Bull. Mater. Sci., Vol. 33, No. 4, August 2010, pp. 351–355. © Indian Academy of Sciences.

# Novel fabrication of silica nanotubes using multi-walled carbon nanotubes as template

**ZHI-HUA YIN, XIANG LIU and ZHONG-XING SU***

College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China

MS received 30 November 2008

**Abstract. Silica nanotubes were synthesized using multi-walled carbon nanotubes (MWCNTs) as template. The as-obtained samples were characterized by infrared spectroscopy (FTIR), X-ray diffraction (XRD), transmission electron microscopy (TEM), field emission scanning electron microscope (FE–SEM) and photoluminescent (PL) spectroscopy. The results indicate that the thickness of the outer walls is about 10 nm and the inner diameter is completely dependent on the size of MWCNTs. The as-fabricated silica nanotubes emit a strong violet light under excitation of 250 nm.**

**Keywords. Silica nanotubes; template; functionalization; MWCNTs.**

## 1. Introduction

In the past few decades, one-dimensional (1D) nanostructure materials (nanotubes, nanowires, nanobelts and nanorods) were extensively studied due to their novel physical and chemical properties (Feldman *et al* 1995; Alivisatos 1996; Ye *et al* 2002; Zhang *et al* 2007), especially with respect to the promising applications in numerous areas such as nanoscale electronics and photonics. Earlier efforts were mainly devoted to the research of carbon nanotubes, metals and II–VI semiconductors (Schonenberger *et al* 1997; Zhang *et al* 2000). Recently inorganic nanotubes derived from non-layered structures such as $SiO_2$, $Al_2O_3$, $TiO_2$, $Ga_2O_3$, CdSe, CdS, ZnS have attracted intense interest for their excellent performance (Nakamura and Matsui 1995; Hoyer 1996; Cheng and Samulski 2001; Xiang *et al* 2003; Golberg *et al* 2005; Guo *et al* 2005; Zollfrank *et al* 2007). Compared with other tubular nanomaterials, pure silica nanotubes not only realize functionalization on the outer and inner walls more easily, but also show exceptional applications in bioanalysis, catalysis and optic devices. Therefore, researchers have paid more attention to the designing and synthesis of more new multifunctional silica nanotubes.

Silica nanotubes can be fabricated by many methods including excimer laser ablation (Yu *et al* 1998), sol–gel template (Zhang *et al* 2002), chemical-vapour-deposition (CVD) (Pan *et al* 2002), and carbothermal reduction (Wu *et al* 2001). To date, fabrication methods of most silica nanotubes have focused on the use of templates. For example, Mitchell (2002) prepared silica nanotubes within the pores of porous alumina membrane templates by a sol–gel coating technique. Yoon (2006) fabricated the silica nanotube with both ends closed from the CdS nanorod template which was removed with controlled photon energy. Chen *et al* (2005) synthesized silica nanotubes using zinc oxide nanowires as templates. Wang (2004) and co-workers synthesized porous hollow silica nanotubes by a sol–gel route using needle-like $CaCO_3$ nanoparticles as the novel inorganic templates, which were prepared by a unique high gravity reactive precipitation technology. Obare *et al* (2001) synthesized hollow silica nanotubes by silica-coated Au nanorods and dissolution of Au core in KCN. However, these templates are not suitable for fabricating silica nanotubes in large quantities, because there is still a long way to realize the commercial application of these templates mentioned above.

In this work, we report a facile method of the synthesis of porous hollow silica nanotubes using MWCNTs as templates. Typically, for the as-obtained samples, the thickness of the outer walls is about 10 nm and the inner diameter is completely dependent on the size of the MWCNTs. What's more, the as-obtained silica nanotubes emit a strong violet light, which is different from the emission bands of silica nanotubes prepared by the sol–gel template method (SGTM).

## 2. Experimental

### 2.1 *Materials*

The MWCNTs with outer diameters of 40–60 nm were supplied by Shen Zhen. Nanotech. Port. Co. 3-APS was purchased from Shang Hai Yao Hua Chemical Co. Nitric acid, sulfuric acid and ammonia were all purchased from

*Author for correspondence (yinzhh06@lzu.cn)

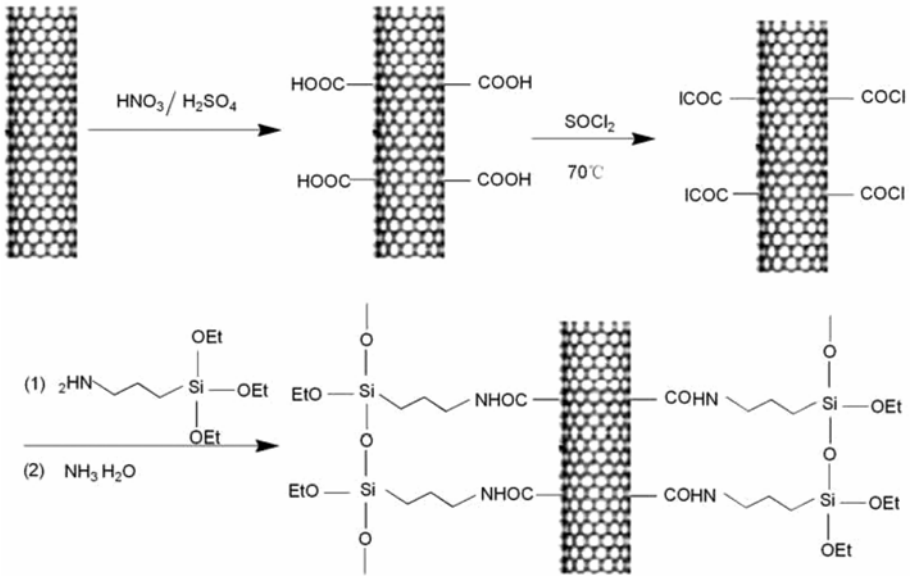


**Figure 1.** Fabrication procedure of silica coated MWCNTs.

Bei Ying Liang You Chemical Co. Tetrahydrofuran, toluene and thionyl chloride were purchased from Tian Jing Chemical Co. All chemical reagents were of analytical grade and used without further purification.

### 2.2 *Preparation of silica nanotubes*

In a typical process, the pristine-MWCNTs were added to a 3 : 1 mixture of concentrated $H_2SO_4$ and $HNO_3$. The suspension was treated in an ultrasonic bath for 15 min and stirring for 4 h under reflux. Then, the mixture was centrifuged and washed with distilled water until pH of the filtrate was 7. The solid was dried under vacuum at 40°C for 24 h for obtaining MWCNT–COOH.

The acid treated MWCNTs (MWCNT–COOH) were suspended in $SOCl_2$ and the suspension was treated in an ultrasonic bath for 15 min and stirred at 70°C for 24 h. The solid was separated by centrifuge and washed with anhydrous tetrahydrofuran, then dried under vacuum at 40°C for 12 h, to produce MWCNT–COCl. The 3-aminopropyltriethoxysilane (3-APS) and anhydrous pyridine were added to a one-neck flask that contained MWCNT–COCl and the mixture was stirred at 120°C for 12 h. After the reaction, the solid was centrifuged and washed for several times with toluene to remove residual 3-APS, thus the MWCNT–APS was obtained.

The resulting MWCNT–APS were added to ammonia (pH = 9). The mixture was treated in an ultrasonic bath for 15 min and stirred at room temperature for 3 h. The solid was centrifuged and washed with distilled water until pH of the filtrate was 7. Then the silica coated MWCNTs were obtained. The as-fabricated samples were calcinated at 800°C for 4 h to remove MWCNT template and the final products were obtained. The detailed reaction scheme is shown in figure 1.

### 2.3 *Characterization*

Nicolet NEXUS 670 Fourier transform infrared (FTIR) spectrometer, Hitachi 600 transmission electron microscopy (TEM), JEOL JSM-6701 field emission scanning electron microscope (FESEM) and Rigaku D/Max 2400 X-ray diffraction (XRD) analysis were used to characterize the changes in chemical structure of silica coated MWCNTs and chemical structure of silica coated MWCNTs after calcination. F-4500 photoluminescent (PL) spectroscopy was used to characterize the optical properties of silica nanotubes.

## 3. Results and discussion

Figure 2 shows the FTIR spectra of MWCNTs obtained at different possessing steps. The bond at 1710 $cm^{-1}$ in figure 2b is clearly assigned to the stretching mode of carboxyl groups, indicating the presence of –COOH on the surfaces of MWCNTs. The bands in 1095 $cm^{-1}$ are assigned to the characteristic absorption peaks of Si–O vibration, as shown in figure 2c. The results reveal that 3-APS has grafted onto the MWCNT–COOH. Figure 2d shows the FTIR spectra of the silica coated MWCNTs after calcination. It has strengthened the characteristic absorption peaks of Si–O which appear at 1170, 1084, 794 and 466 $cm^{-1}$. In addition, a broad shoulder band in the 3200–3600 $cm^{-1}$ and 1630 $cm^{-1}$ regions also appear in figure 2d, which can be attributed to the traces of water in the KBr pellet used for the analysis. The result suggests

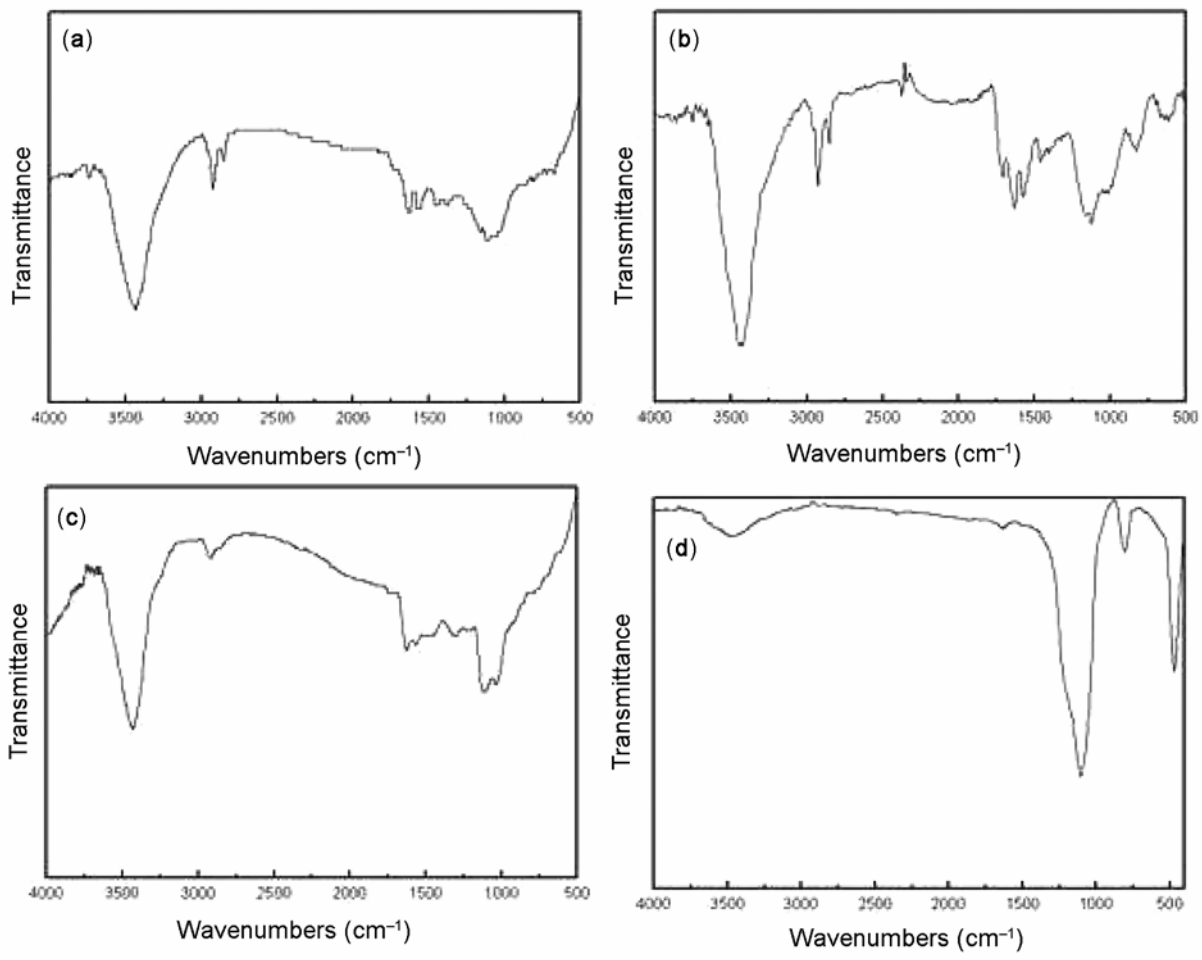


**Figure 2.** FTIR spectra of different MWCNTs: (**a**) the raw MWCNTs, (**b**) the acid treated MWCNTs, (**c**) silica coated MWCNTs and (**d**) the silica coated MWCNTs after calcination.

that the core MWCNTs have been removed from the core-shells nanotubes after calcination and that silica nanotubes have been obtained.

The TEM and FESEM images of silica coated MWCNTs without calcination and silica coated MWCNTs after calcination with different magnifications are shown in figure 3. As seen in figure 3a, the MWCNTs after acid treatment was clean and was not covered with any extra phase with some defects on the wall surface. In contrast, figure 3b exhibited the silica layer to be uniform, which further confirms that the 3-APS has been grafted onto the surface of MWCNTs successfully. Figures 3c and d demonstrate the FESEM and TEM images of the silica nanotubes. It can be seen that the silica nanotubes have a smooth surface and average diameter of silica nanotubes is in the range of 50–70 nm. The thickness of the outer walls is about 10 nm and the inner diameter is completely dependent on the size of MWCNTs.

Figure 4 shows XRD patterns of silica coated MWCNTs after calcination. The broadening of the diffraction peak centred around 23° confirmed the formation of amorphous silica. The ED patterns which display a diffusive ring (inset in figure 3d), also suggests that the as-obtained silica nanotubes are amorphous. No diffraction peaks related to MWCNTs are found in the spectrum of the silica nanotubes, which further prove that the MWCNTs cores are completely removed.

The optical properties of the as-obtained silica nanotubes are investigated by PL spectrum at room temperature. Figure 5 presents the photoluminescence (PL) spectrum. The strong violet light emission at 400 nm is observed under excitation of 250 nm. This result was different from the emission bands of silica nanotubes prepared by the sol-gel template method (SGTM) (Zhang *et al* 2002). The PL spectra of silica nanotubes prepared by SGTM had maxima at 486 nm and 539 nm. This phenomenon indicates that the framework of the as-prepared silica nanotubes is inconsistent with that of silica nanotubes prepared by SGTM. According to the previous report (Jang and Yoon 2004), the luminescence characteristic depends on the silica structure, which is affected by the synthetic variables such as the solvent used, its water

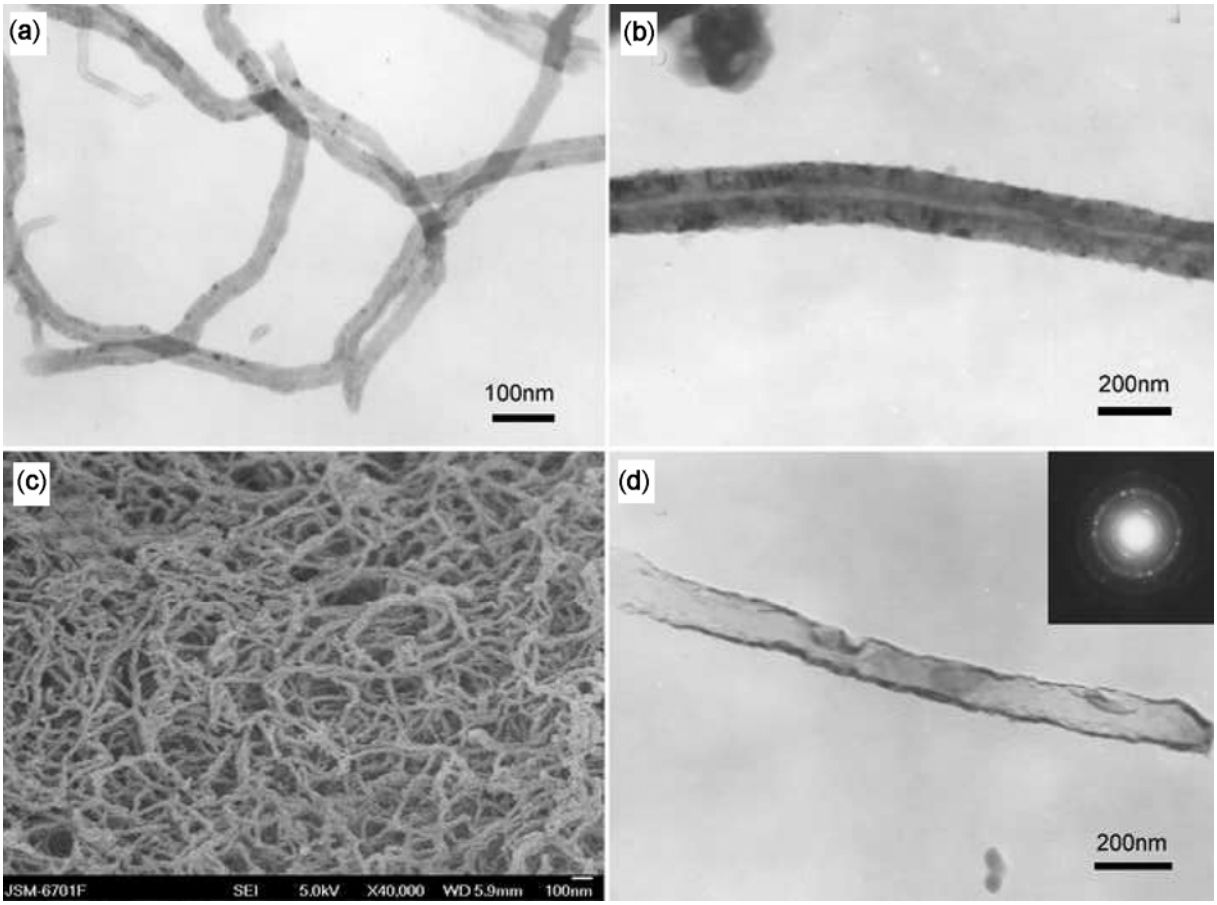


**Figure 3.** TEM images of the (**a**) acid treated MWCNTs, (**b**) MWCNT-APS. FESEM and TEM images and silica coated MWCNTs after calcination (**c**, **d**).

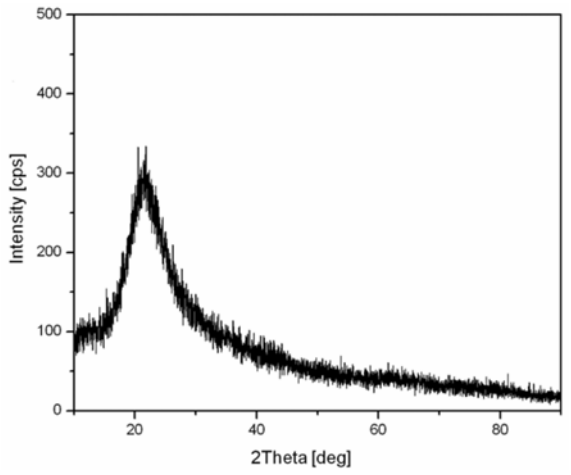


**Figure 4.** XRD patterns of silica nanotubes.

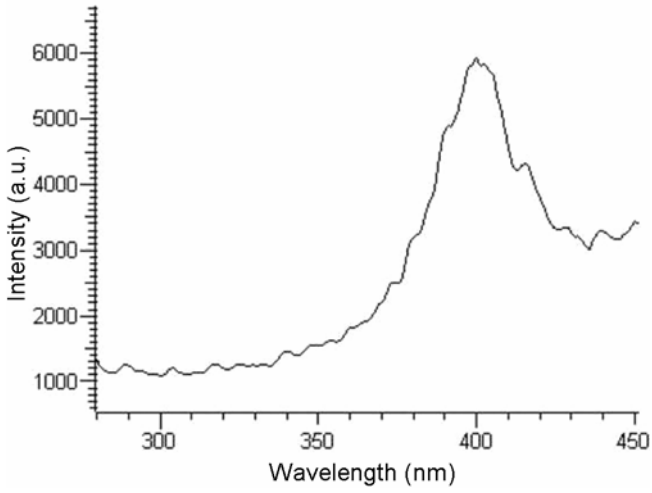


**Figure 5.** Room temperature PL spectrum of the as-fabricated silica nanotubes.

content, and pH of the reaction solution. So, we think the noticeable PL spectra of the as-fabricated silica nanotubes can be attributed to their special structure. Nevertheless, the extra nature of the silica nanotubes remains unclear and requires more detailed systematic investigations.

## 4. Conclusions

In summary, silica nanotubes were synthesized using the multi-walled carbon nanotubes (MWCNTs) as template.

The outer wall thickness of the silica nanotubes was about 10 nm. The inner diameter is completely dependent on the size of MWCNTs. Additionally, the size control of nanotubes materials may be easily achieved by changing the diameter of MWCNTs template. The strong violet light emission at 400 nm is observed under excitation of 250 nm. It could provide potential applications in the fields of light localization, lower dimensional waveguides, and scanning near-field optical microscopy.

## Acknowledgement

The authors would like to thank Jin Chuan Group Limited (JNMC) for financial support.

## References

Alivisatos A P 1996 *Science* **271** 933
Cheng B and Samulski E T 2001 *J. Mater. Chem.* **11** 2901
Chen Y, Xue X and Wang T 2005 *Nanotechnology* **16** 1978
Feldman Y, Wasserman E, Srolovitz D J and Tenne R 1995 *Science* **26** 222
Golberg D, Li Y B, Mitome M and Bando Y 2005 *Chem. Phys. Lett.* **409** 75
Guo Y G, Hu J S, Liang H P, Wan L J and Bai C L 2005 *Adv. Funct. Mater.* **15** 196
Hoyer P 1996 *Langmuir* **12** 1411
Jang B J and Yoon H 2004 *Adv. Mater.* **16** 9
Mitchell D T, Lee S B, Trofin L, Li N, Nevaanen T K, Soderlund H and Martin C R 2002 *J. Am. Chem. Soc.* **124** 11864
Nakamura H and Matsui Y 1995 *J. Am. Chem. Soc.* **117** 2651
Obare S O, Jana N R and Murphy C J 2001 *Nano Lett.* **1** 601
Pan Z W, Dai Z R, Ma C and Wang Z L 2002 *J. Am. Chem. Soc.* **124** 1817
Schonenberger C *et al* 1997 *J. Phys. Chem.* **B101** 5497
Wang J X, Wen L X, Wang Z H, Wang M, Shao L and Chen J F 2004 *Scr. Mater.* **51** 1035
Wu X C, Song W H, Wang K Y, Hu T, Zhao B, Sun Y P and Du J J 2001 *Chem. Phys. Lett.* **336** 53
Xiang Y, Li Z, Zhang R, Xie Y, Yang J and Wu C 2003 *J. Phys. Chem.* **B107** 3697
Ye C H, Meng G W, Jiang Z, Wang Y H, Wang G Z and Zhang L B 2002 *J. Am. Chem. Soc.* **124** 15180
Yoon J H, Chae W S, Cho H M, Choi M G and Kim Y R 2006 *Mater. Res. Bull.* **41** 1657
Yu D P *et al* 1998 *Appl. Phys. Lett.* **73** 3076
Zhang J H, Yang X G, Wang D W, Li S D, Xie Y, Xia Y N and Qian Y T 2000 *Adv. Mater.* **12** 1348
Zhang K F, Liu X, Su Z X and Li H L 2007 *Mater. Letts* **61** 2644
Zhang M, Ciocan E, Bando Y, Wada K, Cheng L L and Pirouz P 2002 *Appl. Phys. Lett.* **80** 491
Zhang M, Ciocan E, Bando Y, Wada K, Cheng L L and Pirouz P 2002 *Appl. Phys. Lett.* **80** 491
Zollfrank C, Scheel H and Greil P 2007 *Adv. Mater.* **19** 984