Nanotube brushes: polystyrene grafted covalently on CN_x nanotubes by nitroxide-mediated radical polymerization†

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Polymer brushes consisting of polystyrene (PS) chains bonded covalently to N-doped multiwalled carbon nanotubes (CN_x) were synthesized by a "grafting from" route using nitroxide mediated radical polymerization (NMRP).

The surface functionalization of carbon nanotubes (CNTs) has become crucial in the fabrication of nanotube polymer composites.[1,2] Among various types of carbon nanotubes, boron and nitrogen-doped multiwalled carbon nanotubes (MWNTs) are expected to be excellent candidates for fabricating composites due to their intrinsic surface reactivity; these being capable of establishing strong filler-matrix interactions without the aid of acid treatments.[1,3,4] In particular, CN_x nanotubes could be synthesized with different stoichiometries ($x < 0.05$ to $x < 0.32$).[4] For these CN_x tubes, N is bonded to C in two fashions: 1) two bonded N (pyridine-type) and 2) three bonded N (substitutional-site in the hexagonal carbon lattice).[3,4]

Polymer brushes are typically synthesized by the covalent attachment of polymer chains to a substrate (*e.g.* CNTs) by either "grafting to" or "grafting from" techniques.[5] The "grafting to" routes involve the bonding between end-functionalized polymer chains and a suitable substrate. The "grafting from" route requires immobilization initiators on the substrate, followed by the *in situ* surface-initiated polymerization of the polymeric chains.[5] Particularly, in the "grafting from" approach, the molecular weight and the molecular weight distribution of the grafted polymers could be controlled using radical, anionic, carbocationic and ring metathesis polymerization. In fact, *in situ* surface-initiated controlled polymerization of single-walled (SWNTs) and multiwalled (MWNTs) carbon nanotubes has been recently reported using either atom transfer radical polymerization (ATRP)[6,7] or nitroxide mediated radical polymerization (NMRP).[8] However, to the best of our knowledge, *in situ* NMRP polymerization of CN_x nanotubes has not been reported hitherto. In addition, the use of CN_x nanotubes would not involve any acid treatment, a drawback that has always been carried out for standard (undoped) SWNTs and MWNTs.

In this communication we report the synthesis of polystyrene (PS) brushes attached to CN_x nanotubes (PS-CN_x) *via in situ* NMRP. This technique exploits the radical scavenging properties of CN_x tubes.[9–11] The obtained materials were fully characterized using high resolution transmission electron microscopy (HRTEM), electron energy loss spectroscopy (EELS), thermogravimetric analysis (TGA), FTIR studies, Raman spectroscopy, and electron spin resonance (ESR).

We have used purified styrene (Aldrich, >98%), TEMPO ($C_9H_{18}NO$), OH-TEMPO ($C_9H_{18}NO_2$), PR CGX505 (all nitroxide regulators from Ciba Specialty Chemicals, NO_x), benzoyl peroxide (BPO, initiator from Baker), and reactive grade solvents. CN_x nanotubes were produced by pyrolysing solutions of ferrocene ($Fe(C_5H_5)_2$) and benzylamine ($PhCH_2NH_2$) at 850 °C under an Ar atmosphere.[4] The raw tubes were dispersed ultrasonically in benzene for 60 min. Subsequently, the nanotube suspension was precipitated, filtered (0.5 μm PTFE filter) and dried under vacuum at 60 °C for 4 h. Note that it is not necessary to use acid treatments on the doped tubes in order to activate their surfaces.

The grafting reactions took place in a combinatorial design experiment using a parallel polymerization reactor module (PPR) involving various types of nitroxides (TEMPO, OH-TEMPO and PR CGX505), different molar initiator–controller ratios (1 : 1.3 and 1 : 2.6), and solvents (benzene and xylene). The reactions were carried out in two steps (Fig. 1): (i) the free radical functionalization of CN_x tubes with an initiator and a nitroxide controller (CN_x–BPO/NO_x), followed by (ii) *in situ* "controlled/living" styrene *via* NMRP (PS-CN_x). In the first step, 10 mg of sonicated

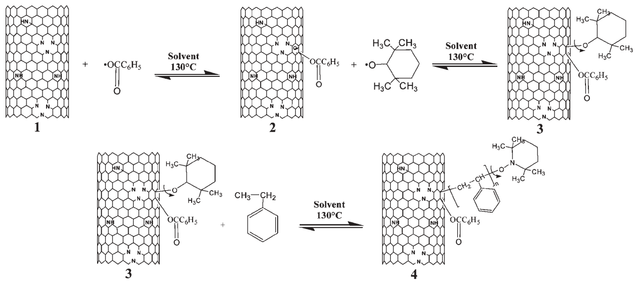

Fig. 1 Polymer brushes synthesis reaction scheme: functionalization of CN_x (**1**) with the BPO initiator (CN_x–BPO–$R^\bullet$) (**2**), the nitroxide controller (CN_x–BPO/NO_x) macroinitiator (**3**), and *in situ* polymerized PS–CN_x brushes (**4**).

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† Electronic supplementary information (ESI) available: Relative elemental compositions obtained by EELS on the different samples; comparative TGA studies of radical functionalized and PS-grafted CN_x nanotubes, and comparative Raman spectra of radical functionalized CN_x nanotubes using BPO and several nitroxides. See http://dx.doi.org/10.1039/b510471h

CN_x, initiator and controller solutions were heated in each reactor at 130 °C for 2 h. After the reaction, CN_x nanotubes were filtered off and washed. Subsequently, functionalized CN_x and fixed amounts of solvent–monomer (3 : 2) and monomer–initiator (96 : 1) solutions were added and heated in each reactor to polymerize for 24 h. The resultant materials were then purified, dried and characterized in order to separate PS-grafted CN_x or PS brushes.

In our reaction scheme (Fig. 1), the peroxide groups are first attached to the surface of the CN_x tube (**2**), thus creating a resonant radical that could trap the nitroxide controllers (**3**). In order to confirm this radical trapping behavior in CN_x, the spin concentration was measured using ESR. In particular, the radical concentration in solution obtained was commensurate with CN_x–BPO/NO_x (**3**) > CN_x–BPO–R$^\bullet$ (**2**) > CN_x (**1**). Our studies suggest that: (i) CN_x tubes are able to trap radicals, (ii) free controlled radical sites could be formed in CN_x–BPO/NO_x nanotubes (these being the NMRP-macroinitiators for grafting PS chains), and (iii) the number of radicals on the nanotube surface was increased when BPO and NO_x are in the solution media.

Soon after polymerization, we noted that our CN_x nanotubes disperse well in the reaction medium, indicating that polystyrene chains could have been fixed on the nanotube surface. This was further confirmed by HRTEM studies (Fig. 2), in which a uniform coating (*ca.* 7 nm thick and identified as PS) is observed, always covering the outer surface of the tubes (Fig. 2a and b). This observation is in contrast to physically mixed PS and CN_x tubes that were dispersed in a solvent; this material usually reveals fragmented and extremely irregular PS adhesion (Fig. 2c and d). In addition, we noted that our purified PS-grafted tubes easily disperse in organic solvents (Fig. 3). This confirms the enhanced surface adhesion of PS and the CN_x tube surface when the tubes are polymerized *via in situ* NMRP.

EELS studies in the low energy loss demonstrate that the amorphous regions surrounding the tubes correspond to PS. Fig. 4 depicts the spectra for PS, raw CN_x and the two types of polymer composites synthesized in this study. The peak located at 5.4 eV corresponds to π→π* excitations of the C=C bonds within CNTs,[12] and the peak at 6.8 eV arises from π→π* excitations of the C=C aromatic rings in PS.[13] These two peaks overlap for the physically blended material. In contrast, these features could not be observed in the amorphous layer covering the NMRP reacted sample (PS–CN_x), where there is only an individual peak centered at 6.6 eV, which could be associated with the excitation of aromatic rings located near the interface between PS and the CN_x nanotubes. In addition, a shift in the plasmon occurred in the NMRP reacted sample. These results could be attributed to covalent bonds established between PS and the CN_x tube surface.

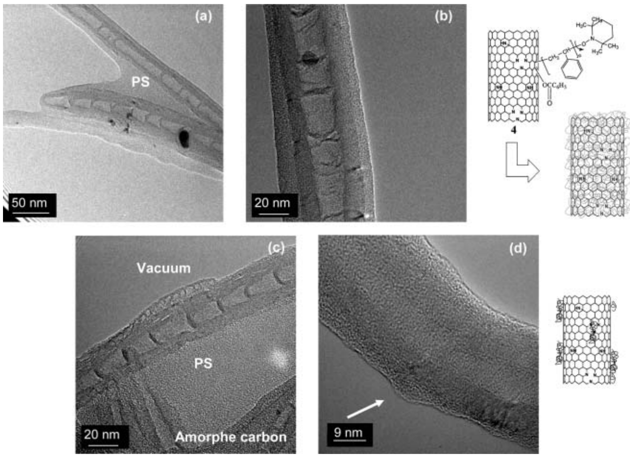

Fig. 2 HRTEM images of polymerized nanotubes: (a, b) using the NMRP method in which an outer layer is composed of PS and its thickness is *ca.* 7 nm; (c, d) sample obtained by physical blending, revealing irregular PS coating with a thickness of *ca.* 3 nm.

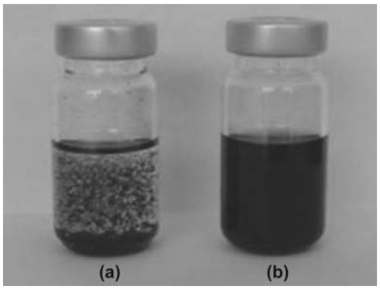

Fig. 3 Solubility differences in organic solvents (*i.e.* toluene) between (a) physically blended PS and CN_x, and (b) PS–CN_x.

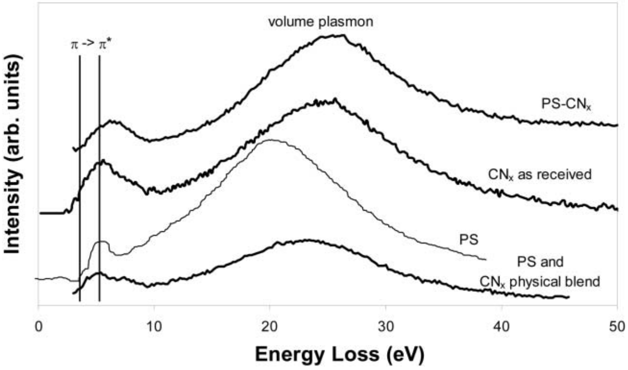

Fig. 4 EEL comparative spectra for the PS, raw CN_x, PS–CN_x using a NO_x controller (*i.e.* PR CGX505) and physically blended CN_x and PS (see text for details).

EEL spectra of PS-CN_x samples obtained for high loss energies and elemental mapping (not shown here) reveal the presence of excitation edges associated with the C-K edge (284 eV), N-K edge (401 eV) and O-K edge (532 eV) in the amorphous layer coating the tube. The concentrations of these elements appear to be higher for the nanotube brushes when compared to those observed for pristine CN_x tubes, and physically blended samples (see ESI†). These changes in the chemical content could be explained in terms of the radical functionalization (additional incorporation of N and O) that arises from the polymer-grafting of CN_x nanotubes.

Raman spectroscopy studies carried out on raw CN_x tubes and polymer brushes (PS–CN_x) are shown in Fig. 5. N-Doped MWNTs indicate the presence of the D (1374 cm^{-1}) and G (1580 cm^{-1}) bands arising from graphite-like materials. Additional peaks related to PS could also be observed in the polymer brushes (*e.g.* 1104, 1342, 1597 and 1604 cm^{-1}). For the BPO/NO_x tubes and the PS–CN_x brushes, we noticed down-field shifts in the D-band varying from 5–12 cm^{-1}. We also observed up-field shifts

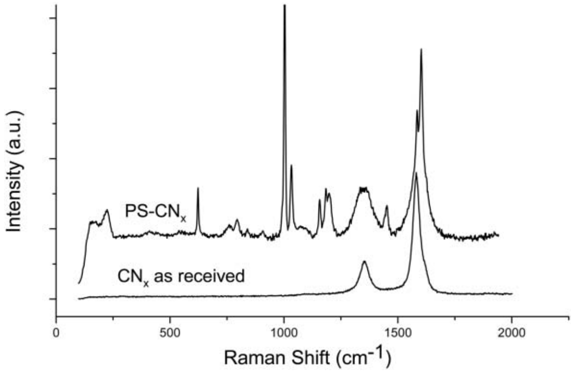

Fig. 5 Comparative Raman spectra of CN$_x$ as received and PS–CN$_x$.

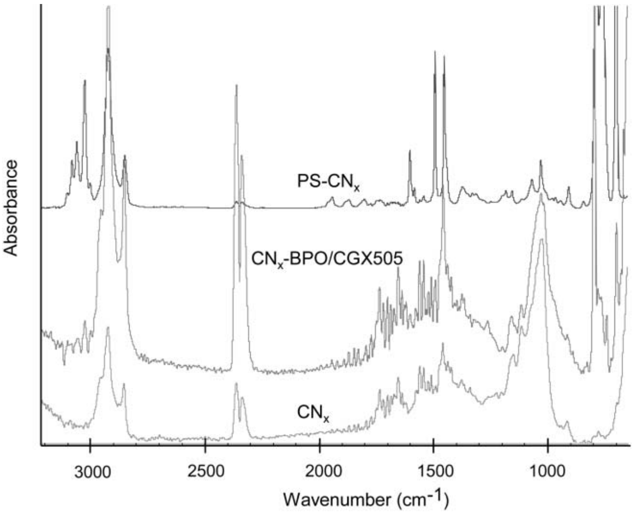

Fig. 6 Comparative FTIR spectra of CN$_x$ as received, CN$_x$–BPO/PR CGX505 and PS–CN$_x$.

within the G-band of *ca.* 2–13 cm^{-1} for the PS–CNx nanotubes. These shifts could be clearly associated with PS chains bonded to the CN$_x$ tubes. The intensity ratios between the D- and G-bands (I_D/I_G) increased in the PS–CN$_x$ brushes to 0.8; note that I_D/I_G = 0.36 for pure CN$_x$ tubes. The enhancement of the D band indicates the breakage of the perfect hexagonal symmetry of the tube surface, and the covalent attachment of PS chains to the surface of the doped tubes (see ESI†).

FTIR spectra from CN$_x$ tubes (as received) were compared with the radical functionalized CN$_x$–BPO/NO$_x$ and the polymer brushes PS–CN$_x$. As depicted in Fig. 6, the radical functionalized CN$_x$ tubes reveal peaks above 3000 cm^{-1}, associated with mono substituted aromatic hydrocarbons arising from the attachment of nitroxide molecules to the tube surface, and peaks at *ca.* 1450 cm^{-1} come from the aliphatic carbons present within the attached BPO molecules. It is also possible to observe C=O bonds from carbonyl compounds at 1600 cm^{-1}, and aromatic ethers located at 1260 cm^{-1}; both associated with initiator–controller attached molecules. PS–CN$_x$ spectra reveal peaks associated with PS, in addition to some variations below 800 cm^{-1} that could be related to the grafting reaction. After performing all these careful spectroscopic studies, we could state that CN$_x$ nanotubes were effectively radical functionalized and grafted.

Thermogravimetric (TGA) analyses show clear differences in thermal stability among CN$_x$ tubes, the CN$_x$–BPO/NO$_x$ material and the PS–CN$_x$ polymer brushes (see ESI†). The plot clearly reveals an abrupt weight loss for the CN$_x$–BPO/NO$_x$ material (at ~10%) that could be associated with the degradation of the adsorbed species on the tube surface casued by the initiator–controller molecules immobilized on the CN$_x$ tube. A higher mass loss was observed for the polymer brush (~35%w), which could be explained in terms of the degradation of PS chains that were covalently attached to the tube surface.

We also determined the average diameters of pristine and PS-grafted CN$_x$ nanotubes. In particular, we observed that by grafting the doped tubes, it is possible to separate the tubes according to their diameters. For example, the obtained average diameters in the supernatant for pristine CN$_x$ was 35 ± 3 nm, whereas for PS–CN$_x$ tubes this corresponded to 26 ± 2 nm (see ESI†).

We have demonstrated that CN$_x$ nanotubes could be successfully functionalized using radicals such as BPO and NO$_x$, without performing acid treatments. In addition, *in situ* controlled polymerization of PS-grafted on the CN$_x$ nanotubes was achieved using NMRP without inducing extensive damage on CN$_x$ surface structure. This technique constitutes an alternative route to synthesize nanostructured homogenous composite materials.

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