A Simple Route to Coat Multiwalled Carbon Nanotubes with Silica

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The pristine multiwalled carbon nanotubes (MWCNTs) without oxidation or covalent decoration were homogeneously coated with silica through a simple modified sol–gel method.

Carbon nanotubes (CNTs) have been the focus of considerable research since 1991 because of their unique properties and tremendous potential applications.[1–4] One of the most popular methods to use their attractive properties is preparing various composites based on metal,[5] polymer,[6,7] and ceramics.[8,9] As to incorporating CNTs into matrix, problems still exist because of the difficulty in dispersing CNTs uniformly throughout the composite and the poor adhesion between them.[10,11] Coating CNTs with materials may be an excellent candidate, because it could eliminate the undesirable attractive interactions between the nanotubes and improve the interfacial bonding with matrix.[6,12,13] Studies on the systems of CNTs interacting with silica include the strengthening effect,[14] microwave attenuation properties,[15] the potential as optical limiting materials,[16] etc. In order to achieve better performance of the composites, a range of methods have been used to coat CNTs with silica, such as plasma-enhanced chemical vapor deposition,[17] vapor-phase method,[18] colloidal method,[19] reverse micelle method,[20] precipitation,[13,21] sol–gel method,[22,23] and other solution-based methods.[6,12] However, some of the methods require strong oxidation or covalent decoration before coating which would disrupt the unique properties of CNTs, and some of them are comparatively complicated, therefore, not suitable for large-scale production.

Here, we report a very simple and efficient route to achieve homogeneous coverage of MWCNTs with silica choosing cetyltrimethylammonium bromide (CTAB) as surfactant and 3-aminopropyltriethanoxysilane (APTES) as coupling agent. The detailed coating procedure was conducted as follows: a mixture (MI) of 250 mg of pristine MWCNTs (provided by Shenzhen Nanotech Port Co., Ltd., China, which were prepared by the catalytic decomposition of CH_4 and then washed in diluted nitric acid to remove the catalytic metals effectively) with 0.5 mL of APTES, 100 mg of CTAB, and 48 mL of H_2O were sonicated for 20 min under 40 °C, and then stirred for 3 h. Another mixture (MII) of 5 mL of tetraethoxylsilane (TEOS) with 3 mL of H_2O and 50 mL of ethyl alcohol was treated exactly as MI. Subsequently, MI and MII were mixed together and then sonicated for 60 min under 40 °C followed by stirring for 10 min. After that, 2.0 mol·L^{-1} aqueous ammonia was added dropwise until the pH value reached 9.5. Then, the obtained black suspension was filtered and washed with distilled water and absolute alcohol for several times. Finally, the product was dried at 100 °C and then characterized.

Figure 1 is the transmission electron microscopy (TEM) image of MWCNTs coated with silica. As seen from the TEM image, all the MWCNTs were homogeneously coated with a uniform layer, and almost each MWCNT had a length more than 1 micron. Figure 2 is the high-resolution transmission electron microscopy (HRTEM) image of MWCNT coated with silica and the corresponding energy-dispersive spectrum. From the HRTEM image, one can see that the thickness of coating was about 6 nm and that the characteristic carbon layer separation arose from MWCNTs was about 0.34 nm.[24] The corresponding energy-dispersive spectrum indicated the expected elemental signals of Si, O, and C and thus confirmed the presence of a silica coating on MWCNT.

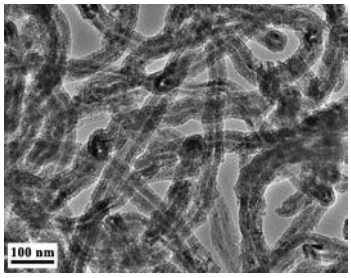

Figure 1. TEM image of MWCNTs coated with silica.

CTAB has been considered as a useful cationic surfactant to disperse CNTs efficiently[12], and APTES could interact with CNTs thus change the surface property of CNTs into more hydrophilic, which would facilitate the growth of silica by the hydrolysis of TEOS.[22] In order to identify the effect of APTES and CTAB individually, a control experiment was done without CTAB as surfactant. As seen from Figure 3, in the absence of CTAB, the coating layer of silica on MWCNTs was not homogenous and lots of dissociating silica particles aggregated into silica spheres. It is probable that APTES mainly interact with the carboxyl or hydroxyfunctional group of MWCNTs.[20,25] In our experiment, little carboxyl or hydroxy functional group was introduced to the pristine MWCNTs without pretreat-

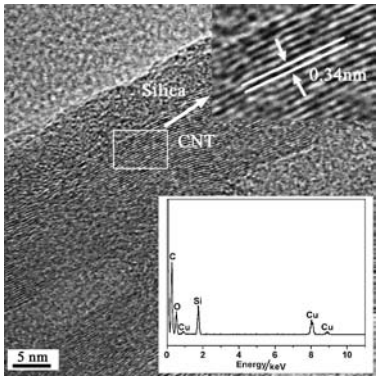

Figure 2. HRTEM image of MWCNT coated with silica and corresponding energy-dispersive spectrum (the bottom right inset).

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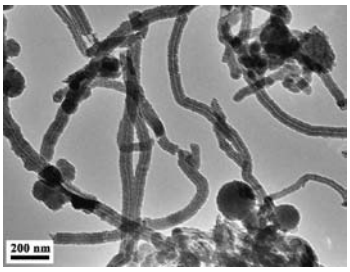

Figure 3. TEM image of MWCNTs coated with silica in the absence of CTAB.

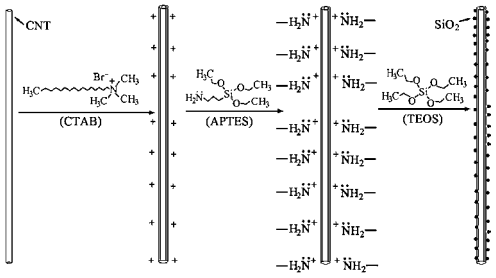

Figure 4. Scheme for the formation of silica coating on MWCNTs.

ment.[26,27] As a result, the interaction between APTES and MWCNTs was restricted and the coating process was blocked to some extent. However, CTAB could interact with pristine MWCNTs through its long hydrophobic alkyl section and exposed the hydrophilic ammonium section, forming a positively charged "wrapping"[28,29] which could strongly attract the lone pair electrons of aminofunctional group of APTES. The same ethoxyl group between APTES and TEOS facilitated the growth of silica on MWCNTs by the hydrolysis of TEOS, thus we proposed the scheme for the coating procedure (Figure 4). It is worthy to note that, as no strong oxidation procedure or covalent decoration on pristine MWCNTs was done before coating, this method is a simple and efficient way to coat MWCNTs with silica and retain their large length/diameter ratio as well as the intrinsic nanotube sp^2 structure and conjugation at the same time.[29] Further conditional experiments showed that the thickness of the coating layer on CNTs could be controlled by varying the content of APTES, and the thermal analysis conformed the stability of silica coating layer on CNTs' surface.[27]

In conclusion, we homogeneously coated MWCNTs with silica through a simple way using CTAB as surfactant and APTES as coupling agent accompanied by the hydrolysis of TEOS. CTAB could interact with the pristine MWCNTs, forming a positively charged "wrapping" which could strongly attract APTES. The similarity between APTES and TEOS facilitated the coating of silica on MWCNTs, and the thickness of stable coating layer could be controlled by altering the experimental conditions. The mild noncovalent decoration retained their large length/diameter ratio as well as the intrinsic nanotube sp^2 structure and conjugation of the pristine MWCNTs at the same time. We anticipate this method would be more suitable for large-scale production and yield composites with better performances.

The authors are grateful for the financial supports from the Nanotechnology Projects of Shanghai (No. 0352nm053) and the Major Basic Research Programs of Shanghai (No. 04DZ14002).

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Published on the web (Advance View) July 28, 2007; doi:10.1246/cl.2007.1098