

One-pot synthesis of net-like silica materials with double mesoporous structure

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A novel net-like silica material with double mesoporous structure had been synthesised by one-pot hydrothermal synthesis method. In the synthesis process, pluronic copolymer P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) and non-ionic surfactant OP-10 were used as templates and potassium fluoride (KF) was chosen as the additive. A study was carried out by small-angle X-ray scattering, scanning electron microscopy and transmission electron microscopy for the physical properties of the resultant products. It was found that the net-like silica materials exhibited a unique three-dimensional morphology with the addition of KF and preserved mesoporous structure. Moreover, the samples had double mesopores of 3.6 and 6.5 nm by the result of the nitrogen adsorption isotherm.

1. Introduction: Mesoporous silica materials have been focused in the past decades because of their potential applications in areas ranging from medicine, pharmaceuticals to materials science and electronics [1–7], due to their extremely high surface areas combined with large and uniform pore sizes. The pore size and morphology of these materials can be tailored during synthesis by variation of the reactant stoichiometry, the nature of the surfactant molecule, the auxiliary chemicals, the reaction conditions or by post-synthesis techniques to realise their functionalisation [8]. In this regard, the controlled morphologies of the mesoporous materials have attracted much significant research attention such as sphere, tubes, belts [9–12] etc. Particularly, three-dimensional (3D) morphology of mesoporous materials has been considered in recent years as promising nanomaterials for a wide range of applications. For example, Dennenwaldt *et al.* [13] have prepared an amorphous silica-based nanotubes formed 3D hyperbranched assemblies by template-free method and it shows a better resistance to extreme pH conditions than pure amorphous silica nanotubes. In addition, Zhao *et al.* have synthesised a kind of novel uniform monodispersed 3D dendritic mesoporous silica nanospheres for the first time and it shows excellent biocompatibility than inorganic mesoporous materials [14]. Chen *et al.* have fabricated hollow carved single-crystal mesoporous silica with mesomorphous polyelectrolyte-surfactant complexes as dynamic template and it possesses both the functions of crystal such as regularity and high diffusion efficiency of hierarchical pores [15].

In this work, we have successfully prepared 3D net-like silica materials with double mesoporous structure by a one-pot hydrothermal synthesis method, using pluronic copolymer P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) and non-ionic surfactants OP-10 as the templates and potassium fluoride (KF) as the additive. XRD, scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen (N_2) adsorption/desorption were performed to characterise the textural properties of the net-like mesoporous silica.

2. Experimental

2.1. Material synthesis: Net-like molecular sieves with double mesoporous were prepared using tetraethyl orthosilicate (TEOS) as silica source, pluronic copolymer P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) and surfactant OP-10 (average $M_n=603$, 98%) as the mesostructure-directing agents and KF as the additive.

Net-like molecular sieves with double mesoporous were hydrothermally synthesised as follows. In a typical synthesis, 1.0 g of P123 was dissolved in 30 ml of 2 mol/l HCl and the solution was

marked as A. About 0.055 g of OP-10 was dissolved in 7.5 ml of deionised water and the solution was marked as B. After that, A and B were mixed at 37°C under vigorous stirring for 1.5 h. About 2.43 ml of TEOS and 0.01 g of KF were then added to the obtained mixture under stirring for 6 h. The resultant mixture (OP-10:P123:KF:SiO₂:HCl: H₂O = 0.0085:0.017:0.01:1:5.8:197) was sealed in one teflon-lined autoclave and aged statically at 100°C for 24 h. The product was filtered, washed with water and calcined at 550°C for 6 h. The obtained sample was denoted as NDM.

To investigate the influence of KF, salt-free synthesis of the sample was also performed by the same procedure as a comparison, but in the absence of KF, and the obtained sample was denoted as DM.

2.2. Characterisation: Small-angle X-ray scattering (SAXS) data were collected on an SAXS pace small-angle SAXS system using copper target Ka-ray at 40 kV and 50 mA. SEM images were performed on a scanning electron microscopy (S-4300; Hitachi) with an acceleration voltage of 20 kV. The TEM images were characterised by a Tecnai G2 F30 TWIN instrument with an accelerating voltage of 200 kV. The TEM samples were suspended in ethanol under ultrasonic treatment for 100 min at room temperature and supported on a carbon-coated copper grid. N₂ adsorption–desorption isotherms were collected in a Quantachrome NOVA2000e gas adsorption analyser at 77 K after degassing the samples at 573 K for 180 min. Pore size distributions were determined using the Barrett–Joyner–Halenda method from the adsorption branch. The surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The mesopore surface area and pore volume were calculated by *t*-plot method.

3. Results and discussion: SAXS patterns of DM and NDM are shown in Fig. 1. The DM exhibits three well-defined peaks in the range of 0.5°–5° (Fig. 1a) that can be indexed as (100), (110) and (200) Bragg reflections, and the pattern can be assigned to an ordered structure of 2D hexagonal *p6mm* symmetry [16]. The NDM sample synthesised with the addition of KF shows only one weak diffraction peak (1 0 0) around $2\theta=0.88^\circ$ (Fig. 1b). It indicates that ordered mesostructure is preserved.

The SEM and TEM images of the DM and NDM samples are shown in Fig. 2. The as-synthesised DM sample consists of rod-like morphology with a diameter of 2–5 μm (Fig. 2a). Further TEM characterisation (Fig. 2c) evidences ordered pore structures,

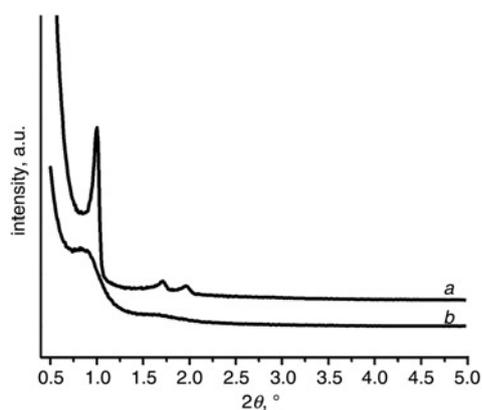


Fig. 1 SAXS patterns of the samples
a DM
b NDM

which is in good accordance with the SAXS observation. However, with the addition of KF the morphology of NDM sample is completely different as shown in Fig. 2*b*. They consist of 3D non-woven networks of b-oriented bundles. The bundles grow on and connect with each other to form net-like macroscopic structure with length of about 150–250 nm and diameter of around 45 nm. The interconnections between bundles give rise to irregular meshes under tension and the diameters of meshes span are 200–400 nm. TEM examination (Fig. 2*d*) indicates that the mesopores of the NDM could be observed and exhibit same alignment, but arrangement order is lower. Moreover, it further confirms the net-like morphology with the mesh. This result indicates that the addition of KF does not significantly disturb the interior texture and pore structure of NDM is remained, but the morphology of NDM has been changed. The possible formation process for the NDM samples under hydrothermal condition can be expressed as follows. In the present synthesis system, when KF is dissolved in water, it can be hydrolysed to the K^+ cation, OH^- anion and HF molecule.

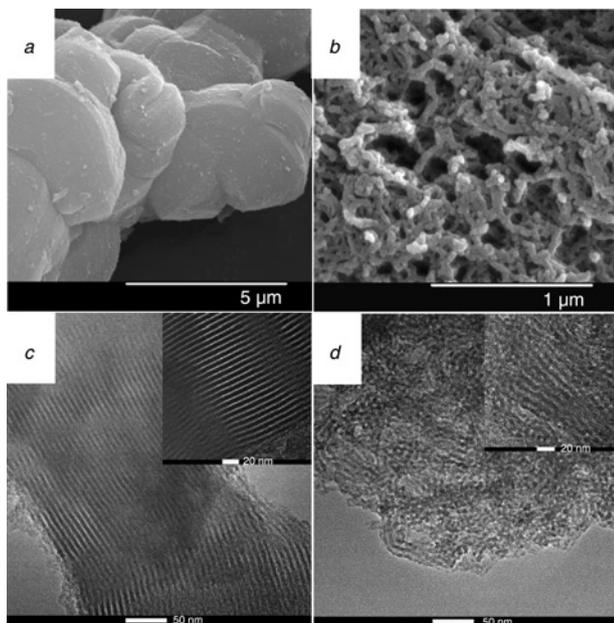


Fig. 2 SEM and TEM images of the samples and their high-resolution TEM image in the upper-right inset
a, b SEM
c, d TEM
a, c DM
b, d NDM

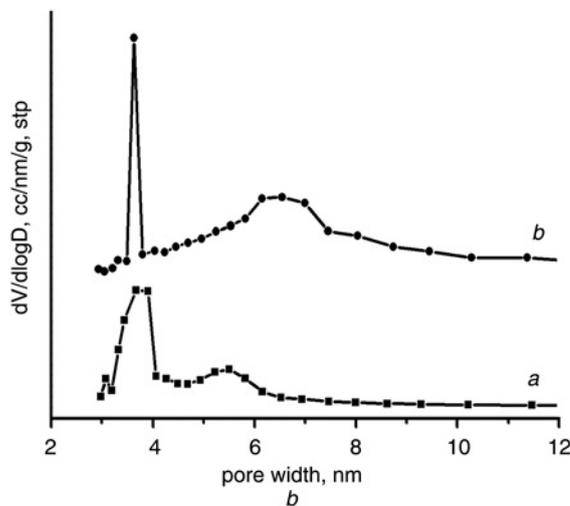
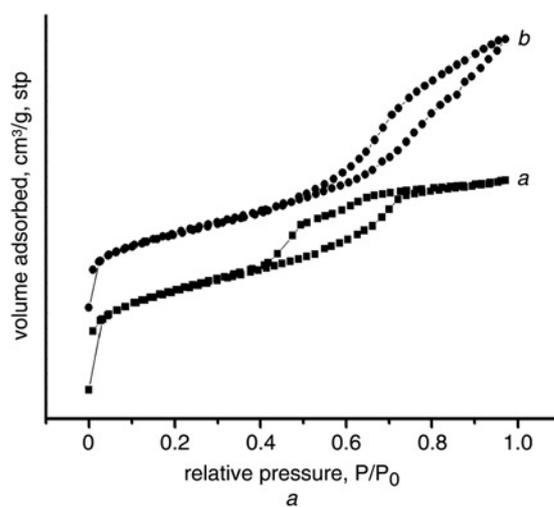


Fig. 3 N_2 adsorption/desorption isotherms and corresponding pore size distributions
a DM
b NDM (the isotherms *b* for sample were vertically shifted by $130 \text{ cm}^3 \text{ g}^{-1}$ STP for clarity)

This process raises the concentrations of the structure-breaking cation and OH^- anion, thus markedly reducing the particle sizes of SiO_2 [17]. The particles connect with each other to form bundles and further expand meshes.

Fig. 3 shows the N_2 adsorption/desorption isotherms of the DM and NDM. All the isotherms of the samples are of type IV with a clear hysteresis loop, indicating mesoporous character according to the International Union of Pure and Applied Chemistry classification. This can also be confirmed by the TEM images. For DM, the measured BET surface area and pore volume are $574.3 \text{ m}^2/\text{g}$ and $0.41 \text{ cm}^3/\text{g}$, while the mean pore size is 3.80 and 5.46 nm, respectively. The NDM displays a surface area of $467.6 \text{ m}^2/\text{g}$ and a pore volume of $0.65 \text{ cm}^3/\text{g}$ and the pore size distribution is narrow with an average pore diameter of 3.6 and 6.50 nm. The above results indicate that the addition of OP-10 affects the nanostructure of mesoporous silica. It should be mentioned that typical SBA-15 will be formed without the addition of OP-10 and KF [16].

4. Conclusion: In summary, a new net-like silica material with double mesoporous structure was successfully synthesised by one-pot hydrothermal synthesis method. The characterisation results of XRD, SEM, TEM and N_2 adsorption indicated the presence of double mesoporous system in the silica materials.

The net-like silica material showed 3D morphology with the addition of KF.

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6 References

- [1] Shi C., Deng S., Wang J., *ET AL.*: 'Hierarchically mesoporous silica single-crystalline nanorods with three dimensional cubic Fm-3m mesostructure', *J. Mater. Chem. A*, 2013, **1**, pp. 14555–14561
- [2] Wan Y., Zhao D.: 'On the controllable soft-templating approach to mesoporous silicates', *Chem. Rev.*, 2007, **107**, pp. 2821–2860
- [3] Lai C.Y., Trewyn B.G., Jęfinija D.M., *ET AL.*: 'A mesoporous silica nanosphere-based carrier system with chemically removable CdS nanoparticle caps for stimuli-responsive controlled release of neurotransmitters and drug molecules', *J. Am. Chem. Soc.*, 2003, **125**, pp. 4451–4459
- [4] Mamak M., Coombs N., Ozin G.: 'Self-assembling solid oxide fuel cell materials: mesoporous yttria-zirconia and metal-yttria-zirconia solid solutions', *J. Am. Chem. Soc.*, 2000, **122**, pp. 8932–8939
- [5] Gañan J., Silva M., Morante-Zarero S., *ET AL.*: 'Application of hybrid mesoporous silica for extraction of hormones in milk by matrix solid phase dispersion', *Mater. Lett.*, 2014, **119**, pp. 56–59
- [6] Hasanzadeh M., Shadjou N., Guardia M., *ET AL.*: 'Mesoporous silica-based materials for use in biosensors', *TRAC-Trends Anal. Chem.*, 2012, **33**, pp. 117–129
- [7] Tang F., Li L., Chen D.: 'Mesoporous silica nanoparticles: synthesis, biocompatibility and drug delivery', *Adv. Mater.*, 2012, **24**, pp. 1504–1534
- [8] ALOthman Z.A.: 'A review: fundamental aspects of silicate mesoporous materials', *Materials*, 2012, **5**, pp. 2874–2902
- [9] Li Y., Li B., Yan Z., *ET AL.*: 'Preparation of chiral mesoporous silica nanotubes and nanoribbons using a dual-templating approach', *Chem. Mater.*, 2013, **25**, pp. 307–312
- [10] Dou J., Zeng H.C.: 'Targeted synthesis of silicomolybdic acid (keggin acid) inside mesoporous silica hollow spheres for friedel-crafts alkylation', *J. Am. Chem. Soc.*, 2012, **134**, pp. 16235–16246
- [11] Ma Y., Guan J., Wu S., *ET AL.*: 'Synthesis and characterization of belt-like silicalite-1 nanocrystals with mesoporous structure', *Mater. Lett.*, 2010, **64**, pp. 2523–2525
- [12] Wang H., Van der Voort P., Qu H., *ET AL.*: 'A simple room-temperature synthesis of mesoporous silica rods with tunable size and porosity', *J. Nanoparticle Res.*, 2013, **15**, pp. 1501–1508
- [13] Dennenwaldt T., Sedlmaier S.J., Binek A., *ET AL.*: 'Bonding behavior and chemical stability of silica-based nanotubes and their 3D assembly', *J. Phys. Chem. C*, 2014, **118**, pp. 8416–8423
- [14] Shen D., Yang J., Li X., *ET AL.*: 'Biphase stratification approach to three-dimensional dendritic biodegradable mesoporous silica nanospheres', *Nano Lett.*, 2014, **14**, pp. 923–932
- [15] Wang J., Zhou H., Sun P., *ET AL.*: 'Hollow carved single-crystal mesoporous silica templated by mesomorphous polyelectrolyte-surfactant complexes', *Chem. Mater.*, 2010, **22**, pp. 3829–3831
- [16] Zhao D., Huo Q., Feng J., *ET AL.*: 'Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures', *J. Am. Chem. Soc.*, 1998, **120**, pp. 6024–6036
- [17] Ke J.A., Wang I.: 'Elucidation of the role of potassium fluoride in the chemical and physical nature of ZSM-5 zeolite', *Mater. Chem. Phys.*, 2001, **68**, pp. 157–165