

Fabrication of lotus-leaf-like nanoporous silica flakes with controlled thickness†

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Lotus-leaf-like silica flakes with a three-dimensionally (3D) connected nanoporous structure and controllable thickness have been facilely synthesized; the flakes produced exhibited superior performance in adsorbing enzymes to their microspheric analogues.

Since the first synthesis of ordered mesoporous silica in 1992,^{1a} considerable effort has been devoted to adapting such materials to the desired applications through controlling pore size and structure.¹ However, more and more evidence has recently revealed that the morphology of mesoporous silica could greatly affect its performance, especially in those processes involving diffusion and adsorption.² Moreover, the studies concerning the morphology of mesoporous silica would also shed light on the morphogenesis of biosilica owing to their similarities.³ Therefore, the rational design of the morphology of mesoporous silica has lately aroused much attention. One important piece of work in this aspect was the restriction of one or more dimensions of mesoporous silica on the submicrometer or nanometer scales,^{4–6} because the resultant short pore channels and more exposed pore-openings could facilitate mass transfer in adsorption and catalysis.⁴ Nanoparticles⁵ and nanofibers⁶ of mesoporous silica have already been fabricated through various methods.

Porous nanoflakes possess similar advantages to porous nanoparticles/nanofibers, and provide another geometric form of building block for the fabrication of nanodevices and composite materials.⁷ Besides, their manipulation and recovery during the preparation and application processes are more facile than those of nanoparticles. Herein, lotus-leaf-like nanoporous silica flakes were fabricated in a homogeneous ethanol/water solution of 1-alkylamine, and the thickness of the silica flakes could be finely controlled from nanometer to submicrometer scale. Different from the two-dimensional mesoporous lamellar silica,⁸ the nanopores of the silica flakes in this work were 3D-connected, leading to abundant pore-openings on the flake surface for the diffusion of guest molecules. In combination with the inherent characteristics of porous nanomaterials (*e.g.* large external surface area and short diffusion path), the nanoporous silica flakes exhibited advantages such as higher rate and larger quantity in adsorbing enzymes over their microspheric analogues.

The typical synthesis process of the nanoporous silica flakes was as follows: 0.6 g of 1-hexadecylamine (2.5 mmol) was dissolved in

60 mL of ethanol through ultrasonification. Then 60 mL of distilled water and 2.0 g of ammonia solution (25 wt%) were added and the solution was stirred until the 1-hexadecylamine was redissolved. Afterwards 2.4 g of tetraethylorthosilicate (TEOS) (11.5 mmol) was added and the solution was kept stirring until the TEOS was homogeneously dispersed. After being statically placed at ambient temperature (*ca.* 25 °C) overnight, the product was recovered by filtration, washing with ethanol twice and drying at 90 °C overnight. The remaining surfactant in the product was removed by calcination in air at 600 °C for 4 h. Nanoporous silica microspheres (see ESI†) were synthesized according to the literature⁹ for comparison with the silica flakes. The experiment of adsorbing enzymes (including ribonuclease A, cytochrome c and lysozyme) was carried out as follows: 2.0 mg of nanoporous silica was dispersed in 1.0 mL of 1.0 mg mL⁻¹ enzyme solution (buffered at pH = 7.0) and kept in a water bath at 37 °C. The adsorbed amount of enzyme was obtained through measuring the UV absorbency at $\lambda = 280$ nm of enzyme solution before and after adsorption.

Figs. 1a and 1b show the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the nanoporous silica flakes obtained under the aforementioned typical synthesis conditions. It is clear that the product possesses typical lotus-leaf-like morphology with rippling fringes. The diameter and thickness of the silica flakes are *ca.* 3 μ m and 200 nm, respectively. The nanopores of the silica flakes are 3D-connected and extend across the whole flake (see ESI†). Only one diffraction peak is

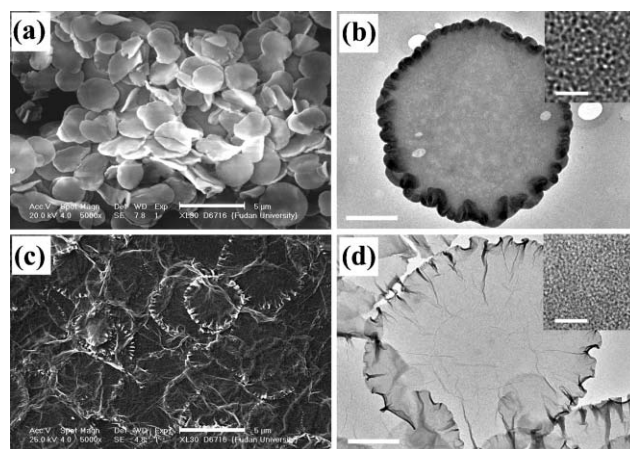


Fig. 1 SEM (a, c) and TEM (b, d) images of nanoporous silica flakes obtained with different concentrations of TEOS in the typical synthesis system: (a, b) 2.1 wt% and (c, d) 0.27 wt%, respectively. The scale bars in SEM, TEM and the inset of TEM are 5 μ m, 1 μ m and 20 nm, respectively.

† Electronic supplementary information (ESI) available: SEM/TEM images and nitrogen sorption isotherms of nanoporous silica. See <http://www.rsc.org/suppdata/cc/b4/b418006b/>

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observed in the small-angle X-ray diffraction (XRD) pattern of the product (Fig. 2a). According to the N₂ sorption isotherms (Fig. 2b), the BET surface area and pore size of the product are 581 m² g⁻¹ and 2.4 nm, respectively.

It was found that silica flakes could only be obtained in a relatively narrow range of ethanol/water ratio (E/W). As shown in Fig. 3a, when E/W was over 1.4 (vol : vol), the morphology of product gradually transformed from flake to sphere with increasing E/W. Accompanied with the morphological transformation, the pore size of the product appreciably decreased owing to the shrinking effect of alcohol,¹⁰ though the 3D-connected nanoporous structure was still retained. However, when E/W was further raised to 3.0, only nonporous silica nanoparticles were obtained, probably because the too strong shrinking effect of ethanol at such a high E/W hindered the formation of micelles. Conversely, if E/W was below 0.9, both 1-hexadecylamine and TEOS could not be well dissolved and a product with irregular morphology was obtained.

The thickness of the silica flakes could be controlled from nanometer to submicrometer scale by simply adjusting the concentration of TEOS in the typical synthesis system (see the line symbolized with '▲' in Fig. 3b). The thickness of the flakes decreased with decreasing concentration of TEOS and ultrathin silica flakes with thicknesses below 100 nm (Figs. 1c and 1d) could be obtained when the concentration of TEOS was lower than 0.54 wt%. However, under these circumstances, the pore size of the silica flakes was smaller than those obtained with typical concentrations (*i.e.* 2.1 wt%) of TEOS (insets of Figs. 1d and 1b), probably because a deficiency in the silica source led to a low-density silica framework that tended to shrink during drying and calcination. Conversely, when the concentration of TEOS was increased to 3.2 wt%, silica flakes as thick as 400 nm were obtained. On the other hand, if the concentration of TEOS was fixed, the higher the concentration of 1-hexadecylamine in the synthesis system, the thinner the silica flakes obtained (see the line symbolized with '●' in Fig. 3b).

Ribonuclease A (RNase A), which could enter the nanopores of the silica product,¹¹ was selected as the model guest molecule to validate that the flake morphology is more advantageous for the mass transfer in adsorption than sphere. As we expected (Fig. 4), the silica flakes (thickness ≈ 200 nm, diameter ≈ 3 μm) possessed a much higher initial adsorbing rate than their microspherical analogues (diameter ≈ 1 μm). For example, the adsorbed amount of RNase A in the silica flakes reached 120 mg g⁻¹ in 4 h, while it

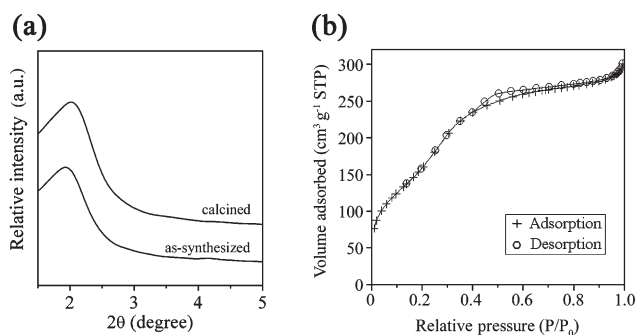


Fig. 2 XRD patterns (a) and N₂ sorption isotherms (b) of nanoporous silica flakes.

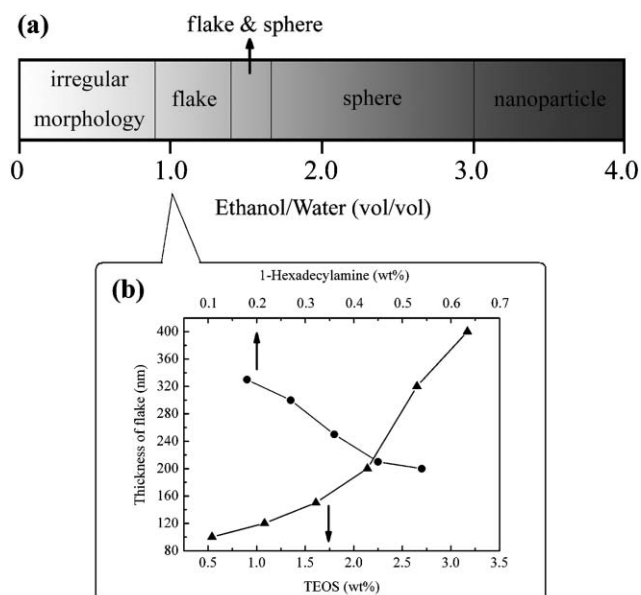


Fig. 3 (a) Schematic illustration of the effect of ethanol/water ratio on the product morphology. The amount of 1-hexadecylamine, the amount of TEOS and the total volume of ethanol and water were fixed at 0.6 g, 2.4 g and 120 mL, respectively. (b) Relationship between the thickness of the flake and the concentration of TEOS or 1-hexadecylamine in the mixed solvent of 60 mL ethanol and 60 mL water. The amount of 1-hexadecylamine was fixed at 0.6 g for the solid triangular symbols. The amount of TEOS was fixed at 2.4 g for the solid circular symbols. The thickness of the flake was the average value obtained through measuring on the SEM image.

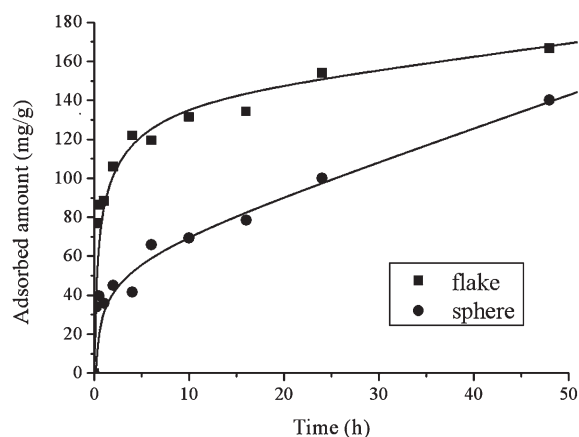


Fig. 4 Adsorbed amount of RNase A in nanoporous silica flakes and spheres as a function of time.

took the silica spheres more than 40 h to reach the same value, indicating that the short nanopore channels and rich pore-openings of the silica flakes greatly facilitated the diffusion and adsorption of guest molecules. Moreover, the equilibrium adsorbed amount of RNase A in the silica flakes was 180 mg g⁻¹, which was also higher than that of the spheres (145 mg g⁻¹). Additionally, the larger external surface of the silica flakes would also benefit the adsorption of enzymes whose size is larger than that of the nanopores. For example, the equilibrium adsorbed amount of cytochrome c or lysozyme on the silica flakes was about

twice as large as that on the spheres, which was approximately consistent with the ratio of theoretical external specific surface area between these two silica samples¹² (see ESI†).

In conclusion, nanoporous silica flakes have been synthesized through a facile method. Their thickness could be well controlled through adjusting the composition of the synthesis system. The silica flakes exhibited superior performance in adsorbing biomolecules to their microspheric analogues and could also be expected to show advantages when applied as a support for catalysts.

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Notes and references

- (a) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710; (b) P. T. Tanev and T. J. Pinnavaia, *Science*, 1995, **267**, 865; (c) D. Y. Zhao, J. L. Feng, Q. S. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548.
- J. Fan, J. Lei, L. M. Wang, C. Z. Yu, B. Tu and D. Y. Zhao, *Chem. Commun.*, 2003, 2140.
- H. Yang, N. Coombs and G. A. Ozin, *Nature*, 1997, **386**, 692; J. N. Cha, G. D. Stucky, D. E. Morse and T. J. Deming, *Nature*, 2000, **403**, 289; B. Wang, W. Shan, Y. H. Zhang, J. C. Xia, W. L. Yang, Z. Gao and Y. Tang, *Adv. Mater.*, 2005, DOI: 10.1002/adma. 200401574.
- H. Zhang, J. M. Sun, D. Ma, X. H. Bao, A. Klein-Hoffmann, G. Weinberg, D. S. Su and R. Schlögl, *J. Am. Chem. Soc.*, 2004, **126**, 7440.
- R. I. Nooney, D. Thirunavukkarasu, Y. M. Chen, R. Josephs and A. E. Ostafin, *Chem. Mater.*, 2002, **14**, 4721; K. Suzuki, K. Ikari and H. Imai, *J. Am. Chem. Soc.*, 2004, **126**, 462; S. Sadasivan, C. E. Fowler, D. Khushalani and S. Mann, *Angew. Chem., Int. Ed.*, 2002, **41**, 2151.
- J. F. Wang, J. P. Zhang, B. Y. Asoo and G. D. Stucky, *J. Am. Chem. Soc.*, 2003, **125**, 13966.
- L. Z. Wang, Y. Ebina, K. Takada and T. Sasaki, *J. Phys. Chem. B*, 2004, **108**, 4283.
- J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834; I. Díaz, J. Pérez-Pariente and O. Terasaki, *J. Mater. Chem.*, 2004, **14**, 48; P. T. Tanev, Y. Liang and T. J. Pinnavaia, *J. Am. Chem. Soc.*, 1997, **119**, 8616.
- M. Grün, G. Büchel, D. Kumar, K. Schumacher, B. Bidlingmaier and K. K. Unger, *Stud. Surf. Sci. Catal.*, 2000, **128**, 155.
- F. Di Renzo, F. Testa, J. D. Chen, H. Cambon, A. Galarneau, D. Plee and F. Fajula, *Microporous Mesoporous Mater.*, 1999, **28**, 437.
- R. Ravindra, S. Zhao, H. Gies and R. Winter, *J. Am. Chem. Soc.*, 2004, **126**, 12224.
- The ratio of the external surface area of the silica flakes and spheres was estimated by supposing that the densities of the two samples were equal.