % (35.83), H wt % (6.97), N wt % (4.60), S wt % (10.62); Found: C wt % (34.39), H wt % (7.64), N wt % (5.0), S wt % (10.89). \(^1^3^C\) NMR data: 7.751, 18.5, 20.2, 45.1, 46.9, 47.9, 49.8.

**Synthesis of Mesoporous Silica Nanospheres.** 3.52 g of CTAC was dissolved in a mixture of 400 mL of deionized water, 505 mL of methanol, and 2.2 mL of NaOH (1.0 mol/L). After stirring for 30 min at room temperature, a mixture of \(n\)-octyltrimethoxysilane and TMOS dissolved in methanol was added dropwise to this solution. After vigorously stirring for 90 min, TMOS (dissolved in 2 mL of methanol) and zwitterionic organosilane (dissolved in 2 mL of deionized water) were simultaneously added dropwise into the above system. After further stirring for 10 h at room temperature, the resulting solid was isolated, washed with water and ethanol, and then dried at room temperature. The obtained solid powders were extracted twice with a CH\(_2\)OH/H\(_2\)O solvent containing NaCl (1.0 g of solid material: 290 mL of methanol: 60 mL of H\(_2\)O: 3.4 g of NaCl) at refluxing temperature and then washed with an ethanol solution of HCl. The obtained samples were denoted as \(x\)CTAC@\(Z\)m according to the amounts of added siliceous precursors (the total amount of siliceous precursors were kept at 10.1 mmol for all the cases), where \(x\) and \(y\) reflect the molar fraction of siliceous precursors added in the first step and the second step, \(n\) represents the molar fraction of octyl silane added in the first step, and \(m\) means the molar fraction of zwitterionic organosilane used in the second step.

For the sake of comparison, octyl-monofunctionalized and zwitterionic group-monofunctionalized mesoporous silica nanospheres were synthesized through one step of condensation instead of the delayed condensation. The obtained materials are denoted as C10 and Z10, respectively, where the molar fraction of octylsilane or zwitterionic organosilane in the total siliceous precursors is 10%. Octyl-zwitterionic group-bifunctionalized mesoporous silica nanosphere was also synthesized through one step of condensation (octyltrimethoxysilane and zwitterionic organosilane were simultaneously added). This material is denoted as C10/Z10 (the molar fractions of both octyltrimethoxysilane and zwitterionic silane in total siliceous precursor are 10%). Meanwhile, we synthesized a reversed core/shell structured mesoporous silica nanosphere (doped as opposed to 1C10@1Z10).

**Adsorption of Water Vapor and Hydrophobic Compound in Water.** Water adsorption experiment was performed on ASAP2020. Before adsorption, the sample was degassed at 150 °C for 6 h. The highly pure, degassed water is obtained from a Microdynamics. The adsorption is performed at 0 °C. Water vapor pressure was recorded by the pressure sensor, similar to the \(N_2\) sorption.

8 mg of the solid materials was added into 36 mL of an aqueous 4-heptylphenol solution with a concentration of 11.5 ppm. The adsorption tests were conducted under the stirring conditions. The concentration of the residual 4-heptylphenol in water was monitored with high performance liquid chromatography (HPLC, \(V_{n\text{ethanol}}/V_{n\text{H}_2\text{O}} = 90:10\), at 278 nm).

**Characterization.** The small-angle X-ray powder diffraction analysis was performed on Rigaku D/max max a X-ray diffractometer (40 kV and 30 mA with Cu K\(_\alpha\) radiation). \(N_2\) physical adsorption was measured by using an an instrument (ASAP2020 volumetric adsorptiometer). Before measuring, all samples were outgassed at 120 °C under vacuum for 6 h, and the pressure was decreased down to 1 μmHg. The specific surface area was calculated from the adsorption branch in the relative pressure range of 0.05–0.12 using the Brunauer–Emmett–Teller (BET) equation. The pore diameters were calculated from the desorption branch of the isotherm using the BJH method. The total pore volume was measured at a relative pressure of \(P/P_0 > 0.99\). FT-IR spectra were performed on Thermo-Nicolet-Nexus 470 infrared spectrometer. Transmission electron microscope (TEM) images were obtained on a JEOL-2000EX (operated at 200 kV) 300 MHz spectrometer; for \(^29^Si\) MAS NMR, 75.4 MHz resonant frequency, 4 kHz spin rate, 4 s pulse delay. 1.0 ms contact time, hexamethyldisilane as a reference compound; for \(^29^Si\) MAS NMR, 79.6 MHz resonant frequency, 4 kHz
Spin rate, 4.0 s pulse delay, TMS as a reference compound. C, N, and S content analysis was conducted on Vario EL (Elementar). X-ray photoelectron spectra (XPS) were recorded on a Kratos Axis Ultra DLD, and the C1S line at 284.8 eV was used as a reference. Water contact angles were measured on KRUSS DSA100 by using contact mode (the images was taken after 0.03 s for all the samples). Before measurement, the powder sample was pressed into flake under the pressure of 4 MPa. The concentration of 4-heptylphenol in water was determined by the HPLC (LC-20AT, Shimadzu).

RESULTS AND DISCUSSION

Synthesis. As aforementioned, the keys for the simulation of a micelle are to create a spherical morphology, hydrophobic core/hydrophilic shell structure, and abundant nanopores that interconnect core and shell domains, like the apertures between surfactant molecules of a micelle. We followed a delayed condensation strategy to synthesize mesoporous silica microspheres because this method allowed a selective location of the molecular functionality through a stepwise addition of siliceous precursors.\(^\text{47−52}\) We implemented a co-condensation of commercial hydrophobic octyltrimethoxysilane and methyl orthosilicate (TMOS) in the presence of template to construct a hydrophobic mesoporous core. A hydrophilic organosilane 3-((3-(trimethoxysilyl)propyl)ammonio)propane-1-sulfonate that was synthesized through one-step reaction of 3-aminopropyltrimethoxysilane with 1,3-propane sulfonate\(^\text{53}\) was used to grow a hydrophilic shell around the core. This hydrophilic organosilane was found to be highly soluble in water due to owning a zwitterionic unit. The synthesis follows up the steps shown in Scheme 2. After two steps of hydrolysis-condensation, the resultant materials were subjected to an extraction with a hot CH\(_3\)OH/H\(_2\)O solution containing NaCl for removing templates.\(^\text{54}\) The zwitterionic moieties could be resumed through washing with an ethanolic solution containing HCl (deprotonation of N atom probably occurred under the basic conditions during the synthesis). The core diameter and shell thickness can, in principle, be adjusted by varying the molar fraction of the siliceous precursors added in the formation of core and shell (keeping the total siliceous precursors constant). The loadings of octyl group in the core and zwitterionic group on the shell were adjusted through changing their molar fractions in preparation. The synthesized materials were denoted as \(\text{xCn@yZm}\) (see Experimental Section). Take 6C10@1N10 for example; the molar fraction of siliceous precursors added for the core formation is 6/7 of the total siliceous precursors, and the molar fraction of siliceous precursors added for the shell formation is 1/7 of the total siliceous precursors. The molar fraction of octyltrimethoxysilane in the mixed siliceous precursors in the first step is 10%, and the molar fraction of zwitterionic organosilane in the mixed siliceous precursors in the second step is also 10%. To systematically investigate the relationship of composition—structure properties, we synthesized three series of samples: \(\text{xC10@yZ10}, \text{4Cn@1Z10}, \text{and 1C10@1Zm}\). Their synthesis conditions are summarized in Table 1. For the sake of comparison, we also synthesized an octyl-monofunctionalized material \(\text{C10}\), a zwitterionic-monofunctionalized material \(\text{Z10}\), a reversed core/shell-structured material \(\text{1Z10@1C10}\) (as opposed to \(\text{1C10@1Z10}\)), and an octyl-zwitterionic-bifunctionalized material \(\text{C10@Z10}\) through the one-step condensation instead of the delayed condensation.

Structure Characterization. The structures of the synthesized samples were characterized with \(\text{N}_2\) sorption, XRD, and TEM. The \(\text{N}_2\) sorption plots of \(\text{Z10}, \text{C10}, \text{and xC10@yZ10s}\) are displayed in Figure 1, and the determined parameters are summarized in Table 2. \(\text{Z10}\) and \(\text{C10}\) both show a sorption isotherm close to the type IV in spite of somewhat deviation and possess a moderate specific surface area and pore volume. As expected, \(\text{xC10@yZ10s}\) exhibit isotherms, also close

<table>
<thead>
<tr>
<th>samples</th>
<th>synthesis conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{xC10@yZ10})(^a)</td>
<td>changing the core and shell dimensions but fixing the loadings of functionalities</td>
</tr>
<tr>
<td>(\text{4Cn@1Z10})(^a)</td>
<td>changing the loading of octyl group but fixing dimensions of the core and shell, and the loading of zwitterionic group</td>
</tr>
<tr>
<td>(\text{1C10@1Zm})(^a)</td>
<td>changing the loading of zwitterionic group but fixing dimensions of the core and shell, and the loading of octyl group</td>
</tr>
<tr>
<td>(\text{C10})</td>
<td>octyl-monofunctionalized mesoporous material, the molar fraction of octylsilane was 10%</td>
</tr>
<tr>
<td>(\text{Z10})</td>
<td>zwitterionic-group functionalized mesoporous material, the molar fraction of zwitterionic organosilane was 10%</td>
</tr>
<tr>
<td>(\text{1Z10@1C10})</td>
<td>zwitterionic-group functionalized core/octyl-functionalized shell, loadings of functionalities are both 10%</td>
</tr>
<tr>
<td>(\text{C10@Z10})</td>
<td>octyl-zwitterionic bifunctionalized mesoporous material, synthesized through a one-step condensation instead of the delayed condensation</td>
</tr>
</tbody>
</table>

\(^a\)Italic letters represent the variables.

Figure 1. \(\text{N}_2\) adsorption/desorption isotherms of the samples \(\text{xC10@yZ10s}\), \(\text{C10}\), and \(\text{Z10}\). Notes: \(\text{1C10@1Z10}\), offset vertically by 100; \(\text{4C10@1Z10}\), offset vertically by 200; \(\text{6C10@1Z10}\), offset vertically by 300; \(\text{8C10@1Z10}\), offset vertically by 400; \(\text{C10}\), offset vertically by 400.
Table 2. Textural Parameters of xC10@yZ10s, Z10, and C10

<table>
<thead>
<tr>
<th></th>
<th>( S^* ) (m(^2)/g)</th>
<th>( V^b ) (cm(^3)/g)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z10</td>
<td>457</td>
<td>0.32</td>
<td>2.3</td>
</tr>
<tr>
<td>1C10@1Z10</td>
<td>624</td>
<td>0.49</td>
<td>2.4</td>
</tr>
<tr>
<td>4C10@1Z10</td>
<td>687</td>
<td>0.45</td>
<td>2.3</td>
</tr>
<tr>
<td>6C10@1Z10</td>
<td>631</td>
<td>0.46</td>
<td>2.3</td>
</tr>
<tr>
<td>8C10@1Z10</td>
<td>509</td>
<td>0.40</td>
<td>2.3</td>
</tr>
<tr>
<td>C10</td>
<td>623</td>
<td>0.40</td>
<td>2.3</td>
</tr>
</tbody>
</table>

\(^*\)BET surface area. \(^*\)Single point pore volume determined at relative pressure of \( P/P_0 = 0.99 \). \(^\circ\)Pore size, BJH method from desorption branch.

Figure 2. XRD patterns of xC10@yZ10s, C10, and Z10.

The capillary condensation steps are not so evident. Their surface area, pore volume, and pore size are correspondingly in the range of 509–824 m\(^2\)/g, 0.40–0.58 cm\(^3\)/g, and 1.5–2 nm, which are smaller than those of a typical mesoporous silica. The pore formation originates from the micelle template and the pore size is thus related to the micelle dimension. However, in the process of self-assembly, the hydrophobic part of the bulky organosilane probably interposes the micelle interiors. As a result, this part of functionality occupies the space of the resultant mesoporous channel after removing templates, leading to a decrease in pore size. As indicated by the results of xC10@yZ10s, variation of the molar fraction of siliceous precursors added in the first and second step does not cause significant changes of the textual parameters. The \( N_2 \) sorption results of 4C\(_n\)@1Z10s and 1C\(_n\)@1Z10s are supplied in Figures S1, S2 and Table S1 (in Supporting Information), also exhibiting features of typical mesoporous materials. One can find that changing the loadings of functionalities leads to evident changes of \( N_2 \) sorption isotherm and textual parameters. The specific surface area and pore volume decrease with increasing the loading of functionalities. For 4C\(_20\)@1Z10 and 4C\(_{30}\)@1Z10, their specific surface areas decrease down to 126 and 38 m\(^2\)/g due to the incorporation of a large amount of functionalities.

The XRD patterns of xC10@yZ10s in Figure 2 exhibit one diffraction peak in the range of \( 2\theta = 2^\circ–3^\circ \), confirming the presence of the micelle template and the pore size is thus related to the micelle dimension. In contrast to a standard MCM-41 material that often exhibits three diffraction peaks, xC10@yZ10s seem less ordered. This may be explained by the possibility that the presence of the bulky organosilane affects the interactions between silicon oligomers and template molecules, and the assembly ability (especially in CH\(_3\)OH/H\(_2\)O system) is thus discounted. The diffraction peak position shifts toward low angles with increase in the molar fractions of siliceous precursors for the core formation. The reason may be that solubilization of CTAC micelles toward hydrophobic octylsilane leads to a size increase of micelle templates. 4C\(_n\)@1Z10s and 1C\(_n\)@Z\(_m\)s show XRD patterns similar to xC10@yZ10s (shown in Figures S3 and S4). The diffraction peak shifts toward low angles with the increase in the molar fraction of octylsilane and toward high angles with the increase in the molar fraction of zwitterionic organosilane. These results reflect the different influences of organosilanes on the mesoporous structures.

The selected TEM images of 4C\(_10\)@1Z10 and 1C\(_{10}\)@1Z10 are displayed in Figure 3. 4C\(_10\)@1Z10 and 1C\(_{10}\)@1Z10 both consist of uniform nanospheres with diameters of about 200–300 nm (Figure 3a,c). Abundant mesopores throughout each sphere (ca. 2 nm) are clearly observed in the more magnified images (Figure 3b,d). Although the pore ordering is distorted to some extent, most of pores are radially aligned. The core and the shell domains are well connected through nanopores without obvious boundaries.

**Composition Characterization.** The compositions of xC10@yZ10s were characterized with Fourier transform infrared spectroscopy (FT-IR), solid state NMR, and elemental analysis. In the FT-IR spectra of xC10@yZ10s (Figure 4), the peaks at 2900–3000 and 1485 cm\(^{-1}\) that correspond to the C–H stretching vibrations and C–H scissoring vibrations are clearly observed, indicating that the functionalities are bound with the solid materials. The peak of \(-\text{SO}_3^-\) is not clearly observed because it is suppressed by the strong, wide absorbance of Si–O–Si vibrations (980–1250 cm\(^{-1}\)). The \(^{13}\)C CP-MAS NMR spectrum of 1C\(_{10}\)@1Z10 (Figure 5a) gives carbon signals in the range 12–54 ppm. The resonance at 50–54 ppm is attributed to the C atom that bonds with N atom [solid-state NMR investigation of C10 revealed that the signals
for residual CH\textsubscript{3}O groups are weak, which are often at 49−51 ppm. In the \textsuperscript{29}Si CP-MAS NMR spectrum (Figure 5b), 1C10@1Z10 shows Q and T bands. The signals at −100 and −110 ppm are attributed to Q\textsuperscript{3} [[Si(OH)(OSi)\textsubscript{3}]] and Q\textsuperscript{4} [[Si(OSi)\textsubscript{4}]] silicon, respectively. The signals at −58 and −66 ppm are attributed to T\textsuperscript{2} [[Si(OH)(OSi)\textsubscript{2}]] and T\textsuperscript{3} [[SiC(OH)(OSi)\textsubscript{3}]] silicon sites, respectively. The strong signal for Q bands confirms that the solid material is subjected to a high degree of condensation. The presence of T bands points to the fact that the organic moieties are integrated with the solid materials through Si−C linkages.

The quantitative results of C, N, and S contents on the solid materials are listed in Table 3. The determined values for N and C are slightly higher than the theoretic values. These results could be explained by the possibility that a small amount of templates remained on the solid materials even after solvent extractions. It should be noted that as the core diameter decreases and shell thickness increases, the C content gradually decreases, while the N and S contents gradually increases. These results are consistent with the changing tendency of the amounts of octylsilane and zwitterionic organosilane added in the preparation. The elemental analysis results suggest that the organic moieties are nearly quantitatively incorporated onto the solid materials.

In order to clarify the distribution of functional groups on the solid materials, we employed X-ray photoelectron spectroscopy (XPS) to investigate the elemental compositions on the surface layer (ca. 10 nm in the detection depth for nonporous materials).\textsuperscript{55} For comparison, 1C10/1Z10, on which octyl and zwitterionic groups are expected to be homogeneously distributed on the solid materials since octylsilane and zwitterionic organosilane are simultaneously added, was investigated. The XPS spectra of 1C10/1Z10, 1C10@1Z10, and 1Z10@1C10 are shown in Figure 6. C, N, S, Si, and O elements were clearly found on these two samples (Na signal was found which was introduced during treatment with a CH\textsubscript{3}OH/H\textsubscript{2}O solution containing NaCl). Notably, the surface C/N molar ratio of 1C10@1Z10 is lower than that of 1C10/1Z10 and much lower than that of 1Z10@1C10 (Figure 6). These results give a clear indication that the shell of 1C10@1Z10 is rich in zwitterionic moiety, as expected (the shell of 1Z10@1C10 is rich in octyl group). But the determined surface N concentration for 1C10@1Z10 is lower than the theoretic value (10%, assuming that the elements only on the shell layer can be detected). It is possible that the shell was contaminated with a little amount of octyl groups due to the surface inhomogeneity caused by the delayed condensation method.\textsuperscript{47,49}

**Dispersion in Water and Distribution in the Water/Oil Biphase.** With the defined “micelle-like” solid materials in hand, we first checked their dispersion in water and the

![Figure 4. FT-IR spectra of xC10@yZ10s, C10, and Z10.](image)

![Figure 5. Solid-state NMR spectra of 1C10@1Z10: (a) \textsuperscript{13}C CP-MAS NMR spectrum; (b) \textsuperscript{29}Si CP-MAS NMR spectrum.](image)

| Table 3. Results of Elemental Analysis of Core/Shell Structured Materials |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| samples                     | N (wt %) found | C (wt %) found | S (wt %) found | octyl loading (mmol/g)   | zwitterionic loading (mmol/g)|
| 8C10@1Z10                   | 0.36          | 0.22          | 16.11         | 0.46                      | 0.50                      |
| 6C10@1Z10                   | 0.40          | 0.28          | 14.99         | 0.67                      | 0.64                      |
| 4C10@1Z10                   | 0.38          | 0.39          | 13.83         | 0.94                      | 0.89                      |
| 1C10@1Z10                   | 1.05          | 0.95          | 10.27         | 2.05                      | 2.16                      |
| 1C10/1Z10                   | 0.80          | 0.95          | 10.76         | 1.98                      | 2.16                      |

\textsuperscript{a}Calculation based on ignoring template.
distribution in the aqueous/organic biphasic system. Figure 7 displays the visual appearances of \(\text{xC10@yZ10s, C10, and Z10}\) in water and a biphasic water/hexane system. C10 floats on water and fails to disperse in water, whereas Z10 is well dispersed in water. The remarkable contrast is a result of the differences in their functionality properties on the solid surfaces. The highly hydrophobic octyl group makes the former surface strongly repel water. The zwitterionic group confers the latter high affinity to water due to bearing charges. Interestingly, as the core dimension decreases and the shell thickness increases, their water dispersion undergoes a remarkable change. Similar to C10, 8C10@1Z10 still floats on water, whereas 6C10@1Z10, 4C10@1Z10, and 1C10@1Z10 become dispersible in water (these samples can suspend in water). More interesting phenomena are observed in the biphasic water/hexane system. C10 is distributed in the upper layer (hexane), while Z10 suspends in the bottom layer (water). 8C10@1Z10 still resides in the hexane layer. But, 6C10@1Z10, 4C10@1Z10, and 1C10@1Z10 are distributed in the water layer. These observations clearly indicate that the dispersion behavior of the solid materials in water and the distribution behaviors in oil/water biphase are highly dependent on the core/shell structures, and the encapsulation of a hydrophobic core with a suitable hydrophilic shell enables the hydrophobic materials to be dispersible in water. To further check the roles of the core/shell structure, we examined 1C10@1Z10 and 1Z10@1C10 (hydrophilic core and hydrophobic shell, as opposed to 1C10@1Z10). Their appearances for the dispersion in water and distribution in the biphasic system are also included in Figure 7. Obviously, they behave differently from 1C10@1Z10 in terms of dispersion. These two samples both float on water and are distributed in the hexane layer for the biphasic system. These distinct differences highlight that the encapsulation of hydrophobic core with a hydrophilic shell is crucial for the high dispersion in water.

Interestingly, the dispersion of our core/shell structured materials can be also adjusted through varying the loadings of the hydrophobic and hydrophilic groups. The appearances of 4Cn@1Z10s on which the loading of octyl group are gradually increased but the loading of zwitterionic group is kept at 10%, are reflected in Figure 8. 44C@1Z10 is well dispersed in water. The samples with octyl loading of 15% and 20% are still dispersible in water. But, further increasing the octyl loading up to 30% leads to a poor dispersion, and this sample begins to float on water. In the biphasic water/hexane system, 4Cn@1Z10s also show different distribution behavior. 4C10@1Z10, 4C15@1Z10, and 4C20@1Z10 prefer to stay in water, whereas 4C30@1Z10 shifts to the oil phase. In parallel, the appearances for 1C10@1Zm and C10 are displayed in Figure 9. As aforementioned, C10 fails to be dispersible in water. Introduction of a little amount of zwitterionic group on the shell leads to significant changes of water dispersion and distribution in the oil/water biphasic. 1C10@1Z5 begins to disperse in water and partition in the water layer for the biphasic oil/water system.

The water contact angle measurements (wettability) may provide some insights into the variations of dispersion behavior. The measured results of \(\text{xC10@yZ10s, C10, and Z10}\) are shown in Figure 10. The water contact angles of C10 and Z10 were determined as 112.7° and 38.8°, respectively. Interestingly, the water contact angles of 8C10@1Z10, 6C10@1Z10, 4C10@1Z10, and 1C10@1Z10 correspond to 101.1°, 94.6°, 84.2°, and 70.8°. These values fall in between the values of C10 and Z10. The wettability shows a monotonous decrease as the
core dimension decreases and the shell thickness increases, which may be partially caused by contamination of the hydrophilic shell with a little amount of hydrophobic octyl groups in the delayed condensation.47,49 The remarkable distinctness in water contact angle reflects the difference in the wettability of our solid materials, which accounts for the observations in water dispersion. As shown in Figures S5 and S6, the water contact angle gradually increases with increasing the loading of octyl group and decreases with increasing the loading of zwitterionic group. These quantitative results confirm that our synthesis protocol allows the dispersion and distribution of functional mesoporous materials in water or in the biphasic system to be tuned in a controllable fashion.

The above three sets of experimental findings reveal that varying the core or shell dimensions, and the loadings of hydrophobic and hydrophilic functionalities lead to controllable changes in the dispersion in water and the distribution in the biphasic water/oil system. These changes may be attributed to the variations in the hydrophobic/hydrophilic balance of the core/shell structured materials. In this regard, it may be really like a surfactant because the hydrophilic/lipophilic balance (the well-known HLB value) of surfactant can be varied through changing the carbon chain length and headgroup type. Our findings allow us to envision that the hydrophobic/hydrophilic balance of our core/shell structured materials can be systematically tuned according to the application requirements, like the well-established surfactant system.

Adsorption of Water Vapor. Adsorption is a fundamental property of porous materials, on which many important applications strongly depend. To further know the adsorption performances of our materials, we first measured the adsorption toward water vapor. The water vapor adsorption plots with vapor pressure for C10, Z10, and 4C10@1Z10 are presented in Figure 11. C10 exhibits a very low adsorption capacity toward water vapor, while Z10 exhibits a high adsorption capacity toward water vapor under the same conditions. These distinct differences clearly reflect the variation of the surface properties: the former is hydrophobic, and the latter is hydrophilic. Interestingly, 4C10@1Z10 shows a slightly higher adsorption ability toward water vapor than C10 but much lower than Z10. That is to say, the inner core domain can efficiently prevent water from intruding the hydrophobic nanospaces. These findings preliminarily imply that although 4C10@1Z10 can be
highly dispersible in water it can prevent water from entering the inner surface.

**Adsorption of Organic Compounds from Water.** To check whether our materials own “solubilization” ability, we determined the adsorption ability toward a hydrophobic organic compounds (HOC) in water, which were ubiquitous environmental contaminants.56

We chose hydrophobic 4-heptylphenol to examine the adsorption ability of our materials because it is one of endocrine disrupters.57−59 The concentration of 4-heptylphenol in water was monitored with time (the initial concentration is 11.5 ppm). The adsorption profile (residual 4-heptylphenol percentage with time, which is the residual 4-heptylphenol concentration/the initial 4-heptylphenol concentration) is reflected in Figure 12. C10 shows a relatively low adsorption rate and capacity (Table S2). After 5 and 20 min, the residual 4-heptylphenol percents are 63% and 42%, respectively (Figure 12a). During the process of adsorption, C10 was observed to fail to disperse in water in spite of stirring. The poor dispersion is responsible for the low adsorption efficiency. Although Z10 is dispersible in water, the strong hydrophilicity leads to a low adsorption ability toward the hydrophobic organic molecule. After 20 min, the residual 4-heptylphenol percent was determined as 40%. Interestingly, 4C10@1Z10 exhibits a much higher adsorption ability. After 5 and 20 min, the residual 4-heptylphenol percents decreased down to 37% and 21%, respectively. In comparison with C10, the increased adsorption efficiency is ascribed to the high dispersion in water because of providing more possibilities for 4-heptylphenol to access to the solid material surface. Increasing the hydrophobic core dimension causes an increase in adsorption ability, as exhibited by the results of 6C10@1Z10. For this material, the residual 4-heptylphenol percent decreases down to 12.9% (i.e., ca. 1.4 ppm). Obviously, the core/shell structured 6C10@1Z10 and 4C10@1Z10 significantly outperform a mesoporous pure silica MCM-41, C10, and Z10 in terms of adsorption ability.

These comparisons confirm that the hydrophobic core/hydrophilic shell structure is crucial for the effective adsorption of HOC in water. Notably, further increasing the core dimensions, however, leads to a decrease in adsorption ability, as indicated by the results of 8C10@1Z10. This result is not surprising because 8C10@1Z10 fails to be dispersible in water owing to the increased hydrophobicity.

To further verify the role of the hydrophobic core, we examined the adsorption ability of 1Cn@1Z10s. As shown in Figure 12b, the adsorption ability remarkably increased with increasing the loading of octyl group from 5% to 15% although the specific surface area gradually decreased. It should be noted that 1C10@1Z10 is much superior to 1C10/1Z10. After 20 min, the residual concentration of 4-heptylphenol over 1C10@1Z10 is 2 ppm, which is much lower than that over 1C10/1Z10 (5 ppm). These results again highlight the role of the hydrophobic core/hydrophilic shell structure. Another set of experiments with 4Cn@1Z10s also support this conclusion (Figure 12c). The adsorption ability also increases with the loading of octyl group. For 4C20@1Z10, the concentration of residual 4-heptylphenol decreases down to less than 1 ppm within 20 min.

Next, we checked the role of zwitterionic group. The results of 1C10@1ZMs (gradually increasing the loading of zwitterionic group but keeping the core and shell dimensions, and the loading of octyl group constant) are reflected in Figure 12d. It was found that the adsorption ability only slightly increased with increasing the loading of hydrophilic group. It is may be possible that the high loading of hydrophilic group results in strong repulsions between silica nanospheres due to electric charge interactions. The increased repulsion makes the solid more dispersible in water (without aggregation), which leads to a high adsorption interface.
CONCLUSIONS

Inspired by the structure features of micelle, we successfully synthesized hydrophobic core/hydrophilic shell structured mesoporous silica nanospheres. Our synthesis protocol with the particular combination of hydrophobic and hydrophilic organosilanes allows their fundamental properties such as dispersibility in water, wettability, and distribution in a biphasic water/oil system to be facilely tuned by changing the core/shell dimensions or the loading of the hydrophobic and hydrophilic groups. Impressively, such “micelle-like” solid materials exhibit an excellent adsorption ability toward the hydrophobic compounds in water. Their adsorption ability is much higher than that of the monofunctionalized mesoporous silica and bifunctionalized mesoporous silica synthesized through a one-step of condensation, clearly confirming the superiority of the hydrophobic core/hydrophilic shell structure. Although the application investigation here is preliminarily focused on the adsorption of hydrophobic organic compounds, we believe that the improvement of the fundamental performances may make mesoporous materials more accessible to the applications in the aqueous systems such as catalysis in water and delivery of hydrophobic drugs.

ASSOCIATED CONTENT

Supporting Information

Textural parameters of the synthesized samples; the adsorption capacity of various materials toward 4-heptylphenol; N2 sorption isotherms of 4C10@1Z10s and 1C10@1Zms; XRD patterns of 4C10@1Z10s and 1C10@1Zms; water contact angles of 4C10@1Z10s; water contact angles of 1C10@1Zms. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

Fax +86-351-7011688; Tel +86-351-7010588; e-mail huyang@sxxu.edu.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge the Natural Science Foundation of China (20903064, 21173137), Program for the Top Young Academic Leaders and the Top Young of Higher Learning Institutions of Shanxi (2011002), and Middle-aged Innovative Talents of Higher Learning Institutions of Shanxi (20120202).

REFERENCES

Encapsulation of Hydrophobic Fluorescent Dyes.


(43) Trentin, F.; Chapman, A. M.; Scarso, A.; Sgarbossa, P.; Michelin, R. A.; Strukul, G.; Wess, D. F. Platinum(II) Diphosphin-