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Fabrication of Carbon Nanotube/SiO₂ and Carbon Nanotube/SiO₂/Ag Nanoparticles Hybrids by Using Plasma Treatment

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Abstract Based on plasma-treated single wall carbon nanotubes (SWCNTs), SWCNT/SiO₂ and thiol groups-functionalized SWCNT/SiO₂ hybrids have been fabricated through a sol–gel process. By means of thiol groups, Ag nanoparticles have been in situ synthesized and bonded onto the SiO₂ shell of SWCNT/SiO₂ in the absence of external reducing agent, resulting in the stable carbon nanotube/SiO₂/Ag nanoparticles hybrids. This strategy provides a facile, low–cost, and green methodology for the creation of carbon nanotube/inorganic oxides-metal nanoparticles hybrids.

**Keywords** Carbon nanotubes · Nanocomposites · Plasma treatments · Silica · Silver nanoparticles

Introduction

Carbon nanotube (CNT)/inorganic composites are a new type of functional materials that gained tremendous interest in recent decades owing to their exceptional optical, mechanical, electrical, and thermal properties, thus enabling the use in photochemical, catalytic, and electrochemical technologies [1–3]. To date, varied CNT-based composite structures resulting from the deposition of metallic, semiconducting, and insulating nanoparticles/nano lusters on the CNT side walls have been created successfully [4–6].

To efficiently synthesize CNT-based nanocomposites, it is necessary to activate the graphitic surface of CNT that tend to be chemical inert and lack of dispersibility in solvents. In this direction, many synthesis strategies have been designed to covalently or non-covalently decorate the side walls of the CNTs with molecular or polymeric entities to create dispersible CNT derivatives. One of the most popular protocols is achieved under strong oxidizing conditions, such as refluxing in concentrated HNO₃, followed by the use of carboxylic acid chemistry or direct sidewall reactions [7]. Although these strong oxidizing treatments functionalize the CNTs, the defects are introduced to the pristine CNTs simultaneously and thus undesirably compromise the electronic and mechanical properties [8]. To conquer these drawbacks, non-covalent techniques for modifying CNTs surfaces have been developed in recent decades. By means of π–π stacking and/or wrapping interactions in the presence of surfactants and/or polymers, aqueous-based CNT sols can be achieved [5, 8, 9]. These modified CNTs can be further assembled with a variety of nanoparticles or ceramic materials by means of in situ synthesis techniques [5, 8, 9]. The resulting CNT-based hybrids exhibit tailored properties while still reserving nearly all the intrinsic properties of CNTs.

The above described pioneering works are very interesting but unfortunately, during all those processes for modifying CNT surfaces, more chemicals such as modifier agents, surfactants, organic solvents, amphiphilic polymers, or other additives are indispensable. These would inevitably increase the hazard to environment; enhance the preparation cost and complex the functionalization processes. Therefore, it is still a challenging work to develop a facile, low-cost, and green CNT surface modification method for fabricating CNT-based nanocomposites.

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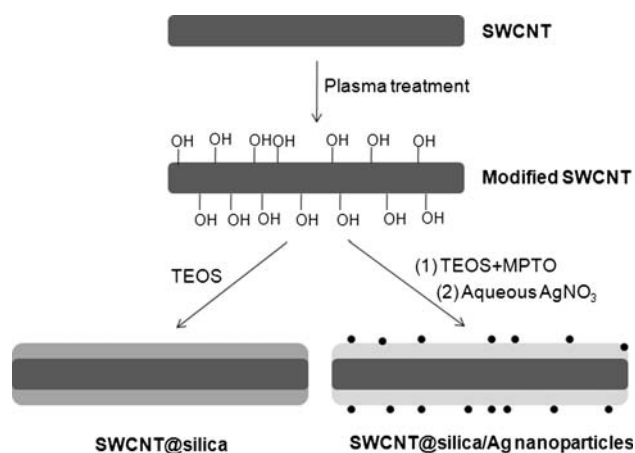
Scheme 1 Schematic illustration of fabrication of SiO$_2$-coated single wall carbon nanotubes (SWCNT@SiO$_2$) and Ag nanoparticles immobilized SWCNT@SiO$_2$ (SWCNT@SiO$_2$/Ag nanoparticles) based on the plasma-treated SWCNTs. TEOS and MPTO in scheme are tetraethoxysilane and 3-mercaptopropyl-triethoxysilane, respectively

Recently, we have demonstrated a novel modification approach, plasma treatment, to modify the polystyrene microspheres surface with hydroxyl groups [10]. In this whole modification process, no more solvent and chemicals are involved, which simplifies the modification process, reduces the preparation cost, and decreases the hazard to environment. Herein, we explored this simple, low-cost, and green protocol to introduce the hydroxyl groups on the side walls of single wall carbon nanotubes (SWCNTs) and use these surface-modified SWCNTs as substrate to fabricate SiO$_2$-coated SWCNTs (SWCNT@SiO$_2$) nanocomposite by the co-condensation reaction between hydroxyl groups bearing on the surface of SWCNT@SiO$_2$ with tetraethoxysilane (TEOS) in a sol–gel process. Following the similar procedures, the SiO$_2$ shell of SWCNT@SiO$_2$ can be further functionalized with thiol groups by using suitable amount of 3-mercaptopropyl-triethoxysilane (MPTO) as co-condensation agent together with TEOS. Subsequently, the silver nanoparticles (Ag NPs) can be further in situ synthesized and immobilized on the thiol-modified surface of SiO$_2$ shell through covalent bonds. The schematic procedures were shown in Scheme 1.

Experimental

Modification of SWCNT by Plasma Treatment

The SWCNTs commercially obtained from Carbon Nanotechnologies Inc. were firstly dispersed in 2 mL of acetone by sonication. When the acetone was evaporated completely under vacuum, the dry samples were transferred to the chamber of plasma cleaner (Harrick Plasmer Cleaner PDC-32G). After evacuating chamber to low-pressure residual air (0.2 mbar), the SWCNTs were subject to plasma treatment at 10.5 W for 20 s. The treatment processes were repeated 3 times to introduce hydroxyl groups homogeneously on the side walls of SWCNTs.

Preparation of SWCNT@SiO$_2$ Composite

In a typical process, 5 mg of surface-modified SWCNTs was transferred to 50-mL flask containing 10 mL of absolute ethanol. After sonicating for 5 min, 0.4 mL of ammonia water (28 wt %), and 0.1 mL of TEOS were injected into the mixture under gentle stirring. And then the mixture was kept stirring at ambient temperature for 3 h. The SWCNT@SiO$_2$ core/shell heterostructures were obtained after removal of supernatants by three circles of centrifugation and redispersion in absolute ethanol. Following the similar procedures, thiol groups modified SWCNT@SiO$_2$ composites (SWCNT@SiO$_2$–SH) can be prepared. In a typical reaction, 0.4 mL of ammonia water (28 wt %), 6 μL of MPTO, and 0.1 mL of TEOS were orderly added to the reactor containing 10 mL of absolute ethanol and 5 mg of plasma-treated SWCNTs under vigorous stirring. After continuous stirring for 3 h at ambient temperature, the resulting SWCNT@SiO$_2$–SH hybrid was collected after purification by three circles of centrifugation and redispersion in absolute ethanol. To immobilize Ag nanoparticles onto the surface of SWCNT@SiO$_2$–SH, the resulting SWCNT@SiO$_2$–SH composites were redispersed in 2 mL of aqueous silver nitride (0.01 M) under vigorous stirring at room temperature for 3 h. After three circles of centrifugation and redispersion in water, the SWCNT@SiO$_2$/Ag nanoparticles composite was obtained.

Characterization

Samples for transmission electron microscopy (TEM) were deposited onto carbon-coated copper electron microscope grids and dried in air. TEM analysis was performed using JEOL 1200 EX at 120 keV. Fourier Transform Infrared (FTIR) spectra were obtained at a resolution of 1 cm^{-1} with a Bruker FT-IR spectrophotometer between 4,000 and 400 cm^{-1}. The IR measurements of the powder samples were performed in the form of KBr pellets. Energy dispersive X-Ray spectroscopy (EDS) analysis was performed using an OXFORD ISIS system attached to the SEM.

Results and Discussion

Plasma Treatment of SWCNT and Fabrication of SWCNT@SiO$_2$ Therby

The side walls of SWCNTs can be modified with hydroxyl groups by means of plasma treatment. The presence of hydroxyl groups bearing on the surface of resulting plasma-treated SWCNTs can be evidenced by FTIR analysis. Figure 1 shows the FTIR spectra of SWCNTs samples before and after plasma treatment. By comparison, it is observed that the plasma-treated SWCNTs exhibit a broad band at around 3,430 cm^{-1} (curve b), which is attributed to the stretching frequency of hydroxyl groups [11]. This fact illustrates that the hydroxyl groups have been successfully introduced onto the sidewalls of SWCNTs by plasma treatments.

Through a co-condensation process between the hydroxyl groups bearing on the plasma-treated SWCNTs and TEOS, a SiO$_2$ layer can be coated onto the surface of SWCNTs. Figure 2a shows a typical TEM image of the as-prepared SWCNT@SiO$_2$. In this context, the SiO$_2$ layer clearly exhibits fairly smooth surface and uniform thickness. And the average thickness of the shell layer and inner core of SWCNT@SiO$_2$ are about 14 and 3 nm respectively determined by TEM o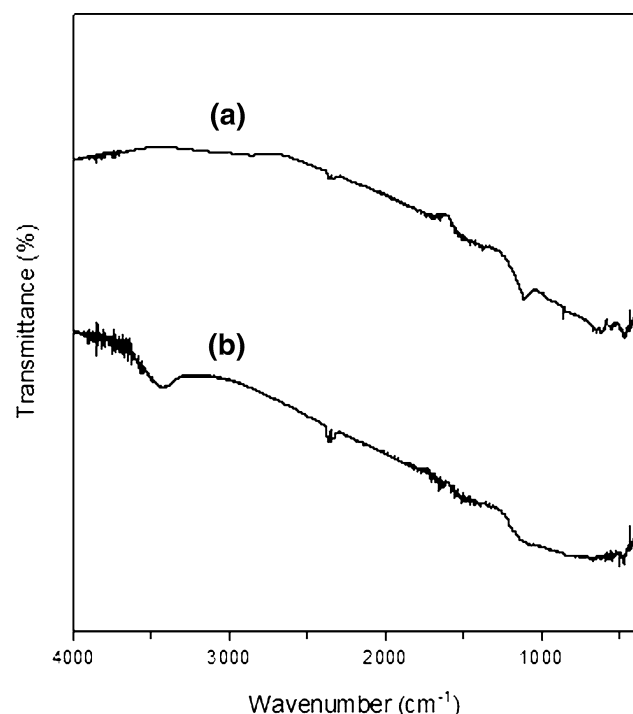bservations. Moreover, no more free SiO$_2$ beads are observed. As the arrows in Fig. 2a indicate, however, partial incomplete SiO$_2$ coatings are also visualized, which is caused by the incomplete plasma treatments of SWCNTs. The formation of SiO$_2$ coating is further confirmed with EDS analysis. Figure 2b shows the sharp peaks of Si and O (with an atomic ratio 1:2), demonstrating the presence of SiO$_2$ on the surface of SWCNTs. More interestingly, when the hydrolysis time is extended to 12 h, the average diameter of the resulting SWCNT@SiO$_2$ is further increased from 31 nm (Fig. 2a) to 38 nm (Fig. 2c), and the corresponding SiO$_2$ coating exhibits a quite rough surface. These are attributed to the combined effects of the nucleation and growth processes of SiO$_2$ derived from TEOS on the surface of plasma-treated SWCNTs [10, 12]. During coating an inorganic oxide layer on a substrate, the surface nucleation-controlled process is favorable to form smooth surfaces, and the nuclei growth–controlled process is beneficial for generating rough surface morphology [10]. In the case of our current study, it is believed that the employed reaction conditions are more favorable for the nuclei growth–controlled process for the hydrolysis of TEOS during the extended reaction period. Therefore, the thickness of SiO$_2$ coating is tunable by prolonging hydrolysis time of TEOS at the expense of surface smoothness.
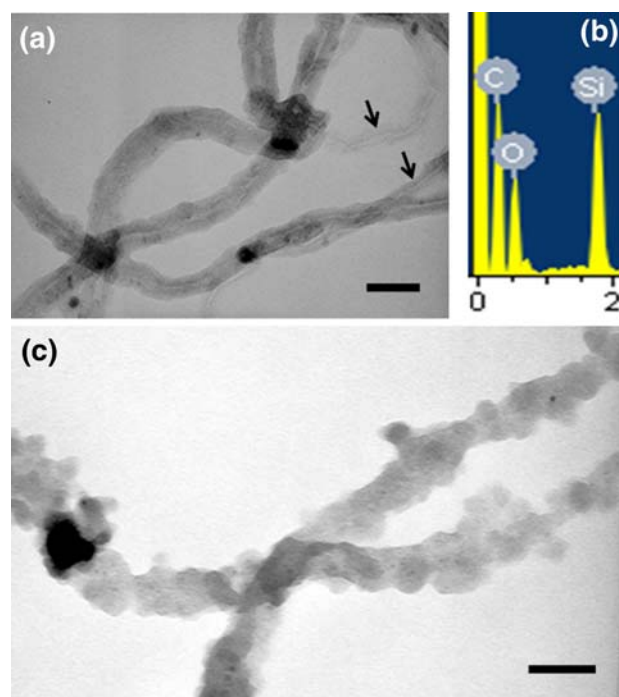

Fig. 1 FTIR spectra of single wall carbon nanotubes before (**a**) and after (**b**) plasma treatment

Fig. 2 TEM image (**a**) and EDS spectrum (**b**) of SiO$_2$-coated single wall carbon nanotube (SWCNT@SiO$_2$) composites resulting from a co-condensation reaction between plasma-treated SWCNTs and TEOS for 3 h; TEM image of SWCNT@SiO$_2$ (**c**) obtained by co-condensation reaction between plasma-treated SWCNTs and TEOS for 12 h. The *scale bars* are 50 nm

Fabrication of SWCNT@SiO$_2$/Ag

The resulting SWCNT@SiO$_2$ hybrid is comprised of SWCNT core with a shell of bonded SiO$_2$, which combines specific properties from each component into a single homogeneous phase. Moreover, the straightforward manufacture, mechanical strength, non-toxicity, and diverse surface chemistry of SiO$_2$ offer an ideal basis for advancing novel SWCNT-based hybrids with desirable functionalities and inherent properties. It is worth noting that the hydroxyl groups usually formed on the SiO$_2$ surface by dissociation adsorption of water molecules provide the capability required for the reduction of metal ions, which offers an effective rout to form SiO$_2$/metal nanoparticles nanocomposites at low temperature without applying any external reducing agent or media [13]. Unfortunately, these hetero-nanostructures are not stable owing to the weak interactions between the metal deposit and SiO$_2$ substrate.

To overcome this disadvantage, a promising alternative is to immobilize metal nanoparticles on the SiO$_2$ surface through covalent bonds. Thiol groups tend to interact with metal ions by the cleavage of an S–H bond and the spontaneous formation of an S-metal bond [14]. These combined sites on the SiO$_2$ surface (S-metal) act as nucleation sites, on which the reduced silver species successively deposit and in situ grow into larger metal nanoparticles. In this process, thiol groups are used as a chemical protocol to attach the metal nanoparticles to the SiO$_2$ surface, resulting in a stable heterogeneous nanocomposite containing metal nanoparticles.

In our current research, the further functional SWCNT@SiO$_2$ was explored to create by immobilizating Ag nanoparticles onto the SiO$_2$ sheath. A SiO$_2$ layer bearing thiol groups was firstly coated onto the plasma-treated SWCNTs. Figure 3a shows the resulting thiol groups modified SWCNT@SiO$_2$ hybrid (SWCNT@SiO$_2$–SH), exhibiting a fairly uniform SiO$_2$ coating (26 nm in average diameter) with smooth surface, which is similar to the SWCNT@SiO$_2$ (Fig. 2a). It is obvious that the involvement of the third condensation agent MPTO has negligible effects on the morphology of the resulting SWCNT@SiO$_2$ heterostructures. The presence of the thiol groups in the heterostructures can be further evidenced by EDS analysis (inset of Fig. 3a), in which the obvious S signal originated from the thiol groups is observed.

Aimed to immobilize Ag nanoparticles on the functional SiO$_2$ shell of SWCNT@SiO$_2$–SH, the SWCNT@SiO$_2$–SH composites were redispersed in 2 mL of aqueous silver nitride (0.01 M) under vigorous stirring at room temperature for 3 h. In this process, Ag nanoparticles are in situ formed and immobilized onto the SiO$_2$
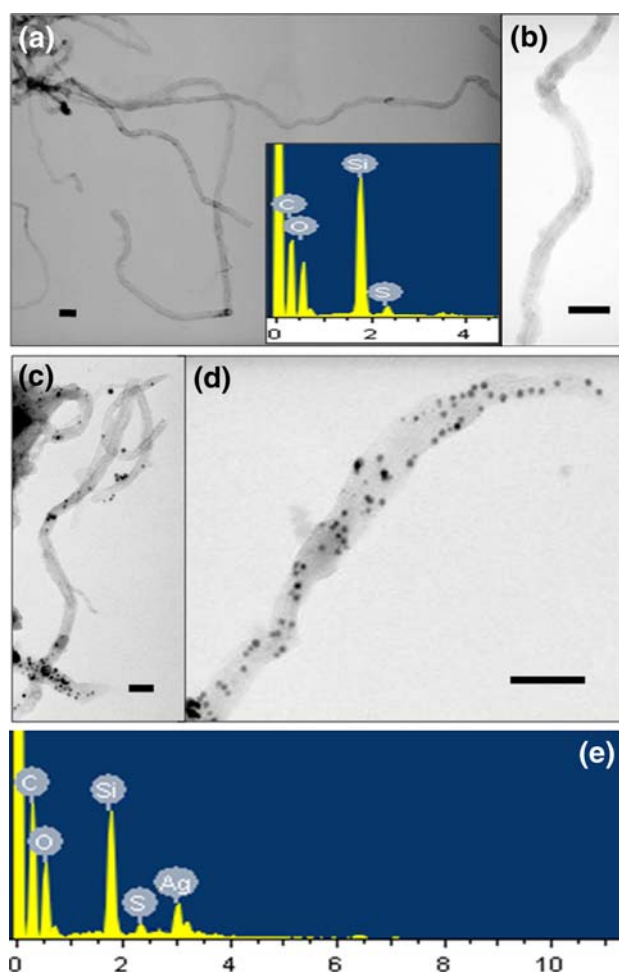

Fig. 3 TEM images with lower (**a**) and higher magnification (**b**) and EDS spectrum [inset of (**a**)] of SiO$_2$-coated SWCNTs bearing thiol groups (SWCNT@SiO$_2$–SH); TEM images with lower (**c**), higher magnification (**d**) as well as EDS spectrum (**e**) of Ag nanoparticles immobilized SWCNT@SiO$_2$–SH. The *scale bars* are 50 nm

surface, resulting in the formation of SWCNT@SiO$_2$/Ag hybrids. The Direct evidence for the formation of Ag nanoparticles on the SiO$_2$ surface is obtained from TEM observation. Figure 3c, d shows the surfaces of SWCNT@SiO$_2$ are decorated with Ag nanoparticles. Although the in situ formed Ag nanoparticles are randomly distributed on the SiO$_2$ shell, their size is quite uniform (with an average diameter of ca. 5 nm). The further evidence of the existence of Ag nanoparticles is provided by EDS (Fig. 3e), which reveals the presence of S and Ag on the surface of SWCNT@SiO$_2$/Ag. Similarly, by using different metal oxides and metal precursors, a variety of CNT/inorganic oxide/metal nanoparticles hybrid materials can be expected. It is worth noting that this protocol provides a facile, low-cost, and green alternative to create the CNT-based inorganic oxide heterostructures/metal nanoparticle hybrids.

Conclusions

An effective rout to introduce hydroxyl groups onto the side walls of pristine SWCNTs by means of plasma treatment technique has been demonstrated. By means of a co-condensation process between these hydroxyl groups bearing on the SWCNTs and TEOS (or together with MPTO), an uniform SiO_2 and thiol groups-functionalized SiO_2 coating on the SWCNTs can be fabricated effectively. Utilizing SWCNT@SiO_2–SH, a stable SWCNT@SiO_2/Ag heterogeneous hybrid has been generated via in situ growth process in the absence of any additional reducing agents. These SWCNT-based composites may provide considerable potential in applications like catalysis, bactericide, and electrode materials. Particularly, it is worthy to note that this facile procedure could offer a promising alternative to create varied SWCNT/inorganic oxide (TiO_2, GeO_2 et al.) composites and the corresponding SWCNT/inorganic oxide/metal nanoparticles hybrids.

References

1. J. Dimaio, S. Rhyne, Z. Yang, K. Fu, R. Czerw, J. Xu, S. Webster, Y.P. Sun, D.L. Carroll, J. Ballato, Inf. Sci. **149**, 69 (2003)
2. V.G. Gavalas, R. Andrews, D. Bhattacharyya, L.G. Bachas, Nano. Lett. **1**, 719 (2001)
3. J.S. Moon, P.S. Alegaonkar, J.H. Han, T.Y. Lee, J.B. Yoo, J. Appl. Phys. **100**, 10403 (2006)
4. L. Han, W. Wu, K.F. Louis, J. Luo, M.M. Maye, N.N. Kariuki, Y. Lin, C. Wang, C.J. Zhong, Langmuir **20**, 6019 (2004)
5. G. Mountrichas, S. Pispas, N. Tagmatarchis, Small **3**, 404 (2007)
6. Y. Liu, J. Tang, X. Chen, R. Wang, G.K.H. Pang, Y. Zhang, J.H. Xin, Carbon **44**, 165 (2006)
7. M.W. Marshall, S. Popa-Nita, J.G. Shapter, Carbon **44**, 1137 (2006)
8. X. Li, Y. Liu, L. Fu, L. Cao, D. Wei, Y. Wang, Adv. Funct. Mater. **16**, 2431 (2006)
9. D. Wang, Z. Li, L. Chen, J. Am. Chem. Soc. **128**, 15078 (2006)
10. H. Li, C.-S. Ha, I. Kim, Langmuir **24**, 10552 (2008)
11. T. Ramanathan, F.T. Frank, R.S. Ruoff, L.C. Brinson, Res. Lett. Nanotech. **2008**, 1 (2008). doi:10.1155/2008/296928
12. M. Agrawal, A. Pich, S. Gupta, N.E. Zafeiropoulos, P. Simon, M. Stamm, Langmuir **24**, 1013 (2008)
13. H. Hofmeister, P.-T. Miclea, W. Mörke, Part. Part. Syst. Charact. **19**, 359 (2002)
14. P.N. Floriano, O. Schlieben, E.E. Doomes, I. Klein, J. Janssen, J. Hormes, E.D. Poliakoff, R.L. McCarley, Chem. Phys. Lett. **321**, 175 (2000)