# Hybrid silica nanotubes with chiral walls†‡

Yuanli Chen,[a] Baozong Li,[a] Xiaojian Wu,[a] Xiulin Zhu,[a] Masahiro Suzuki,[b]
Kenji Hanabusa[b] and Yonggang Yang*[a]

*Received (in Cambridge, UK) 20th June 2008, Accepted 11th July 2008*
*First published as an Advance Article on the web 30th August 2008*
**DOI: 10.1039/b810517k**

**Hybrid silica nanotubes with chiral aromatic rings in the walls were prepared using self-assemblies of a low molecular weight amphiphile as a template; transmission electron microscopy images of the nanotubes at different formation steps showed that the co-structure-directing agent plays an important role in this chiral transfer.**

Because chirality and helicity have a strong relationship with the origin of life, many groups are focusing on preparing chiral and helical structures at molecular and nano-size levels and studying their chiral transfer and amplification properties.[1,2] Single-handed helical silica nanotubes[3,4] and coiled titania ones[5] have been successfully prepared through sol–gel transcription processes. Meanwhile, many efforts have been carried out to prepare chiral and helical mesoporous silicas using self-assemblies of surfactants as templates.[6–10] Generally, self-assemblies of chiral low molecular weight gelators, lipids, and surfactants were used as the templates. Namely, chiral and helical nanostructures were prepared by the transcription of the chirality and helicity of organic self-assemblies.

Compared with helical silica nanostructures, only very few helical organic–inorganic hybrid silica nanostructures have been created, such as nanotubes,[4] nanofibers[9] and mesoporous nanofibers.[10] Compared to mesoporous hybrid silica nanofibers or nanotubes, since they are more easily modified through the organic groups within the walls than the silica ones, they are more suitable to be applied in many fields such as catalysis[11] and optical materials.[12] To be applied in the fields of chiral separation, recognition, and catalysis, it is essential to obtain chiral and helical materials at a molecular level. Although single-handed helical silica nanotubes have been successfully prepared using self-assemblies of cationic and nonionic amphiphiles as templates,[13] it is still hard to transfer the chirality of the self-assemblies at a molecular scale. The main cause is that the obtained silicas are amorphous. If the walls of the nanotubes were both crystal-like and helical, the obtained helical nanostructures could have the potential to show chirality at a molecular level. Here, a sol–gel transcription method was used to prepare helical 1,4-phenylene silica nanotubes, and aromatic rings were built into the walls of helical nanotubes to increase the degree of crystalline order.[14–17] Circular dichroism (CD) spectra indicates that at least some of the aromatic rings are chiral within the walls of the hybrid silica nanotubes. Transmission electron microscopy (TEM) images at different reaction times revealed a spatio-temporal coordination (dynamic templating) mechanism which is different from the classical sol–gel transcription process.[3] The morphologies of the organic self-assemblies were gradually changed during the sol–gel transcription process.

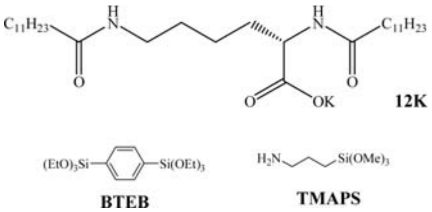

**Fig. 1** Molecular structures of gelator **12K**, BTEB, and TMAPS.

Compound **12K** can form a gel in water, cyclohexane, cyclohexanone, THF, DMSO, and DMF (Fig. 1). The minimum gel concentration for **12K** in pure water is 20 g dm$^{-3}$ at 25 °C.[18] The preparation procedure for the coiled nanotubes in the mixture of water and ethanol was as follows. Gelator **12K** (20 mg, 0.036 mmol) was dissolved in a mixture of 2.2 mL of de-ionized water and 1.8 mL of ethanol to form a transparent solution. Then 10 mg (0.056 mmol) of TMAPS was dropped into the solution under strong stirring at 0 °C. Five seconds later, 30 mg (0.075 mmol) of BTEB was dropped into the mixture. Around 10 min later, after a white precipitate came out, stirring was stopped. The mixture was kept at 0 °C for 1 d and 80 °C for 4 d under static conditions. Finally, the template was removed by boiling with a mixture of 5.0 mL of 36.0 wt% HCl aq. and 100 mL of methanol. The obtained sample was dried in air.

To visually study the morphological shapes and internal pore-architectures of the hybrid silicas, we used a field emission scanning electron microscope (FESEM) and TEM. Before taking FESEM images, 10 nm of Pt metal was coated onto the surface the silica nanostructures. Fig. 2 shows the FESEM and TEM images of the left-handed coiled tubular nanoribbons and tubes-in-tubes (ESI, Fig. S1†). All of the coiled tubular nanoribbons are left-handed, with helical pitches around 600 nm. The relationship between these nanostructures could be understood clearly from Fig. 2a and b. By increasing the width of the coiled tubular nanoribbons, tubes-in-tubes were obtained. To prepare uniform hybrid silicas, sol–gel transcriptions were carried out by changing gelator concentrations. Unfortunately, mixtures as above were obtained.

---

[a] *Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215123, P. R. China. E-mail: ygyang@suda.edu.cn*
[b] *Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda 386-8567, Japan*

† Electronic supplementary information (ESI) available: FESEM and TEM images of left-handedly coiled tubular ribbons and tube-in-tube structures; TEM images of the reaction mixture at different reaction times. See DOI: 10.1039/b810517k

‡ TEM images were obtained using a TecnaiG220. FESEM images were taken on a Hitachi S-4700. Specific surface areas and pore-size distributions were determined by the BET and BJH methods using an $N_2$ adsorption isotherm measured by a Gemini V 2380 instrument. The PXRD spectrum was taken on an X'Pert-Pro MPD X-ray diffractometer. The circular dichroism spectrum was taken on an AVIV 410 spectrometer.

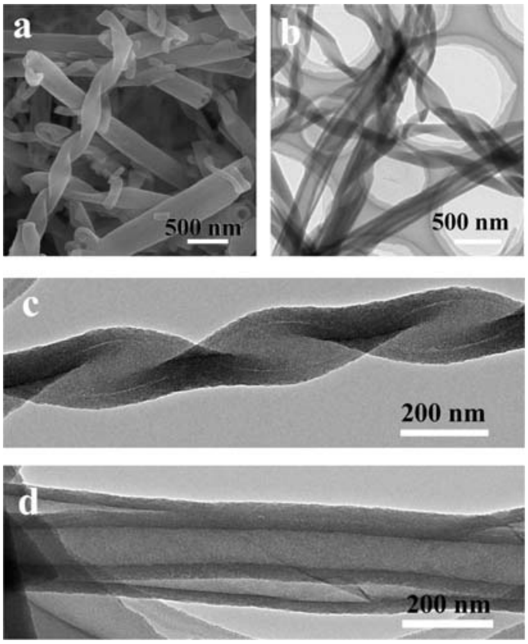

**Fig. 2** FESEM (a) and TEM (b, c, and d) images of left-handed coiled tubular ribbons and tube-in-tube structures.

The PXRD pattern at medium scattering angles shows two broad peaks around $d$ = 8.0 and 4.0 Å (Fig. 3a). These results indicate that molecular scale periodicity exists within the wall of the nanotubes. The monomer length is around 8.0 Å. Because the thickness of the hybrid silica nanotubes is less than 30 nm, the distances between the aromatic rings is hard to be detected by means of XRD techniques.[19] Moreover, the hybrid nanotubes did not show high crystalline order.

For potential applications in biology and materials science, many efforts were carried out to prepare water-soluble nanotubes, such as carbon, titania, and boron nitride ones. The obtained materials here are cotton-like. Because $-NH_3^+$ groups can enhance the solubility of this hybrid silica, these hybrids may partially dissolve in pure water. Unfortunately, they did not dissolve even under ultrasonication. However, it is very interesting to find that these hybrids were somewhat solubile in water on addition of cetyltrimethylammonium chloride (CTAC) or alcohols such as ethanol. The hydrophobicity generated by benzene rings in the wall would be the reason for the enhancement in solubility. For the sake of the solubility in ethanol, we can take CD spectra at a concentration of 2.0 mg of hybrid silica in 50 mL of ethanol. Although a light scattering effect is identified from UV spectra, no linear dichroism signs are identified. A negative peak in the CD spectrum at 278 nm is found (Fig. 3b). It indicates that at least some of the aromatic rings are chiral within the walls of the nanotubes. Although neither TMAPS nor BTEB are chiral, it should be noted that the chirality of the organic self-assemblies could be transferred to aromatic rings in the hybrid silicas through non-local interactions.

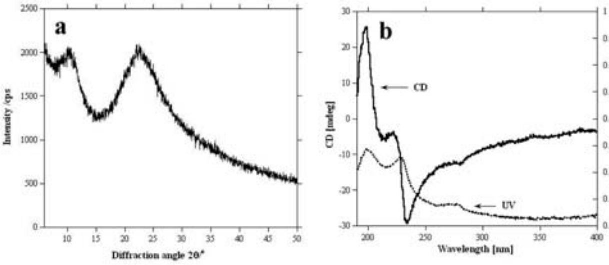

**Fig. 3** (a) PXRD graph and (b) CD and UV spectra of hybrid silica nanotubes.

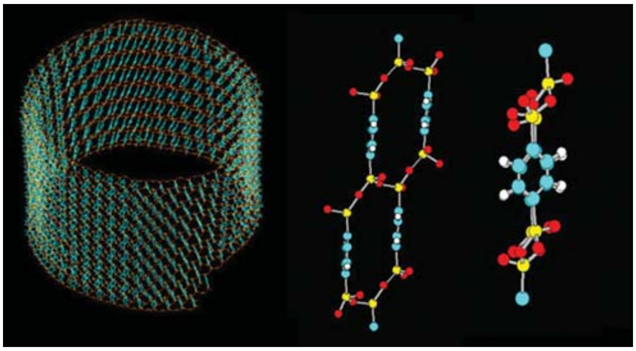

**Fig. 4** Model showing coiled hybrid silica nanotubes and chiral π–π stacking between two benzene rings. Silicon, yellow; oxygen, red; carbon, blue; hydrogen, white.

The structure shown in Fig. 4 was minimized using the force field MM+ in the HyperChem Pro 6.0 program package. Here we show only two layers. Hydrophobic benzene layers and hydrophilic silica layers array alternately at an interval of 7.98 Å. The benzene rings tilt within the wall of the nanotube. Moreover, there is a small tilt angle between two neighboring benzene rings. This model indicates that there exists chiral benzene packing.

The mechanism of the formation of organic–inorganic hybrid silica nanostructures was studied using TEM at different reaction times (Fig. 5). Because the sol–gel transcription process was carried out under dilute gelator conditions, before dropping in TMAPS and BTEB, only fine aggregates were recognized (Fig. 5a). The diameters of the aggregates are around 100 nm. After dropping in TMAPS and BTEB, twisted ribbons and hybrid silica oligomers were identified at 90 s (Fig. 5b). Some of

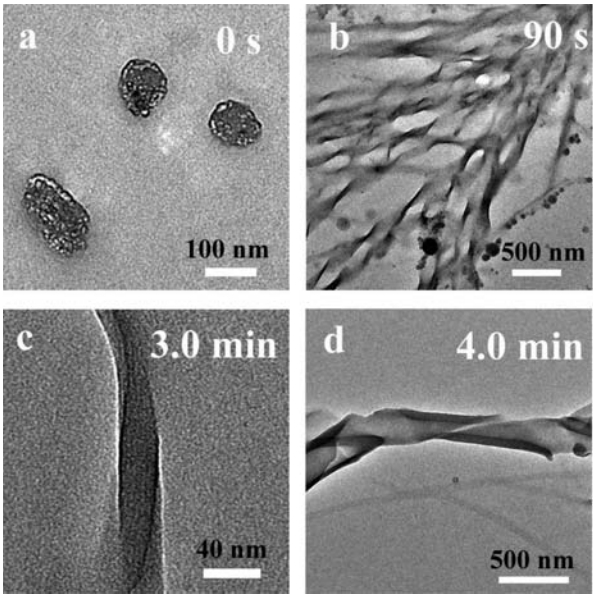

**Fig. 5** TEM images of the reaction mixture at different reaction times. (a) 0 s; (b) 90 s; (c) 3.0 min and (d) 4.0 min.

the hybrid silica oligomers adsorbed on the surfaces and edges of the twisted ribbons. Because the reactions were carried out in mixtures of water and ethanol, alcohols hydrolyzed from the silica sources should not be the main factor to induce the reorganization of **12K**. Therefore, the hydrolysized TMAPS on the surface of organic self-assemblies should play an important role in inducing the reorganization of **12K**. Apparently, the formation of the chiral hybrid silica follows a spatio-temporal coordination mechanism which is different from the classical sol–gel transcription process. In the classical sol–gel transcription process, the organic self-assemblies form firstly. Then silica oligomers adsorb and polycondense on the surface. It is interesting to see from Fig. 5c that the ribbons were formed by multilayer organic self-assemblies. The aromatic rings can be well-organized during the reaction process. At 4.0 min, with the width of the nanoribbons gradually increasing, coiled ribbons were obtained (Fig. 5d). The results shown above indicated the chiral transfer from organic self-assemblies to aromatic rings within hybrid silicas occurred through non-local interactions.

Without adding TMAPS to the reaction mixture, and only using BTEB as silica source, hybrid silica balls were obtained. It seems that TMAPS plays an important role in the reorganization of the organic self-assemblies of **12K** during the sol–gel transcription process. For a better understanding the effect of TMAPS, sol–gel polycondensation was carried out using only TMAPS as the silica and basic sources (ESI, Fig. S2†). The organic aggregates reorganized into twisted nanoribbons at 45 s (Fig. S2a†). The diameters of the nanoribbons are around 40 nm. The width of the nanoribbons gradually increased with extending reaction time (Fig. S2b†). In conclusion, the addition of TMAPS into the reaction system strongly induced the organic self-assemblies to reorganize into chiral nanoribbons.

To further understand the effect of the trimethoxysilyl group of TMAPS, we used 1-propylamine as a basic source. 1-Propylamine did not strongly affect the morphologies of the organic self-assemblies of **12K**. When the sol–gel transcription process was carried using 1-propylamine as the basic source and BTEB as the silica one, twisted nanoribbons were identified at 180 s (Fig. S2c†). Before 150 s, only ball-shape aggregates were identified. These nanoribbons were organized into balls gradually with extending reaction time (Fig. S2d†). Because there are no strong interactions between 1-proylamine and BTEB, BTEB oligomers were trapped within the balls due to hydrophobic association, only hybrid silica balls were obtained finally. Therefore, the interactions between TMAPS oligomer and the organic self-assemblies of **12K** induced the formation of chiral nanoribbons (Fig. S2a†). After that, BTEB oligomers adsorbed on the surface of helical organic self-assemblies were supported by TMAPS oligomers and polycondensed with the silica part of the TMAPS oligomers. During the further polycondensation process, because **12K** and its organic self-assemblies are chiral, the benzene rings linked with TMAPS are forced to form chirality. Therefore, the organic self-assemblies go beyond directing a structure-inducing effect on the morphologies on the nano-scale and induce organic–inorganic hybrid silica to form chirality at a molecular level.

In summary, we successfully transferred the chirality of an organogel to a hybrid silica nanostructure on both the nano- and molecular levels. Some of the benzene rings within the walls are chiral. This chiral transfer follows a dynamic templating mechanism. The morphologies of the organic self-assemblies changed gradually during the silica sources' adsorption process. TMAPS plays an important role on this chiral transfer at a molecular level. This material may be useful in chiral separation, recognition, and catalysis, at least it shows optical activity. Further research will be carried out in these fields.

This work was partially supported by the Jiangsu Provincial Key Laboratory of Organic Chemistry Foundation, Natural Science Foundation of Jiansu Province (No. BK2007047).

## Notes and references

1 E. Yashima, K. Maeda and Y. Okamoto, *Nature*, 1999, **399**, 449; E. Yashima, T. Nimura, T. Matsushima and Y. Okamoto, *J. Am. Chem. Soc.*, 1996, **118**, 9800.

2 M. M. Green, C. Khatri and N. C. Peterson, *J. Am. Chem. Soc.*, 1993, **115**, 4941; H. Nakashima, J. R. Koe, K. Torimitsu and M. Fujiki, *J. Am. Chem. Soc.*, 2001, **123**, 4847; G. Guo, M. Naito, M. Fujiki, A. Saxena, K. Okoshi, Y. Yang, M. Ishikawa and T. Hagihara, *Chem. Commun.*, 2004, 276.

3 J. H. Jung, Y. Ono, K. Hanabusa and S. Shinkai, *J. Am. Chem. Soc.*, 2000, **122**, 5008; J. H. Jung, H. Kobayashi, M. Masuda, T. Shimizu and S. Shinkai, *J. Am. Chem. Soc.*, 2001, **123**, 8785.

4 Y. Yang, H. Fukui, M. Suzuki, H. Shirai and K. Hanabusa, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 2069.

5 S. Kobayashi, N. Hamasaki, M. Suzuki, M. Kimura, H. Shirai and Kenji Hanabusa, *J. Am. Chem. Soc.*, 2002, **124**, 6550.

6 T. E. Gier, X. Bu, P. Feng and G. D. Stucky, *Nature*, 1998, **395**, 154; S. Che, Z. Liu, T. Ohsuna, K. Sakamoto, O. Terasaki and T. Tatsumi, *Nature*, 2004, **429**, 281; T. Ohsuna, Z. Liu, S. Che and O. Terasaki, *Small*, 2005, **11**, 233; S. Yang, L. Zhao, C. Yu, X. Zhou, J. Tang, P. Yuan, D. Chen and D. Zhao, *J. Am. Chem. Soc.*, 2006, **128**, 10460.

7 Y. Yang, M. Suzuki, H. Shirai, A. Kurose and K. Hanabusa, *Chem. Commun.*, 2005, 2032; Y. Yang, M. Suzuki, S. Owa, H. Shirai and K. Hanabusa, *Chem. Commun.*, 2005, 4462; Y. Yang, M. Suzuki, S. Owa, H. Shirai and K. Hanabusa, *J. Am. Chem. Soc.*, 2007, **129**, 581; Y. Yang, M. Suzuki, S. Owa, H. Shirai and K. Hanabusa, *J. Mater. Chem.*, 2006, **16**, 1644.

8 W.-J. Kim and S.-M. Yang, *Adv. Mater.*, 2001, **13**, 1191; H. Jin, Z. Liu, T. Ohsuna, O. Terasaki, Y. Inoue, K. Sakamoto, T. Nakanishi, K. Ariga and S. Che, *Adv. Mater.*, 2006, **18**, 593; A. M. Seddon, H. M. Patel, S. L. Burkett and S. Mann, *Angew. Chem., Int. Ed.*, 2002, **41**, 2988.

9 J. J. E. Moreau, L. Vellutini, M. Wong Chi Man and C. Bied, *J. Am. Chem. Soc.*, 2001, **123**, 1509; Y. Yang, M. Nakazawa, M. Suzuki, M. Kimura, H. Shirai and K. Hanabusa, *Chem. Mater.*, 2004, **16**, 3791.

10 Y. Yang, M. Suzuki, H. Fukui, H. Shirai and K. Hanabusa, *Chem. Mater.*, 2006, **18**, 1324.

11 A. Stein, B. J. Melde and R. C. Schroden, *Adv. Mater.*, 2000, **12**, 1403.

12 Q. Huo, D. Zhao, J. Feng, K. Weston, S. K. Buratto, G. D. Stucky, S. Schacht and F. Schüth, *Adv. Mater.*, 1997, **9**, 974.

13 K. Sugiyasu, S.-I. Tamaru, M. Takeuchi, B. Berthier, I. Huc, R. Oda and S. Shinkai, *Chem. Commun.*, 2002, 1212; J. H. Jung, K. Yoshida and T. Shimizu, *Langmuir*, 2002, **18**, 8724; S. Tamary, M. Takeuchi, M. Sano and S. Shinkai, *Angew. Chem., Int. Ed.*, 2002, **41**, 853.

14 T. Asefa, M. J. MacLachlan, N. Coombs and G. A. Ozin, *Nature*, 1999, **402**, 867.

15 S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna and O. Terasaki, *J. Am. Chem. Soc.*, 1999, **121**, 9611; S. Guan, S. Inagaki, T. Ohsuna and O. Terasaki, *J. Am. Chem. Soc.*, 2000, **122**, 5660.

16 S. Inagaki, S. Guan, T. Ohsugna and O. Terasaki, *Nature*, 2002, **416**, 304.

17 Q. Yang, M. P. Kapoor and S. Inagaki, *J. Am. Chem. Soc.*, 2002, **124**, 9694; S. S. Park, D. H. Park and C.-S. Ha, *Chem. Mater.*, 2007, **19**, 2709.

18 M. Suzuki, M. Yumoto, M. Kimura, H. Shirai and K. Hanabusa, *Helv. Chim. Acta*, 2004, **87**, 1.

19 C. Pham-Huu, G. Winé, J.-P. Tessonnier, M.-J. Ledoux, S. Rigolet and C. Marichal, *Carbon*, 2004, **42**, 1941.