

Azobenzene-Derived Surfactants as Phototriggered Recyclable Templates for the Synthesis of Ordered Mesoporous Silica Nanospheres

Jing Wei, Yuyun Liu, Jia Chen, Yuhui Li, Qin Yue, Gaoxiang Pan, Yanlei Yu,*
Yonghui Deng,* and Dongyuan Zhao

Azobenzene has two isomers, the *trans* and *cis* forms; reversible switching between the two forms is possible using photo-irradiation. The transformation of molecules containing azobenzene can lead to the changes in the molecular size and polarity.^[1] They are consequently regarded as powerful molecular switches and have been applied to a broad range of applications such as switchable catalysts,^[2] liquid crystals,^[3] and drug delivery.^[4] Various azobenzene-derived building blocks, including metal and metal-oxide nanoparticles, surfactants, and block copolymers, have been used to induce self-assembly and disassembly in solutions in response to light stimulus. The azobenzene-derived surfactants exhibit amphiphilicity and photocontrollable spatial structures. They can self-assemble into photoresponsive micelles with various morphologies in solutions, making it possible to generate organic/organic (inorganic) nanocomposites with unique nanostructures and novel properties in catalysis and optics^[2–5] via the co-assembly of the azobenzene-derived surfactants and organic (or inorganic) species.

Silica-based materials exhibit good biocompatibility, transparency, controllable sol–gel processes, and easy postmodification. Ordered mesoporous silica nanospheres (MSNs) with large pore size, high surface area, and various pore structures are ideal nanocontainers for guest molecules and nanocatalysts.^[6] The incorporation of azobenzene-containing groups into the framework can endow the MSNs with unique photoreversible properties.^[7,8] In addition, the rigid silica framework

can enhance the mechanical, chemical, and thermal stability of the photocontrollable nanocomposites, thus extending their applicability for potential applications. Several research groups have reported the introduction of azobenzene-derived silanes on the pore walls of mesoporous silicas, and they have explored their photoresponsive properties and controllable release of cargo materials from the mesopores;^[8] however, all of these reports have relied on regular cationic surfactants (e.g., cetyltrimethylammonium bromide) as the template and the modification of the mesoporous silicas with azobenzene-derived silanes. Reports have not yet been made involving investigations into the direct co-assembly process of silica species and azobenzene-derived surfactants into ordered mesostructures, where azobenzene-derived surfactants act as a structure-directing agent as well as a functional group to modify the silica framework uniformly.

In the synthesis of ordered mesoporous materials, it is necessary to remove the organic templates from the silica matrix to create accessible mesopores and open frameworks. Usually, the templates are removed by calcination in air at high temperature (ca. 550 °C). However, this process not only releases large amounts of pollutants, but it also causes severe framework shrinkage, and even results in distorted mesostructures (especially in the case of ordered mesoporous silica films). Moreover, it eliminates silanol groups in the silica frameworks, reducing the water dispersibility, which is disadvantageous for biological applications. Without silanol groups, it is difficult to further modify the surface of mesoporous silicas for specific applications. Solvent extraction is an alternative method for the removal of template molecules, which can be conducted under mild conditions and typically avoids severe framework shrinkage or loss of silanol groups. In addition, through solvent extraction, the template molecules extracted from the silica matrix are recyclable;^[9] solvent extraction has therefore been widely used to remove templates for the synthesis of water-dispersible MSNs, which are highly desirable for biomedical applications. However, the common solvent extraction method is usually a long process (ca. 24 h).

Herein, we designed a cationic azobenzene-derived surfactant, 6-(4'-ethoxy-4-azophenyl)hexyloxytrimethyl ammonium bromide (abbreviated as AZTMA) as a soft template for the synthesis of ordered MSNs with a uniform diameter (ca. 300 nm); the synthesis uses tetraethyl-orthosilicate (TEOS) as a precursor in an alkaline aqueous solution under UV light irradiation. Owing to the electrostatic interactions between the positively charged AZTMA and negatively charged silicate oligomers, they

Dr. J. Wei,^[†] Y. H. Li,^[†] Q. Yue, Prof. Y. H. Deng,
Prof. D. Y. Zhao
Department of Chemistry
Shanghai Key Laboratory of Molecular Catalysis
and Innovative Materials
State Key Laboratory of Molecular Engineering of
Polymers and Laboratory of Advanced Materials
Fudan University, Shanghai, 200433, P. R. China
E-mail: yhdeng@fudan.edu.cn

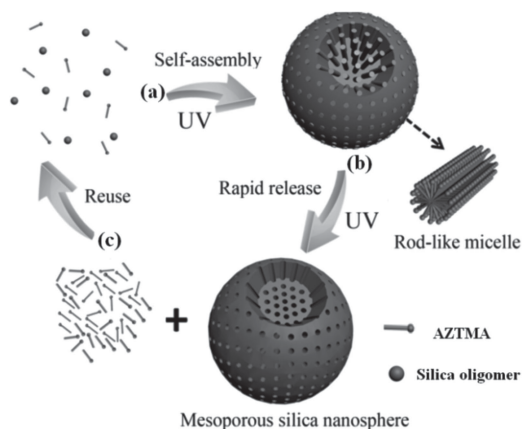
Y. Y. Liu, G. X. Pan, Prof. Y. L. Yu
Department of Materials Science
Fudan University
Shanghai, 200433, P. R. China
E-mail: ylyu@fudan.edu.cn

J. Chen
Department of Chemistry
Princeton University
Princeton, New Jersey, 08544, USA

^[†]J. Wei and Y.Y. Liu contributed equally to this work.



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Scheme 1. a) The co-assembly of azobenzene-derived AZTMA and silica precursor into AZTMA/silica composites with unique mesostructure and spherical morphology. b) The release of AZTMA molecules under UV light irradiation, forming mesoporous silica nanospheres (MSNs) with mesopores perpendicular to the surface, and (c) the recycling and reuse of AZTMA for further synthesis of MSNs.

co-assemble into rodlike AZTMA/silica composite micelles that further organize into mesostructured composite nanospheres (Scheme 1). Interestingly, the azobenzene-derived AZTMA surfactants confined in the silica matrix were found to maintain good photoresponse with alterable molecular size and polarity. The surfactants can be released rapidly (1 h) from the silica framework in a water/ethanol solution under UV light irradiation, resulting in uniform MSNs with a unique mesostructure and highly accessible mesopores that are perpendicular to the surface of the nanospheres. The MSNs obtained after removal of the AZTMA template have high surface area (381 m²/g), uniform pore size (2.7 nm), and regular spherical morphology with a mean diameter of ~300 nm. Through the mild extraction method, the released AZTMA surfactants can be recycled and reused as the template to synthesize more MSNs.

The synthesis of azobenzene-derived AZTMA involves three steps (Figure S1, Supporting information (SI)): the synthesis of i) 4'-ethoxy-4'-hydroxy azobenzene; ii) 4-(6-bromohexyloxy)-

4'-ethoxy azobenzene, and iii) 6-(4'-ethoxy-4-azophenyl) hexyloxytrimethyl ammonium bromide. UV-vis spectroscopy was employed to study the photoresponsive properties of the obtained AZTMA (Figure 1). Before UV light irradiation, a strong absorption band at around 360 nm is clearly observed, which is attributed to the π - π^* transition of the *trans* form of AZTMA, i.e., the more stable isomer (Figure 1A). After UV irradiation at a wavelength of 365 nm at room temperature for 1 s (illumination intensity: 100 mW/cm²), the absorption band at around 360 nm disappears due to the formation of the *cis* isomer. The new adsorption bands of the *cis* AZTMA at 338 and 450 nm are due to the π - π^* and n- π^* electron transitions, respectively. The change of the absorption band suggests that the AZTMA molecules possess photoisomerization behavior from *trans* to *cis* forms under UV light, suggesting that the photoresponsive properties of azobenzene were well retained in the AZTMA surfactants.

As azobenzene transforms from *trans* to *cis* form, the molecular size decreases from 9.0 to 5.6 Å.^[1] The *trans*-azobenzene has no dipole moment, while the nonplanar *cis* isomer has a dipole moment of 3.0 D.^[1] In this study, the molecular sizes of the AZTMA surfactant in *trans* and *cis* forms were investigated via theoretical calculations. Structure relaxation calculations were performed within the plane-wave pseudopotential scheme as implemented in the Quantum Espresso package^[10] by density functional theory (DFT) with the exchange and correlation functional of Perdew-Burke-Ernzerhof.^[11] Ultrasoft pseudopotentials were used, and the valence electrons included the 2s and 2p states of C, N, and O and the 1s states of H.^[12] Plane-wave energy cut-offs were 30 Ry for the smooth part of the wavefunction and 300 Ry for the augmented density. The molecular size of the *trans* form is calculated to be 23.3 Å × 2.5 Å × 2.5 Å, while that of the *cis* form is 14.8 Å × 10.0 Å × 4.0 Å (Figure 2). These results indicate that, similar to other azobenzene derivatives, this novel cationic AZTMA template can change its molecular size and polarity in response to UV irradiation, which makes it possible to construct smart nanosystems with photoresponsive properties.

In the synthesis of MSNs, the AZTMA soft template was first dissolved in an alkaline aqueous solution at 80 °C. The UV-vis spectrum that was recorded in situ indicates that the AZTMA molecules take the *trans* form in the hot solution (SI: Figure S2); however, after UV irradiation (at a wavelength of $\lambda = 365$ nm), they transform into the *cis* isomers even at 80 °C (SI: Figure S2). The silica precursor, TEOS, was added to the solution under magnetic stirring, followed by further irradiation by UV light for 10 min. After that, the reaction was allowed to proceed at 80 °C without UV irradiation. After 2 h, a colloidal suspension of the mesostructured silica/AZTMA nanocomposites (denoted as the as-made MSN-UV) were obtained. The UV-vis spectrum of the as-made MSN-UV shows an obvious absorption band at around 360 nm, indicative of the *trans* form of AZTMA. This implies that the *cis* isomer formed at the early stage of the synthesis isomerizes to

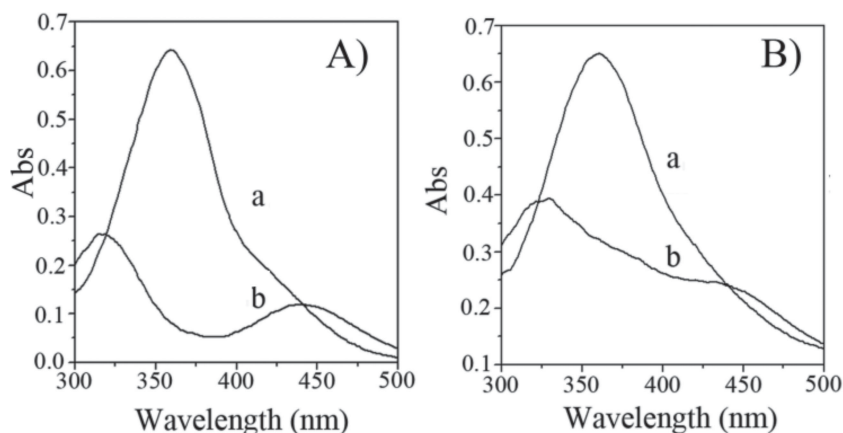


Figure 1. The UV-vis spectra of A) AZTMA surfactant and B) AZTMA/silica mesostructured nanocomposites a) before and b) after UV light irradiation ($\lambda = 365$ nm), indicating the photoisomerization between *trans* (a) and *cis* (b) forms.

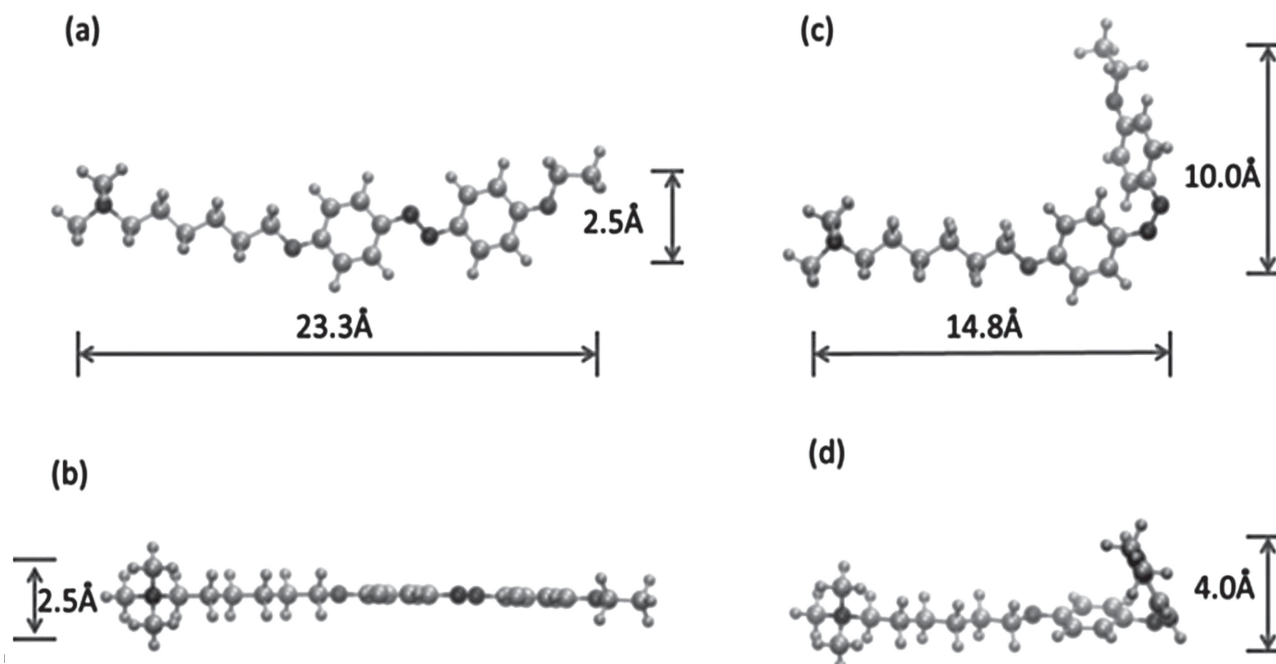


Figure 2. (a) The side view and (b) top view of *trans* form AZTMA, (c) side view and (d) top view of *cis* form AZTMA. The gray balls (●) represent carbon, red balls represent oxygen; the two connected black balls (●●) are for nitrogen (N=N) and the smallest balls (●) are for hydrogen.

trans after removing the UV light with heat (80 °C) during the subsequent reaction (Figure 1B,a). After irradiation with UV light, the absorption at 360 nm of the as-made MSN-UV decreases significantly, and new absorption bands at 338 and 450 nm appear. These results clearly indicate that a photoisomerization from the *trans* to *cis* form occurs, implying that the photoresponsive property of the AZTMA were retained in the mesostructured composites after the organic–inorganic co-assembly. This is the first time that amphiphilic molecules confined in mesostructured nanocomposites were found to be able to adjust their configuration in response to external stimulus.

Since the photoresponsive properties of AZTMA are retained after co-assembly with the inorganic silicate oligomers, AZTMA can be made to decrease in molecular size and to increase in solubility in polar solution through molecular isomerization under the UV light irradiation, and thus induce the disassembly of the nanocomposites. To study the possibility of photocontrollable disassembly of AZTMA and the silica framework, the as-made MSN-UV were dispersed in mixed water/ethanol solvent at 60 °C, and the release behavior of AZTMA with or without UV irradiation were studied. The release rate of the *cis* AZTMA surfactant at 60 °C under UV light is much faster than that under natural light (Figure 3). In 15 min, 70% of the AZTMA molecules can be released under UV light irradiation; however, without UV irradiation, only 40% AZTMA was released. This indicates that the UV light irradiation can significantly promote the extraction process of AZTMA surfactant. After irradiation for 60 min, over 80% of the surfactant templates were removed from the mesostructured nanocomposite, indicative of an ultra-fast template removal process as compared to common solvent

extraction.^[13] Such an improvement in the extraction process is probably attributed to the fact that the AZTMA molecule after UV light irradiation has a stronger hydrophilicity and better solubility in polar solvent. Therefore, it can be viewed as a

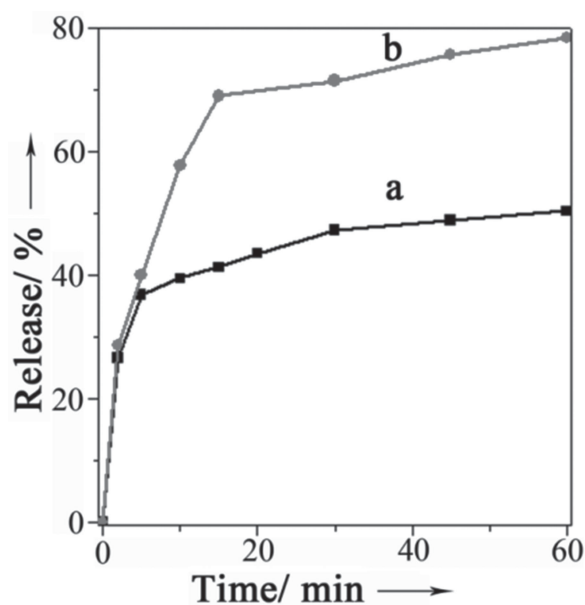


Figure 3. The release curves of azobenzene-derived AZTMA surfactant from the silica framework in mixed water/ethanol solvent (v/v = 3:1) at 60 °C: a) under natural light and b) under UV light with a light density of 300 mW/cm².

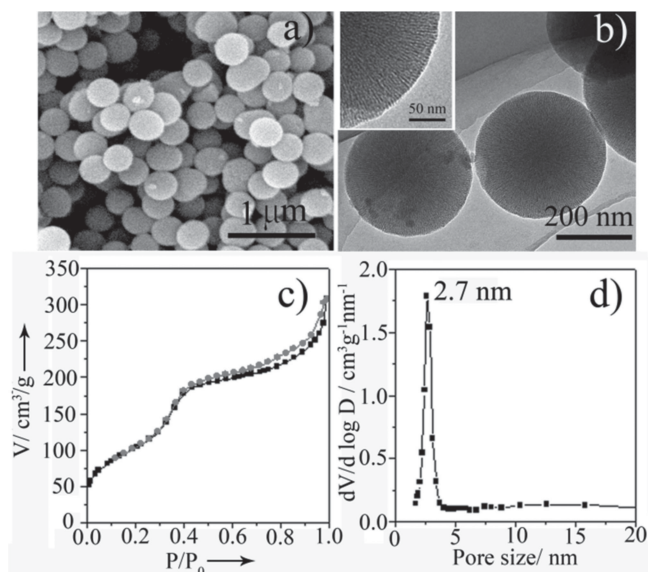


Figure 4. a) SEM image of as-made MSN-UV. b) TEM image, c) N_2 -sorption isotherms, and d) pore size distribution of MSNs after the removal of azobenzene-derived AZTMA templates. The inset in (b) is the high-resolution TEM image, revealing the radial pore channels.

photocontrollable disassembly between the organic surfactants and inorganic silica framework; this is expected to be a facile and fast method to remove the template from the mesostructured organic/inorganic composites.

The as-made MSN-UV exhibit uniform spherical morphology with a diameter of about 300 nm, as observed by scanning electron microscopy (SEM; **Figure 4a**). No obvious phase separations, such as aggregation of templates, were observed, owing to the electrostatic attraction between the cationic surfactant and the negatively charged silica oligomer in the alkaline aqueous solution. By comparison, the as-made MSN samples synthesized under natural light exhibit an irregular morphology, implying that UV light plays a key role in the formation of the uniform spherical morphology (SI: **Figure S3**). AZTMA molecules become the *cis* form under UV light irradiation, and they exhibit increased polarity and better solubility in water. The *cis* form of the template is discrete in the solution due to the improved solubility. In contrast, due to inferior solubility of the *trans* form in water, the aggregation of the template molecules lead to irregular morphology. After removal of the templates, MSNs with well-maintained spherical morphology and uniform size can be obtained, as revealed by transmission electron microscopy (TEM; **Figure 4b**). Interestingly, all the mesopore channels are found to be radial, and perpendicular to the surface of the spheres, indicating an open framework with accessible pores (**Figure 4b**, inset). The nitrogen adsorption–desorption isotherms of the MSNs exhibit type IV curves with a sharp capillary condensation step in the relative pressure range of 0.2–0.3 and an H_1 -type hysteresis loop, indicating that uniform channel-like mesopores are generated (**Figure 4c**). The pore size distribution curves calculated from the adsorption branch using the Barrett–Joyner–Halenda (BJH) model show a uniform pore size centered at 2.7 nm (**Figure 4d**). The

Brunauer–Emmett–Teller (BET) surface area and pore volume are 381 m^2/g and 0.48 cm^3/g , respectively.

The recycled surfactant can be reused as the template to synthesize new MSNs under the same conditions. The TEM image of the obtained MSNs shows spherical morphology with radial mesopore channels similar to the MSN-UV sample (SI: **Figure S4**), indicating that the recycled cationic template molecules were not destroyed during the solution extraction assisted by the UV light irradiation. The pore size, BET surface area, and pore volume were 2.7 nm, 360 m^2/g , and 0.47 cm^3/g , respectively, close to the results for the initial MSN-UV sample. It is worth noting that, although some previously reported amphiphilic molecules could be degraded under UV irradiation and give rise to ordered mesoporous materials, they could not be recycled and reused for the templating synthesis of mesoporous materials.^[14]

As a photosensitive moiety, the azobenzene group undergoes a reversible *trans*–*cis* isomerization under light irradiation, which is accompanied by spatial and polarity changes. By grafting the azobenzene group into a cationic surfactant, the obtained azobenzene-derived AZTMA surfactant retains its photoresponsive properties (SI: **Figure S1,S2**). Similar to the frequently used cationic surfactant, cetyltrimethylammonium bromide (CTAB), AZTMA surfactants can assemble into micelles during the synthesis of mesoporous silica because their concentration (4.3×10^{-3} mol/L) is much higher than their critical micelle concentration (3.5×10^{-5} mol/L; SI: **Figure S5**). The micelles can further co-assemble with silica oligomers into silica/surfactant nanocomposites with ordered mesostructures, where the AZTMAs form rodlike micelle in the silica matrix (**Figure 5**). After irradiation by UV light, the AZTMA molecules

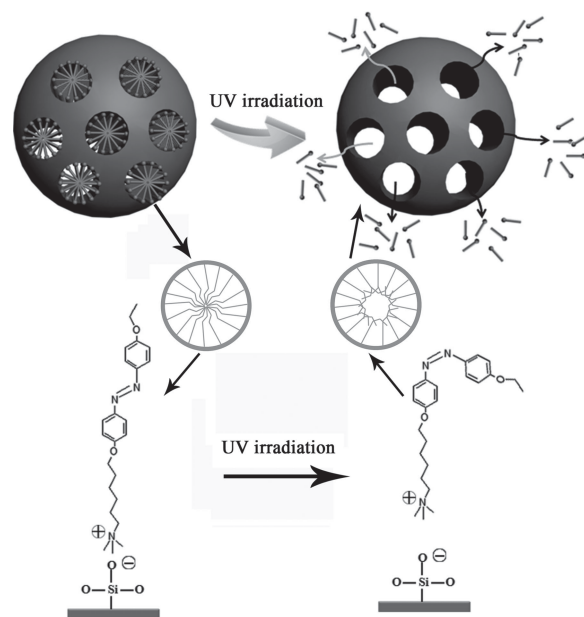


Figure 5. Schematic illustration of the release process of azobenzene-derived surfactant from the silica framework in water/ethanol ($v/v = 3:1$) at 60 °C under UV light. The azobenzene-derived surfactant transforms from the *trans* to the *cis* form under UV irradiation. The molecular polarity increases and molecular size decreases, which induces the releasing process.

attached to the silica surface via electrostatic interactions switch from the more stable *trans* to the *cis* form, resulting in spatial and polarity changes. The *cis* form is smaller and more polar, and it can rapidly escape from the silica framework and dissolve in the polar water/ethanol mixture. After releasing the AZTMA molecule, the radially aligned mesopores were produced. The release of AZTMA molecules via the facile photocontrolled extraction method is a mild and nondestructive process, and the recycled AZTMA can be used as a template to synthesize ordered MSNs repeatedly.

In summary, an azobenzene-derived cationic surfactant with photoresponsive properties is reported for use as a smart structure-directing agent in the synthesis of ordered MSNs. The surfactant confined in the silica matrix retains its photoresponsiveness and its tunable molecular size and polarity via *cis-trans* isomerism. After 1-h UV light irradiation, 80% of the surfactants in the silica framework can be released into mixed water/ethanol solvent and recycled from the solution. The recycled surfactant can be used again as the structure-directing agent in the templating synthesis of new MSNs. After removal of the AZTMA templates, the MSNs exhibit an open framework with accessible pores, radial mesopores, high surface area (~381 m²/g), uniform pore size (2.7 nm), and uniform diameter (~300 nm). The high surface area, unique mesoporous structure, and uniform spherical morphology of the MSNs makes them potential candidates for numerous applications such as adsorption, catalysis, and drug delivery.

Experimental Section

Synthesis of Azobenzene-Derived Surfactant: i) **4-Ethoxy-4'-hydroxy-azobenzene (a):** 4-Ethoxyaniline (5.0 g, 36.5 mmol) was dissolved in 0.2 M HCl (40 mL). The solution was cooled below 5 °C, and with vigorous stirring, 10 mL of an aqueous solution of sodium nitrite (2.52 g, 36.5 mmol) was slowly added. A mixture of sodium hydroxide (1.46 g, 36.5 mmol) and phenol (3.42 g, 36.45 mmol) in water (15 mL) was added dropwise to the resulting diazonium solution. The reaction solution was stirred for 3 h and then acidified to give pH ≈ 4. The precipitate was collected and purified via silica-gel column chromatography (petroleum ether:ethyl acetate = 1:3) (Yield: 85%). ¹H-NMR (500 MHz, CDCl₃, δ, ppm): 1.46 (t, 3H, CH₃), 4.09 (m, 2H, OCH₂), 5.41 (s, 1H, Ar-OH), 6.91–6.98 (d, 4H, Ar-H), 7.83–7.92 (d, 4H, Ar-H).

ii) **4-(6-Bromohexyloxy)-4'-ethoxy-azobenzene (b):** a (5.5 g, 22.2 mmol) was dissolved in *N,N*-dimethylformamide (DMF) (50 mL). Then potassium carbonate (3.10 g, 22.2 mmol) and 1,6-dibromohexane (7.1 mL, 5.0 mmol) were added to the solution. The reaction solution was refluxed with stirring for 24 h, and then cooled to room temperature. Water was added to the mixture to precipitate the crude product, which was then purified via silica-gel column chromatography (petroleum ether:dichloromethane = 2:1) (Yield: 52%). ¹H-NMR (500 MHz, CDCl₃, δ, ppm): 1.46–1.91 (m, 8H, CH₂), 4.05 (t, 2H, OCH₂), 4.10 (m, 2H, OCH₂), 3.65 (t, 3H, BrCH₂), 6.91–7.01 (d, 4H, Ar-H), 7.92–7.98 (d, 4H, Ar-H).

iii) **6-(4'-Ethoxy-4-azophenyl)hexyloxytrimethylammonium Bromide:** b (0.8 g, 2 mmol) was dissolved in a mixture of dichloromethane (10 mL) and ethanol (20 mL). Trimethylamine (30% in ethanol, 10 mL) was added to the mixture. The mixture was stirred for 96 h at room temperature. The product was collected by filtration and washed with dichloromethane and dried in vacuum at room temperature, and thus 6-(4'-ethoxy-4-azophenyl)hexyloxy-trimethyl ammonium bromide (AZTMA) was obtained. ¹H-NMR (500 MHz, D₂O, δ, ppm): 1.42 (t, 3H,

CH₃), 1.31–1.91 (m, 8H, CH₂), 4.01 (t, 2H, OCH₂), 4.10 (m, 2H, OCH₂), 3.05 (s, 9H, NCH₃), 3.36 (t, 2H, CH₂N), 6.95–7.11 (d, 4H, Ar-H), 7.78–7.88 (d, 4H, Ar-H).

Synthesis of the MSNs: AZTMA (50 mg) and sodium hydroxide (17 mg) were dissolved in deionized water (25 g) at 80 °C in an oil bath. After stirring for 30 min with UV irradiation, TEOS (0.19 g) was added to the solution, and the solution was irradiated with UV for an additional 10 min. After stirring for 2 h, the yellow precipitate was collected by centrifugation and washed with deionized water 3 times, followed by drying at 50 °C, and the obtained sample was denoted as the as-made MSN-UV. For comparison, a similar synthesis procedure under natural light was also conducted, and the obtained sample was denoted as the as-made MSN.

Removal of the Surfactant Templates: The surfactant templates were removed in a mixed solvent of water and ethanol under UV irradiation. Typically, as-made MSN-UV (20 mg) was added to the water (45 mL) and ethanol (15 mL) and refluxed at 60 °C. In order to detect the surfactant release amount, 1 mL of solution was withdrawn periodically and centrifuged to remove the silica nanoparticles for UV-vis spectroscopy. The total amount of surfactant was measured via UV-vis spectroscopy. The as-made MSN-UV was dissolved in an NaOH aqueous solution of the same volume as the extraction solvent. For comparison, the extraction was also conducted using the same conditions without the UV light.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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