Coating carbon nanotubes with polymer in supercritical carbon dioxide†

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A facile and efficient method has been developed for coating MWNTs with solvent resistant polymer in scCO$_2$, which permits the selective deposition of high molecular weight fluorinated graft poly(methyl vinyl ether-*alt*-maleic anhydride) polymer onto MWNTs in scCO$_2$ under 100–170 bar at 40 °C and forms quasi one-dimensional nanostructures with conducting cores and insulating surfaces.
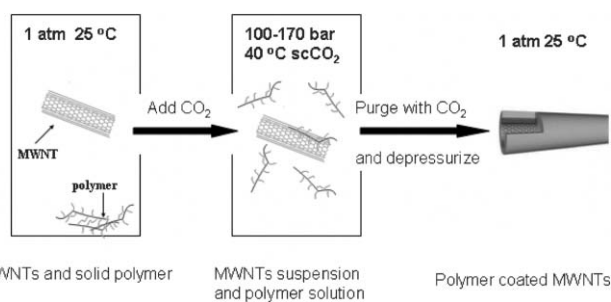
Because of their unique electronic and mechanical properties,[1] carbon nanotubes (CNTs) have been proposed as materials for nanotechnology to replace silicon-based electronics in the near future. To assemble nanoscale electronic devices, an insulating layer has to be coated onto the CNTs to avoid short circuits. Polymer-coated nanotubes have recently been used as a scanning tip for atomic force microscopy and have shown great promise for nanoscale bio- and electrochemical probing.[2] Despite the recent progress, nanotube coating still poses a significant problem because the electronic and mechanical properties of CNTs are often affected by the molecules[3] deposited onto the nanotubes through either conventional solution methods[4] or *in situ* polymerization.[5] Here we report a new and facile solvent-free method for coating solvent-resistant insulating polymer onto carbon nanotubes using supercritical carbon dioxide (scCO$_2$). Carbon dioxide is non-flammable, non-toxic and naturally abundant,[6] and is consequently promoted as a sustainable solvent in chemical processing. It can be viewed as a good alternative to organic solvents for coating nanotubes with a polymer layer while retaining the intrinsic properties of CNTs.

Supercritical carbon dioxide has been already used in many nanostructure processes, such as filling nanotubes,[7] nanopore expansion[8] and functionalization of mesoporous silica.[9] Further benefit of scCO$_2$ is its pressure-dependent density. This property of scCO$_2$ allows selective fractioning of polymers by molecular weight,[10] which potentially can be used to control the thickness of a polymer layer simply by changing the operating pressure. Very recently, scCO$_2$ has also been shown to be useful for the functionalization of multi-walled carbon nanotubes with molecular anchors.[11]

The fluorinated graft poly(methyl vinyl ether-*alt*-maleic anhydride) (F-g-PMVE-MA, the structure is shown in the supplementary information†) was chosen as the coating polymer, not only because it is electrically insulating and soluble in supercritical carbon dioxide, but also because it is insoluble in conventional organic solvents. This property is important because it allows the coating layer to stay intact during further processing of the nanotubes where various organic solvents are normally used. The coating process includes four steps (Scheme 1): (1) a mixture of multi-walled nanotubes (Aldrich, 95%) and F-g-PMVE-MA with a weight ratio of 0.07:1 was put into a high pressure view cell with a sapphire window. (2) The system was then heated up to 40 °C and pressurized with carbon dioxide (up to 300 bar) until polymer particles were no longer visible in the cell. The MWNTs were suspended by mechanical stirring during the process. (3) The stirrer was stopped, and the pressure was slowly released under isothermal conditions through a back pressure regulator down to 170 bar, which was below the cloud point. When the pressure reached the cloud point, the system became opaque. The stirrer was restarted, and the pressure and temperature were kept constant for one hour. (4) Finally the system was purged with fresh carbon dioxide until the fluid was clear (*ca.* 2 hours). The system was then fully depressurized and the sample was collected and labelled as P-MWNT.

The polymer coated nanotubes P-MWNT maintained the morphology and the visual appearance of uncoated MWNTs, indicating that the resultant material did not form a bulk continuous polymer with nanotubes suspended in it (see supplementary information†). The structure of P-MWNT was characterized by high-resolution transmission electron microscopy (HRTEM) (Fig. 1a) confirming that the polymer and nanotubes do not form bulk composite. High magnification micrographs (Fig. 1b) show MWNTs coated with an amorphous layer indicated by arrows, while the nanotube internal cavity is empty. The average thickness of the polymer layer is about 2 nm. Energy dispersive X-ray (EDX) spectroscopy (Fig. 1c) performed for the coated nanotubes P-MWNT using a ~10 nm electron beam probe confirmed the presence of fluorine ($K\alpha_{1,2}$ = 0.677 keV) in the amorphous layer, which is a component of the block copolymer F-g-PMVE-MA used for coating.

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† Electronic supplementary information (ESI) available: Experimental section and figures of fluorinated graft poly(methyl vinyl ether-*alt*-maleic anhydride) and coated carbon nanotubes. See DOI: 10.1039/b600441e
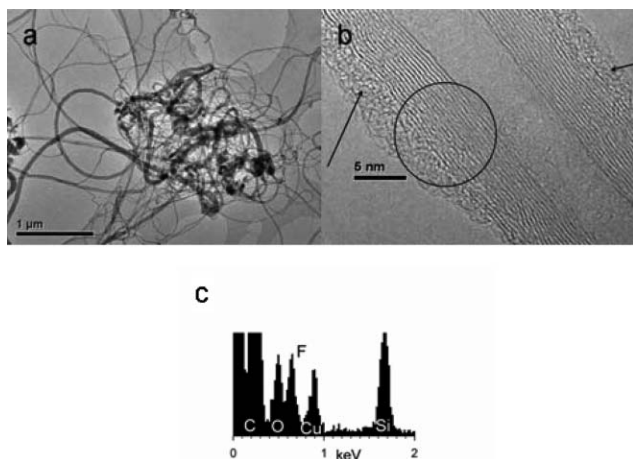

Scheme 1 Schematic procedure for coating MWNTs with fluorinated graft poly(methyl vinyl ether-*alt*-maleic anhydride) copolymer in supercritical carbon dioxide.

Fig. 1 (a) Low magnification HRTEM micrograph of coated MWNTs, (b) high magnification HRTEM images of one MWNT with the polymer layer indicated by arrows, (c) EDX spectrum obtained from the area in (b) marked by a circle. Note the F-peak is characteristic of the polymer layer (only the bottom part of the C-peak is shown and the other peaks are from the sample holder).

Fourier transform infrared (FT-IR) spectra of P-MWNT show a significant IR absorption in the range of 1000–1300 cm^{-1} (Fig. 2, region 1), which corresponds to vibration of C–F bonds in the polymer. IR peaks at 2925 cm^{-1} and 2853 cm^{-1} are also observed (Fig. 2, region 2), which are assigned to C–H bond vibrations.

Thermal gravimetric analysis (TGA) for P-MWNT, carried out under an N_2 atmosphere (Fig. 3), showed a 35% weight loss below 450 °C, associated with polymer decomposition. This weight loss for P-SWNT below 450 °C is 60% less than the weight loss for pure polymer F-g-PMVE-MA over the same temperature range. Uncoated MWNTs show no detectable weight loss up to 700 °C. Thus, the content of the polymer in P-MWNT calculated from the TGA data is about 35%, which is consistent with the average thickness of the coating layer observed in HRTEM. The temperature (T_d) for the onset of decomposition of F-g-PMVE-MA deposited onto nanotubes is 370 °C, 20 °C higher than that of
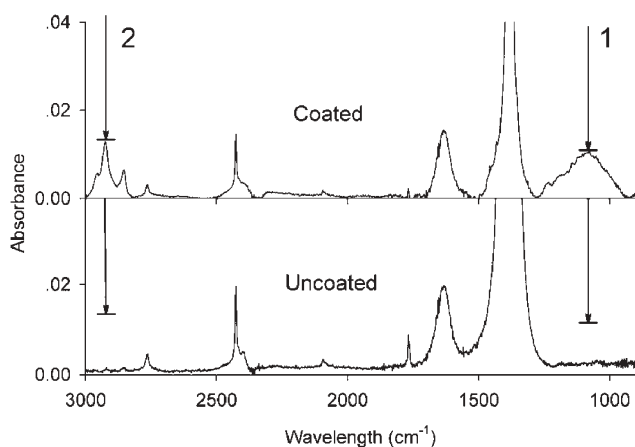

Fig. 2 FT-IR spectra of the coated nanotubes, P-MWNT (top) and uncoated MWNTs (bottom). Note the characteristic bands 1, v(C–F) and 2, v(C–H), which are present on the coated sample but not on the uncoated.
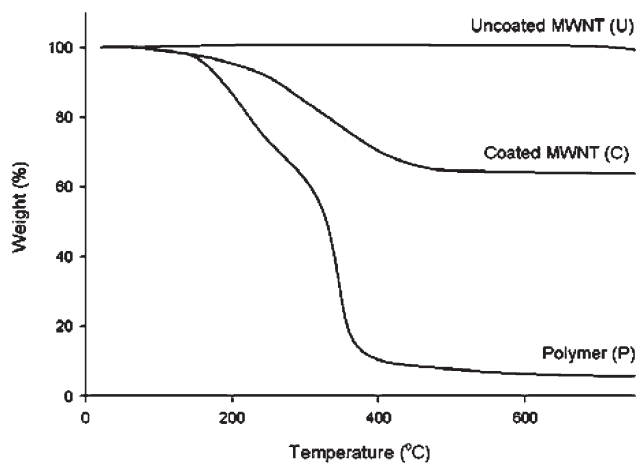

Fig. 3 TGA curves of uncoated MWNTs (U), polymer-coated MWNTs (C) and pure polymer F-g-PMVE-MA (P). The trace C suggests that the weight of the coating is *ca.* 35% of the total weight of the coated MWNTs.

pure F-g-PMVE-MA (*ca.* 350 °C). This indicates that the F-g-PMVE-MA coating in P-MWNT has a higher molecular weight than the average molecular weight of the bulk F-g-PMVE-MA originally put into the high pressure cell. This is to be expected because as the pressure of scCO$_2$ reaches the cloud point, polymer molecules with high molecular weight precipitate preferentially as the solubilising ability of scCO$_2$ decreases. Similar techniques of isothermal pressure decrease have been used for supercritical fractionation of polymers.[10] The purging process at low pressure will remove the remaining low molecular weight polymer from the chamber, and leaves the higher molecular weight polymer coating on the nanotube walls.

In conclusion, we have developed a facile and efficient method for coating MWNTs with solvent resistant polymer in scCO$_2$. It permits the selective deposition of high molecular weight fluorinated graft poly(methyl vinyl ether-*alt*-maleic anhydride) polymer onto MWNTs in scCO$_2$ under 100–170 bar at 40 °C.‡ The coating layer has an average thickness of ~2 nm around the multi-walled carbon nanotubes. These materials have a high potential for a range of important applications including nanoelectronics and nanomaterials.
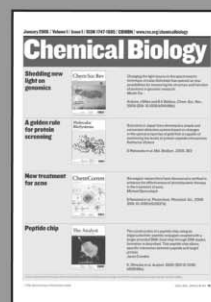
Notes and references

‡ **Caution**: Such experiments involve high pressures and require an appropriate safety assessment.

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