Chinese Chemical Letters Vol. 14, No. 11, pp 1175 – 1178, 2003 1175
http://www.imm.ac.cn/journal/ccl.html

"Noodle-like" Mesoporous Silica Templated by Polyelectrolyte/Surfactant Complex

Cheng TAO[1], Jian Guo HUANG[2], Jun Bai LI[1,*]

[1]International Joint Lab, The Center for Molecular Science, Institute of Chemistry
Chinese Academy of Sciences, Beijing 100080
[2]Frontier Research System, RIKEN, Wako, Saitama 351-0198, Japan

Abstract: "Noodle-like" mesoporous silica with a diameter of about 180 nm and a length of *ca.* 10 μm was prepared through sol-gel process by using poly(sodium 4-styrenesulfonate) (PSS)/ cetyltrimethylammonium bromide (CTAB) complex as template. Parallel oriented regular mesopores with a diameter of around 2−4 nm are distributed along the wall of the particles, while the "worm-like" disordered mesopores can be found in the fringe part. This approach provides a new series of templates and a novel route to prepare inorganic mesoporous materials with special morphology.

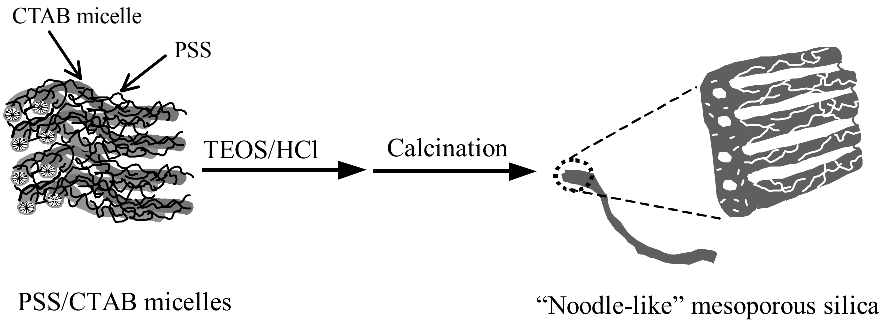
Keywords: Mesoporous, polyelectrolyte, surfactant, template.

Mesoporous materials have been widely investigated since the discovery of M41S family of mesoporous molecular sieves [1, 2]. Various organic templates, such as microemulsion [3], block copolymers [4, 5], latex particles [6], colloidal crystals [7], spongelike polymer gels [8] and bacterial superstructures [9], were employed for pores formation, aiming to control of the pore structures. Polyelectrolyte (PE) and oppositely charged surfactant assemblies can easily form stable stoichiometric complexes in aqueous solution [10], which could be used as templates for synthesis of mesoporous materials with novel structures. The synthesis of mesoporous materials by the templates of the polyelectrolyte/surfactant complex has not been reported. In our study, "noodle-like" mesoporous silica with different oriented mesopores was prepared by using the complex of an anionic polyelectrolyte [poly(sodium 4-styrenesulfonate), Mw=70,000, PSS] and a cationic surfactant (cetyltrimethylammonium bromide, CTAB) as template.

The synthetic process is described in **Figure 1**. PSS/CTAB micelle assemblies were firstly formed in acid aqueous solution *via* electrostatic interaction. The PSS chains were adsorbed onto/between the CTAB micelles. Polymer molecules inserted in surfactant micelles leads to a so-called polyelectrolyte stabilized phase at micrometer level [11], which forms a well-defined, long-range organized self-assembled structure. Tetraethyl orthosilicate (TEOS) was thereafter added as silica source. Silica frameworks and "noodle-like" morphology were then formed due to the hydrolysis and

* E-mail: jbli@infoc3.icas.ac.cn

Figure 1 Schematic illustration of the formation of "noodle-like" mesoporous silica particles (the PSS/CTAB templates were removed by calcination to yield mesopores)

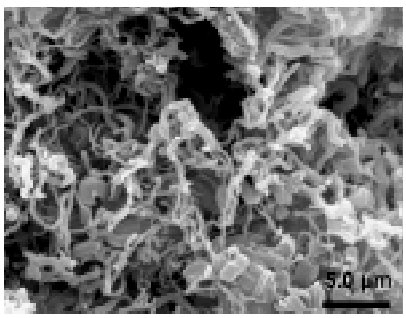


condensation of TEOS. The original PSS/CTAB templates were removed by calcination to yield mesopores. Finally, two kinds of mesopores were obtained from the contributions of CTAB micelles and PSS molecules, respectively.

A typical synthetic process is that PSS was dissolved in hydrochloric acid aqueous solution and then CTAB was added with vigorous stirring. After one hour stirring at ambient temperature, TEOS was added dropwise. The final reactant mole ratios were: 1 TEOS : 130 H_2O : 10.4 HCl : 1.143×10^{-4} PSS : 0.13 CTAB. The resulted reaction mixture was again vigorously stirred for 24 hours at 85 °C. The white precipitate yielded was filtered and washed thoroughly with deionized water, followed by drying with air. Template was removed by calcination in air at 550 °C for three hours.

Figure 2 shows the SEM image of the calcined sample, from which randomly accumulated "noodle-like" particles can be clearly seen. The diameter of silica particles is in range of about 180 nm, and in length *ca.* 10 μm. The silica morphology varied with the amount of PSS in the reaction mixture, and inner structures could not be formed with a comparatively high PSS concentration, which means that proper PSS/CTAB molar

Figure 2 SEM image of the calcined silica, showing "noodle-like" morphology



ratio plays a key role in the "noodle-like" particles' structure formation. It was also found that the reaction temperature and ageing time did not make obvious differences in the silica morphologies. The adding sequence of PSS and CTAB also applied little influence. These experimental features reflect that the PSS/CTAB complex templates have been assembled by the electrostatic interaction, and the hydrolysis and condensation of TEOS occurred at the initial stage of sol-gel process.

TEM images of the silica particles are shown in **Figure 3**. The low magnification image (**Figure 3a**) distinctly displays the "noodle-like" morphology, which is similar to the SEM images. The regular mesoporosity in the silica "noodle-like" particles can be obviously observed from **Figure 3b**. The pore has a diameter of around 2−4 nm and the pore shape is regularly oriented to the long axis. However, a randomly distributed "worm-like" mesopores with a size of 2 − 4 nm were formed in the particles fringe part, which may be templated by PSS. Therefore, the prepared mesoporous silica is in the form of "noodle-like", and two different kinds of mesopores are formed inside, giving the present material a unique structure.

Nitrogen adsorption-desorption isotherm of the present "noodle-like" mesoporous silica particles is displayed in **Figure 4**, from which the pore size distribution can be determined. The sample surface area was found to be 827 m^2/g. The P/P_0 position of reflection points clearly shows that the pore diameter is in the mesopore range, while the broad hysteresis loop reflects some mesopores are disorder in shape. The disordered mesopores may be attributed to those pores in the fringe part of the particles. The pore size is estimated to be mainly in a range of 2.0 − 4.0 nm, while a very small proportion at relatively large dimension (> 20 nm) can also be found. Small-angle X-ray diffraction pattern (not shown here) of the present sample displayed (100) reflection at around 2.0°, and the relatively weak intensity of the d_{100} peak suggesting part of the mesopores is irregular in shape.

Figure 3 Low (a) and high (b) magnification TEM images of the mesoporous "noodle-like" silica particles

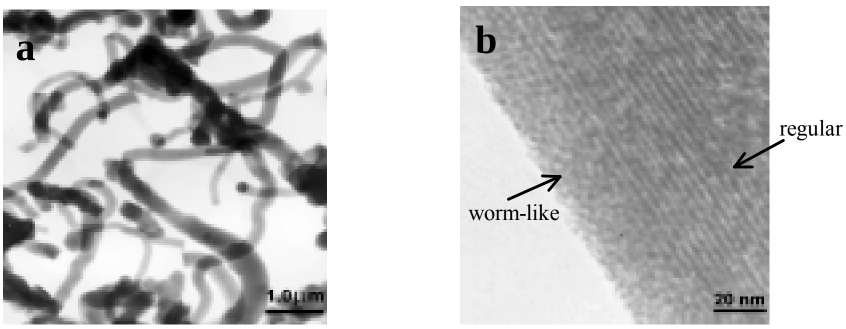
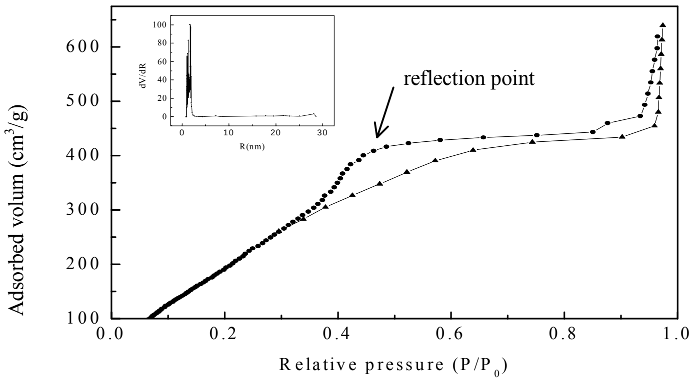


Figure 4 N_2 adsorption (▲)-desorption (●) isotherm and pore size distribution (inert)



In summary, “noodle-like” mesoporous silica can be easily prepared by using PSS/CTAB complex as template. By changing the mole ratio of polyelectrolyte to surfactant, the pore structure of the “noodle-like” morphology can be controlled. The
In summary, “noodle-like” mesoporous silica can be easily prepared by using PSS/CTAB complex as template. By changing the mole ratio of polyelectrolyte to surfactant, the pore structure of the “noodle-like” morphology can be controlled. The mesoporous material obtained from this experiment has potential applications in the separation, catalysis, and drug release, *etc*. The current study may inspire an approach for the syntheses of the special morphological inorganic mesoporous materials and is helpful for understanding the formation of biomimetic inorganic material.

References

1. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature,* **1992**, *359*, 710.
2. J. S. Beck, J. C. Vartuli, W. J. Roth, *et al.*, *J. Am. Chem. Soc.*, **1992,** *114*, 10834.
3. D. Walsh, S. Mann, *Nature*, **1995**, *377*, 320.
4. C. G. Goltner, S. Henke, M. C. Weisenberger, *et al*., *Angew. Chem. Int. Ed.*, **1998**, *37*, 613.
5. D. Zhao, J. Feng, Q. S. Huo, *et al.*, *Science*, **1998,** *279*, 548.
6. Y. Ono, K. Nakashima, M. Sano, *et al*., *Chem.Commun*., **1998**, 1477.
7. O. D. Velev, T. A. Jede, R. F. Lobo, *Chem. Mater.*, **1998,** *10*, 3597.
8. M. Breulmann, H. Coelfen, H. P. Hentze, *et al*., *Adv. Mater.*, **1998**, *10*, 237.
9. D. D. Archibald, S. Mann, *Nature*, **1993,** *364*, 430.
10. B. A. Elsa, J. C. Scaiano, *J. Am. Chem. Soc.*, **1984,** *106*, 6274.
11. M. Antonietti, J. Conrad, A. Thünemann, *Macromolecules*, **1994**, *27*, 6007.

Received 4 November, 2002