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Facile synthesis of mesoporous silica by CO₂/N₂ switchable templates using a convenient compound†

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A facile synthesis method for the preparation of mesoporous silica with CO₂/N₂ switchable templates using a commercially available compound was described. Dodecyl dimethyl ammonium bicarbonate, which can be *in situ* formed by *N,N*-dimethyldodecylamine and CO₂, was used as a soft template, and 98% of the templates could be easily removed.

Mesoporous silica nanoparticles (MSNs) have attracted extensive attention in recent years and have been applied in various fields such as catalysis, adsorption and storage, controlled drug release, targeted drug delivery, and simultaneous diagnosis, owing to their low density, large void space, large specific surface area, and good biocompatibility.¹

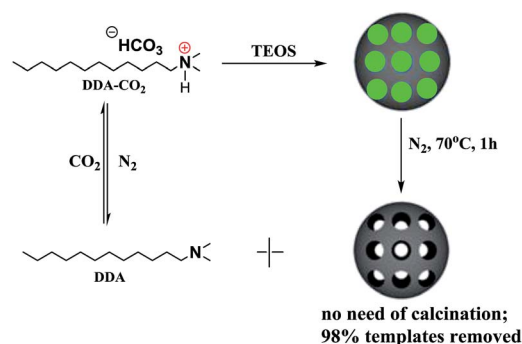
Soft templates are most commonly used in the preparation of various mesoporous silica materials. MSNs with spherical pores can always be obtained after the removal of the templates. The use of different removal methods certainly influence the characteristics of mesoporous materials. The most common method to remove the templates is calcination. The calcination process causes structure shrinkage or collapse, no recovery of the surfactants, and sacrifice of the surface hydroxyl groups.² Pinnavaia and co-workers have extensively studied alkylamines as silica templates;³ however, solvent extraction was needed to remove the templates. Although solvent extraction allows the recovery and reuse of expensive templates,⁴ a great amount of solvent is needed. Supercritical carbon dioxide extraction,⁵ ultrasonic extraction,⁶ microwave-assisted methods,⁷ and oxidative treatment, such as UV/H₂O₂ treatment⁸ and oxidation using perchlorates,⁹ have also been employed to remove the templates. Recently, Zhao *et al.* reported UV irradiation and solvent extraction to remove an azobenzene-derived surfactant template that was used to prepare MSNs, and 80% of the surfactant could be recycled.¹⁰ However, new strategies are still needed for the facile and non-destructive preparation of MSNs.

Jessop *et al.* have developed CO₂-switchable surfactants.¹¹ Compared to other triggers, such as light or pH, CO₂ is an

inexpensive, environmentally benign, and effective trigger for switchable surfactants. Hydrophobic long-chain alkyl amidines could be protonated and become water-soluble surfactants upon the addition of CO₂. Amidinium ion could then be deprotonated by removing CO₂ using N₂. However, most of the switchable surfactants need complex synthesis methods and are commercially unavailable.

Herein, we described a CO₂/N₂ switchable template for the synthesis of MSNs using a commercially available compound, *N,N*-dimethyldodecylamine (abbreviated as DDA), which can be *in situ* converted to amphiphilic dodecyl dimethyl ammonium bicarbonate (abbreviated as DDA-CO₂) by bubbling CO₂. The templates collapsed after the preparation of the MSNs and could be easily removed from the mesopores by bubbling N₂ at 70 °C and washing with water/acetone. Most of the template (98%) could be removed without calcination (Scheme 1).

In an initial experiment, DDA was used as a template for the preparation of MSNs. As shown in Fig. 1a, there was no peak in the X-ray diffraction (XRD) curve, which indicated that DDA was not a suitable template for MSNs. Pinnavaia *et al.* have reported that primary amines can be used as a silica template. However,



Scheme 1 The synthesis of MSNs using a CO₂/N₂ switchable template.

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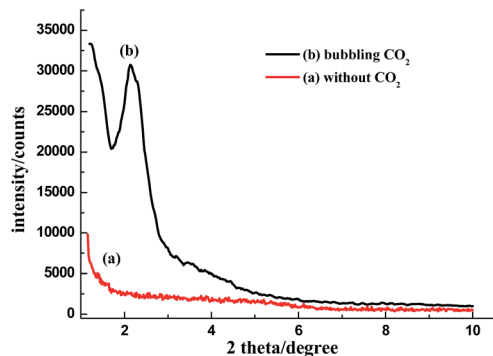


Fig. 1 The X-ray diffraction (XRD) curves obtained for the MSNs fabricated using *N,N*-dimethyldodecylamine aqueous solution: (a) without bubbling CO₂ and (b) after bubbling CO₂ (0.1 MPa).

contrary to primary amines, *N,N*-dimethyldodecylamine is too hydrophobic to form micelles in water.

DDA can be protonated to amphiphilic ammonium bicarbonate (DDA-CO₂, surface-active form) by bubbling CO₂, and the opaque aqueous solution of DDA quickly turns transparent. Bubbling the latter solution with N₂ or air converts the surface-active form to its uncharged surface-inactive form (Scheme 1). The interconversion can be monitored by measuring the conductivity of the aqueous solution (Fig. S1†). Therefore, the *in situ* formed amphiphilic DDA-CO₂ was used as a soft template for the preparation of MSNs.

As shown in Scheme 1, tetraethyl orthosilicate (TEOS) and Na₂EDTA were then added into the DDA aqueous solution in a bottle under stirring. The bottle was connected to a CO₂ cylinder (0.1 MPa). The reaction was carried out under static conditions at a certain temperature for 6 days. N₂ was then bubbled into the suspension at 70 °C for an hour when the reaction was completed. The product was ultrasonically washed 6 times using distilled water and acetone (5 minutes per washing step) at room temperature.

Silica was investigated using XRD. There was one strong and narrow peak at 2 degree in the XRD curve, as shown in Fig. 1b, which indicated the disordered mesopores in the silica product. The result is similar to that previously reported in the literature.^{2a,12} At neutral pH ~7, only disordered amorphous silica was obtained.

Thermogravimetric analysis (TGA) was performed to determine the template residue in the mesopores (Fig. 2). The weight loss can be divided into the following stages: the first stage is associated with the removal of physically adsorbed water (temperature below 150 °C), the second stage is associated with the decomposition of organic compounds (150 to 350 °C), and the third stage is associated with the dehydroxylation of the silicon hydroxyl groups (temperature higher than 350 °C).¹³ It was calculated that the template residue in the as-made silica without any treatment was 30% (Fig. 2a). Although the template residue was decreased to 22% after washing with acetone and water, the washing process did not efficiently remove the template from the mesopores (Fig. 2b). The template residue in silica was only 2% after bubbling N₂ and washing (Fig. 2d), which was close to the residue value obtained after calcination (~1%, Fig. 2e).

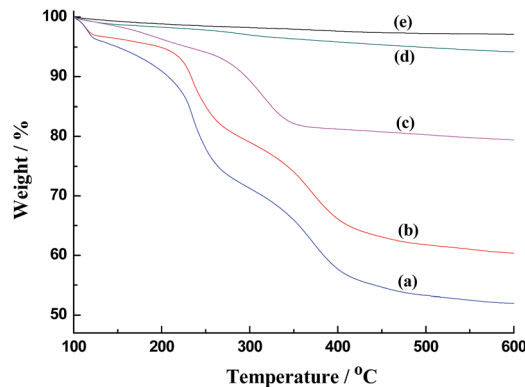


Fig. 2 Thermogravimetric analysis of the MSNs fabricated using the CO₂/N₂ switchable template (DDA-CO₂, 1.1 × 10⁻⁴ M). (a) The as-made sample without any treatment; (b) with washing 20 times with distilled water and acetone; (c) the as-made MSNs without Na₂EDTA and bubbling N₂ to the remove template, (d) with bubbling N₂ and washing with water/acetone, and (e) calcination.

The IR transmission spectra show a slight peak at 2900 cm⁻¹ corresponding to the stretching vibration band of -CH₃ and -CH₂, which indicates the efficient removal of the organic templates by calcination and bubbling N₂ (Fig. S2†). The relative intensity of the Si-OH bending bands around 960 cm⁻¹ was nearly the same as that observed for the as-made and bubbling N₂ samples, whereas a much weaker peak intensity was observed for the calcined sample. This result indicated that calcination would inevitably reduce the level of silanol groups.

Compare with the time-consuming process of calcination or solvent extraction, the entire process of bubbling N₂ and washing only required 1.5 h. There are three reasons that DDA-CO₂ template could be efficiently removed just by switching off the template upon bubbling N₂. The first reason is that DDA-CO₂ can be easily deprotonated into its surface-inactive compound (DDA). The hydrophilic DDA cannot form micelles as amphiphilic DDA-CO₂. Therefore, the micelles collapse after the DDA-CO₂ is deprotonated by bubbling N₂.^{11b} The second reason is that the negative charges on the wall of the mesopores in a neutral solution were much lower than those under basic conditions. The electrostatic attraction between the micelles and the wall of the mesopores is weaker under neutral conditions. The third reason is the addition of Na₂EDTA to the surfactant solution. Wong and Xiao have reported that EDTA²⁻ can co-assemble with the micelles of the cationic surfactant *via* electrostatic interactions to afford a low incorporation of the surfactant on the mesoporous,¹⁴ which facilitates the removal of the template. The TGA results show that the addition of Na₂EDTA decreases the template residue from 15% to 2% (Fig. 2c and d).

The recyclability of the template was also studied. The solution after bubbling N₂ and washing was obtained, evaporated, and then extracted with diethyl ether. The diethyl ether layer was evaporated and DDA was then obtained. Most of the DDA could be obtained (~97%) and could be reused at least 10 times although there was a small weight loss during the entire process (Fig. S3†).

Scanning electron microscopy (SEM) (Fig. 3a) and transmission electron microscopy (TEM) (Fig. 3b) were also



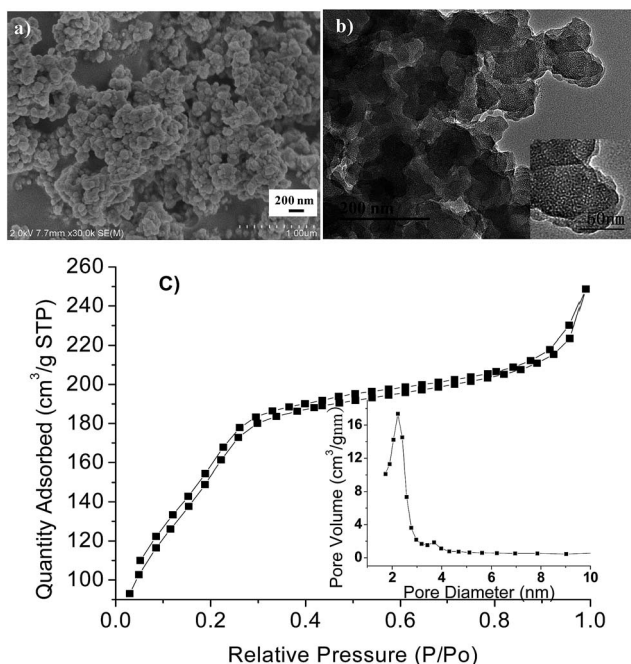


Fig. 3 (a) SEM image of the MSNs after removal of the template by bubbling N_2 , (b) TEM image, and (c) the N_2 adsorption isotherm and pore size distribution.

performed to observe the morphology and structure of the silica product. It was seen that the silica product comprised aggregated particles with sizes of 150 nm and had a clear mesoporous structure. Moreover, the N_2 adsorption isotherm shown in Fig. 3c was a type IV isotherm according to IUPAC nomenclature.¹⁵ The steep increase at a relative pressure of $0.9 < p/p_0 < 1.0$ indicated

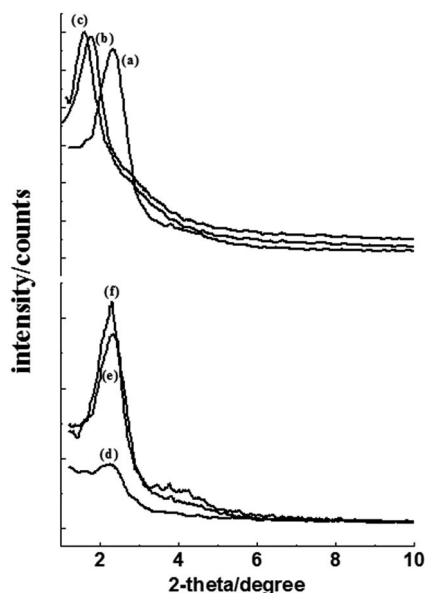


Fig. 4 (a)–(c): The XRD patterns of the silica products synthesized using tertiary amines with different carbon number in the alkyl chain (a: 12, b: 14, and c: 16). (d)–(f): The XRD patterns of the silica products synthesized using DDA- CO_2 at different temperatures (d: 10 °C, e: 20 °C, and f: 30 °C).

that the pores were formed by stacked particles. The pore size distribution curve indicated a uniform pore size of 2.3 nm. The Brunauer–Emmett–Teller (BET) surface area S_{BET} was $565.8 \text{ m}^2 \text{ g}^{-1}$ and pore volume at $P/P_0 = 0.99$ was $0.4 \text{ cm}^3 \text{ g}^{-1}$.

As the hydrocarbon chain length is an important factor that can affect the surface activity of a surfactant and the size of the micelles, tertiary amines with a carbon number of 12, 14, and 16 in the alkyl chain were used under the same conditions (Fig. 4a–c). The particle size decreased upon increasing the alkyl chain (Fig. S4†). In general, the longer the cation alkyl chain, the stronger the cation amphiphilicity. The tertiary amines with a longer alkyl chain have a higher surface activity, which can facilitate the surfactant assembly with the silica monomer, resulting in smaller particles.^{16,17} The 2-theta of peak in the XRD pattern decreased as the alkyl chain increased (Fig. 4a–c), which indicated larger cell spacing.

As shown in Fig. 4d–f, the intensity at higher temperature was stronger, which indicated better long-range order. In addition, the morphology at higher temperature was more uniform (Fig. S5†). DDA- CO_2 with a much lower surface activity at lower temperature could not effectively assemble with the silica monomer; thus, it was harder to form the uniform mesoporous particles.^{1b}

In conclusion, a new method to synthesize mesoporous silica using an inexpensive N_2/CO_2 switchable surfactant as the template was introduced, in which the template could be easily removed *via* bubbling N_2 .

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