Chem. Mater. **2006,** *18,* 2929−2934

Articles

Single-Step in Situ Preparation of Polymer-Grafted Multi-Walled Carbon Nanotube Composites under ^{60}Co γ-Ray Irradiation

Hangxun Xu,[†] Xingbo Wang,[†] Yanfeng Zhang,[†] and Shiyong Liu,*[,†,‡]

Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui Province, 230026, People's Republic of China, and The Hefei National Laboratory for Physical Sciences at Microscale, Hefei, Anhui Province, 230026, People's Republic of China

Received December 23, 2005. Revised Manuscript Received March 26, 2006

We present single-step in situ syntheses of polystyrene-grafted multi-walled carbon nanotubes (MWNTs) under ^{60}Co γ-ray irradiation. Pristine MWNTs were first dispersed in pure styrene under sonication, and polystyrene (PS) was then covalently attached to the surface of MWNTs when the mixture was subjected to γ-ray irradiation. The polymer content in PS functionalized MWNTs can be up to ~15 wt %, as determined by thermal gravimetric analysis (TGA). The functionalized MWNTs can be dispersed well in common organic solvents such as THF, toluene, and $CHCl_3$, etc. The presence of PS in the functionalized carbon nanotube composites was further evidenced by Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM/HRTEM). The mechanism of the irradiation grafting process was also proposed. The reported γ-ray irradiation grafting technique is expected to be suitable for industrial scale-up preparation of functionalized carbon nanotubes (CNTs).

Introduction

Carbon nanotubes (CNTs) exhibit potential applications in the production of molecular wires, the next generation of electronic devices, fibers with exceptionally high tensile length, and high-performance composites, etc.[1−10] Their unique structural and electronic properties have been extensively investigated, which further expanded their scope of applicability. Now, they are very close to real-world applications.[11] Nevertheless, the problem of processability remains a severe hindrance to the extensive applications of CNTs, which explains the recent interests in the functionalization or surface modification of CNTs to improve their processability in a wide range of solvents and the performance of the nanocomposite materials.

Until now, several strategies have been proposed based on the noncovalent and covalent bonding of organic molecules to the surface of CNTs.[12−15] With respect to polymer functionalization of CNTs, "grafting to" and "grafting from" techniques have recently been developed with the purpose of rendering CNTs dispersible in organic or aqueous solvents.[16,17] The "grafting from" approach relies on the immobilization of initiators at the surface of CNTs, followed by in situ surface-initiated polymerization to generate tethered polymer chains. Besides the anionic polymerization of

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* To whom correspondence should be addressed. E-mail: sliu@ustc.edu.cn.
[†] University of Science and Technology of China.
[‡] The Hefei National Laboratory for Physical Sciences at Microscale.

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10.1021/cm052840o CCC: \$33.50

styrene from the surface of CNTs,[16a] initiators for the controlled free radical polymerization of butyl methacrylate, methyl methacrylate, styrene, and *N*-isopropylacrylamide by atom transfer radical polymerization (ATRP) and reversible addition−fragmentation chain transfer (RAFT) have also been covalently attached to the nanotube surface.[16] Other examples are ring-opening polymerization,[16e,16f] electropolymerization,[16g] and traditional free radical polymerization.[16h] The "grafting to" technique involves the bonding of preformed end functionalized polymer chains to the surface of CNTs.[17] This method is self-limiting because the grafted polymer chains will prohibit a further high extent of polymer grafting. Functionalization of CNTs via noncovalent approaches or "polymer wrapping" has also been reported.[18]

However, the aforementioned schemes for the functionalization of CNTs usually involve multistep organic syntheses. Sometimes, the preparation protocols are rigorous and time-consuming. The most obvious drawback is that the prepared carbon nanotube composites are only on a milligram scale. This precludes their widespread applications such as molecular electronics, blending with conventional polymers, and the preparation of homogeneously dispersed conducting layers within electroluminescent devices, etc. Therefore, it is still a big challenge for relevant scientists and engineers to functionalize CNTs in a much simpler and more economical manner.

γ-Ray irradiation has been extensively applied in initiating polymerizations, grafting polymer chains onto polymeric backbones, modifying polymer blends, and preparing interpenetrating polymer networkss.[19] γ-Ray irradiation generates free radicals via radiolysis of monomers and can also produce radicals on polymer surfaces (e.g., polypropylene). Generally, γ-ray irradiation-induced polymerizations exhibit the following advantages: the products are free of residual initiators or catalysts and polymerizations can be conducted at low temperatures and in gaseous, liquid, or even solid-state phases. Moreover, it is also well-known that γ-ray irradiation is an effective and facile technique for surface modification of either organic or inorganic materials. During revision of this paper, we noticed a recently published paper by Wu et al.,[20] who reported a two-step irradiation approach for poly(acrylic acid) (PAA) functionalized multi-walled carbon nanotubes (MWNTs). MWNTs were successively irradiated in ethanol and acrylic acid, respectively. The prepared PAA functionalized MWNTs showed good solubility in water.

Herein, we report single-step in situ preparation of CNT composites by covalently grafting polystyrene (PS) at the surface of MWNTs under ^{60}Co γ-ray irradiation. The reported γ-ray irradiation grafting technique is expected to be suitable for industrial scale-up preparation of functionalized CNTs.

Experimental Procedures

Materials. Multi-walled carbon nanotubes were obtained from Chengdu Organic Chemicals Co., Ltd. They were manufactured by the chemical vapor deposition method (purity >95%, 20−30 nm overall diameter) and used without further purification. Styrene was distilled under vacuum and stored at −20 °C prior to use. *N,N*-Dimethylformamide (DMF), anhydrous THF, and all other reagents were used as received from Shanghai Experiment Reagent Co., Ltd.

Functionalization of MWNTs. Dried pristine MWNTs (50 mg) were dispersed in styrene (10 mL) after sonication for 30 min. The mixture was then deoxygenated by bubbling with high-purity nitrogen. The black dispersion was irradiated in the field of a 2.6×10^{15} Bq ^{60}Co γ-ray source, and the dose rate was ∼80 Gy/min. For comparison, pristine MWNTs were also irradiated in the absence of styrene monomer at the same dose rate. After irradiation for different time periods, a gel-like mixture was obtained. It was diluted with 200 mL of anhydrous THF and then sonicated for 15 min. The mixture was subjected to centrifugation at ∼2500*g* for 15 min. After removal of the homogeneous black supernatant, the black sediment was redispersed in THF by sonication and centrifuged for 15 min again, and the black supernatant was collected. This dispersion−centrifugation−collection cycle was repeated 3 times.

The combined black supernatant was first vacuum-filtered through a 0.2 μm PTFE membrane, and the collected black solids were thoroughly washed 5 times with 50 mL of THF. The collected black solids were then redispersed in 200 mL of THF by sonication for 15 min, filtered, and washed with excess THF again. This dispersion−filtration−washing cycle was repeated at least 3 times to remove any residual monomers or PS homopolymers. During each cycle of vacuum-filtration, several drops of filtrate were added into 10 mL of fresh methanol from time to time, and the absence of cloudiness can be used to indicate the complete removal of PS homopolymers.[17a] The collected black solids were dried overnight in a vacuum oven at room temperature. Typicall, ∼40 mg of functionalized MWNTs was obtained.

On the basis of a previous report by Ford et al.,[17a] ultracentrifugation is a powerful technique to completely remove any residual homopolymer from the functionalized CNTs. We then employed ultracentrifugation to check whether the purified functionalized MWNTs are free of PS homopolymer or not. A total of 10.0 mg of the functionalized MWNTs was dispersed in 20 mL of THF, and the black dispersion was then subjected to ultracentrifugation at 250 000*g* for 3 h. After the supernatant was discarded, the combined black sediment was dried overnight under vacuum, yielding 9.9 mg of functionalized MWNTs. This indicated that functionalized MWNTs purified by vacuum-filtration still contained ∼1 wt % PS homopolymer. However, this will not alter the basic conclusions drawn in this study. In subsequent characterizations, we still used the functionalized MWNTs purified by vacuum-filtration.

Instruments and Characterization. The sonication was performed on a JL-180DTH (180 w, 40 kHz, bath temperature at 30 °C) sonicator. The separation of the functionalized MWNTs from

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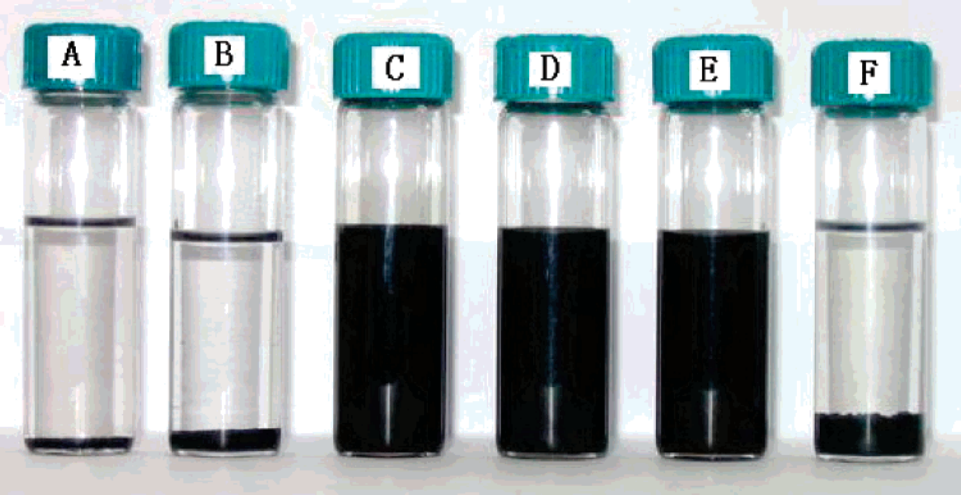

Figure 1. Photographs of MWNT samples in THF: (A) pristine MWNTs; (B) MWNTs irradiated in the absence of styrene for 48 h; (C) functionalized MWNTs prepared after irradiation in styrene for 48 h; (D) functionalized MWNTs prepared after irradiation in styrene for 24 h; (E) functionalized MWNTs prepared after irradiation for 16 h; (F) mixture of pristine MWNTs (80 wt %) and PS homopolymer (20 wt %); the total concentration is 5.0 g/L. All photos were taken after 15 days of storage at room temperature. The concentrations of functionalized MWNTs in samples C−E are 0.5 g/L, respectively.

impurities was first conducted by centrifugation at ∼2500*g* using a General Purpose centrifuge (TGL-16C). Ultracentrifugation was performed on a Beckman Optima L-100K at ∼250 000*g*. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker VECTOR-22 IR spectrometer. Raman spectra were obtained on a LABRAM-HR confocal laser MicroRaman spectrometer with an argon-ion laser at an excitation wavelength of 514.5 nm. The samples for Raman measurements were prepared by evaporating the functionalized MWNT dispersion in THF on a microscope cover glass. Thermal gravimetric analyses (TGA) were conducted on Perkin-Elmer Diamond TG/DTA, with a heating rate of 15 °C/min in a nitrogen atmosphere. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG ESCALAB MK II X-ray photoelectron spectrometer, using a Mg Kα line (1486.6 eV) as the excitation source under high vacuum (5×10^{-9} Pa). The C 1s peak (284.6 eV) was used as the internal reference of binding energy values. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) measurements were conducted on a Hitachi model H-800 and a JEOL 2010 electron microscope, respectively. The samples for TEM/HRTEM measurements were prepared by placing one drop of sample dispersion in THF on carbon-coated copper grids.

Results and Discussion

To disentangle the MWNTs that typically tend to clump together to form bundles, the first step of γ-ray irradiation grafting of PS was the dissolution/dispersion of MWNTs in a proper solvent/styrene mixture. Several organic solvents such as *N*,*N*-dimethylformamide (DMF) and THF were tried initially, and eventually we found out that the styrene monomer itself was the best solvent. After sonication of MWNTs in styrene to disentangle the bundles, a black dispersion was obtained. After the reaction mixture was subjected to irradiation for 16, 24, or 48 h, a more homogeneous dispersion was obtained with a small amount of black sediment. The black sediment should be ascribed to impurities such as amorphous carbon, nonfunctionalized MWNTs, and functionalized MWNTs with low PS grafting density. The black sediment was removed by centrifugation at ∼2500*g*. A total of 50 mg of pristine MWNTs typically produced ∼40 mg of functionalized MWNTs after purification. Addition of DMF or THF into the MWNTs/styrene mixture decreased the yield of functionalized MWNTs. Only ∼20 and 15 mg of functionalized MWNTs was obtained when 1:1 v/v styrene/DMF and styrene/THF (10 mL in total) were used, respectively. Thus, all subsequent γ-ray irradiation experiments were carried out in the absence of any organic solvents.

Figure 1 compares the solubility in THF of pristine MWNTs and MWNTs irradiated in the absence and presence of styrene. In contrast to pristine MWNTs and MWNTs irradiated in the absence of styrene, which is insoluble in THF, functionalized MWNTs prepared after irradiation in styrene can be easily dispersed in THF. They are also soluble in other common organic solvents such as toluene, $CHCl_3$, etc. Upon addition of the THF dispersion of functionalized MWNTs into an excess of *n*-hexane, which is a poor solvent for polystyrene, insoluble black solids quickly phase separated out. Thus, by visual inspection, polystyrene chains have been successfully grafted at the surface of MWNTs. The dispersion of functionalized MWNTs in THF is indefinitely stable, and no sedimentation is observed up to the present (more than 8 months). In the control experiment, we mixed pristine MWNTs and PS homopolymers (prepared via free radical polymerization, $M_n = 24000$ and $M_w/M_n = 1.8$) at a weight ratio of 8:2 in THF, and the mixture was subjected to sonication for ∼30 min. After storage for ∼0.5 h, the MWNTs precipitated out (Figure 1F). This suggests that the good solubility of functionalized MWNTs is due to the covalent grafting of PS instead of physisorption of PS chains onto the surface of MWNTs.

The presence of PS in the CNT composites was further confirmed by FT-IR, which can provide rich information about the functional groups grafted onto the sidewall of MWNTs. The FT-IR spectrum (Figure 2) of functionalized MWNTs exhibits characteristic vibration bands for PS (in KBr: absorbance peaks at 3025, 1602, 1492, 756, and 698 cm^{-1} correspond to the phenyl group, the peaks at 2922 and 2850 cm^{-1} correspond to the methylene and methenyl groups, and the peaks at 1028 cm^{-1} correspond to the C−Ph groups).

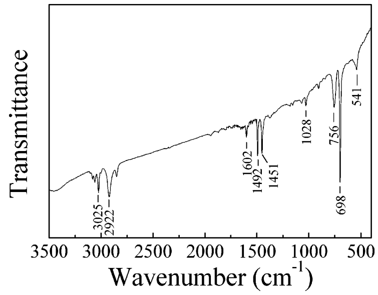

Figure 2. FT-IR spectrum of functionalized MWNTs prepared after irradiation in styrene for 48 h.

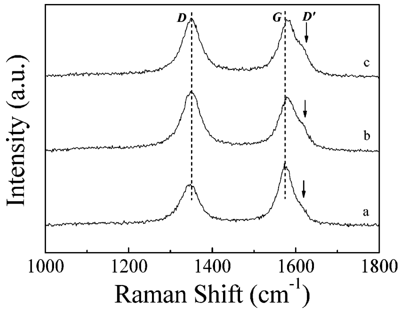

Figure 3. Raman spectra of MWNTs irradiated in the absence of styrene for 48 h (a) and functionalized MWNTs prepared after irradiation for 16 h (b) and 24 h (c).

This suggests the presence of PS in the functionalized MWNTs.[16c]

Raman spectroscopy is a powerful tool to characterize the extent of disorder or the degree of crystallinity in the functionalized MWNTs.[21,22] As shown in Figure 3, the D- and G-bands at ~1350 and ~1580 cm^{-1}, respectively, attributed to the defects/disorder-induced modes and in-plane vibrations of the graphitic wall,[21d] can be clearly observed for MWNTs irradiated in the absence and presence of styrene. The D- to G-band intensity ratio (I_D/I_G) for MWNTs irradiated in the absence of styrene (Figure 3a) is ca. 0.85, which is generally comparable to that reported for pristine MWNTs.[22] For the functionalized MWNTs prepared after irradiation in styrene for 16 and 24 h, the I_D/I_G intensity ratios are ~1.17 and 1.03, respectively. The D′-band at ~1615 cm^{-1} is barely discernible in nonfuntionalized MWNTs (Figure 3a), while the peaks are more clearly evident in the functionalized MWNTs (Figure 3b,c). It is well-known that the D′-band is also associated with the defects and disorder in nanotubes.[21d] Thus, both the increase in I_D/I_G intensity ratios and the enhancement of the D′-band for MWNTs after functionalization indicate the relative increase of defects in nanotubes due to covalent attachment of PS chains under irradiation.[21,22]

It is worthy to be noted that the Raman signals of PS were not detected for the functionalized MWNTs. Baskaran et al.[16c] reported that functionalized MWNTs prepared by ATRP with a PS content of 33 wt % also did not exhibit characteristic Raman signals of PS. The absence of PS signals in our case is possibly due to the low PS grafting densities (~15 wt %, see TGA results described next).[16c,22] After functionalization with PS, the D-band shows no noticeable peak shift, while the G-band slightly shifts upfield for ~4−8 cm^{-1}, as compared to that of the control. This shift should be associated with PS chains covalently attached to the nanotube surface.[21e,23,24]

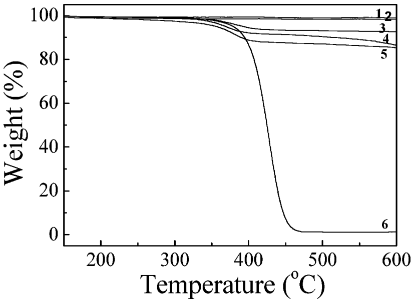

Figure 4. TGA curves of pristine MWNTs (1); MWNTs irradiated in the absence of styrene for 48 h (2); functionalized MWNTs prepared after irradiation in styrene for 16 h (3), 24 h (4), and 48 h (5); and PS homopolymer (6).

To determine the PS content in the CNT composites, TGA measurements were performed on the functionalized MWNTs after purification (Figure 4). Pristine MWNTs will decompose at around 500 °C in air, whereas they start to decompose at around 800 °C under nitrogen atmosphere. TGA results (up to 800 °C) of PS functionalized MWNTs reveal that the majority of weight loss occurs in the temperature range of 300−450 °C, corresponding to the decomposition of PS. A weight loss of ~15% was observed for functionalized MWNTs prepared after irradiation in styrene for 48 h. Considering that functionalized MWNTs purified by vacuum-filtration still contain ~1 wt % residual PS homopolymer, the actual content of PS covalently grafted to the MWNT surface is thus estimated to be ~14 wt %. With decreasing duration of irradiation, the TGA weight loss decreases (Figure 4). The PS contents in the functionalized MWNTs decrease from 15 to 9% when the duration of irradiation decreases from 48 to 16 h. This indicates that the degree of functionalization can be easily tuned by the duration of irradiation. Previous reports revealed that even low loading levels (ca. 1−5%) of the CNTs can dramatically enhance the conductivity and mechanical properties of CNT composites.[25−27] So, ^{60}Co γ-ray irradiation is an effective and facile technique for scale-up preparation of CNT composites.

The nanostructures of the functionalized MWNTs were then investigated by TEM. The TEM image shown in Figure

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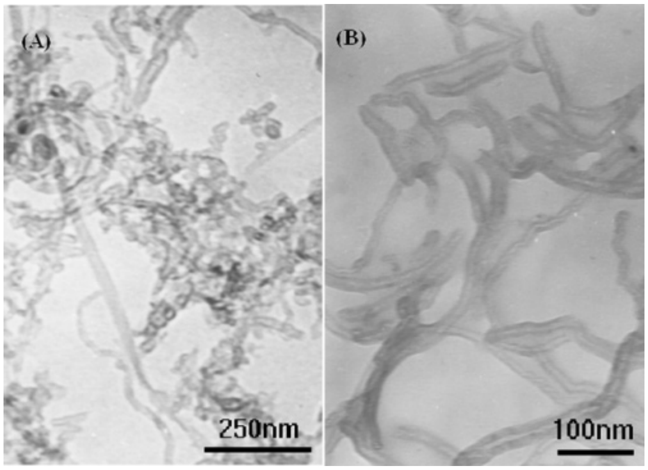

Figure 5. TEM images of pristine MWNTs (A) and functionalized MWNTs prepared after irradiation in styrene for 48 h (B).

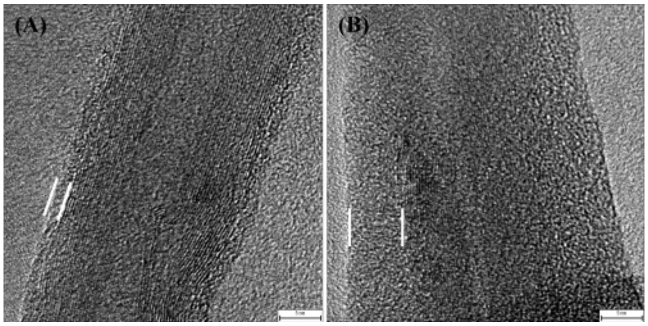

Figure 6. HRTEM images of functionalized MWNTs prepared after irradiation in styrene for 16 h (A) and 48 h (B).

5A reveals densely entangled networks for pristine MWNTs, indicating that pristine MWNTs are piled up to form large bundles. In contrast, functionalized MWNTs can be dispersed well in THF, and only individual tubes can be observed (Figure 5B). HRTEM images of functionalized MWNTs prepared after irradiation in styrene for different durations are shown in Figure 6. We can clearly observe the core−shell nanostructure consisting of a nanotube core and a polymer outer shell. The wrapped PS layer around the nanotube is generally uniform in distribution.[20,22] The thicknesses of the polymer shell of the functionalized MWNTs prepared after irradiation in styrene for 16 and 48 h are 1−2 and 5−6 nm, respectively. This suggests that a longer duration of irradiation leads to a thicker polymer shell. This is also in agreement with the TGA results as shown in Figure 4.

XPS was further employed to determine the surface composition of functionalized MWNTs. The typical information depth of XPS is ∼5 nm.[28] Figure 7 shows the XPS survey spectra of pristine and functionalized MWNTs. Both spectra reveal the presence of only carbon (284.6 eV) and oxygen (532. 3 eV). For pristine MWNTs, the relative atomic concentrations of carbon and oxygen are 95.5 and 4.5%, respectively (Figure 7a). After irradiation in styrene for 48 h, the atomic concentration of oxygen in the functionalized MWNTs decreases to ∼1.2%. This strongly supports that the nanotube is coated with a PS layer. Because of XPS peak overlapping of PS and MWNTs,[29] we do not further analyze the C 1s core level spectra by peak fitting. However, a comparison between Figure 7, spectra a and b tells us that a new peak at ∼291.0 eV can be clearly observed for functionalized MWNTs. This peak should be ascribed to the $\pi \rightarrow \pi^*$ shake-up of aromatic groups, which is barely discernible in pristine MWNTs.

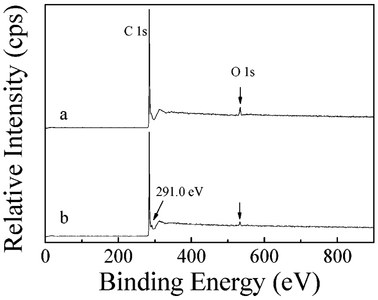

Figure 7. XPS full-scan spectra of pristine MWNTs (a) and functionalized MWNTs prepared after irradiation in styrene for 48 h (b).

Thus, we have successfully established that MWNTs can be conveniently functionalized with PS via irradiation-induced covalent grafting and that the polymer content in the CNT composites can be up to 15 wt %. In the irradiation grafting process, both “grafting to” and “grafting from” mechanisms should be effective. The propagating PS chains, generated by the radiolysis of styrene monomers and subsequent polymerization under γ-ray irradiation, have a high tendency to react with unsaturated double bonds on MWNTs and readily functionalize them via the “grafting to” method. The radical addition to the CNT surface has been extensively studied, as both small molecular radicals and polymer chain radicals have been reported to be able to effectively functionalize CNTs.[17b,17c,30−35] For the “grafting from” mechanism, the tips and defects of MWNTs might be easily destroyed by the high-energy γ-ray,[23,24] which will produce radicals in situ at the CNT surface. The radicals can then readily initiate the polymerization of styrene. Therefore, the functionalization of MWNTs under γ-ray irradiation should involve both “grafting to” and “grafting from” mechanisms.

Conclusion

In conclusion, we have developed a straightforward and facile technique for the functionalization of MWNTs. The

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polymer grafting occurs in a single-step manner under γ-ray irradiation, and the structural integrity of the nanotubes is well-maintained during irradiation. The polymer content in the functionalized MWNTs can be up to ∼15% depending on the duration of irradiation. Currently, ongoing projects further reveal that the irradiation-induced functionalization technique is amenable to other monomers, such as methyl methacrylate, methyl acrylate, and vinyl acetate, etc. This technique is expected to be suitable for industrial scale-up preparation of functionalized CNTs.

Acknowledgment. This work was supported by an Outstanding Youth Fund (50425310) and a key research grant (20534020) from the National Natural Scientific Foundation of China (NNSFC), the "Bai Ren" Project of the Chinese Academy of Sciences, and the Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT).

CM052840O

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