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# Mesoporous silica with *Ia*3*d* cubic structure and good thermal stability†

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***Ia*3*d* cubic mesoporous silica with unusual thermal stability has been synthesized using cetyltrimethylammonium bromide (CTAB) and sugar surfactant dodecyl-β-D-maltoside (DM) as co-templates.**

Studies of mesoporous materials have been extensive research subjects during the last decade since the M41S family was developed by Kresge *et al.*[1] These materials are potential candidates for a variety of applications in the fields of catalysis, sorption, separation, drug delivery, optics, electronics, sensors, *etc.*[2] However, among the various types of mesophases[3] such as 2D-hexagonal *P*6*mm*, 3D-hexagonal $P6_3/mmc$, cubic *Pm*3*n* and cubic *Ia*3*d*, the *Ia*3*d* cubic mesostructure (typical of MCM-48)[1] has recently attracted the most attention due to its unique interpenetrating bicontinuous networks of channels, which are very useful for applications requiring easy molecular accessibility and fast molecular transport.[4] Several methods have been developed to synthesize *Ia*3*d* cubic mesoporous silica by using cationic alkylammonium surfactants,[1,5–7] mixed cationic/anionic surfactants,[8] mixed cationic/nonionic surfactants,[4] laboratory-synthesized block copolymers,[9] and commercially available nonionic triblock copolymers (*e.g.*, Pluronic 123) incorporating with sulfur-containing silane additives,[10] NaI salt,[11] or butanol,[12] as structure-directing agents.

It has been recognized that the stabilities (thermal, hydrothermal and mechanical) are crucial parameters for industrial applications of mesoporous materials.[2,13] The pure silica M41S materials prepared from tetraethylorthosilicate (TEOS) may collapse upon calcination at a temperature higher than 750 °C or degrade by treating in a hydrothermal condition due to the hydrolysis of the amorphous silicate wall.[13,14] Generally, mesoporous silicas (*e.g.*, SBA-15) templated by copolymer surfactants exhibit better thermal and hydrothermal stabilities than M41S due to the thicker pore walls.[14] Enormous efforts have been made to improve the stabilities of mesoporous materials either by adjusting the synthesis conditions or by post-synthesis modification. One of the most attractive examples is the MAS-5[15] type mesoporous aluminosilicate showing extraordinary thermal and hydrothermal stability due to the crystalline zeolite-structured pore wall. Incorporation of metal ions in the synthesis can also increase the stability of mesoporous silica.[2,13,16]

In this communication, *Ia*3*d* cubic mesoporous silica has been successfully synthesized using cationic CTAB and functional nonionic sugar surfactant DM as co-templates. More interestingly, the *Ia*3*d* cubic mesostructure is very stable even under calcination (carbonization) at 900 °C for 4 h in nitrogen due to the possible protection from carbon that is produced from the sugar head groups of the DM sugar surfactant.

In a typical synthesis, 0.392 g of CTAB (Aldrich) and 0.183 g of DM (Aldrich) was dissolved in 4.65 g of 1 mol $L^{-1}$ NaOH and 19.75 g of deionized $H_2O$. 1.87 g of TEOS (Aldrich) was then added, and the solution was stirred for 1.5 h at room temp. The molar ratio of TEOS:CTAB:DM:NaOH:$H_2O$ = 1:0.12:0.04:0.5:150. The mixture was then placed in a static autoclave at 100 °C for 20 h. The powder products were recovered by filtration, washed with deionized $H_2O$ and dried at 100 °C. The powders were calcined in air at 500 °C for 6 h to remove all the organic template, or calcined in nitrogen at 900 °C for 4 h to carbonize the sugar groups in DM molecules. Powder X-ray diffraction (XRD) patterns were recorded on a Siemens D500 diffractometer operating at 40 kV, 30 mA (Cu-K$\alpha$ radiation, $\lambda$ = 0.15406 nm). $N_2$ Adsorption–desorption isotherms were measured at 77 K on a micromeritics ASAP 2010 analyzer. The transmission electron microscopy (TEM) images were taken using a JEOL 2010 microscope operated at 120 kV.

Fig. 1 shows the XRD patterns of the as-synthesized powders (a), the powders calcined in air at 500 °C for 6 h (b) and the powders calcined in nitrogen at 900 °C for 4 h (c). All the patterns exhibit typical diffraction peaks indexed as (211), (220), (420) and (332) corresponding to the *Ia*3*d* space group.[4–12] The calculated cell parameters *a* are 9.72, 9.02 and 8.36 nm for the as-synthesized powders, the powders calcined in air at 500 °C for 6 h and the powders calcined in nitrogen at 900 °C for 4 h, respectively. The decrease of the cell parameters indicates structure contraction due to the increased condensation and/or degradation within the walls at high temperatures. However, the *Ia*3*d* cubic structure is preserved very well upon calcination. In particular, the materials exhibit highly ordered structures under calcination in nitrogen at 900 °C for 4 h, indicating the unusual thermal stability.

Fig. 2 shows the nitrogen adsoption–desorption isotherms and Barrett–Joyner–Halenda (BJH) pore size distributions (inset) of the powders calcined in air at 500 °C for 6 h (a) and calcined in nitrogen at 900 °C for 4 h (b), respectively. The isotherms exhibit sharp

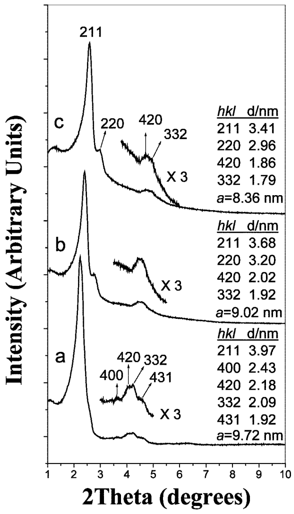

**Fig. 1** XRD Patterns of the as-synthesized powders (a), the powders calcined in air at 500 °C for 6 h (b) and the powders calcined in nitrogen at 900 °C for 4 h (c).

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† Electronic Supplementary Information (ESI) available: XRD and $N_2$ sorption isotherms of the as-synthesized powders calcined in air at 900 °C for 4 h, and the as-synthesized powders calcined in air at 500 °C for 6 h and then calcined in air or nitrogen at 900 °C for 4 h; XRD of the as-synthesized powders when the molar ratio of DM:CTAB is 1:2; EDS spectrum and TGA curve of the powders carbonized in nitrogen at 900 °C for 4 h; proposed formation mechanism of the *Ia*3*d* cubic mesostructure in nitrogen at high temperatures such as 900 °C. See http://www.rsc.org/suppdata/cc/b3/b316501a/

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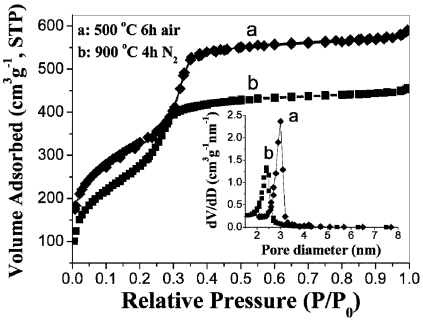

**Fig. 2** The nitrogen adsoption–desorption isotherms and BJH pore size distributions (inset) of the powders calcined in air at 500 °C for 6 h (a) and calcined in nitrogen at 900 °C for 4 h (b).

capillary condensation steps at relative pressures of 0.25–0.35 (a) and 0.2–0.3 (b) for the samples calcined at 500 and 900 °C, respectively, resulting in very narrow pore size distributions centered at 3.0 and 2.4 nm (see the inset of Fig. 2). The difference in the pore size may result from an increase in structure shrinkage at 900 °C compared to 500 °C and the carbon produced upon calcination at 900 °C in nitrogen. The sample calcined at 500 °C in air has a high surface area of 1196 $m^2\ g^{-1}$ and a large pore volume of 0.893 $cm^3\ g^{-1}$. Although the other sample was carbonized at 900 °C for 4 h, it still has a high surface area of 1034 $m^2\ g^{-1}$ and a pore volume of 0.694 $cm^3\ g^{-1}$.

Fig. 3 shows a representative TEM image of the powders after calcination in nitrogen at 900 °C for 4 h. The highly ordered mesostructure is typical for *Ia*3*d* cubic mesophase viewed along the [110] direction.[6,9,10] It also suggests the mesostructure is stable even after calcination at 900 °C. X-Ray energy dispersive spectroscopy (EDS) and thermogravimetric analysis (TGA) studies (see ESI†) confirmed the existence of carbon in the frameworks.

For comparison, when the as-synthesized powders were calcined in air at 900 °C for 4 h, the mesostructure is completely destroyed as evidenced from the XRD and nitrogen sorption studies (see ESI†). In addition, the *Ia*3*d* cubic mesostructure of the sample calcined in air at 500 °C for 6 h is not yet very stable, and when the sample was further calcined either in air or in $N_2$ at 900 °C for 4 h the mesostructure was degraded (see ESI†). For these two cases, most of the organic components were removed by calcining in air without forming carbon. Although the mesostructure is more stable in $N_2$ than that in air, it lost 70% of pore volume when the sample was further calcined in $N_2$ at 900 °C for 4 h after calcination in air at 500 °C for 6 h. Therefore, the sugar surfactant may play an important role on the thermal stability of the *Ia*3*d* cubic mesophase by producing carbon at 900 °C in nitrogen. As illustrated in Scheme 1 (see ESI†), the *Ia*3*d* cubic mesophase is formed by using cationic CTAB and nonionic DM as co-templates, which is similar to the pioneering work of Ryoo *et al*[4] who mixed cationic quaternary ammonium surfactant and neutral polyethylene oxide surfactant to form *Ia*3*d* cubic mesophases. In this work, the functional surfactant containing a sugar head group is employed with CTAB. After carbonization at high temperature in nitrogen, the sugar groups may be transformed into carbon on the silica pore surface, which largely contributes to the thermal stability of the *Ia*3*d* cubic mesostructure at high temperatures such as 900 °C.

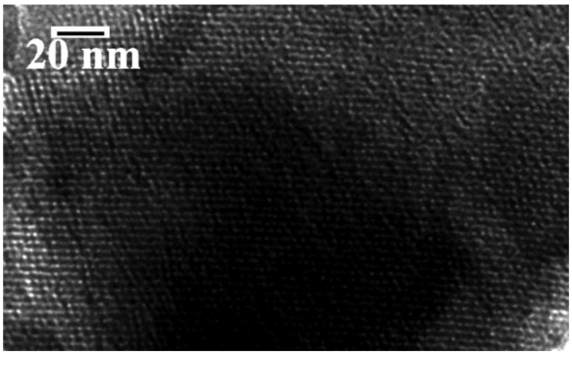

**Fig. 3** A representative TEM image of the powders after calcination in nitrogen at 900 °C for 4 h. (taken along the [110] direction)

When the molar ratio of DM:CTAB was increased from 1:3 to 1:2, the mesostructure transformed from a cubic structure to a hexagonal structure (see ESI†). Although we have not yet confirmed the carbon structure by TEM observation, as proposed in Scheme 1 (see ESI†) tubular carbon networks may be obtained by removing the silica frameworks using HF. Further studies are currently in progress to analyze this. Since the carbon precursor is introduced in the synthesis procedure by covalently attaching to the surfactant molecules, the strategy to get a tubelike carbon network should be more efficient than the two-step infiltration process reported recently.[17] Therefore, the significance of this work includes not only providing an efficient route to synthesize thermally stable *Ia*3*d* cubic mesostructured silica, and providing a possible facile pathway to fabricate the tubular carbon network, but also providing a possible strategy to modify or functionalize the pore surface of mesoporous silica by using surfactant containing functional head groups.[18]

In conclusion, a reproducible method is presented to synthesize *Ia*3*d* cubic mesostructured silica by using cationic quaternary ammonium surfactant CTAB and functional nonionic sugar surfactant DM as co-templates. The *Ia*3*d* cubic mesostructure has excellent thermal stability under calcination in nitrogen at 900 °C for 4 h.

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