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A facile method to fabricate silica-coated carbon nanotubes and silica nanotubes from carbon nanotubes templates

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Abstract Silica-coated multiwalled carbon nanotubes (MWCNTs) have been prepared by the sol–gel polymerization of tetraethoxysilane (TEOS) in the presence of the acid-oxidized MWCNTs at room temperature, followed by oxidizing the MWCNTs templates at high temperature in air to produce hollow silica nanotubes. The thickness and architectures of silica shell were well controlled by rationally adjusting the concentration of TEOS, and by adding cationic surfactant as a structure-directing agent. These results also give a clear answer to prove the fact that the structures of spherical silica particles can be fully "copied" to the coating shell and the wall of silica nanotubes when prepared by the same method as the synthesis of silica particles in the presence of templates.

Introduction

The fabrication of versatile nanostructured materials such as nanoparticles, nanowires, nanorods, and nanotubes has attracted considerable attentions in fundamental science and industrial research, since they have fascinating geometries and physicochemical properties as well as various potential applications [1–5]. Among them, inorganic nanotubes with a unique hollow structure allow the independent modification of their inner and outer surface with desired functional molecules to develop smart multifunctional nanotubes [6] and provide straight nanochannels for the nanofluidic sensors [7]. Moreover, some novel properties of molecules or ions confined within the nanotubes are of great current interest [8]. Carbon nanotubes (CNTs) with remarkable structure-dependent properties have triggered intensive research towards the fabrication of novel advanced materials since their discovery [9–12]. CNTs are expected to be controllably designed into the desirable architectures as integral components. At present, versatile strategies have been developed to functionalize CNTs with organic, inorganic, and biological species [13–18]. Among them, the linkage of insulating materials to CNTs has emerged as a new strategy for the applications in field effect transistors, gas sensors, molecular circuits, switches, and others [19]. In this regard, recent investigation has demonstrated that silica-coated CNTs can serve as a good candidate for high-toughness composites, and open up new possibilities for the fabrication of advanced reinforced materials due to the high stiffness and bending strength of the nanaotubes [20]. Enhancement in thermal conductivity [21] and nonlinear optical properties [22] has also been found for the homogeneous silica/CNT composites as compared with the unmodified-CNTs. As silica is an insulator, silica-coated CNTs appear to be a super-dielectric with a very large

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low-frequency dielectric constant and low dielectric loss [23]. Moreover, with a biocompatible silica shell, silica-coated CNTs have many potential applications in biotechnology and nanoelectric devices. To date, silica-coated CNTs have been successfully synthesized by the liquid-phase deposition [24], electrodeposition [25], and sol–gel methods [26]. However, control over the thickness and architectures of silica coating are highly desirable but little reported [25].

Silica nanotubes (silica-NTs) are hydrophilic, biocompatible, and photoluminescent and can be applied in bio-separation, biocatalysis, biosensors, drug/gene delivery carriers, and optoelectronic nanodevices [27]. Till now, silica-NTs have been typically fabricated by applying the various templates [28], and using a surfactant-mediated sol–gel method [29] and a thermal oxidation-etching approach to convert the silicon nanowires into silica-NTs [30]. Though silica-NTs with different thickness, dimensions, and helicity have been fabricated by changing the reaction parameters, the control and design of wall structure remain contentious but desirable.

Many techniques have been developed for the preparation of spherical silica particles with various structures by the sol–gel chemistry [31–33], but they cannot be directly adopted for synthesizing silica tubes under comparable conditions. However, can these methods be further used for reference of producing similar coating shell and wall of silica in the presence of templates? That is, can the structures of silica particles can be fully "copied" to the coating shell and the wall of silica nanotubes by employing the methods of synthesizing particles? There are in fact, to the best of our knowledge, few reports that address these issues. Herein, we attempt to find out the answer for developing a facile and feasible methodology to produce silica-coated CNTs and subsequent silica nanotubes. Although the preparation of silica-NTs by calcination of the CNTs templates from silica-coated CNTs has been reported previously [34], our proposed technique can provide additional control over the thickness and architecture of the silica shell. Specifically, the application of sol–gel chemistry allows us to control the nanostructure of silica wall coating [35].

Experimental

The methodology employed in this study is outlined in Fig. 1. Pristine multi-walled carbon nanotubes (MWCNTs, with an average outer diameter of 50 nm, China Shenzhen Nanotech Port Co., Ltd.) were cut and purified by reflux in strong acids as described previously [15], producing oxygenated functional groups (–COOH, –OH, and C=O) on the CNTs surface. The resulting acid-oxidized MWCNTs (denoted as *o*-MWCNTs) become hydrophilic, which makes them well-dispersed in the reaction mixture. Typically, *o*-MWCNTs (50 mg) are ultrasonically dispersed into a fixed-volume mixture of ethanol (250 mL) and NH_4OH (8 mL, 25.0–28.0 wt%) for 30 min, followed by vigorous mechanical agitation for another 15 min to obtain a stable and homogeneous suspension. Immediately afterward, the appropriate amount of tetraethoxysilane (TEOS) is quickly added to achieve the desired volume ratio (vol.%) of TEOS with respect to ethanol, and kept there for 12 h under stirring. The whole reaction is carried out at room temperature. After the reaction, the mixture is centrifuged at a moderate speed (2000 rpm). In order to fully remove free silica particles, the resultant sediment is ultrasonically re-dispersed in water for 15 min, and vacuum filtered. The same procedure is repeated at least four cycles. Finally, the darkish product is obtained by filtration through a 0.8-μm nylon membrane and vacuum dried, yielding silica-coated MWCNTs (silica@MWCNTs). Silica@MWCNTs are then oxidized in an oven (NEY2-525) at 600 °C for 8 h to remove the CNTs templates giving the silica nanotubes (silica-NTs). The morphology and structure of silia@MWCNTs and silica-NTs can be examined by transmission electron microscopy (TEM, Tecnai G220 and Philips CM 20).

Fig. 1 Scheme for the preparation of silica-coated MWCNT (silica@MWCNT) and subsequent silica nanotube (silica-NT)

Results and discussion

Figure 1 demonstrates the procedure to synthesize silica-coated MWCNT and subsequent silica-NT by oxidation of the MWCNT template in air. In previous articles, coating of CNTs with silica has been mainly performed by reacting siloxanes with the precursor-modified CNTs [36, 37], rather than with the acid-oxidized MWCNTs as described here. The latter appears to be relatively facile and fast. Figure 2 shows the FT-IR spectra of pristine MWCNTs, acid-oxidized MWCNTs (*o*-MWCNTs), and silica-coated MWCNTs (silica@MWCNTs). For pristine MWCNTs, there is only a weak peak at 1580 cm^{-1}, corresponding to the C=C stretching of the MWCNTs backbone (Fig. 2a). After oxidation of MWCNTs with the concentrated acid, two new

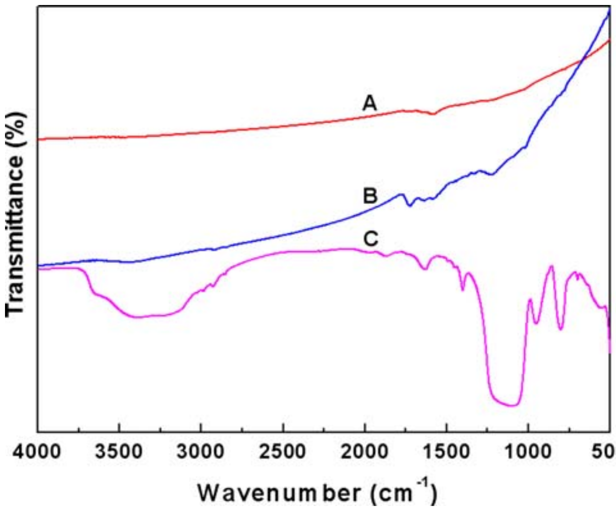


Fig. 2 FT-IR spectra of pristine MWCNTs (a) o-MWCNTs (b) and silica@MWCNTs (c)

bands occur at 1720 and 1230 cm^{-1} (Fig. 2b), which are assigned to the C=O vibration of the carboxylic group and C–O stretching, respectively. In the spectrum of silica@MWCNTs (Fig. 2c), a strong band centered at 1100 cm^{-1} can be clearly observed due to the Si–O–Si asymmetric stretching, and two peaks at 950 and 800 cm^{-1} are attributed to the Si–OH stretching and Si–O–Si symmetric vibration, respectively. Moreover, a broad band centered at 3400 cm^{-1} corresponds to the OH stretching that originates from both silanol and adsorbed water. These results indicate that the MWCNTs surfaces are effectively coated by silica shell.

From the TEM images of silica@MWCNTs (Fig. 3a–c), a sharp contrast structure that consists of an inner and an outer layer can be observed along the axial direction of the nanotubes. These appear to be clear core–shell structures. As compared with the smooth and clear surface of *o*-MWCNTs (Fig. 3d), the surface of silica coating is rough with some nanoparticles attached to the surface of silica@MWCNTs. However, the thickness of the silica shell is relatively uniform. The coupling of silica shell to MWCNTs core is considerably strong, and they cannot be detached from each other even after prolonged ultrasonication. One reason involves the chemical binding that the surface functional groups (–COOH, –OH) of MWCNTs react with silanol from the hydrolyzed-TEOS to form Si–O–C linkages. Another possibility is hydrogen-bonding interaction between silanol and C=O groups on the CNTs surface [38]. In some cases, the silica shells of the *o*-MWCNTs surface are not so clear (as indicated by the arrows in Fig. 3). Moreover, the thickness of silica shell is clearly dependent on the volume ratio of TEOS with respect to ethanol. With the addition of 3.2 vol.% (8 mL), 4.0 vol.% (10 mL), and 4.8 vol.% (12 mL) of TEOS into the reaction system, the resulting silica thickness is about 9.2 nm (Fig. 3a), 11.6 nm (Fig. 3b), and 13.4 nm (Fig. 3c), respectively.

After calcination of silica@MWCNTs at high temperature, the carbon atoms of MWCNTs are converted to CO or CO_2 gas due to the oxidation of O_2 in air. This removes the MWCNTs templates leaving silica nanotubes [34]. It is generally accepted that the resulting H_2O and alcohol during the hydrolysis and condensation of TEOS remain in

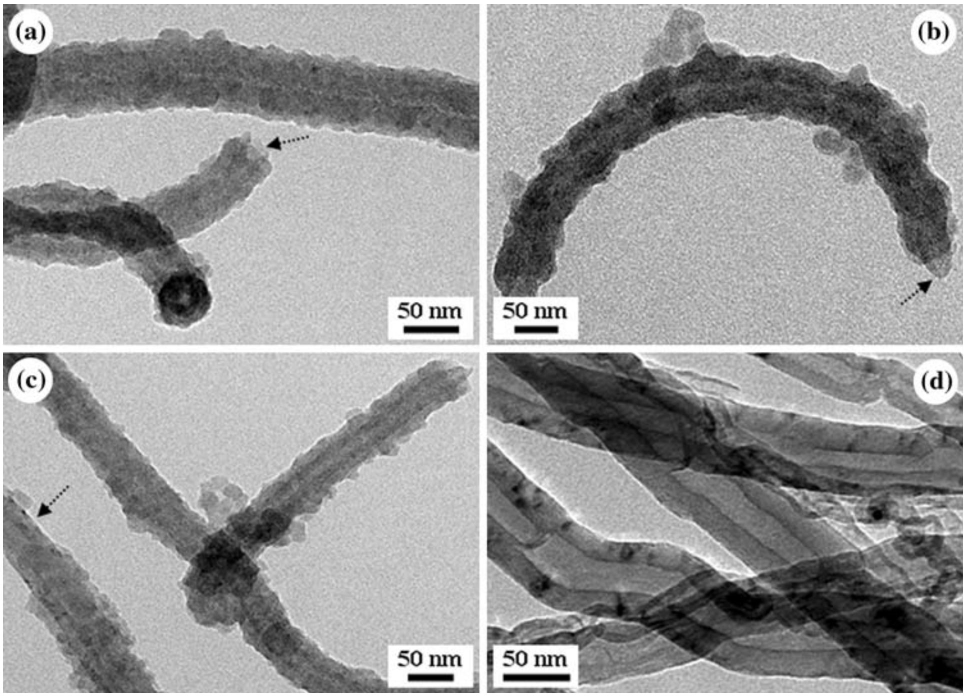


Fig. 3 TEM images of silica@MWCNTs (**a**–**c**) and o-MWCNTs (**d**). The concentration of TEOS is 3.2, 4.0, and 4.8 vol.%, corresponding to the image of **a**, **b**, and **c**, respectively

the pore of the Si–O–Si network [35]. Therefore, H_2O and alcohol are easily removed at high temperature leaving lots of holes, which provide the channels for the entrance of O_2 and the release of CO or CO_2. As represented in Fig. 4(a–e), TEM images show the typical hollow structure of silica-NTs with a relatively smooth inner wall, and no graphitic-type fringes are seen in silica-NTs. The inner diameters for the silica-NTs range from 30 to 80 nm, which are in agreement with the outer diameter of the MWCNTs templates. The measured wall thicknesses for silica-NTs are ca. 9.2 nm (Fig. 4a, b), 11.6 nm (Fig. 4c, d), and 13.4 nm (Fig. 4e), respectively, which is in agreement with the thickness of silica coating on the MWCNTs surface. Figure 4f gives the energy dispersive X-ray spectrum (EDX) of silica-NTs, in which three distinct peaks of silicon, oxygen, and copper are observed. The copper signal originates from the grid used for TEM analysis. These results further confirm that the nanotubes are only composed of silica, and the MWCNTs templates are fully removed under calcination. In some cases, silica-NTs are either closed (Fig. 4c) or open-ended tubes (Fig. 4b) on both ends. Alternatively, some of silica-NTs have one closed end and the other open-ended (Fig. 4e). These tubes (i.e., Fig. 4e) could be treated as nano-test-tubes, which allow the biomolecules of interest to be encapsulated by capillary filling. The encapsulated biomolecules can be stored inside the tubes until it is ready to be delivered [39].

The above results show that the silica thickness on silica@MWCNTs (and hence, the wall thickness of silica-NTs) can be effectively controlled by adjusting the concentration of TEOS. However, the desirable silica shell structure is not fabricated in a simple sol–gel process. In fact, spherical silica with various structures have been prepared by addition of structure-directing agents [40, 41]. Recently, monodispersed spherical silica particles with dense silica core and ordered-mesoporous shell had been

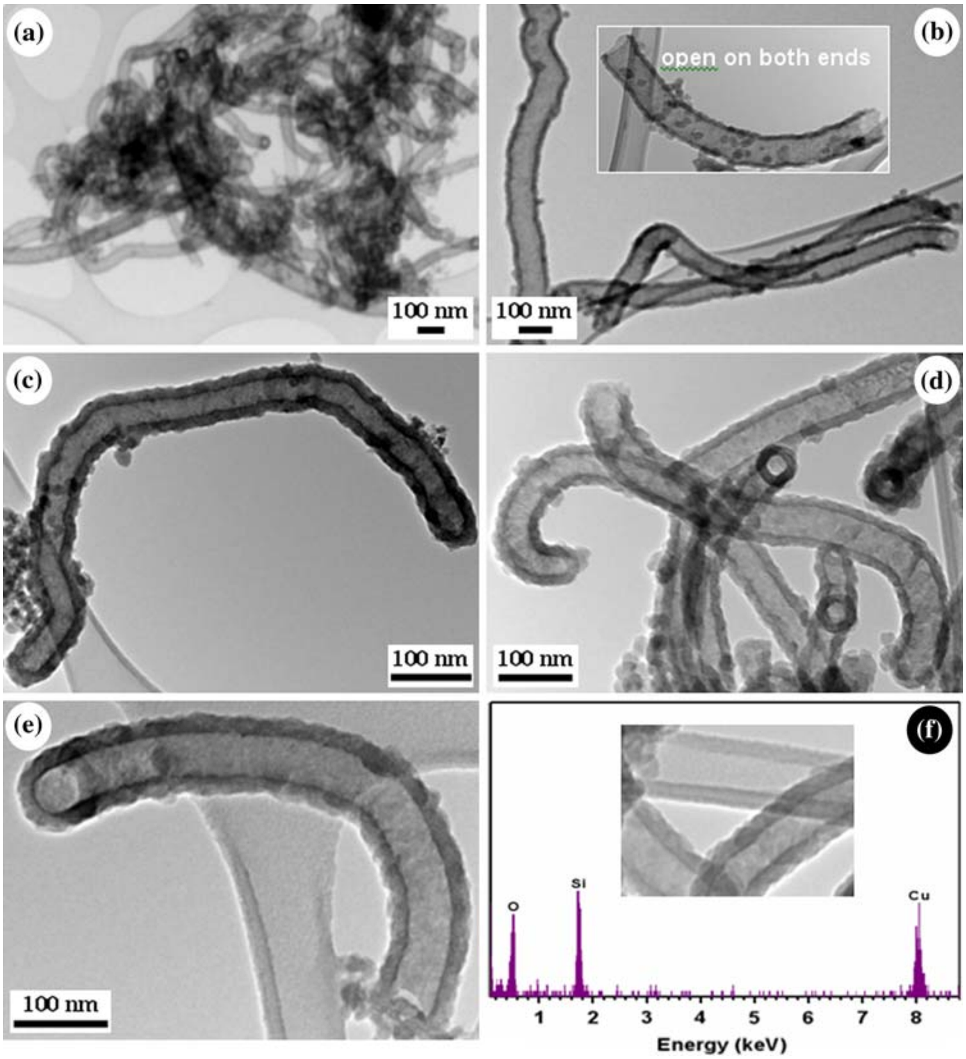
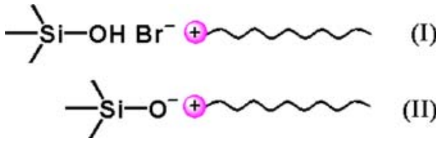


Fig. 4 TEM images of hollow silica-NTs obtained by calcining silica@MWCNTs at high temperature (**a**–**e**), and EDX spectrum of silica-NTs shown in the inset (**f**). The concentration of TEOS is 3.2 vol.% (**a** and **b**), 4.0 vol.% (**c** and **d**), and 4.8 vol.% (**e**), respectively

reported by employing alkyltrimethylammonium bromide as a structure-directing agent [41]. Therefore, it is to be expected that novel structure of spherical silica particles can be transferred to the coating shell or the wall of silica-NTs. Herein, one-pot two-step synthesis developed by Yu and coauthors [41] is employed in this investigation. In this study, *o*-MWCNTs (50 mg) are pre-coated by hydrolysis, and polycondensation of TEOS (5 mL) is performed in the presence of a mixture of ethanol (100 mL), NH_4OH (4 mL), and H_2O (10 mL) with mechanical stirring for 6 h, resulting in a dense silica (solid-structured) inner shell. Then, 200 mL of hexadecyltrimethylammonium bromide (CTAB, 0.015 M) aqueous solution is added to the reaction mixture. At the end of stirring for 30 min, an additional TEOS (2 mL) is quickly added to the above prepared suspension, followed by stirring for 12 h at room temperature. The final product can be obtained by purification and calcination to remove free particles and CTAB as described before.

As shown in Fig. 5a, free silica particles have a dense core with diameter of ca. 270 nm and an ordered-mesoporous shell with thickness of about 50 nm, in which mesoporous channels are perpendicular to the surface of the inner shell, similar to the previously reported results [41]. Noticeably, similar mesoporous channel structure can also been clearly observed on the wall of silica-NTs (see insert in Fig. 5b), which is composed of a dense silica inner shell and an ordered-mesoporous outer shell with thicknesses of ca. 94 and 21 nm, respectively. When silica@MWCNTs are calcined at 400 °C (not 600 °C) in air, only CTAB micelles are removed and MWCNTs backbone can be kept due to higher thermal stability of MWCNTs. From Fig. 5c, a clear protruded-MWCNT tip can be observed together with double silica shells. These results demonstrate that the structure of silica particles is fully transferred to the silica shell, which implies that the synthesis method of silica particles is easily applied to control the structure of silica coating or silica-NTs. Interestingly, when the sol–gel polymerization is carried out by simultaneously adding a TEOS/CTAB mixture to a suspension of previously prepared *o*-MWCNTs, the resulting silica particles and silica-NTs have totally different structures after the removal of CTAB by calcination. TEM images (e.g., Fig. 5d) demonstrate that the structure consists of random and disordered mesoporous silica, and no multi-walled layers can be found on the surface of silica-NTs (and silica particles). Only on increasing the concentration of CTAB (0.02 M), the resultant silica particles and silica-NTs are, however, made up of mesopore with a relative proportional spacing (Fig. 5e, f).

In the reaction system, CTAB might interact with hydrolyzed silanol to form weak electrostatic interaction (I) or stronger association (II) under basic conditions, as follows:



Therefore, the surface of previously prepared silica acts as an interface template to assist the self-assembly of positively charged CTAB micelles under basic conditions, followed by inducing the oriented propagation of mesopore to form a dense silica core and a mesoporous-ordered shell after heating (Fig. 5a–c). With simultaneous addition of TEOS and CTAB to the reaction system, the hydrolysis and polycondensation reactions initiate at numerous sites within the TEOS/NH_4OH solution to form Si–O–Si bonds, which are also synchronously surrounded by CTAB micelles. When sufficient interconnected Si–O–Si bonds are formed in a region, they respond cooperatively as colloidal particles or silica shell, and CTAB molecules remain in the pores of the network as a result. At lower concentration of CTAB, CTAB micelles cannot alternately interact with the Si–O–Si network, which leads to relative aggregate of Si–O–Si bonds without interference of CTAB in a certain region, forming the little dense silica dots (Fig. 5d). However, CTAB with a higher concentration can alternately interact with the propagated Si–O–Si bonds during the course of hydrolysis and condensation of TEOS, and evenly distributes and remains in the pore of the Si–O–Si network. After CTAB molecules are removed by calcination, the left mesopores are homogeneous distribution within the silica particles or the wall of silia-NTs (Fig. 5e, f). Further study is under way to determine the specific surface area according to the BET (Brunauer–Emmett–Teller) method, and the pore size (diameter and volume) according to the BJH (Barrett–Joyner–Halenda) method and Gurvitch rule.

In addition, the inside diameter and length of the resulting silica-NTs are clearly dependent on the outside diameter and length of the MWCNTs templates (Figs. 4, 5). This indicates that the diameter and length of silica-NTs can be tailored according to the CNTs used. The theoretical investigation has also demonstrated that the silica-coating has structure dependence on the CNTs backbone [42]. Such a template-directed synthesis strategy is an ideal tool to fabricate the desired oxidated-nanotubes in which their dimensions can be precisely controlled, which allows us to prepare the specially structured materials. For example, helical polymer nanotubes could be obtained by utilizing

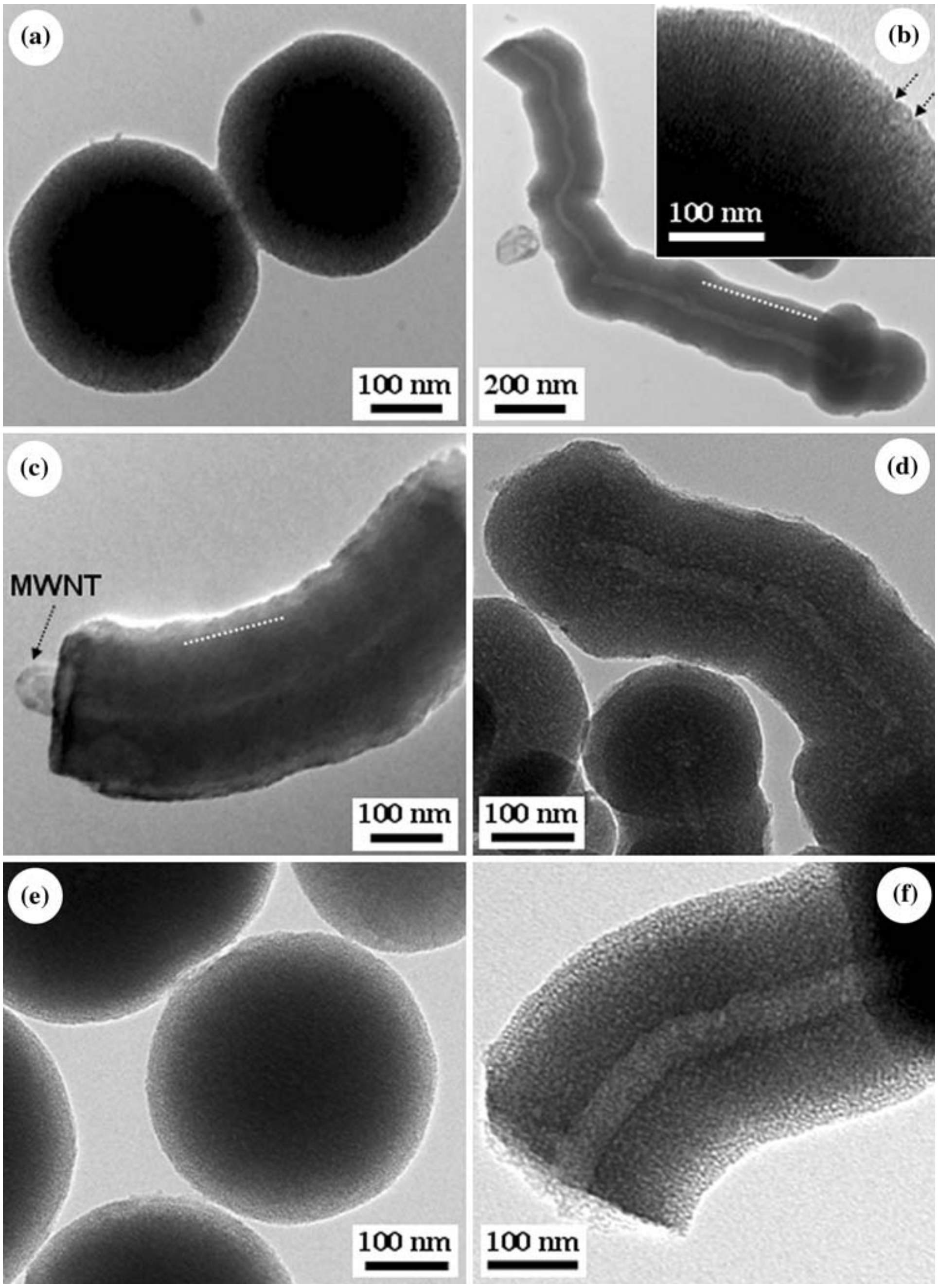


Fig. 5 TEM images of free silica particles (**a**, **e**) and silica-NTs (**b**, **d**, **f**) obtained by heating (600 °C) silica-coated MWCNTs in which a structure-directing agent (CTAB) is added during the course of hydrolysis and condensation of TEOS, and (**c**) TEM image of silica@MWCNTs that are calcined at 400 °C (not 600 °C) in air

polymer-grafted helical silica-NTs when helical CNTs are used as templates, since silica can be easily etched away by hydrofluoric acid treatment.

Conclusions

A facile sol–gel process has been successfully employed to prepare silica-coated MWCNTs in the presence of the acid-oxidated MWCNTs. The proposed methodology has several advantages in that the thickness and architectures of silica coating can be easily controlled by rationally adjusting reaction parameters such as precursor or catalyst concentration, as well as addition of structure-directing agents. Silica-coated MWCNTs can be further calcined at high temperature in air to form hollow silica nanotubes after removing the MWCNTs templates. The wall structure of silica nanotubes can be designed by adding CTAB surfactant to the reaction system. These results clearly prove that the structures of silica shell can be derived from those of particles by employing the synthesis methods of silica particles in the presence of additional templates. Considering that the silica surface and structured tubes are functionally versatile, silica-coated CNTs and silica nanotubes with novel structure prepared by the authors are expected to have potential applications for tunable nanoelectric and photonic devices. The sol–gel process developed is facile and efficient for the fabrication of silica-coated CNTs and silica nanotubes, which could be applied in large scale production. The synthesis methods for preparation of silica partilces also open up new opportunities to the surface-coating techniques of the supports by adopting the versatile sol–gel chemistry.

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References

1. Goldberger J, Fan R, Yang P (2006) Acc Chem Res 39:239
2. Suhr J, Koratkar NA (2008) J Mater Sci 43:4370. doi:10.1007/s10853-007-2440-x
3. Oliphant CJ, Arendse CJ, Malgas GF, Motaung DE, Muller TFG, Halindintwali S, Julies BA, Knoesen D (2009) J Mater Sci 44:2610. doi:10.1007/s10853-009-3341-y
4. Wang B, Yang YH, Li LJ, Chen Y (2009) J Mater Sci 44:3285. doi:10.1007/s10853-009-3444-5
5. Zhao YY, Yang J, Frost RL, Kristóf K, Horváth E (2009) J Mater Sci 44:3662. doi:10.1007/s10853-009-3489-5
6. Mitchell DT, Lee SB, Trofin L, Li N, Nevanen TK, Soderlund H, Martin CR (2002) J Am Chem Soc 124:11864
7. Fan R, Karnik R, Yue M, Le DY, Majumdar A, Yang P (2005) Nano Lett 5:1633
8. Chen S, Wu G, Sha M, Huang S (2007) J Am Chem Soc 129:2416
9. Lu CS, Mai YW (2008) J Mater Sci 43:6012. doi:10.1007/s10853-008-2917-2
10. Song R, Yang DB, He LH (2008) J Mater Sci 43:1205. doi:10.1007/s10853-007-2277-3
11. Lu K (2008) J Mater Sci 43:652. doi:10.1007/s10853-007-2155-z
12. Wang SR (2008) J Mater Sci 43:5837. doi:10.1007/s10853-008-2847-z
13. Tasis D, Tagmatarchis N, Bianco A, Prato M (2006) Chem Rev 106:1105
14. Yang YK, Xie XL, Wu JG, Mai YW (2006) J Polym Sci Part A Polym Chem 44:3869
15. Yang YK, Xie XL, Wu JG, Yang ZF, Wang XT, Mai YW (2006) Macromol Rapid Commun 27:1695
16. Yang YK, Xie XL, Yang ZF, Wang XT, Cui W, Yang JY, Mai YW (2007) Macromolecules 40:5858
17. Yang YK, Wang XT, Liu L, Xie XL, Yang ZF, Li RKY, Mai YW (2007) J Phys Chem C 111:11231
18. Chang QF, Zhao K, Chen X, Li MQ, Liu JH (2008) J Mater Sci 43:5861. doi:10.1007/s10853-008-2827-3
19. Postma HWC, Teepen T, Yao Z, Grifoni M, Dekker C (2001) Science 293:76
20. Olek M, Kempa K, Jurga S, Giersig M (2005) Langmuir 21:3146
21. Ning J, Zhang J, Pan Y, Guo J (2003) J Mater Sci Lett 22:1019
22. Zhan H, Zheng C, Chen W, Wang M (2005) Chem Phys Lett 411:373
23. Kempa T, Carnahan D, Olek M, Correa M, Giersig M, Cross M (2005) J Appl Phys 98:034310
24. Whitsitt EA, Barron AR (2003) Nano Lett 3:775
25. Kanungo M, Isaacs HS, Wong SS (2007) J Phys Chem C 111:17730
26. Liu Y, Tang J, Chen X, Wang R, Pang GKH, Zhang Y, Xin JH (2006) Carbon 44:165
27. Llusar M, Sanchez C (2008) Chem Mater 20:782
28. Hillebrenner H, Buyukserin F, Kang M, Mota MO, Steward JD, Martin CR (2006) J Am Chem Soc 128:4236
29. Jang J, Yoon H (2004) Adv Mater 16:799
30. Fan R, Wu Y, Li D, Yue M, Majumdar A, Yang P (2003) J Am Chem Soc 125:5254
31. Trewyn BG, Slowing II, Giri S, Chen HT, Lin VSY (2007) Acc Chem Res 40:846
32. Chae WS, Braum PV (2007) Chem Mater 19:5593
33. Kim JW, Kim LU, Kim CK (2007) Biomacromolecules 8:215
34. Satishkumar BC, Govindaraj A, Vogl EM, Basumallick L, Rao CNR (1997) J Mater Res 12:604
35. Hench LL, West JK (1990) Chem Rev 90:33
36. Bottini M, Tautz L, Huynh H, Monosov E, Bottini N, Dawson MI, Bellucci S, Mustelin T (2005) Chem Commun 758
37. Li X, Liu Y, Fu L, Cao L, Wei D, Wang Y (2006) Adv Funct Mater 16:2431
38. Shanmugharaj AM, Bae JH, Lee KY, Noh WH, Lee SH, Ryu SH (2007) Compos Sci Technol 67:1813
39. Gasparac R, Kohli P, Mota MO, Trofin L, Martin CR (2004) Nano Lett 4:513
40. Yoon SB, Sohn K, Kim JY, Yu JS, Hyeon T (2002) Adv Mater 14:19
41. Yoon SB, Kim JY, Kim JH, Park YJ, Yoon KR, Park SK, Yu JS (2007) J Mater Chem 17:1758
42. Chernozatonskii LA, Artyukhpv VI, Sorokin PB (2006) Phys Rev B 74:045402