

## Preparation of Chiral 4,4'-Biphenylene-silica Nanoribbons

LI, Haitao(李海涛) LI, Baozong(李宝宗) CHEN, Yuanli(陈媛丽) ZHANG, Ming(张明)  
WANG, Sibing(王思兵) LI, Yi(李艺) YANG, Yonggang\*(杨永刚)

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, Jiangsu 215123, China

A sol-gel transcription process was carried out using an anionic gelator **12K** and TMAPS as the co-structure-directing agent, as well as 4,4'-bis(triethoxysilyl)biphenyl as a hybrid silica source. It is interesting to find that the chirality of the organic self-assemblies of **12K** was successfully transferred to the 4,4'-biphenylene-silica nanoribbons which are potentially applied in chiral catalysis

**Keywords** silica, nanoribbon, sol-gel, self-assemble

### Introduction

Varieties of chiral and helical nanomaterials have been prepared. Up to now, helical carbon,<sup>1</sup> silicon carbide,<sup>2</sup> ZnO,<sup>3</sup> SnO<sub>2</sub>,<sup>4</sup> and silica nanofibers<sup>5</sup> have been prepared using physical methods. These materials are potentially applied to electronics, optoelectronics, sensing and actuating, and electromechanically coupled nanodevices.<sup>3c</sup> However, it is still hard to control them in single-handedness. Chiral transfer and amplification are well-known in chiral catalysis. To a typical reaction mixture, a small amount of chiral catalyst can induce the formation of a large quantity of chiral compounds. Chiral transfer and amplification can be also applied to control helical nanostructures. During the last decade, a variety of single-handed coiled silica nanotubes<sup>6</sup> and helical mesoporous silica nanofibers<sup>7</sup> have been prepared. The chirality of organic self-assemblies was transferred to silica nanostructures on a nano scale. Although the nanostructures could be controlled in single-handed helix, because the silicas are amorphous,<sup>8</sup> they are not chiral at molecular levels. Therefore, they are not suitable for application to chiral catalysis.

Organic-inorganic hybrid silicas have been widely studied. Recently, several series of chiral silsesquioxanes were synthesized,<sup>9</sup> which can self-assemble into helical morphologies. After polycondensation, helical hybrid silica bundles were obtained. Because the hybrid silicas are chiral, they are suitable for application to chiral catalysis.<sup>10</sup> For the potential applications of mesoporous hybrid silicas to chiral catalysis, it is better to build chiral function groups in the walls.<sup>11</sup> Because it is hard to synthesize chiral silsesquioxanes which are suitable to be used as the precursors for the preparation of mesoporous hybrid silicas, it is still hard to prepare chiral mesoporous hybrid silicas.<sup>12</sup> Recently, it was re-

ported that the chirality of organic self-assemblies could be transferred to 1,4-phenylene-silica nanotubes and mesoporous 1,4-phenylene-silica nanofibers through non-covalent interactions.<sup>13,14</sup> Some of the aromatic rings pack in helix within the walls of the nanotubes. Here, we show that the chirality of organic self-assemblies was transferred to 4,4'-biphenylene-silica nanoribbons. Stronger signals were identified in circular dichroism (CD) spectrum.

### Experimental

#### Materials and methods

3-Aminopropyltrimethoxysilane (APTMS) and 4,4'-bis(triethoxysilyl)biphenyl (BTSB) were purchased from Aldrich.

Field emission scanning microscope (FESEM) observations were carried out on a Hitachi S-4700 FESEM at 10 kV with 10 nm of Pt coating. Transmission electron microscope (TEM) observations were carried out on a JEOL JEM-2010 TEM at 200 kV. The powder X-ray diffraction (PXRD) pattern was taken on an X'Pert-Pro MPD X-ray diffractometer. CD and UV spectra were measured on an AVIV 410 spectrophotometer (cell diameter 1.0 cm).

#### General procedure

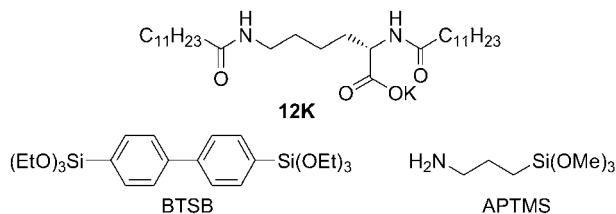
The synthesis and physical gelation properties of amphiphile **12K** (Figure 1) has been reported before.<sup>13,15</sup> The preparation procedure of the coiled nanotubes in the mixture of water and ethanol was shown as follows. Gelator **12K** (20 mg, 0.036 mmol) was dissolved in the mixture of 2.2 mL of de-ionized water and 1.8 mL of ethanol to form a transparent solution. Then 10 mg (0.056 mmol) of APTMS was dropped into the solution

\* E-mail: ygyang@suda.edu.cn; Tel.: 0086-0512-65880047; Fax: 0086-0512-65880047

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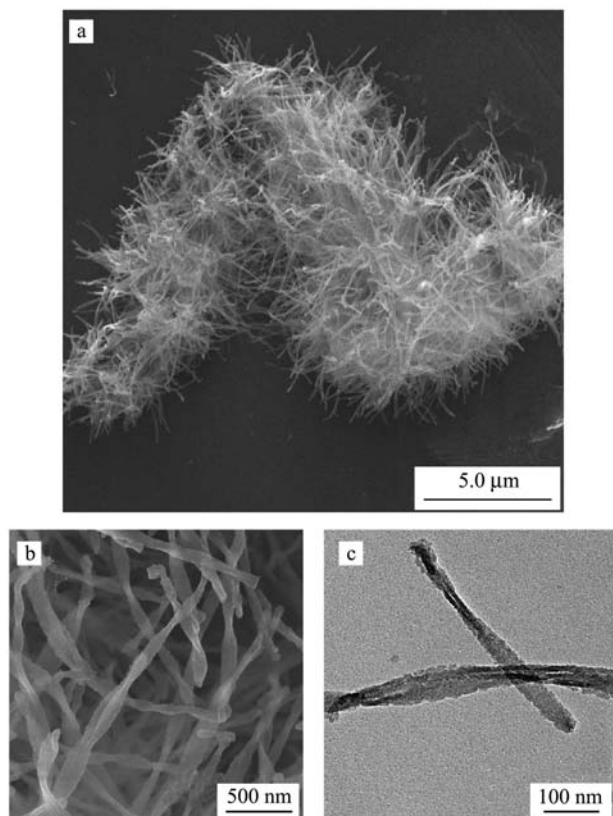
under strong stirring at 0 °C. 5 s later, 30 mg (0.075 mmol) of **12K** was dropped into the mixture. Stirring was stopped after white precipitate came out. The mixture was kept at 0 °C for 1 d and 80 °C for 4 d under a static condition. Finally, the templates were removed by extraction with a mixture of 5.0 mL of 36.0 wt% aq. HCl and 100 mL of methanol for 24 h. The obtained sample was dried in air.



**Figure 1** Molecular structures of **12K**, **BTSB** and **APTMS**.

## Results and discussion

To visually study the morphological shapes and internal pore-architectures of hybrid silicas, we used FESEM and TEM. Before taking FESEM images, Pt metal of 10 nm was covered on the surface of the hybrid silica nanoribbons. Figures 2a and 2b show the FESEM images of the left-handed twisted nanoribbons. The lengths of the ribbons are around 5.0 μm. Each hybrid silica ribbon has a relatively uniform width along its entire length, and the typical widths of the ribbons are around 70 nm.



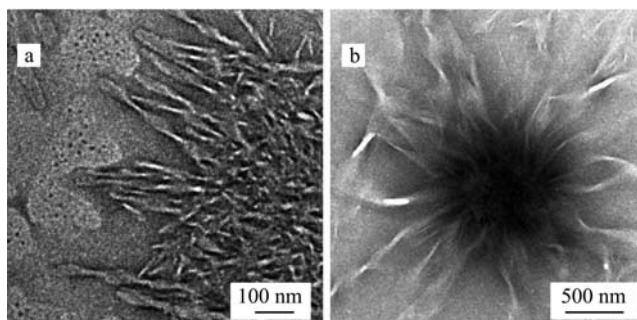
**Figure 2** FESEM (a and b) and TEM (c) images of the 4,4'-biphenylene-silica nanoribbons.

TEM image (Figure 2c) indicated that each nanoribbon shown in FESEM images was constructed by two fine nanoribbons. The distance between these two fine nanoribbons is around 3.0 nm.

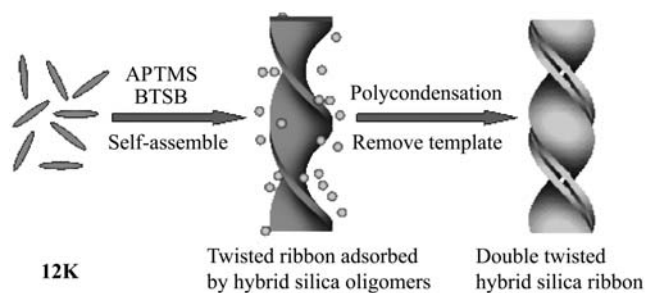
For a better understanding of the formation of the double twisted 4,4'-biphenylene-silica nanoribbons, the interactions between **12K** and APTMS were studied firstly (Figure 3). APTMS was dropped into the **12K** solution. Before dropping APTMS, **12K** has self-assembled into ball shaped aggregates.<sup>13</sup> At 45 s, twisted nanoribbons were identified, due to the interactions of **12K** with APTMS. The lengths and thicknesses of these nanoribbons are around 1.0 μm and 7.0 nm, respectively (Figure 3a). At 180 s, the lengths and the thicknesses of the twisted nanoribbons increased to several μm and 50 nm, respectively (Figure 3b). The formation of the double twisted 4,4'-biphenylene-silica nanoribbons was proposed in Figure 4. The addition of APTMS induces the formation of left-handed twisted self-assemblies. Then, the hybrid silica oligomers adsorb on the two sides of organic nanoribbons through hydrogen-bonding and cationic-anionic ion interactions, and polycondense on the surface of them. After the templates were removed by extraction with the mixture of aq. HCl and methanol, double twisted 4,4'-biphenylene-silica nanoribbons were obtained. Although the thicknesses of the organic nanoribbons were around 10 μm, the voids within the double twisted hybrid silica nanoribbons shrank to around 3.0 nm, after the organic nanoribbons are removed.

The PXRD pattern at medium scattering angles shows three broad peaks at  $2\theta$  of 7.1°, 15.2° and 23.0° (Figure 5). The peaks were assigned as a periodicity with a spacing of 12.4 Å and higher-order reflections. These results indicate that molecular-scale periodicity exists within the nanoribbons. However, the packing of the smallest repeat units does not show high crystalline order.<sup>16</sup>

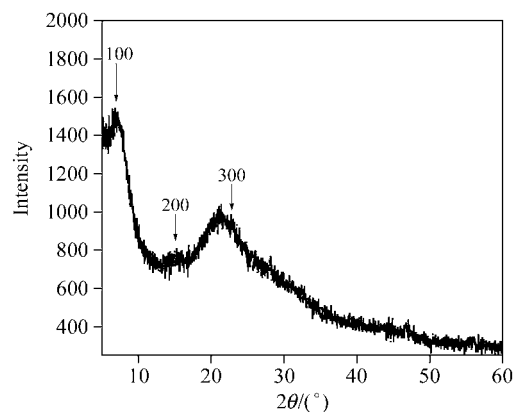
The CD spectrum of the 4,4'-biphenylene-silica nanoribbons was taken at a concentration of 2.0 mg in 50 mL of ethanol (Figure 6), which shows two negative signals at 226 and 295 nm, and one positive signal at 258.5 nm. Two ultra-violet (UV) absorption bands were identified from 200 to 300 nm. Since the first CD signal is negative, at least some of aromatic rings packed in a



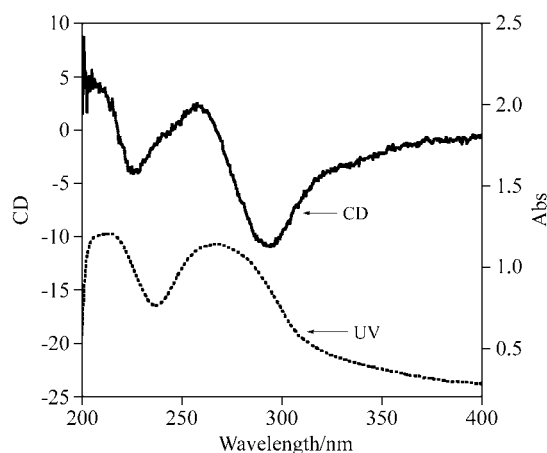
**Figure 3** TEM images of the **12K** solution in the mixture of ethanol and water, after dropping APTMS at 45 s (a) and 180 s (b).



**Figure 4** Schematic presentation of the formation of double twisted hybrid silica nanoribbons.



**Figure 5** PXRD pattern of the 4,4'-biphenylene-silica nanoribbons.



**Figure 6** CD and UV spectra of the 4,4'-biphenylene-silica nanoribbons

left-handed manner within the nanoribbons. Although neither APTMS nor BTSB is chiral, it should be noted that the chirality of the organic self-assemblies could be transferred to the packing of aromatic rings in the hybrid silicas through non-local interactions.

## Conclusion

In summary, chirality of organic self-assemblies was transferred to 4,4'-biphenylene-silica nanoribbons through non-local interactions. This kind of materials is potentially applied to the fields of chiral separation and catalysis.

## References

- (a) Motojima, S.; Hoshiya, S.; Hishikawa, Y. *Carbon* **2003**, *41*, 2653.  
(b) Qin, Y.; Zhang, Z.; Cui, Z. *Carbon* **2003**, *41*, 3063.  
(c) Iijima, S. *Nature* **1991**, *354*, 56.  
(d) Qin, Y.; Zhang, Z.; Cui, Z. *Carbon* **2004**, *42*, 1917.
- (a) Yang, Z. X.; Wu, Y. J.; Zhu, F.; Zhang, Y. F. *Physica E* **2005**, *25*, 395.  
(b) Zhang, D.; Alkhateeb, A.; Han, H.; Mahmood, H.; McIlroy, D. N. *Nano Lett.* **2003**, *3*, 983.
- (a) Yang, R.; Ding, Y.; Wang, Z. L. *Nano Lett.* **2004**, *4*, 1309.  
(b) Kong, X. Y.; Wang, Z. L. *Nano Lett.* **2003**, *3*, 1625.  
(c) Gao, P. X.; Mai, W.; Wang, Z. L. *Nano Lett.* **2006**, *6*, 2536.
- Yang, R.; Wang, Z. L. *J. Am. Chem. Soc.* **2006**, *128*, 1466.
- Zhang, H. F.; Wang, C.-M.; Buck, E. C.; Wang, L.-S. *Nano Lett.* **2003**, *3*, 577.
- (a) Jung, J. H.; Ono, Y.; Hanabusa, K.; Shinkai, S. *J. Am. Chem. Soc.* **2000**, *122*, 5008.  
(b) Yang, Y.; Fukui, H.; Suzuki, M.; Shirai, H.; Hanabusa, K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 2069.
- (a) Yang, Y.; Suzuki, M.; Owa, S.; Shirai, H.; Hanabusa, K. *J. Am. Chem. Soc.* **2007**, *129*, 581.  
(b) Yang, Y.; Suzuki, M.; Fukui, H.; Shirai, H.; Hanabusa, K. *Chem. Mater.* **2006**, *18*, 1324.  
(c) Yang, Y.; Suzuki, M.; Shirai, H.; Kurose, A.; Hanabusa, K. *Chem. Commun.* **2005**, 2032.  
(d) Yang, Y.; Suzuki, M.; Owa, S.; Shirai, H.; Hanabusa, K. *Chem. Commun.* **2005**, 4462.  
(e) Seddon, A. M.; Patel, H. M.; Burkett, S. L.; Mann, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2988.
- Chen, Y.-L.; Pei, X.-F.; Jiang, Y.; Zhou, L.; Zhang, J.; Bi, L.-F.; Li, H.-T.; Yang, Y.-G. *Chin. J. Chem.* **2008**, *26*, 1323.
- (a) Moreau, J. J. E.; Vellutini, L.; Wong Chi Man, M.; Bied, C. *J. Am. Chem. Soc.* **2001**, *123*, 1509.  
(b) Yang, Y.; Nakazawa, M.; Suzuki, M.; Kimura, M.; Shirai, H.; Hanabusa, K. *Chem. Mater.* **2004**, *16*, 3791.
- Kawasaki, T.; Ishikawa, K.; Sekibata, H.; Sato, I.; Soai, K. *Tetrahedron Lett.* **2004**, *45*, 7939.
- Wang, Z.-L.; Wang, L.; Yan, J.-C. *Chin. J. Chem.* **2008**, *26*, 1721.
- MacQuarrie, S.; Thompson, M. P.; Blanc, A.; Mosey, N. J.; Lemieux, R. P.; Crudden, C. M. *J. Am. Chem. Soc.* **2008**, *130*, 14099.
- Chen, Y.; Li, B.; Wu, X.; Zhu, X.; Suzuki, M.; Hanabusa, K.; Yang, Y. *Chem. Commun.* **2008**, 4948.
- Wu, X.; Ji, S.; Li, Y.; Li, B.; Zhu, X.; Hanabusa, K.; Yang, Y. *J. Am. Chem. Soc.* **2009**, *131*, 5986.
- Suzuki, M.; Yumoto, M.; Kimura, M.; Shirai, H.; Hanabusa, K. *Helv. Chim. Acta* **2004**, *87*, 1.
- Kapoor, M. P.; Yang, Q.; Inagaki, S. *J. Am. Chem. Soc.* **2002**, *124*, 15176.

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