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Grafting of 4-(2,4,6-Trimethylphenoxy)benzoyl onto Single-Walled Carbon Nanotubes in Poly(phosphoric acid) via Amide Function

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Abstract Single-walled carbon nanotubes (SWCNTs), which were commercial grade containing 60–70 wt% impurity, were treated in a mild poly(phosphoric acid) (PPA). The purity of PPA treated SWCNTs was greatly improved with or without little damage to SWCNTs framework and stable crystalline carbon particles. An amide model compound, 4-(2,4,6-trimethylphenoxy)benzamide (TMPBA), was reacted with SWCNTs in PPA with additional phosphorous pentoxide as "direct" Friedel–Crafts acylation reaction to afford TMPBA functionalized SWCNTs. All evidences obtained from Fourier-transform infrared spectroscopy, Raman spectroscopy, thermogravimetric analysis, scanning electron microcopy, and transmission electron microscopy strongly supported that the functionalization of SWCNTs with benzamide was indeed feasible.

Keywords Single-walled carbon nanotube · Purification · Grafting · Polyphosphoric acid · Phosphorous pentoxide

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Introduction

Single-walled carbon nanotubes (SWCNTs) are theoretically expected to display outstanding mechanical strength, chemical inertness, and excellent thermal and electrical conductivities [1, 2]. However, as-prepared SWCNTs contain a large amount of impurities such as small-sized catalytic metal particles and carbonaceous materials [3, 4]. They also have difficulty in efficient dispersion to display maximum enhanced properties. Because of their strong intrinsic lateral van der Waals attraction, SWCNTs form bundles that are strictly entangled (http://hnt.hanwha.co.kr/). Thus, the preparation and purification of SWCNTs are equally important for manufacturing efficiencies in practice. There are still a few fundamental issues needed to be resolved first before developing applications. They are related to: (i) cost-effective synthesis with high purity, and (ii) easy purification without or less damaging SWCNTs. Many processes for the synthesis of SWCNTs have been reported [4]. However, as-prepared SWCNTs contain more than 60–70 wt% of impurities regardless what method is used (http://hnt.hanwha.co.kr/). Aside from developing viable SWCNT production on an industrial scale, the purification and functionalization of SWCNTs continue to be important in nanomaterial research and development efforts, thus, it would be of practical interest to be able to develop a scalable, one-pot process for purification and functionalization at the same time in a non-destructive mild medium. Hence, many attempts to purify SWCNTs have been reported by using oxidation in nitric acid [5], burning in air [6], using steam [7], etc. However, some reports have pointed out that significant damage in such harsh conditions has apparently occurred on the sidewall of SWCNTs such as sidewall opening, breaking, etc. [8–10]. Thus, the purification and functionalization without or little damage

on SWCNT framework are prerequisites to maintain and transfer its outstanding properties to corresponding matrix as nanoscale additives. As a result, the maximum effective aspect ratio, which is largely determined by the state of dispersion, could be achieved. In addition, the chemical modification of SWCNTs, which is able to diminish lateral interaction between SWCNTs and also to improve chemical affinity between SWCNT and matrix, would be a viable approach to help efficient dispersion.

We have developed the purification of SWCNTs in a mild and non-destructive medium in PPA. Specifically, commercial grade PPA (83% P_2O_5 assay) with additional amount of phosphorous pentoxide (P_2O_5) medium was optimized condition for "direct" Friedel–Crafts acylation reaction using a carboxylic acid instead of the corresponding acid chloride [11]. The medium appears to be an ideal system to exploit both purification and functionalization in a one-pot process. The PPA reaction medium, which has moderately acidic and viscous characteristics, is expected to play two important roles. Its acidic nature could protonate to promote de-bundling of SWCNTs and also to decompose pre-existing carbonaceous impurities and catalytic residues. Its viscous nature would help to impede reaggregation of SWCNTs after their dispersion. The reaction condition in PPA/P_2O_5 medium at 130 °C has been utilized in both the polymerization of phenoxybenzoic acids [11] and functionalization of closely related carbon materials such as vapor-grown multi-walled carbon nanofibers (MWCNFs) [12, 13] and multi-walled carbon nanotubes (MWCNTs) [14–18].

In this work, we prepared an "amide" model compound, 4-(2,4,6-trimethylphenoxy)benzamide (TMPBA), which was treated with SWCNTs in PPA/P_2O_5 medium. The covalent attachment of TMPBA onto the surface of SWCNTs was studied by elemental analysis (EA), Fourier-transform infrared spectroscopy (FT-IR), Raman spectroscopy, and thermogravimatric analysis (TGA). In addition, the morphology of functionalized SWCNTs was verified by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Experimental

Materials

In this study, all reagents and solvents were purchased from Aldrich Chemical Inc. and used as received, unless otherwise mentioned. The 4-(2,4,6-trimethylphenoxy)benzamide was synthesized following the procedure described in a literature and its melting point was 236–238 °C [19]. Single-walled carbon nanotubes (SWCNTs, 30–40 wt% purity) were obtained from Hanwha Nanotech Co., LTD, Seoul, Korea (http://hnt.hanwha.co.kr/).

Instrumentation

Fourier-transform infrared (FT-IR) spectra were recorded on a Jasco FT-IR 480 Plus spectrophotometer. Solid samples were imbedded in KBr disks. Elemental analysis (EA) was performed by using a CE Instruments EA1110. The melting points (mp) were determined on a Mel-Temp melting point apparatus and are uncorrected. Thermogravimetric analysis (TGA) was conducted both in air and nitrogen atmospheres with a heating rate of 10 °C/min using a Perkin–Elmer TGA7. The field emission scanning electron microscopy (FE-SEM) used in this work was a LEO 1530FE. A FEI Tecnai G2 F30 S-Twin was used for the field emission transmission electron microscope (FE-TEM) study.

PPA Treatment of SWCNTs at 130 °C

In a 250 mL resin flask equipped with a high-torque mechanical stirrer, nitrogen inlet and outlet, as-received SWCNTs (1.0 g) and PPA (50 g, 83% P_2O_5 assay) were placed and stirred under dry nitrogen atmosphere at 130 °C for 48 h. After cooling to room temperature, water was added into the flask. Purified SWCNTs were precipitated as black powder and collected by suction filtration. The SWCNTs were Soxhlet-extracted with water for 3 days to completely remove any residual PPA, and then with methanol for three more days to remove any organo-soluble low molar mass impurities. Finally, the sample was freeze-dried under reduced pressure (0.5 mmHg) for 72 h.

Functionalization of SWCNTs with 4-(2,4,6-Trimethylphenoxy)benzamide (TMPBA)

In a 100 mL resin flask equipped with a high torque mechanical stirrer, and nitrogen inlet and outlet, custom synthesized TMPBA (0.5 g, 1.96 mmol), and PPA treated SWCNTs (0.5 g, 41.6 mmol), and PPA (83% assay, 20 g) were charged and the mixture was stirred under dried nitrogen purging at 130 °C for 3 h. Phosphorous pentoxide (P_2O_5, 5.0 g) was then added in one portion. The initially dark mixture became light brown. The temperature was maintained at 130 °C for 48 h. After cooling down to room temperature, water was added. The resulting precipitates were collected, washed with diluted ammonium hydroxide, Soxhlet-extracted with water for 3 days and methanol for 3 days, and finally freeze-dried under reduced pressure (0.05 mmHg) for 72 h to give 0.85 g (88% yield) of black powdery solid: Anal. Calcd. for $C_{46.19}H_{15}O_2$: C, 90.47%;

H, 3.06%. Found: C, 79.76%; H, 2.61%. FT-IR (KBr, cm^{-1}): 1233, 1648, 2919, 2920.

Results and Discussion

Without purification, most of the as-prepared SWCNTs contain approximately 60–70 wt% of impurities such as carbonaceous fragments, amorphous carbons, and small amount of graphite and metal catalysts (http://hnt.hanwha.co.kr/). Hence, together with the development of efficient manufacturing to minimize persistent impurities, the viable purification of prepared SWCNTs is equally important approach in the field of SWCNT research area. Unlike MWCNTs or MWCNFs, SWCNTs consist of single graphene layer rolled into tubes. SWCNTs are vulnerable to be damaged on their frameworks and thus, they will loose their outstanding properties. Thus, as-received SWCNTs with 30–40 wt% purity treated to remove impurities in a much less corrosive medium in PPA at 130 °C for 48 h. As described in the "Experimental" section, the PPA treated SWCNTs were recovered and rigorously worked up.

The SEM image obtained from as-received SWCNTs shows bulky particle agglomerates (Fig. 1a), while those impurities have practically disappeared from the PPA treated SWCNTs (Fig. 1b). The PPA treated SWCNT bundles appear much coarser than the as-received ones, and thus the average diameter of the PPA treated SWCNT bundles is approximately four times of that of as-received ones. This is simply because carbonaceous impurities coated on the surface of the as-received SWCNT bundles are cleaned up, rendering the surfaces more active (Fig. 1a, inset). The PPA treated SWCNT bundles are able to make better lateral contact each other and forms larger bundles. Apparently, the surface of PPA treated SWCNT bundles is seamless and smooth, whereas the surface of as-received SWCNT bundles is furry and rough due to the impurities. It could be an indication that the larger bundle thickness implies the higher purity of SWCNTs.

The TEM image of the as-received SWCNTs shows that there are large portions of carbonaceous and metallic impurities (Fig. 1c). On the other hand, the PPA treated SWCNTs show that most of carbonaceous impurities have been removed, but some entrapped metallic particles are still present in stable spherical crystalline phases (Fig. 1d, arrows). Since PPA is not as corrosive as superacids, the entrapped metallic particles could not be removed without causing the sidewall opening and breaking of the stable crystalline carbon particles. This implies that PPA can selectively destroy the amorphous carbons. Unlike SWCNTs treated in hydrochloric acid and nitric acid/sulfuric acid treatments [20–22], there were no broken SWCNTs in bundles observed in this study. On the basis of these observations, PPA is indeed a mild and much less destructive medium for the purification of commercial grade SWCNTs and thus, SWCNTs could preserve their structural integrity.

The efficient functionalization of SWCNTs in the same purification medium might be the most important progress,

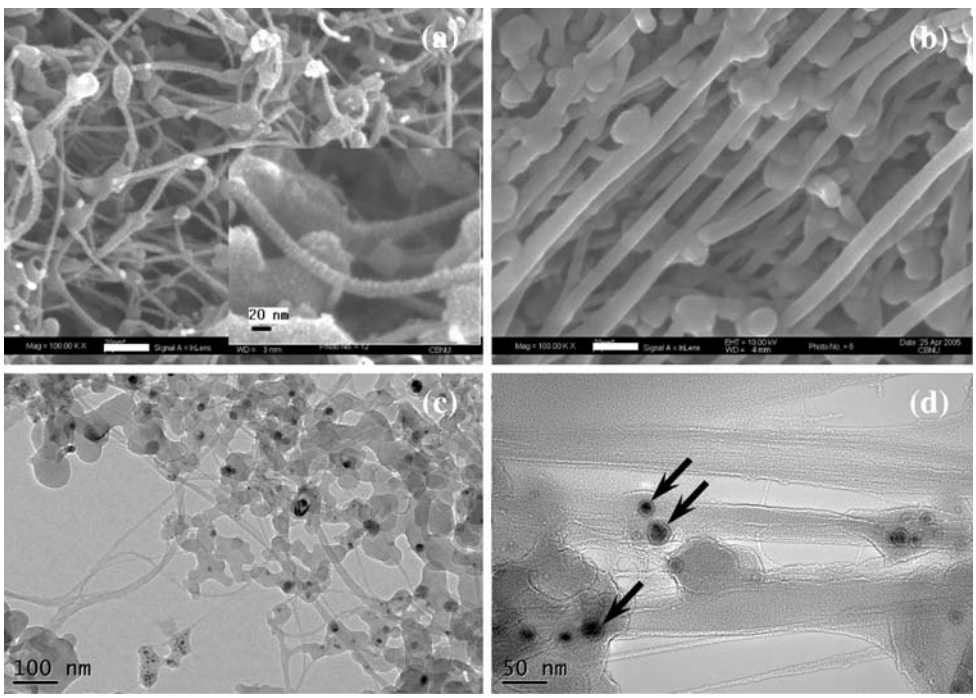

Fig. 1 SEM images: **a** as-received SWCNTs (100000×, scale bar is 100 nm); **b** PPA treated SWCNTs (100000×, scale bar is 100 nm). TEM images: **c** as-received SWCNTs (25000×); and **d** PPA treated SWCNTs (50000×)

since it could allow a one-pot process. For the "direct" Friedel–Crafts acylation reaction of benzamide instead of benzoic acid chloride, 4-(2,4,6-trimethylphenoxy)benzamide (TMPBA) was prepared by two step reaction sequences. It was synthesized via aromatic nucleophilic substitution reaction between 2,4,6-trimethylphenol and 4-fluorobenzonitrile to give 4-(2,4,6-trimethylphenoxy)benzonitrile, followed by acidic hydrolysis to give overall good yield. The "direct" Friedel–Crafts acylation reaction between TMPBA and SWCNTs was carried out to afford TMPBA grafted SWCNTs (TMPBA-g-SWCNT) in PPA/P_2O_5 medium at 130 °C (Fig. 2a). After the reaction mixture had been precipitated in water, the collected product was completely worked up by Soxhlet-extraction with water for 3 days to completely remove residual PPA. An additional Soxhlet-extraction was conducted with methanol for 3 days to ensure the complete removal of any unreacted TMPBA and low molar mass impurities.

The SEM image of TMPBA-g-SWCNT shows that the surface of SWCNTs is apparently decorated with covalently bonded moieties (Fig. 2b). Since the expected product should contain carbonyl groups (Fig. 2a), Fourier-transform infrared (FT-IR) spectroscopy was used to monitor the aromatic ketone υ(C=O) band. The FT-IR spectrum of TMPBA-g-SWCNT shows keto-carbonyl stretching peak at 1648 cm^{-1} (Fig. 2c). In addition, the primary amine bands of TMPBA at 3215 and 3386 cm^{-1} have disappeared in the spectrum from TMPBA-g-SWCNT. The result strongly implies that covalent attachment of TMPBA onto the surface of SWCNT to afford TMPBA-g-SWCNT. Furthermore, FT-Raman spectra were taken from PPA treated SWCNTs and TMPBA-g-SWCNT with 46-mW argon-ion laser (1064 nm) as the excitation source (Fig. 2d). The radial breathing mode (RBM), which appears in low frequency, is a powerful indicator to determine the nanotube diameters [23]. The RBM frequencies of as-received SWCNTs were 83.36–160.50 cm^{-1}. The values correspond SWCNT diameters of 1.39–2.68 nm by equation, $\omega RBM = 223.75/dt$ (ωRBM is the RBM frequency in cm^{-1}; dt is the SWCNT diameter in nm) [24]. In comparison with PPA treated SWCNTs and TMPBA-g-SWCNT, the RBM frequencies of TMPBA-g-SWCNT were almost identical at 85.29 and 162.43 cm^{-1} (Fig. 2d). The diameter values, which correspond well to

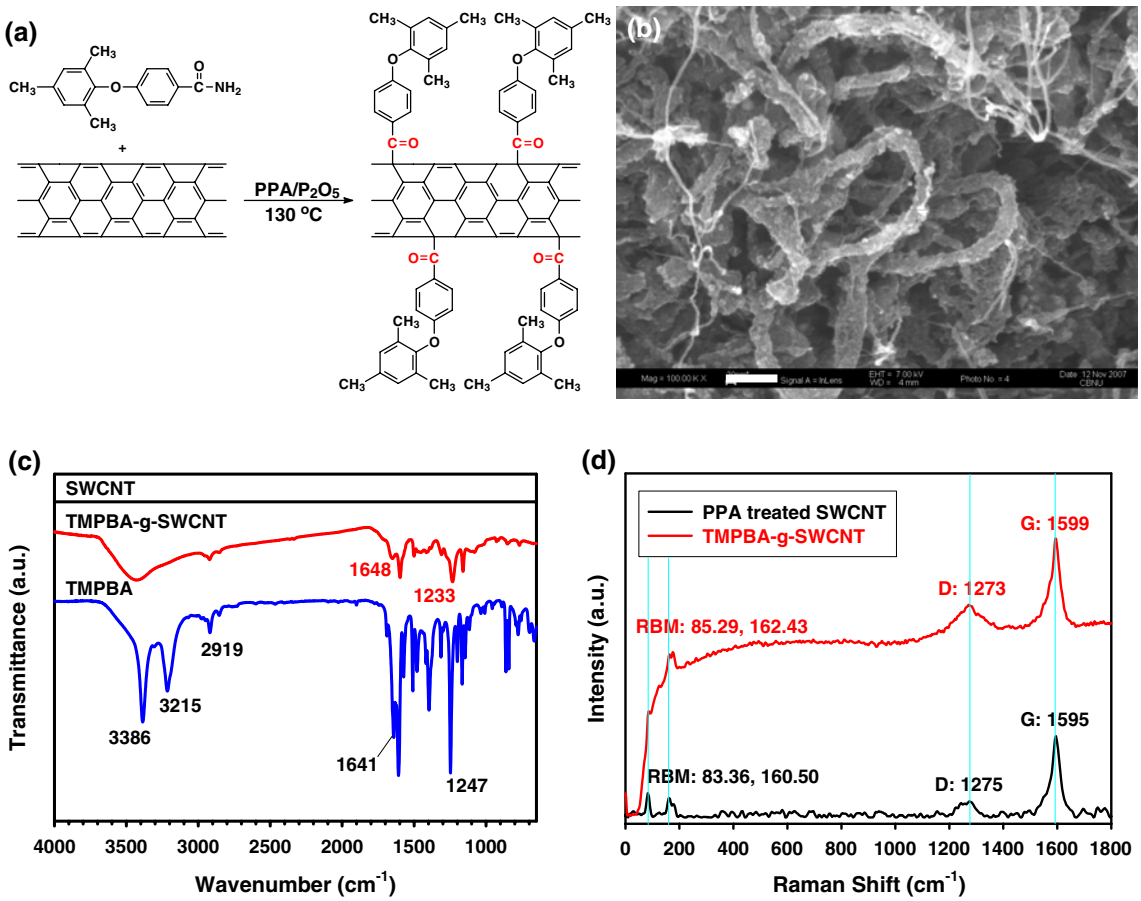

Fig. 2 **a** Functionalization of SWCNTs in PPA/P_2O_5 at 130 °C; **b** SEM image of TMPBA-g-SWCNT (100000×, scale bar is 100 nm); **c** FT-IR spectra; and **d** FT-Raman spectra

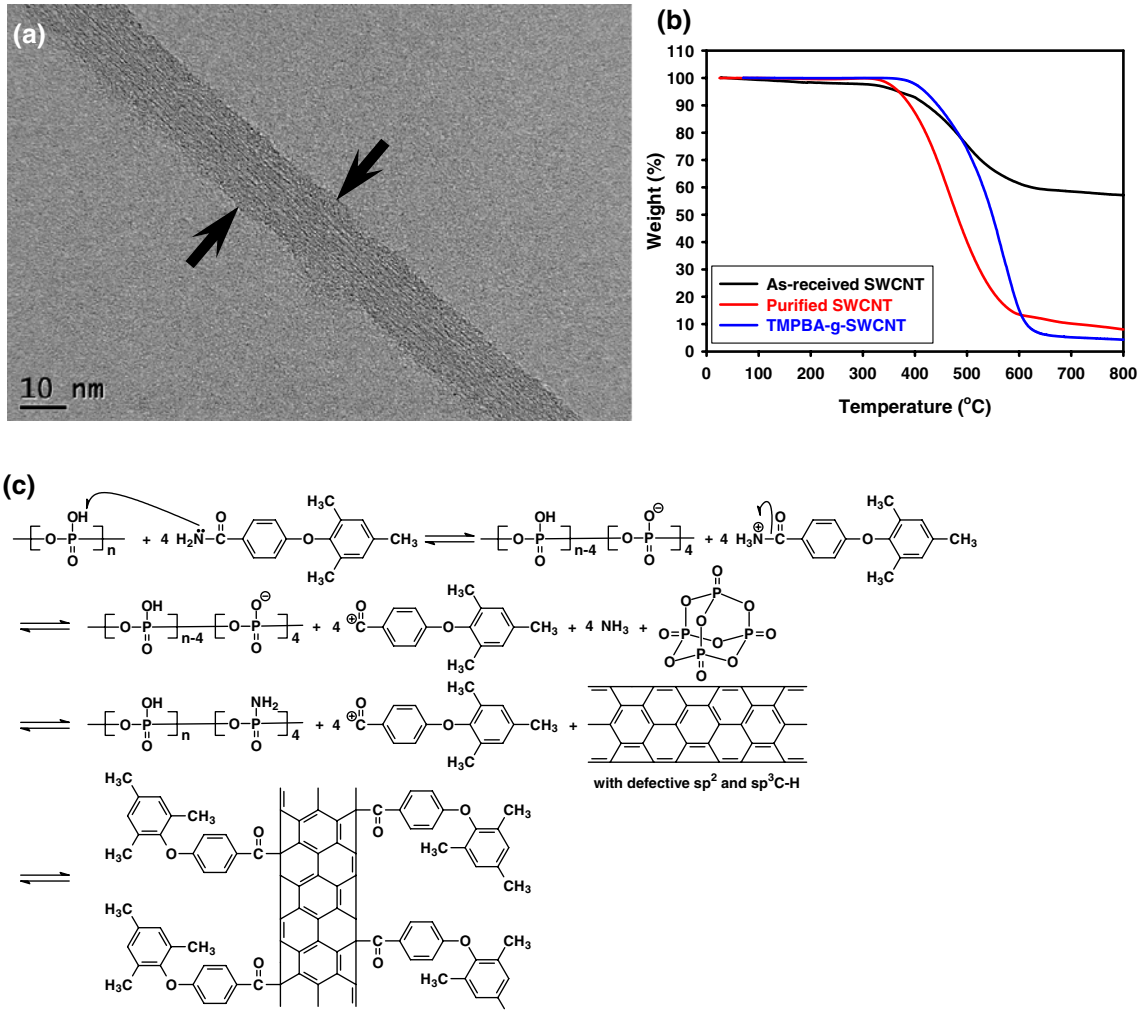

Fig. 3 **a** TEM image of TMPBA-g-SWCNT bundle; **b** TGA thermograms obtained with heating rate of 10 °C/min in air; and **c** proposed mechanism of functionalization of SWCNT with benzamide functional group

SWCNT diameters of 1.37–2.62 nm. It is a strong indication that the framework of SWCNTs was not damaged. The ratio of D/G-band intensity (I_D/I_G) depends on the SWCNT content. The D-band found near 1275 cm^{-1} is used to evaluate the defect density present in the tubular wall structure and the G-band in the 1550–1600 cm^{-1} region of spectrum is due to the tangential C–C stretching of SWCNT carbon atoms [25]. The I_D/I_G value of the TMPBA-g-SWCNT was 1.3, which was much lower than 5.0 of the PPA treated SWCNTs (Fig. 2d). The result indicates that SWCNTs in TMPBA-g-SWCNT are further purified during the functionalization in PPA/P_2O_5 reaction medium. On the basis of combined results from FT-IR and Raman spectra, it could be tentatively concluded that TMPBA had been attached to electron deficient SWCNTs via "direct" Friedel–Crafts acylation reaction to give TMPBA-g-SWCNT and SWCNTs could be further purified in the reaction medium.

A TEM image is provided to further confirm covalent grafting of TMPBA onto SWCNT bundles (Fig. 3a). Clear stripes in the inner part of SWCNT bundle represent that SWCNT frameworks are not damaged. The organics coated on the surface of SWCNT bundle are TMPBA moieties, which are uniformly decorated on the outer surface.

To obtain char yield and thermooxidative stability, the samples were heated to 800 °C with ramping rate of 10 °C/min under air atmosphere during TGA runs (Fig. 3b). The TGA thermogram of as-received SWCNT shows that the thermooxidative weight loss occurred in the broad range of 369–593 °C with approximately 57.1% of char yield at 800 °C (Fig. 3b). The residue at 800 °C in air is expected to be metallic impurities and stable carbonaceous fragments. The PPA treated SWCNTs displayed the weight loss in the range 348–607 °C with only 8.1% of char yield at 800 °C (Fig. 3b). The value was 49 wt% less than that of as-received SWCNTs. The result suggests that the heavy

weight metallic impurities and most of the carbonaceous fragments, which are located at outside of SWCNTs, could almost completely be eliminated by PPA treatment. On the other hand, stable crystalline carbon particles are unaffected by PPA. The thermooxidative stability of TMPBA-g-SWCNT was the best among the samples. It showed the temperature at which 5 wt% weight loss ($T_{d5\%}$) had occurred at 420 °C. The $T_{d5\%}$'s of as-received SWCNTs and PPA treated SWCNTs were the same at 369 °C, which was 51 °C lower than that of TMPBA-g-SWCNT. The weight loss of as-received SWCNTs was gradually started just above 100 °C, indicating that they contained some amount of volatile impurities. The enhanced thermooxidative stability of TMPBA-g-SWCNT could due to defective sp^3C–H and sp^2C–H sites were substituted by aromatic TMPBA. The defects are presumably attributable to the hydrocarbons, which are used as the major components in the feedstock for SWCNT productions [26, 27]. The defects would provide primary sites for "direct" Friedel–Crafts acylation reaction. On the basis of the foregoing rationalization, we have recently reported for the first time that "direct" functionalization and grafting onto as-received vapor-grown MWCNFs are very effective in PPA/P_2O_5 medium [12–18]. However, we believe there must be other type of chemical reaction(s) between SWCNT and carbonium ion to heavily and uniformly functionalize entire SWCNT (see Fig. 2b) [19, 28]. The proposed functionalization mechanism of TMPBA onto SWCNTs is presented in Fig. 3c. The mechanism involves that acylium ions are generated directly from benzamide groups. These ions attack SWCNTs and attach to their surfaces. From combined results, it is fair to say PPA is indeed less destructive to remove the undesired impurities from commercial grade SWCNTs. PPA with additional P_2O_5 is also an efficient medium for covalent attachment of TMPBA onto SWCNTs.

Conclusions

The purification of SWCNTs and the covalent attachment of TMPBA onto the surface of SWCNTs were conducted in a mild and thus less destructive PPA medium. On the basis of the results, it was confirmed that this medium could efficiently remove persisted carbonaceous and metallic impurities in commercial grade SWCNTs with or without little damage to their framework. In addition, the amide functionality on TMPBA is versatile for the covalent functionalization of SWCNTs via a simple one-step "direct" electrophilic substitution reaction. Thus, our approach points out the convenience of purification and functionalization of SWCNT to a one-pot manufacturing process.

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References

1. Y.-P. Sun, K. Fu, Y. Lin, W. Huang, Acc. Chem. Res. **35**, 1096 (2002). doi:10.1021/ar010160v
2. C.A. Mitchell, J.L. Bahr, S. Arepalli, J.M. Tour, R. Krishnamoorti, Macromolecules **35**, 8825 (2002). doi:10.1021/ma020890y
3. C. Journet, W.K. Maser, P. Bernier, A. Loiseau, M.L. de la Chapelle, S. Lefrant, P. Deniard, R. Lee, J.E. Fischer, Nature **388**, 756 (1997). doi:10.1038/41972
4. J. Li, Y. Zhang, Physica E **28**, 309 (2005). doi:10.1016/j.physe.2005.03.022
5. E. Dujardin, T.W. Ebbesen, A. Krishnan, M.M.J. Treacy, Adv. Mater. **10**, 611 (1998). doi:10.1002/(SICI)1521-4095(199805)10:8<611::AID-ADMA611>3.0.CO;2-8
6. Z. Shi, Y. Lian, F. Liao, X. Zhou, Z. Gu, Y. Zhang, S. Iijima, Solid State Commun. **112**, 35 (1999). doi:10.1016/S0038-1098(99)00278-1
7. G. Tobias, D. Shao, C.G. Salzmann, Y. Huh, M.L.H. Green, J. Phys. Chem. B **110**, 22318 (2006). doi:10.1021/jp0631883
8. M. Monthioux, B.W. Smith, B. Burteaux, A. Claye, J.E. Fischer, D.E. Luzzi, Carbon **39**, 1251 (2001). doi:10.1016/S0008-6223(00)00249-9
9. H. Hu, B. Zhao, M.E. Itkis, R.C. Haddon, J. Phys. Chem. B **107**, 13838 (2003)
10. C.G. Salzmann, S.A. Llewellyn, G. Tobias, M.A.H. Ward, Y. Huh, M.L.H. Green, Adv. Mater. **19**, 883 (2007). doi:10.1002/adma.200601310
11. J.-B. Baek, L.-S. Tan, Polymer (Guildf) **44**, 4135 (2003). doi:10.1016/S0032-3861(03)00374-4
12. J.-B. Baek, C.B. Lyons, L.-S. Tan, J. Mater. Chem. **14**, 2052 (2004). doi:10.1039/b401401d
13. J.-B. Baek, C.B. Lyons, L.-S. Tan, Macromolecules **37**, 8278 (2004). doi:10.1021/ma048964o
14. H.-J. Lee, S.-J. Oh, J.-Y. Choi, J.W. Kim, J. Han, L.-S. Tan, J.-B. Baek, Chem. Mater. **17**, 5057 (2005). doi:10.1021/cm051218t
15. S.-J. Oh, H.-J. Lee, D.-K. Keum, S.-W. Lee, D.H. Wang, S.-Y. Park, L.-S. Tan, J.-B. Baek, Polymer (Guildf) **47**, 1132 (2006). doi:10.1016/j.polymer.2005.12.064
16. K. Saeed, S.Y. Park, H.-J. Lee, J.-B. Baek, W. Huh, Polymer (Guildf) **23**, 8019 (2006). doi:10.1016/j.polymer.2006.09.012
17. J.-Y. Choi, S.-J. Oh, H.-J. Lee, D.H. Wang, L.-S. Tan, J.-B. Baek, Macromolecules **40**, 4474 (2007). doi:10.1021/ma0701282
18. J.-Y. Choi, W. Huh, L.-S. Tan, J.-B. Baek, Polymer (Guildf) **48**, 4034 (2007). doi:10.1016/j.polymer.2007.04.073
19. D.-H. Lim, C.B. Lyons, L.-S. Tan, J.-B. Baek, J. Phys. Chem. C **228**, 12188 (2008). doi:10.1021/jp801772r
20. Y. Zhang, Z. Shi, Z. Gu, S. Iijima, Carbon **38**, 2055 (2000). doi:10.1016/S0008-6223(00)00047-6
21. K.B. Shelimov, R.O. Esenaliev, A.G. Rinzler, C.B. Huffman, R.E. Smalley, Chem. Phys. Lett. **282**, 429 (1998). doi:10.1016/S0009-2614(97)01265-7
22. A.G. Rinzler, J. Liu, H. Dai, P. Nikolaev, C.B. Huffman, F.J. Rodrigues-Macias, P.J. Boul, A.H. Lu, D. Hetmann, D.T. Colbert, R.S. Lee, J.E. Fischer, A.M. Rao, P.C. Eklund, R.E. Smalley, Appl. Phys. A **67**, 29 (1998). doi:10.1007/s003390050734
23. U.J. Kim, C.A. Furtado, X. Liu, G. Chen, P.C. Eklund, J. Am. Chem. Soc. **127**, 15437 (2005). doi:10.1021/ja052951o

24. S. Bandow, S. Asaka, Y. Saito, A.M. Rao, L. Grigorian, E. Richter, P.C. Eklund, Phys. Rev. Lett. **80**, 3779 (1998). doi:10.1103/PhysRevLett.80.3779
25. M.S. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio, Phys. Rep. **409**, 47 (2005). doi:10.1016/j.physrep.2004.10.006
26. T. Shimada, H. Yanase, K. Morishita, J. Hayashi, T. Chiba, Carbon **42**, 1635 (2004). doi:10.1016/j.carbon.2004.02.019
27. O.S. Carneiro, J.A. Covas, C.A. Bernardo, G. Calderia, F.W.J.V. Hattum, J.M. Ting, R.L. Alig, M.L. Lake, Compos. Sci. Technol. **58**, 401 (1998). doi:10.1016/S0266-3538(97)00138-3
28. M. Liu, Y. Yang, T. Zhu, Z. Liu, Carbon **43**, 1470 (2005). doi:10.1016/j.carbon.2005.01.023