

Scalable Functional Group Engineering of Carbon Nanotubes by Improved One-Step Nitrene Chemistry

Chao Gao,^{*,†} Hongkun He,[‡] Li Zhou,[†] Xing Zheng,[‡] and Yu Zhang[‡]

Department of Polymer Science and Engineering and Key Laboratory of Macromolecular Synthesis and Functionalization, Ministry of Education, Zhejiang University, 38 Zheda Road, Hangzhou 310027, P.R. China, and College of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P.R. China

Received October 5, 2008. Revised Manuscript Received November 26, 2008

A facile, green, low cost and efficient one-step technology to synthesize highly dispersible functional single-walled and multiwalled carbon nanotubes (f-SWNTs and f-MWNTs) up to supergrams is reported. Large-scale (up to hundreds of grams) synthesis of functional azides was developed at first, and various reactive groups (i.e., $-\text{OH}$, $-\text{NH}_2$, $-\text{COOH}$, and $-\text{Br}$) were then introduced onto the convex surfaces of CNTs in merely one reaction of nitrene addition under a relatively mild condition without causing significant damage to nanotubes. The contents of the functional moieties can be easily controlled by adjusting the feed ratio of the azide compounds to CNTs. In order to demonstrate the reactivity and functions of the immobilized organic moieties, different chemical reactions, including surface-initiated polymerizations, amidation, and reduction of metal ions, were performed on the functional CNTs, affording various CNT-polymer and CNT-Pt nanohybrids. The resulting materials were characterized by various measurements, such as TGA, Raman, XPS, FTIR, NMR, XRD, SEM, TEM, and HRTEM. The presented one-step methodology opens the avenue for industrial production of functional CNTs.

Introduction

Brisk research activities have commenced in the early 1990s, when the carbon nanotubes (CNTs) were originally discovered.¹ With their intriguing unique structural, chemical, optical, electrical, and mechanical properties, both multiwalled carbon nanotubes (MWNTs) and single-walled carbon nanotubes (SWNTs) enkindle profuse interest. Recent years have witnessed numerous applications of CNTs in a wide variety of fields, including polymeric nanocomposites, biological nanoengineering and bionanotechnology, and so forth.² Pristine MWNTs have now been industrially produced with ton-scale and cheapened to approximately 200 euros/kg. With the advancement of preparation technology, MWNTs will become a common kind of chemical or raw material in the near future. However, the key problem for the wide application of CNTs in industry is still their poor wettability/dispersibility which waters down their great potential. Therefore, both academic and commercial organs are looking for a breakthrough technology for scalable production of functionalized CNTs because functionalization or modification of CNTs can improve their dispersibility significantly and render them new property profiles.³ In this regards, diverse strategies designed to functionalize CNTs continuously emerge, such as end and defect-chemistry,⁴ endohedral

functionalization,⁵ ionic chemistry (doping),⁶ covalent side-walls functionalization,⁷ and noncovalent functionalization.⁸

So far, one of the dominant methods to functionalize CNTs is to introduce carboxylic acid groups onto the surface of CNTs via nitric acid oxidation method and then convert them into other functional groups if needed.^{2,6} Although being a currently popular and powerful method, this acid treatment method still possesses several disadvantages: (1) the process is associated with strong corrosion and high pollution due to the raw materials of concentrated HNO_3 and H_2SO_4 and their decomposed gases (e.g., NO_2 , SO_2 , etc.), which is not only complex in laboratory practice but also poses a barrier to large-scale bulk production of functionalized CNTs; (2) the reaction leads to weight-decrease of product (normally, only 60–70 wt % yield), which consumes a big part of good quality of CNTs and thus is quite uneconomical; (3) the serious break of CNTs is inevitable during the acid treatment (some tubes are heavily eroded, truncated, and disinte-

- (3) (a) Ebbesen, T. W.; Hiura, H.; Bisher, M. E.; Treacy, M. M. J.; Shreeve-Keyer, J. L.; Haushalter, R. C. *Adv. Mater.* **1996**, *8*, 155–157. (b) Dujardin, E.; Ebbesen, T. W.; Krishnan, A.; Treacy, M. M. J. *Adv. Mater.* **1998**, *10*, 611–613. (c) Dujardin, E.; Ebbesen, T. W.; Krishnan, A.; Treacy, M. M. J. *Adv. Mater.* **1998**, *10*, 1472–1475. (d) Yao, N.; Lordi, V.; Ma, S. X. C.; Dujardin, E.; Krishnan, A.; Treacy, M. M. J.; Ebbesen, T. W. *J. Mater. Res.* **1998**, *13*, 2432–2437.

- (4) Banerjee, S.; Hemraj-Benny, T.; Wong, S. S. *Adv. Mater.* **2005**, *17*, 17–29.

- (5) Hirsch, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1853–1859.

- (6) Niyogi, S.; Hamon, M. A.; Hu, H.; Zhao, B.; Bhowmik, P.; Sen, R.; Itkis, M. E.; Haddon, R. C. *Acc. Chem. Res.* **2002**, *35*, 1105–1113.

- (7) (a) Blake, R.; Gun'ko, Y. K.; Coleman, J.; Cadek, M.; Fonseca, A.; Nagy, J. B.; Blau, W. J. *J. Am. Chem. Soc.* **2004**, *126*, 10226–10227. (b) Liang, F.; Sadana, A. K.; Peera, A.; Chattopadhyay, J.; Gu, Z. N.; Hauge, R. H.; Billups, W. E. *Nano Lett.* **2004**, *4*, 1257–1260.

- (8) Holzinger, M.; Abrahams, J.; Whelan, P.; Graupner, R.; Ley, L.; Hennrich, F.; Kappes, M.; Hirsch, A. *J. Am. Chem. Soc.* **2003**, *125*, 8566–8580.

* To whom correspondence should be addressed. E-mail: chaogao@zju.edu.cn.

[†] Zhejiang University.

[‡] Shanghai Jiao Tong University.

(1) (a) Iijima, S. *Nature* **1991**, *354*, 56–58. (b) Iijima, S.; Ichihashi, T. *Nature* **1993**, *363*, 603–615.

(2) Sun, Y. P.; Fu, K. F.; Lin, Y.; Huang, W. J. *Acc. Chem. Res.* **2002**, *35*, 1096–1104.

grated),⁹ impairing the intrinsic morphology and properties of CNTs; (4) besides the carboxyl groups, the acid-treated nanotubes also have other groups (e.g., aldehyde, carbonyl, and hydroxyl) on them,¹⁰ and the simultaneous presence of various functional groups may cause troubles in the succeeding chemical modification and characterization; and (5) additional reactions on acid-treated nanotubes are required to gain other surface functional groups.

There is no doubt that these researches improved the dispersibility of CNTs from an academic point of view. However, scalable synthesis of such CNTs is another issue owing to the associated problems of too many steps, complex processes, serious pollution, high cost of reagents, and so forth. Although the recently developed ozone technology may introduce some functional groups onto CNTs, the exfoliation of CNT bundles or networks is quite difficult due to the gas-phase reaction.¹¹

More recently, it has been found that some biradical groups (such as dichlorocarbene and nitrene) could be employed to modify the double bonds of CNTs^{8,12–14} or fullerenes^{15,16} in a covalent way. Moreover, the reaction mechanisms of nitrenes are also investigated in prior researches through theoretical calculations and computational chemistry studies.¹⁷ Such nitrene chemistry may provide a chance for scalable synthesis of functionalized CNTs because of the high reactivity and facile availability of azides. However, detailed investigation on the engineering of this methodology is not reported yet. In addition, the reported solvents, 1,1,2,2-tetrachloroethane (TCE),¹³ for example, are quite expensive and not suitable for industrial production. Herein, we reinvestigate the nitrene chemistry from an engineering point of view and develop it into one-step technology for scalable preparation of soluble CNTs with high density of functional groups. This is, to our knowledge, the first reported technology of facile, green, cost-effective, and super-gram scale preparation of functional CNTs.

To demonstrate the compatibility of the one-step methodology, a series of functional azide compounds (f-azides) are designed and used to react with both MWNTs and SWNTs. Each f-azide molecule contains both azido group

and another functional group (e.g., $-\text{OH}$, $-\text{NH}_2$, $-\text{COOH}$, or $-\text{Br}$). Once the azido group anchors on the sidewall of nanotubes, another functional group extends into the surrounding solvent to solubilize CNTs and is suitable for further chemical modification. An azido group may produce two types of reactive intermediate upon thermolysis, that is, singlet-state nitrenes (have two filled p-orbitals) and triplet-state nitrenes (have one filled p-orbital and two p-orbitals containing unpaired electrons), both of which can attack the convex surface of nanotubes to afford aziridine rings by an electrophilic $[2 + 1]$ cycloaddition and reaction between biradicals and the nanotube sidewalls' π -system, respectively.¹⁴ Meanwhile, it is worth mentioning that we also developed the procedures to scalably prepare f-azides (up to hundreds of grams) from commercially available reagents, which greatly facilitates the economical mass production of f-CNTs.

Our one-step technology based on nitrene chemistry for preparing functional CNTs (f-CNTs) is promising with considerable merits: (1) the materials of azides can be scalably synthesized under relatively mild conditions; (2) the process is green and environmentally friendly since the decomposed gas is nitrogen and the solvent can be used circularly; (3) the functionalization process does not cause severe damage to CNTs; (4) almost no other functional groups except the desired one is anchored on the CNTs, making the f-CNTs structurally well-defined materials; (5) various functional groups (for example, $-\text{OH}$, $-\text{NH}_2$, $-\text{COOH}$, $-\text{Br}$) can be introduced onto the nanotubes in merely one reaction; (6) the engineering leads to a weight increase of product; and (7) the reaction can be performed by either elevated temperature of thermolysis or UV irradiation.¹⁸ In this paper, we focus on the thermolysis engineering.

Experimental Section

Materials. The multiwalled carbon nanotubes (MWNTs) were purchased from Tsinghua-Nafine Nano-Powder Commercialization Engineering Center in Beijing (purity > 95%). The single-walled carbon nanotubes (SWNTs) were purchased from Shenzhen Nanotech Port Co. (purity of CNTs > 90%, purity of SWNTs > 50%). Succinic anhydride (98%), stannous octoate ($[\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{COO}]_2\text{Sn}$, 95%), and ethylene glycol (99%) were purchased from Aldrich and used as received. 2-Bromoisobutyl bromide (98%), N,N,N',N'',N'' -pentamethyldiethylenetriamine (PMDETA, 99%), N,N -(dimethylamino)pyridine (DMAP, 98%), and boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{OEt}_2$, 98%) were purchased from Alfa Aesar and used as received. ϵ -Caprolactone (Acros, 99%) and palmitoyl chloride (Fluke, 97%) were used without further purification. Sodium azide (95%), 2-chloroethanol (99%), 3-chloropropylamine hydrochloride (98%), potassium tetrachloroplatinate(II) (K_2PtCl_4 , 99%), N -methyl-2-pyrrolidinone (NMP), acetone, tetrahydrofuran (THF), N,N -dimethyl formamide (DMF), chloroform, and other solvents were obtained from Shanghai Reagents Company and used as received. Glycidyl methacrylate (GMA, Alfa Aesar, 95%) was purified by passing through a column filled with basic alumina to remove the inhibitor. Triethylamine (Et_3N), dichloromethane (CH_2Cl_2), methyl methacrylate (MMA, Alfa Aesar, 99%), and styrene (St, Alfa Aesar,

- (9) Gao, C.; Vo, C. D.; Jin, Y. Z.; Li, W. W.; Armes, S. P. *Macromolecules* **2005**, *38*, 8634–8648.
- (10) Lordi, V.; Yao, N.; Wei, J. *Chem. Mater.* **2001**, *13*, 733–737.
- (11) Byl, O.; Liu, J.; Yates, J. T. *Langmuir* **2005**, *21*, 4200–4204.
- (12) (a) Zhang, C.; Li, R. F.; Liang, Y. X.; Shang, Z. F.; Wang, G. C.; Xing, Y. M.; Pan, Y. M.; Cai, Z. S.; Zhao, X. Z.; Liu, C. B. *J. Mol. Struct. (Theochem)* **2006**, *764*, 33–40. (b) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y. S.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998**, *282*, 95–98. (c) Qin, S. H.; Qin, D. Q.; Ford, W. T.; Resasco, D. E.; Herrera, J. E. *Macromolecules* **2004**, *37*, 752–757.
- (13) Holzinger, M.; Vostrowsky, O.; Hirsch, A.; Hennrich, F.; Kappes, M.; Weiss, R.; Jellen, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 4002–4005.
- (14) Holzinger, M.; Steinmetz, J.; Samaille, D.; Glerup, M.; Paillet, M.; Bernier, P.; Ley, L.; Graupner, R. *Carbon* **2004**, *42*, 941–947.
- (15) Yashiro, A.; Nishida, Y.; Ohno, M.; Eguchi, S.; Kobayashi, K. *Tetrahedron Lett.* **1998**, *39*, 9031–9034.
- (16) Nakahodo, T.; Okada, M.; Morita, H.; Yoshimura, T.; Ishitsuka, M. O.; Tsuchiya, T.; Maeda, Y.; Fujiwara, H.; Akasaka, T.; Gao, X.; Nagase, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 1298–1300.
- (17) (a) Xu, Y. J.; Zhang, Y. F.; Li, J. Q. *J. Phys. Chem. B* **2006**, *110*, 3197–3205. (b) Mandel, S. M.; Singh, P. N. D.; Muthukrishnan, S.; Chang, M. X.; Krause, J. A.; Gudmundsdottir, A. D. *Org. Lett.* **2006**, *8*, 4207–4210. (c) Muthukrishnan, S.; Mandel, S. M.; Hackett, J. C.; Singh, P. N. D.; Hadad, C. M.; Krause, J. A.; Gudmundsdottir, A. D. *J. Org. Chem.* **2007**, *72*, 2757–2768.

- (18) Pastine, S. J.; Okawa, D.; Kessler, B.; Rolandi, M.; Llorente, M.; Zettl, A.; Frechet, J. M. J. *J. Am. Chem. Soc.* **2008**, *130*, 4238–4239.

98%) were dried with CaH_2 and distilled under reduced pressure before use. CuBr (Aldrich, 99.999%) was obtained from Aldrich and purified according to the published procedures.¹⁹ The monomer of 3-azido-2-hydroxypropyl methacrylate (GMAN_3) was prepared by reaction of GMA and sodium azide in the mixture of water and THF (5/1 by volume) at room temperature for 48 h.

Instruments and Measurements. Thermal gravimetric analysis (TGA) was carried out on a TA Instruments TGA-2050 thermogravimetric analyzer with a heating rate of 20 °C/min under a nitrogen flow rate of 60 mL/min. Fourier transform infrared (FTIR) spectra were recorded on a PE Paragon 1000 spectrometer (KBr disk). Hydrogen nuclear magnetic resonance (^1H NMR) spectra were measured with a Varian Mercury Plus 400 MHz spectrometer with CDCl_3 as the solvent. Transmission electron microscopy (TEM) analysis was performed on a JEOL JEM2010 electron microscope at 200 kV. Scanning electron microscopy (SEM) images were recorded using a FEI SIRION 200 field-emission microscope. X-ray diffraction (XRD) was recorded on a Rigaku X-ray diffractometer D/max-2200/PC equipped with $\text{Cu K}\alpha$ radiation (40 kV, 20 mA) at the rate of 5.0 deg/min over the range of 10–90° (2 θ). Raman spectra were collected on a LabRam-1B Raman spectroscope equipped with a 632.8 nm laser source. X-ray photoelectron spectroscopy (XPS) measurements were made on a RBD upgraded PHI-5000C ESCA system (Perkin-Elmer) with $\text{Mg K}\alpha$ radiation ($h\nu = 1253.6$ eV) at a power of 250 W. Atomic force microscopy (AFM) was performed on a Digital Instrument Nanoscope IIIa scanning probe microscope, operating at the tapping mode.

Large-Scale Synthesis of 2-Azidoethanol.²⁰ Typically, to a 2000 mL three-neck round-bottom flask equipped with a condenser were added a solution of sodium azide (195 g, 3.0 mol) in deionized water (780 mL) and 2-chloroethanol (120.8 g, 1.5 mol). The flask was immersed in an oil bath at 75 °C and kept stirring for 96 h (caution: the azide is quite explosively sensitive to friction during feeding and when the temperature is higher than 80 °C). After cooling to room temperature, the reaction mixture was then extracted with diethyl ether (5 × 100 mL). The combined extracts were dried over anhydrous MgSO_4 overnight, filtered, concentrated on a rotary evaporator, and distilled under reduced pressure to produce a colorless oil. Yield: 216.6 g, 83%. ^1H NMR (CDCl_3 , δ , ppm): 3.79 (t, 2H, CH_2O), 3.44 (t, 2H, CH_2N_3), 2.21 (b, 1H, OH).

Large-Scale Synthesis of 3-Azidopropan-1-amine.²¹ A solution of sodium azide (195 g, 3.0 mol) in deionized water (800 mL) was added into a three-neck round-bottom flask equipped with a condenser. Then 3-chloropropylamine hydrochloride (195 g, 1.5 mol) dissolved in 300 mL of deionized water was added. After continued stirring at 75–78 °C for 96 h, the white precipitate (NaCl) was removed as a byproduct from the reaction mixture by filtration. The yellow filtrate was basified with aqueous NaOH to pH \approx 10–11 and further extracted with diethyl ether (5 × 200 mL). The organic fraction was dried over anhydrous MgSO_4 overnight, filtered, concentrated on a rotary evaporator, and distilled under reduced pressure to produce a colorless oil. Yield: 109.2 g, 73%. ^1H NMR (CDCl_3 , δ , ppm): 3.35 (t, 2H, CH_2N_3), 2.78 (t, 2H, NH_2CH_2), 1.71 (p, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.27 (s, 2H, NH_2).

Synthesis of 4-(2-Azidoethoxy)-4-oxobutanoic Acid. Succinic anhydride (23.0 g, 0.230 mol) was added into a three-neck round-bottom flask equipped with a condenser and a dropping funnel. Under nitrogen atmosphere and magnetic stirring, freshly distilled methylene chloride (150 mL), DMAP (2.3 g, 19 mmol) and freshly

distilled Et_3N (46.46 g, 0.460 mol) was sequentially added. After the flask was immersed into an ice–water bath, 2-azidoethanol (20.0 g, 0.230 mol) was added dropwise into the previous solution. The solution was later heated at 40 °C for 48 h, and the reaction mixture was washed successively with 1 M HCl solution (5 × 100 mL) and deionized water (2 × 100 mL). The organic phase was dried over anhydrous MgSO_4 overnight. After filtering and removal of methylene chloride under reduced pressure, the final product was obtained as a yellow viscous liquid. Yield: 39.1 g, 91%. ^1H NMR (CDCl_3 , δ , ppm): 4.27 (t, 2H, $\text{N}_3\text{CH}_2\text{CH}_2$), 3.48 (t, 2H, N_3CH_2), and 2.68 (m, 4H, $\text{CH}_2\text{CH}_2\text{COOH}$).

Synthesis of 2-Azidoethyl-2-bromo-2-methylpropanoate.²² 2-Azidoethanol (17.40 g, 0.2 mol), freshly distilled methylene chloride (150 mL), and Et_3N (21.21 g, 0.21 mol) were added into a three-neck round-bottom flask equipped with a condenser and a dropping funnel. Under nitrogen atmosphere and magnetic stirring, freshly distilled anhydrous methylene chloride (150 mL), DMAP (1.7 g, 14 mmol), and freshly distilled anhydrous Et_3N (46.5 g, 0.46 mol) were sequentially added. After the flask was immersed into an ice–water bath, 2-bromoisobutyl bromide (48.28 g, 0.21 mol) was added dropwise into the previous solution. Twenty-four hours later, the reaction mixture was washed successively with 1 M HCl (3 × 200 mL) solution and deionized water (1 × 200 mL). The organic phase was dried over anhydrous MgSO_4 overnight. After filter and removal of methylene chloride on a rotary evaporator, the obtained residues were distilled under reduced pressure to give a colorless viscous liquid. Yield: 33.7 g, 71%. ^1H NMR (CDCl_3 , δ , ppm): 4.34 (t, 2H, $\text{N}_3\text{CH}_2\text{CH}_2$), 3.52 (t, 2H, N_3CH_2), 1.96 (s, 6H, $(\text{CH}_3)_2\text{Br}$).

Preparation of MWNT-OH, MWNT-NH₂, MWNT-COOH, and MWNT-Br. In a typical experiment (feed ratio, $R_{\text{feed}} = 20/1$ (w/w)), pristine MWNTs (1.00 g) and *N*-methyl-2-pyrrolidinone (NMP, 80 mL) were placed in a 250 mL Schlenk flask fitted with a condenser. The mixture was treated with an ultrasonic bath (40 kHz) for 2 h and then placed on a magnetic stirrer with an oil bath. After the mixture was bubbled with nitrogen for 15 min, 2-azidoethanol (20.0 g, 0.23 mol) was added via syringe. The reaction mixture was then heated and maintained around 160 °C in a nitrogen atmosphere under constant stirring for 18 h. After cooling down to room temperature, the product was isolated by precipitation into acetone. The resulting precipitates were redispersed in acetone with the aid of an ultrasonic bath and then collected by centrifugation. This centrifugation was repeated until the upper layer was nearly colorless. The separated solid was sequentially redispersed in water and purified by at least five centrifugation cycles. All these centrifugations were performed at a rotation speed of at 14 500 rpm for 3 min using 30 mL plastic centrifuge tubes. The supernatant was decanted and the black solid was dried under vacuum at 60 °C overnight to give 1.02 g of MWNT-OH. So this is a weight-increase process, and the mass loss of neat nanotubes during the preparation methods is less than 10%. We also tried experiments with one batch of 5–10 g of pristine MWNTs, and similar dispersed functional CNTs were obtained.

The same protocol was also used to prepare MWNT-NH₂, MWNT-COOH, and MWNT-Br, except that 2-azidoethanol was substituted by 3-azidopropan-1-amine, 4-(2-azidoethoxy)-4-oxobutanoic acid, and 2-azidoethyl 2-bromo-2-methylpropanoate, respectively.

Synthesis of MWNT-g-PCL by Ring-Opening Polymerization (ROP). Into a 50 mL Schlenk flask, as-prepared MWNT-OH ($R_{\text{feed}} = 20/1$, 50 mg) was charged, and the flask was then sealed with a rubber plug. The flask was evacuated and filled thrice with high-purity nitrogen. ϵ -Caprolactone (6.0 g, 53 mmol) and stannous

(19) Cheng, G. L.; Boker, A.; Zhang, M. F.; Krausch, G.; Muller, A. H. E. *Macromolecules* **2001**, *34*, 6883–6888.

(20) Sumerlin, B. S.; Tsarevsky, N. V.; Louche, G.; Lee, R. Y.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 7540–7545.

(21) Carboni, B.; Benalil, A.; Vaultier, M. J. *Org. Chem.* **1993**, *58*, 3736–3741.

(22) Inoue, Y.; Matsugi, T.; Kashiwa, N.; Matyjaszewski, K. *Macromolecules* **2004**, *37*, 3651–3658.

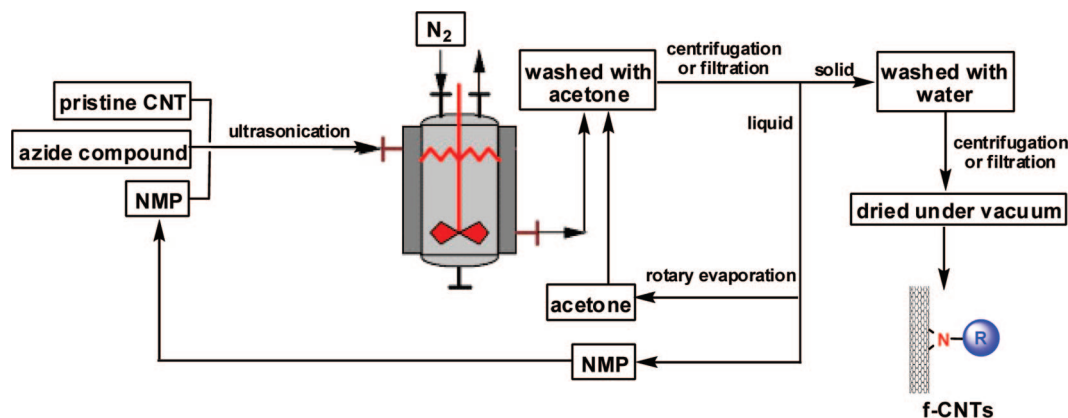


Figure 1. Flowchart for the large-scale production of f-CNTs.

octoate (2 mg) were injected into the flask via a syringe. The reaction was allowed to proceed for 24 h at 120 °C under constant stirring. The product was filtered and washed thoroughly with excess chloroform several times. The final product was dried under vacuum overnight to give 55 mg of MWNT-g-PCL.

Synthesis of MWNT-g-PGMA by Cationic ROP. Into a dried Schlenk flask as-prepared MWNT-OH ($R_{\text{feed}} = 20/1$, 20 mg), dried CH_2Cl_2 (15 mL) and GMA (4.0 g, 28 mmol) were added under nitrogen. The flask was then treated with ultrasonic bath for 1 min before placed into ice–water bath. $\text{BF}_3 \cdot \text{OEt}_2$ (0.1 mL) was injected into the reaction mixture by syringe quickly. After 24 h, the cationic polymerization was ended by adding a little methanol. The resulting product was washed with methanol and separated by centrifuging. The final product was dried under vacuum overnight to give 18 mg of MWNT-g-PGMA.

Synthesis of MWNT-PC by Amidation. MWNT-NH₂ (20 mg) was dispersed via sonication in 8 mL of dried CHCl_3 . After dried Et_3N (3.5 g, 35 mmol) and palmitoyl chloride (3 g, 11 mmol) were added, the reaction was allowed to proceed at room temperature for 24 h. The product was isolated by centrifugation and rinsed in turn with 1 M HCl, deionized water, and acetone. The black solid was collected and dried overnight under vacuum to give 19 mg of MWNT-PC.

Preparation of Pt/MWNT Nanohybrids. The as-prepared MWNT-COOH (20 mg) and 40 mL of ethylene glycol–water solution (3:2 volume ratio) were placed into a 100 mL Schlenk flask, which was then treated with an ultrasonic bath (40 kHz) for 3 min. K_2PtCl_4 (12.8 mg, 0.03 mmol) was added into the flask before the reactive mixture was heated in a 125 °C oil bath under nitrogen atmosphere for 4 h. The product was centrifuged, rinsed several times with deionized water, and dried at 60 °C.

Synthesis of MWNT-g-PMMA by Atom Transfer Radical Polymerization (ATRP). To a 25 mL Schlenk flask containing a magnetic stirrer, 50 mg of MWNT-Br was dispersed in 2 mL of THF upon sonication for 15 min before MMA (0.5 g, 5 mmol), CuBr (11.5 mg, 0.08 mmol), and PMDETA (17 μL , 0.08 mmol) were added under nitrogen. The flask was then sealed and stirred at 40 °C for 24 h. The mixture showed obvious viscosity at the end of the reaction. The mixture was subsequently diluted to THF, centrifuged, and rinsed several times with THF to remove any ungrafted polymer. A black solid MWNT-g-PMMA (66 mg) was obtained after vacuum-drying overnight.

Synthesis of MWNT-g-PS by ATRP. In a 25 mL Schlenk flask, 50 mg of MWNT-Br was dispersed via sonication for 15 min in 0.91 g of styrene. CuBr (18.5 mg, 0.13 mmol) and PMDETA (21 μL , 0.10 mmol) were added under a nitrogen atmosphere. The flask was placed in an oil bath at 80 °C under magnetic stirring. After 24 h, the viscosity had obviously increased. The mixture was cooled

to room temperature and washed by repeated dispersing in THF and centrifuging. The black solid was collected and dried under vacuum at 30 °C to a constant weight, affording 25 mg of MWNT-g-PS.

Synthesis of MWNT-g-GMAN₃ by ATRP. In a 25 mL Schlenk flask, 30 mg of MWNT-Br was dispersed via sonication for 15 min in 1.5 mL of THF. GMAN₃ (0.40 g, 2.2 mmol), CuBr (7.8 mg, 0.05 mmol) and PMDETA (11 μL , 0.05 mmol) was added under a nitrogen atmosphere. The resulting mixture was stirred for 24 h at 25 °C. The solid was then separated from the mixture by centrifuging and washed with acetone. The black solid was collected and dried under vacuum at 30 °C to a constant weight, affording 16 mg of MWNT-g-GMAN₃.

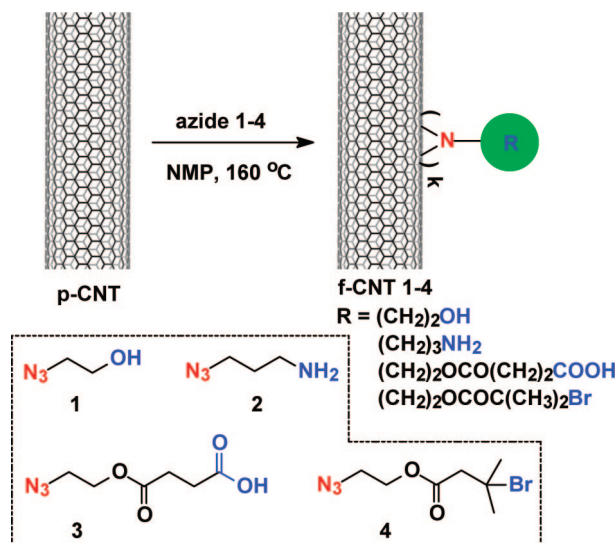
Results and Discussion

General Approach for One-Step Preparation of Functional CNTs. Our engineering aims to prepare functional group-contained CNTs with large-scale productivity, which is directly industrially producible if needed. Therefore, the functionalization technique should meet the requirements of a green process, inexpensive or recyclable materials, as few as possible reaction steps, and controllability of the group density.

In our one-step technology, various functional groups were introduced onto CNTs to obtain the f-CNTs by simply mixing as-purchased pristine CNTs (p-CNTs) and functional azides (f-azides) in *N*-methyl-2-pyrrolidone (NMP) at 160 °C for several hours. The process is depicted in Figure 1. Previously, 1,1,2,2-tetrachloroethane (TCE) was used as the solvent,¹³ and no one considered recycling the solvent in the nitrene chemistry and any other functionalization techniques. Herein, we selected NMP as the best solvent (bp 202 °C) after tens of experiments. Significantly, NMP was recycled in our engineering and is much cheaper than TCE. Before reaction, nitrogen bubbling for several minutes is necessary to prevent the highly reactive intermediates from reacting with oxygen.²³ Since the pristine CNTs dispersed poorly in NMP (or any other solvent), it is significant to treat the mixture with an ultrasonic bath for a period of time to achieve better dispersion and presumably leads to more evenly anchored functional groups on CNTs. Meanwhile, ultrasound cut short CNTs and caused defects in the sidewalls of carbon struc-

(23) Liu, J.; Hadad, C. M.; Platz, M. S. *Org. Lett.* **2005**, 7, 549–552.

Scheme 1. General Approach for One-Step Preparation of f-CNTs by Nitrene Chemistry



tures.²⁴ After reaction, the raw product was separated in two manners: direct filtration with filter paper for a large batch and precipitation in acetone followed by centrifugation for a small batch. Final product of f-CNTs was then obtained after repeated washing with water or organic solvent of reagent.

The general one-step strategy for the synthesis of f-CNTs is illustrated in Scheme 1. Herein, the azides act as a button or an anchor: they carry within themselves the functional groups and attach them to the surface of CNTs. These azide reagents can be easily synthesized from NaN_3 and other readily available chemicals. Triazolines were formed by 1,3-dipolar cycloaddition reactions between organic azides and $\text{C}=\text{C}$ bonds of CNTs, and then a concomitant nitrogen loss occurred upon thermolysis.¹⁵ This thermolysis could be visually confirmed by the continuing bubbles coming out of the reaction flask. In addition, thermal activation alkyl azide precursors also yielded some azo and heterocyclic byproduct, causing the reaction solution to become dark brown.²⁵ Accordingly, we have obtained four types of f-CNTs with different reagents of azides, that is, hydroxyl-functionalized CNTs (CNT-OH), amino-functionalized CNTs (CNT- NH_2), carboxyl-functionalized CNTs (CNT-COOH), and bromine-functionalized CNTs (CNT-Br).

The f-CNTs were characterized by TGA, FTIR, Raman, XPS, SEM, and TEM, and the functional groups of f-CNTs were demonstrated with further chemical reactions. Both f-MWNTs and f-SWNTs were prepared, and the details of f-MWNTs are discussed in the text.

TGA of f-MWNTs. Thermal gravimetric analysis (TGA) is an extensively used analysis method that is capable of

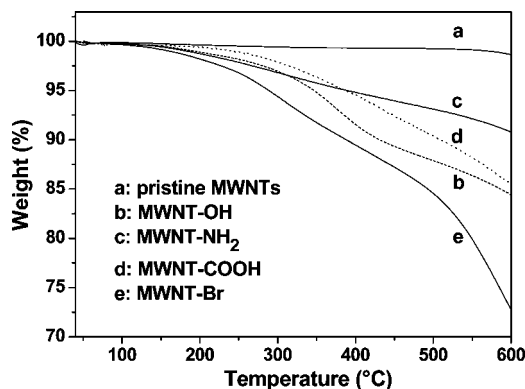


Figure 2. TGA curves of (a) pristine MWNTs, (b) MWNT-OH, (c) MWNT- NH_2 , (d) MWNT-COOH, and (e) MWNT-Br.

Table 1. Data Calculated from TGA Curves of f-MWNTs

samples	f_w^a (%)	concn ^b (mmol/g)	density ^c
MWNT-OH (1:1)	3.1	0.53	6.5
MWNT-OH (10:1)	5.5	0.94	11.9
MWNT-OH (20:1)	10.5	1.78	23.7
MWNT- NH_2	5.3	0.73	9.3
MWNT-COOH	8.2	0.52	6.8
MWNT-Br	12.5	0.60	8.2

^a Weight loss fraction between 200 and 480 °C. ^b The concentration of functional groups per gram of f-MWNTs. ^c The average numbers (density) of functional groups per 1000 carbons.

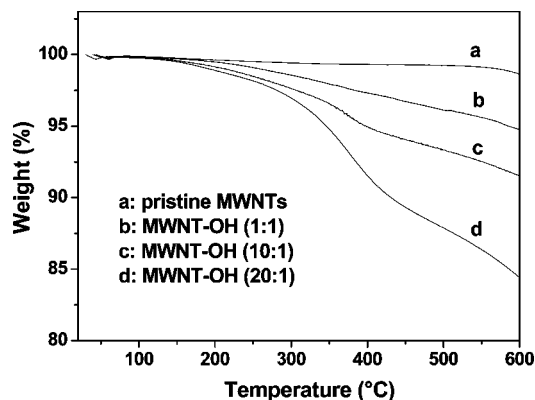


Figure 3. TGA curves of pristine MWNTs (a) and MWNT-OH prepared with different 2-azidoethanol/MWNT mass feed ratios of 1:1 (b), 10:1 (c), and 20:1 (d).

determining the amount of organic groups in the functionalized CNTs.²⁶ The TGA curves of f-MWNTs are shown in Figure 2. The weight loss of pristine MWNTs was only 1.4% at 600 °C, which might arise from decomposing and volatilizing of impurity. This little weight loss suggested that the thermal stability of nanotubes was significantly high and that there were few organic compositions on the pristine MWNTs. MWNT-OH showed distinct weight loss above 200 °C, with a maximum decomposition rate at 380 °C. Given the contrast between the TGA data of pristine MWNTs and MWNT-OH, it is reasonable to attribute the weight loss of MWNT-OH to the loss of functional side chains of MWNTs. So the degree of functionalization of CNTs can be easily obtained by measuring the weight loss. In the temperature range of 200 to 480 °C, MWNT-OH showed a weight loss of 10.5%. This corresponds to ca. 1.78 mmol

(24) Koshio, A.; Yudasaka, M.; Zhang, M.; Iijima, S. *Nano Lett.* **2001**, 1, 361–363.

(25) (a) Singh, P. N. D.; Mandel, S. M.; Sankaranarayanan, J.; Muthukrishnan, S.; Chang, M.; Robinson, R. M.; Lahti, P. M.; Ault, B. S.; Gudmundsdottir, A. D. *J. Am. Chem. Soc.* **2007**, 129, 16263–16272. (b) Singh, P. N. D.; Mandel, S. M.; Robinson, R. M.; Zhu, Z. D.; Franz, R.; Ault, B. S.; Gudmundsdottir, A. D. *J. Org. Chem.* **2003**, 68, 7951–7960.

(26) Kong, H.; Gao, C.; Yan, D. Y. *Macromolecules* **2004**, 37, 4022–4030.

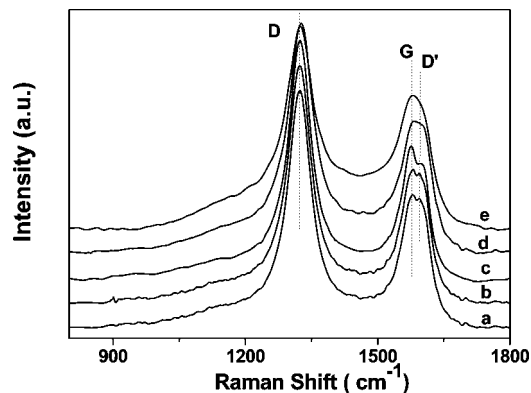


Figure 4. Raman spectra of (a) p-MWNTs, (b) MWNT-OH, (c) MWNT-NH₂, (d) MWNT-COOH, and (e) MWNT-Br.

hydroxyl-terminated group per gram of MWNT-OH, or ca. 23.7 functional groups per 1000 carbons. The data calculated from TGA curves of all the samples (i.e., MWNT-OH, MWNT-NH₂, MWNT-COOH, and MWNT-Br) are listed in

Table 1. These values are close to or higher than that reported previously by Gao and co-workers (0.55 mmol of functional groups per gram of acid-treated MWNTs).⁹ Such a high density of organic moieties indicates the high efficiency of the one-step functionalization method. It is noteworthy that almost the same results (e.g., dispersibility and functional group density) were obtained wherever the raw materials of p-MWNTs are microgram scale or supra-gram scale, indicating the high reproducibility and large-scale productivity of this one-step technology.

Furthermore, we varied the ratio of 2-azidoethanol to MWNTs to investigate the effect of feed ratio (R_{feed}) on the functionalization efficiency. Interestingly, the weight loss of these MWNT-OHs increased considerably with increasing the amount of 2-azidoethanol added to the reaction system (see Figure 3 and Table 1), indicating that the amount of hydroxyl-terminated groups attached on the surface of nanotubes can be generally controlled by adjusting R_{feed} . It

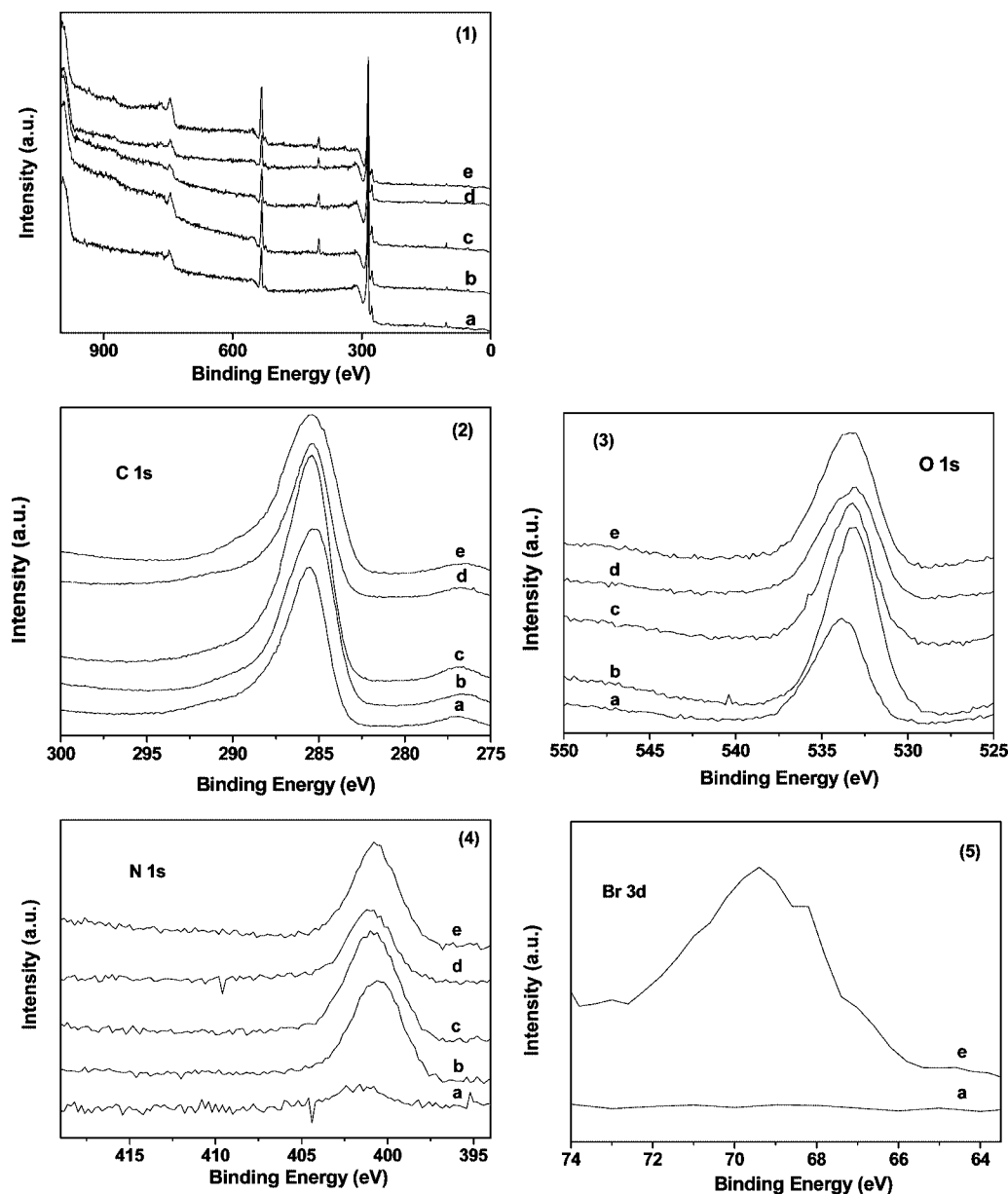


Figure 5. XPS spectra of (a) p-MWNTs, (b) MWNT-OH, (c) MWNT-NH₂, (d) MWNT-COOH, and (e) MWNT-Br: (1) survey of the spectral region from 0 to 1000 eV, (2) the carbon 1s region, (3) the oxygen 1s region, (4) the nitrogen 1s region, and (5) the bromine 3d region.

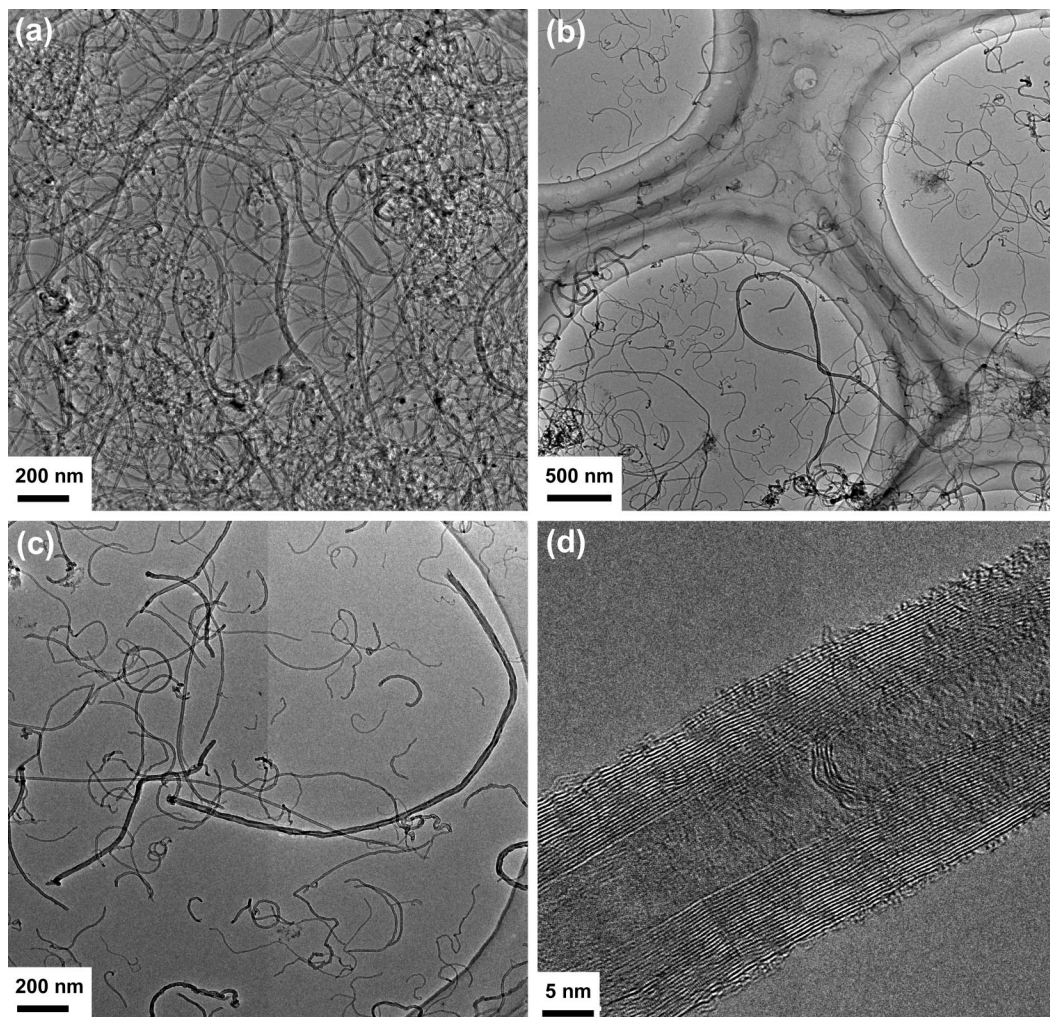


Figure 6. Representative TEM images of p-MWNTs (a) and MWNT-OH (b–d). Other f-MWNTs showed TEM images similar to those of the MWNT-OH.

is noteworthy that high quantity of hydroxyl groups up to 0.53 mmol per gram of f-MWNTs is achieved when the R_{feed} is only 1/1, implying that a small addition amount of azides can result in high density of functional group on MWNTs. This is essentially important to decrease the cost in industrial production. When the R_{feed} was increased from 1/1 to 20/1, the group density rose from 0.53 to 1.78 mmol per gram of MWNT-OH, suggesting that (1) the group density can be adjusted in a wide range by the R_{feed} and (2) multiple kinds of functional groups can be introduced onto CNTs if f-CNTs with lower degree of functionalization were further reacted with other azides.^{18,27,28} To make the functional modification more obvious in the subsequent reactions and characterization, R_{feed} of 20/1 (w/w) was chosen as the standard ratio and applied to the preparation of other f-MWNTs.

Raman Spectroscopy of f-MWNTs. Raman spectra provide reliable structural information on the covalent sidewall functionalization of nanotubes in a nondestructive

way.²⁹ Figure 4 illustrates the Raman spectra of pristine MWNTs and f-MWNTs operating at a laser wavelength of 632.8 nm measured at room temperature. It is clear that all of the spectra display the same pattern, revealing that the intrinsic graphite structure of the nanotubes remains largely intact after functionalization. The typical Raman spectrum for MWNTs shows two prominent bands around 1320 cm^{-1} (D band) and 1580 cm^{-1} (G band). The disorder mode band (D band) is related to the presence of defects in the nanotubes. The strong G band is associated with the vibration of sp^2 -bonded carbon atoms in a graphitic layer (in-plane E_{2g} mode of graphite), accompanying by D' band at 1594 cm^{-1} as a shoulder that may be attributed to the disorder-induced effect originating from the finite size effect or lattice distortion.³⁰ The f-MWNTs exhibit a larger D band with reference to p-MWNTs, indicating some sp^2 -hybridized

(27) Mawhinney, D. B.; Naumenko, V.; Kuznetsova, A.; Yates, J. T.; Liu, J.; Smalley, R. E. *J. Am. Chem. Soc.* **2000**, *122*, 2383–2384.
 (28) Brunetti, F. G.; Herrero, M. A.; Munoz, J. D.; Diaz-Ortiz, A.; Alfonsi, J.; Meneghetti, M.; Prato, M.; Vazquez, E. *J. Am. Chem. Soc.* **2008**, *130*, 8094–8100.

(29) (a) Moreno, J. M. C.; Swamy, S. S.; Fujino, T.; Yoshimura, M. *Chem. Phys. Lett.* **2000**, *329*, 317–322. (b) Mahanandia, P.; Nanda, K. K. *Nanotechnology* **2008**, *19*, 155602 (seven pages). (c) Gao, C.; Jin, Y. Z.; Kong, H.; Whitby, R. L. D.; Acquah, S. F. A.; Chen, G. Y.; Qian, H. H.; Hartschuh, A.; Silva, S. R. P.; Henley, S.; Fearon, P.; Kroto, H. W.; Walton, D. R. M. *J. Phys. Chem. B* **2005**, *109*, 11925–11932.

(30) Liu, L. Q.; Qin, Y. J.; Guo, Z. X.; Zhu, D. B. *Carbon* **2003**, *41*, 331–335.

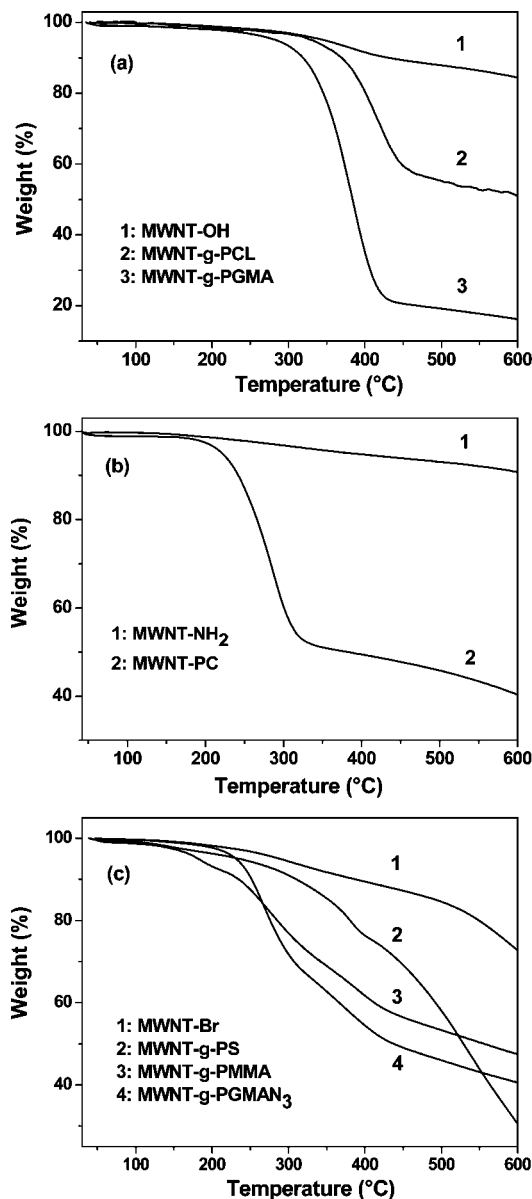


Figure 7. TGA curves of functionalized MWNTs.

simple and cost-effective. To clarify these doubts, various chemical reactions were performed on the f-MWNTs, as shown in Scheme 2.

Surface-initiated polymerization, generally termed “grafting from” approach, has been adopted to covalently graft a wide range of polymer chains from the surface of CNTs.³² To confirm the successful addition of hydroxyl groups to MWNT-OH, ring-opening polymerizations (ROP) of ϵ -caprolactone³³ and cationic polymerization of glycidyl methacrylate (GMA)³⁴ from MWNT-OH were carried out to produce MWNT-g-PCL and MWNT-g-PGMA, respectively. MWNT-NH₂ was reacted with palmitoyl chloride to verify

amino groups introduced onto the nanotubes.³⁵ Pt/MWNT nanohybrids were prepared from MWNT-COOH by reducing K₂PtCl₄ in an ethylene glycol–water solution to show the function of carboxyl groups.³⁶ In order to demonstrate the function of bromine groups linked on MWNT-Br, we also carried out in situ atom transfer radical polymerization (ATRP)³⁷ with MWNT-Br as macroinitiator, and styrene, methyl methacrylate (MMA), and 3-azido-2-hydroxypropyl methacrylate (GMAN₃) as monomers, affording MWNT-g-PS, MWNT-g-PMMA, and MWNT-g-PGMAN₃, respectively.³⁸

To examine the relative quantity of organic compounds grafted from/to the f-MWNTs, TGA measurements were done again to record the weight loss curves of the remodified MWNTs. The amounts of grafted organic compounds calculated from the TGA data, are 42.6 wt % for MWNT-g-PCL and 78.3 wt % for MWNT-g-PGMA (Figure 7a). The results show that the surface hydroxyl groups of MWNT-OH are highly reactive for initiating ROP. The TGA curve of MWNT-PC with a 50.8% weight loss is present in Figure 7b, demonstrating the high density and high reactivity of amino groups on MWNT-NH₂. The samples of MWNT-g-PS, MWNT-g-PMMA, and MWNT-g-PGMAN₃ have weight losses of 33.3%, 50.5%, and 58.6%, respectively (Figure 7c), verifying in turn the existence and high ATRP initiating activity of bromine groups on MWNT-Br. In addition, in the ¹H NMR spectrum of MWNT-g-PCL (Supporting Information, Figure S1), the proton signals of the grafted PCL chains were found as peaks at 4.1 (–CH₂O–), 2.3 (–OCCH₂–), 1.6 (–OCCH₂CH₂CH₂CH₂CH₂O–), and 1.3 ppm (–OCCH₂CH₂CH₂CH₂CH₂O–), respectively.³⁹

Fourier transform infrared (FTIR) spectroscopy is a well-established and informative analytical tool for identifying chemically modified MWNTs. The as-prepared samples after thorough workup as well as the pristine MWNTs were analyzed by FTIR (Supporting Information, Figure S2). In the FTIR of pristine MWNTs, the large band centered at 3430 cm^{–1} and the weak one at 1630 cm^{–1} could be assigned, respectively, to the asymmetrical stretching and scissoring vibrations due to trace amount of ambient atmospheric moisture absorbed in the samples and KBr pellets.⁴⁰ Pristine MWNTs also show symmetrical and asymmetrical stretching vibration and symmetrical deformation vibration (at 2928, 2862, and 1384 cm^{–1}, respectively) of C–H bond that could be ascribed to the defects at outer walls and ends of MWNTs. The C–H defects of MWNTs prepared via chemical vapor

- (32) (a) Kong, H.; Gao, C.; Yan, D. Y. *J. Am. Chem. Soc.* **2004**, *126*, 412–413. (b) Qin, S. H.; Qin, D. Q.; Ford, W. T.; Resasco, D. E.; Herrera, J. E. *J. Am. Chem. Soc.* **2004**, *126*, 170–176. (c) Jin, Y. Z.; Gao, C.; Kroto, H. W.; Maekawa, T. *Macromol. Rapid Commun.* **2005**, *26*, 1133–1139.
- (33) Wang, K.; Li, W. W.; Gao, C. *J. Appl. Polym. Sci.* **2007**, *105*, 629–640.
- (34) Huang, W.; Zhou, Y. F.; Yan, D. Y. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 2038–2047.

- (35) Stevens, J. L.; Huang, A. Y.; Peng, H. Q.; Chiang, L. W.; Khabashesku, V. N.; Margrave, J. L. *Nano Lett.* **2003**, *3*, 331–336.
- (36) Xing, Y. C. *J. Phys. Chem. B* **2004**, *108*, 19255–19259.
- (37) (a) Wang, J.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614–5615. (b) Wang, J.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7572–7573. (c) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921–2990. (d) Matyjaszewski, K.; Davis, T. P., Eds. *Handbook of Radical Polymerization*; Wiley: Hoboken, NJ, 2002. (e) Tsarevsky, N. V.; Matyjaszewski, K. *Chem. Rev.* **2007**, *107*, 2270–2299.
- (38) (a) Kong, H.; Gao, C.; Yan, D. Y. *J. Mater. Chem.* **2004**, *14*, 1401–1405. (b) Kong, H.; Li, W. W.; Gao, C.; Yan, D. Y.; Jin, Y. Z.; Walton, D. R. M.; Kroto, H. W. *Macromolecules* **2004**, *37*, 6683–6686.
- (39) Zeng, H. L.; Gao, C.; Yan, D. Y. *Adv. Funct. Mater.* **2006**, *16*, 812–818.
- (40) (a) Yao, Z. L.; Braid, N.; Botton, G. A.; Adronov, A. *J. Am. Chem. Soc.* **2003**, *125*, 16015–16024. (b) Ramanathan, T.; Fisher, F. T.; Ruoff, R. S.; Brinson, L. C. *Chem. Mater.* **2005**, *17*, 1290–1295.

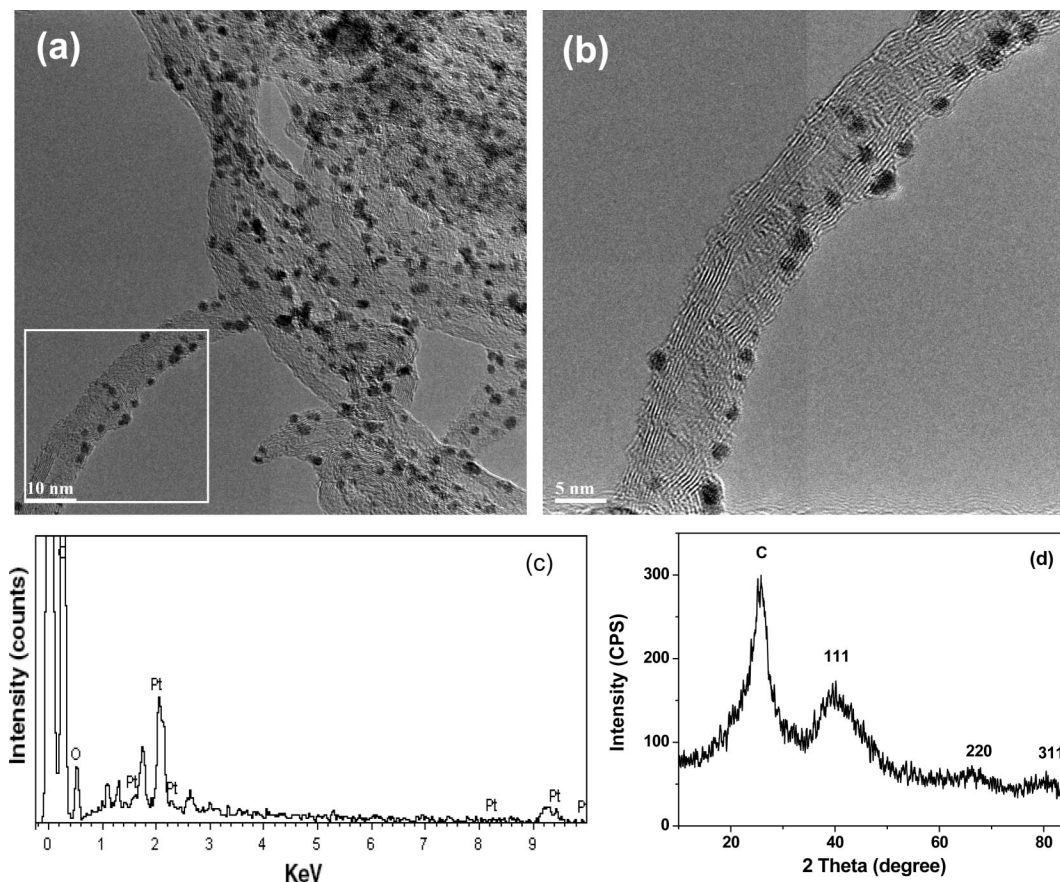


Figure 8. TEM images (a, b), EDS spectrum (c), and XRD pattern (d) of Pt/MWNT-COOH nanohybrids.

deposition (CVD) assumably stem from the hydrocarbon that added as one of the major feedstocks during the producing process.⁴¹ FTIR spectra of MWNT-COOH and MWNT-Br showed characteristic absorption peak of carbonyl (C=O) near 1730 cm^{-1} . In the infrared spectrum of MWNT-PC, the band near 2930 cm^{-1} can be assigned to the stretching mode of the CH_2 groups in alkyl chains that attached onto the surface of MWNT- NH_2 . Although this band also exists in the spectrum of p-MWNTs, its intensity is greatly augmented after reaction with palmitoyl chloride. After MWNT-OH was grafted with PCL, a new band appears at 1726 cm^{-1} , which is ascribed to the carbonyl (C=O) in the polymer. Another band corresponding to ethylene ($-\text{CH}_2-$) is clearly visible at 2924 cm^{-1} , which is more intense than that of MWNT-OH.

SEM and TEM studies were undertaken to characterize the surface structure and nanoscale morphologies of the resulting polymer-grafted MWNTs (Supporting Information, Figures S3 and S4). SEM images of p-MWNTs and MWNT-OH exhibited the similar nanowire-like morphology. A much thicker rodlike morphology was observed in the SEM image of polymer-grafted tubes, and many tubes were tangled and conglutinated. This distinguishing morphology could be caused by interactions among the polymer chains. In the TEM images of polymer-grafted MWNTs, the core-shell

nanostucture was observed with the outer wall of the nanotubes wrapped by several nanometers of polymer layer, demonstrating the even grafting efficiency by the grafting from approach.

It is reported that carboxyl groups help to deposit some metal nanocrystals on CNTs.⁴² So we used the sample of MWNT-COOH as the template to prepare Pt nanocrystals to check the function of the introduced carboxyl groups on MWNTs. Figure 8a,b shows that MWNT-COOH was evenly decorated with Pt nanodots, which are regular spherical particles with relatively uniform size of approximately 2 nm in diameter. Furthermore, energy dispersive X-ray spectroscopy (EDS) analyses (Figure 8c) indicated that the platinum content in this sample is approximately 8.4 wt %. In the X-ray diffraction (XRD) patterns of the Pt/MWNT nanohybrids (Figure 8d), the diffraction peak at $2\theta\ 25.8^\circ$ is assigned to the graphite crystalline phase of CNTs, and the other three peaks are assigned to the diffractions from the (111), (220), and (311) planes of face-centered cubic (fcc) platinum crystals, respectively.⁴³ Control experiments showed that Pt nanoparticles were hardly observed when p-MWNTs were used as the template. Moreover, other nanoparticles such as magnetic iron oxide and metallic silver were also successfully in situ deposited on the MWNT-COOH (data not shown).

(41) (a) Lee, H. J.; Oh, S. J.; Choi, J. Y.; Kim, J. W.; Han, J.; Tan, L. S.; Baek, J. B. *Chem. Mater.* **2005**, *17*, 5057–5064. (b) Carneiro, O. S.; Covas, J. A.; Bernardo, C. A.; Caldeira, G.; Van Hattum, F. W. J.; Ting, J. M.; Alig, R. L.; Lake, M. L. *Compos. Sci. Technol.* **1998**, *58*, 401–407.

(42) (a) Gao, C.; Li, W. W.; Jin, Y. Z.; Kong, H. *Nanotechnology* **2006**, *17*, 2882–2890. (b) Wildgoose, G. G.; Banks, C. E.; Compton, R. G. *Small* **2006**, *2*, 182–193.

(43) Tian, Z. Q.; Jiang, S. P.; Liang, Y. M.; Shen, P. K. *J. Phys. Chem. B* **2006**, *110*, 5343–5350.

herein), confirming the high density of carboxyl groups covalently linked on the surfaces of MWNTs.

Taken all of the evidence aforementioned, our studies explicitly illuminate that various functional groups have been effectively introduced onto MWNTs by the improved one-step nitrene chemistry strategy.

One-step preparation of functional SWNTs. In order to assess the compatibility of our approach to different types of nanotubes, we have also investigated the functionalization of SWNTs using the one-step technology. By examining the TGA, Raman, XPS, SEM, TEM and AFM data (see Supporting Information, Figures S5–S9), it was proved that the SWNTs have also been covalently linked with the functional groups (i.e., -OH, -NH₂, -COOH and -Br).

Conclusions

A facile one-step technology to produce functional carbon nanotubes in large quantity using readily available azide starting materials was set up. The pristine multiwalled carbon nanotubes (p-MWNTs) were reacted with various azide compounds in 1,3-dipolar cycloaddition reactions, affording hydroxyl-, amino-, carboxyl-, and bromine-functionalized MWNTs (MWNT-OH, MWNT-NH₂, MWNT-COOH, and MWNT-Br), respectively. TGA, Raman, and XPS studies indicated the covalent linkage between the functional groups and MWNTs. SEM and TEM observations showed that the nanotube structure remained essentially unaltered during chemical functionalization, and the dispersibility of f-CNTs has been significantly improved compared with p-CNTs. Moreover, it was feasible to control the functionalization

degree simply by adjusting the feed ratio of the azide compounds to CNTs. The functional groups anchored on the CNTs are still highly active and can be further chemically modified. Polymer-coated CNTs were synthesized by surface-initiated polymerizations of different types of monomers; Pt nanoparticles were in situ generated to produce Pt/CNT nanohybrids. In addition, we demonstrated that this approach could work well for both MWNTs and SWNTs. The resulting products are excellent candidate materials for use in biotechnology, nanotechnology, catalytic processes, and other related areas. The strategy described here is feasible in operation, convenient in practice, superior in efficiency, and inexpensive in cost, which paves the way to the industrial scale production of functional CNTs. Further studies are now in progress to expand applications of the one-step functionalized nanotubes.

Acknowledgment. This work was financially supported by the National Natural Science Foundation of China (No. 50773038), National Basic Research Program of China (973 Program) (No. 2007CB936000), Science and Technology Commission of Shanghai Municipality (07pj14048), the Program for New Century Excellent Talents in University of China, and the Foundation for the Author of National Excellent Doctoral Dissertation of China (No. 200527).

Supporting Information Available: Chemical modification of f-MWNTs and detailed characterization data for f-SWNTs. This information is available free of charge via the Internet at <http://pubs.acs.org>.

CM802704C