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Photochemical modification of single-walled carbon nanotubes using HPHMP photoinitiator for enhanced organic solvent dispersion

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Abstract Photochemical modification of single-walled carbon nanotubes (SWCNTs) was carried out by covalent attachment of 2-propanol-2-yl radicals on the surface of SWCNTs, which were engendered by the photolysis of 1-[4-(2-Hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one (HPHMP) under ultraviolet (UV) light. Pristine single-walled carbon nanotubes (p-SWCNTs) were dispersed in acetone along with HPHMP photoinitiator. After that, the mixture was irradiated by UV light to generate the free radicals which were introduced onto the surface of SWCNTs. The modification of SWCNTs was supported by UV/visible spectroscopy, Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, thermal gravimetric analysis–mass spectrometry (TGA–MS), and transmission electron microscopy (TEM). UV/visible results revealed the loss of van Hove singularities due to covalent modification. The modification was further verified by FT-IR showing the signals at 3421 and 1100 cm^{-1} due to stretching and bending of O–H group, respectively. Moreover, other peaks at 2927 and 2858 cm^{-1} indicated the asymmetric and symmetric stretching modes of aliphatic C–H bond, respectively. Raman spectra illustrated that the intensity ratio of the tangential mode to the disorder mode (I_G/I_D), for modified SWCNTs (F-SWCNTs), decreased nearly four times than p-SWCNTs. TGA–MS also evidenced the signal corresponding to m/z 59 at 400 °C indicating the presence of 2-propanol-2-yl groups. TEM and dispersibility data demonstrated that the sidewall modification detached the bundled structure, enhanced the dispersion in common organic solvents and retained the original size of SWCNTs without hefty modification, which could cut or damage the nanotubes.

Introduction

Since their discovery, carbon nanotubes have attracted a great deal of interest, not only in scientific fields but also in the field of nanotechnology applications, such as electronic devices, energy-related applications [1], and fiber reinforcement materials in polymer matrix composites [2]. A single-walled carbon nanotube (SWCNT) is unique among solid state materials in that every atom is on the surface [3]. SWCNTs are known as strikingly inert materials, which due to van der Waals attractive interactions are usually present in the form of bundles [4]. The SWCNT sidewalls are largely defect-free and therefore, rather inert to chemical attack during reactions. Limited reactivity occurs at defects on the sidewalls generated by curvature-induced stresses due to non-planar sp^2 carbons and the misaligned orbitals, and at dangling bonds located at the tube ends. Chemical modification of SWCNTs is critical for the applications of nanotubes. Because, the insoluble SWCNTs are rendered soluble, resulting in easy and efficient chemical processibility [5].

The progress in this field of SWCNT research has been limited up to now, and the main reason is the poor dispersion of SWCNTs in solvents. Then, the modification of SWCNTs is advantageous because functional groups can prevent the aggregation of nanotubes and in addition favor their dispersion in organic solvents [6, 7]. The attached

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functional groups can be used as precursors for the subsequent attachment of a wider variety of other functional groups [8]. Chemical modification of carbon nanotubes allows the change of their solution properties and subsequent understanding of the chemistry of these nanomaterials [9, 10].

Although many studies have addressed the covalent modification of SWCNTs by using thermal methods, but little attention has been devoted to photochemical methods. There have been few publications focused on the chemical modification techniques of the carbon nanotubes by the introduction of radicals. In general, radicals may be formed photochemically, thermally, in oxidation/reduction reactions by inorganic ions resulting in single electron transfer, and by electrolysis. For the photochemical generation of radicals, different precursors can be used, e.g., perfluoroazooctane [11], 1,2-dithiane, and acetonitrile [12].

In photochemical method, photoinitiator generates free radicals on photolysis. Then, the radicals would modify the surface of SWCNTs by covalent attachment. Consequently, these functional groups disturb the charge balance around the SWCNTs and induce an electronic polarity, leading to an enhanced dispersion in common organic solvents. For example, the chemical oxidation that occurs in a strong acidic solution improves the dispersion of CNTs in various polar solvents including dimethylformamide and water [13]. Moreover, photochemical modification is direct and selective for the introduction of respective functional groups. It improves the dispersibility of SWCNTs and enhances their adhesive properties [14], to utilize them in different applications and for further chemical processing [15]. An easy and mild chemical modification technology is worthy of more efforts.

In this article, we report on a useful method of modification of SWCNTs by covalent attachment of 2-propanol-2-yl radicals $(CH_3)_2C^*OH$ generated by the photolysis of 1-[4-(2-Hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one (HPHMP) in acetone. Commonly, HPHMP is used as radical initiator in polymerization reactions, but currently, it is used as a source of functional group to modify the SWCNTs. On the other hand, the photochemical process is one step in spite of multi-steps, which is a direct way of modification. Furthermore, photochemical method did not require the exact control of the temperature, because it was carried out at room temperature. The results showed that photochemical method is selective and retentive to the electronic and chemical properties of SWCNTs.

Experimental

SWCNTs (purity >90%, diameter range 1–2 nm, length about 30 µm) were obtained from Chengdu Organic Chemicals Co., Ltd. synthesized by the chemical vapor deposition method. Irgacure 2959 (HPHMP) was obtained from Ciba Inc., Ltd. Acetone, tetrahydrofuran, 2-propanol, toluene, *N*,*N*-dimethylformamide (DMF), and carbon disulfide were used as received from Beijing Chemical Co., Ltd.

In a typical experiment, SWCNTs (5 mg) were added into a three-neck flat bottom quartz flask along with acetone (30 mL), and dispersed through sonication for 30 min. After that, HPHMP (3 mg) was added and reaction contents were degassed by continuous purging of argon gas with constant stirring. After 30 min, the contents were irradiated with a low-pressure mercury lamp for 8 h at room temperature in an argon atmosphere with stirring as shown in Fig. 1. The ultraviolet (UV) output at the distance of 10 cm from the lamp was 9,000 µW per cm^2 at a wavelength of 254 nm. After the removal of acetone from the reaction mixture by centrifuging at the rate of 5,000 rpm for 30 min, the residual powder was first washed with acetone (10 mL) and then three times with toluene (10 mL each time). The product was dried in vacuum oven at 50 °C for 12 h and characterized by several analytical techniques.

UV–visible spectra were recorded on a Cintra 20 UV–Visible spectrometer by dispersing the pristine and modified SWCNTs in dimethylformamide. Fourier transform infrared spectroscopy (FT-IR) spectra were measured on a Thermo Nicolet Nexus 670 spectrometer by KBr pellet method. Raman spectra were recorded on a JY-HR 800 Raman spectrometer operating at 532 nm laser light. Nuclear magnetic resonance spectroscopy (NMR) measurements were recorded on a Bruker AV 600 NMR spectrometer by dispersing the F-SWCNTs in deuterated chloroform ($CDCl_3$). Thermal gravimetric analysis (TGA) measurements were carried out on a NETZSCH TG 209 thermal analysis system under a flowing nitrogen atmosphere at a scan rate of 10 °C/min.

TGA–MS analysis was carried out on a Perkin Elmer Pyris Diamond TGA–MS equipped with a ThermoStar

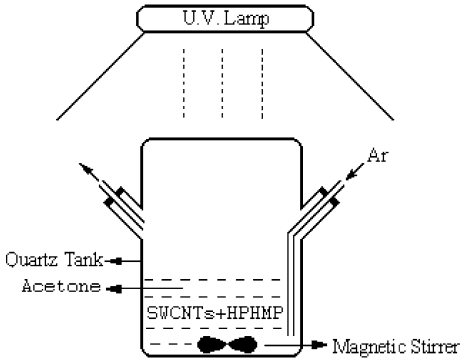

Fig. 1 Reaction assembly

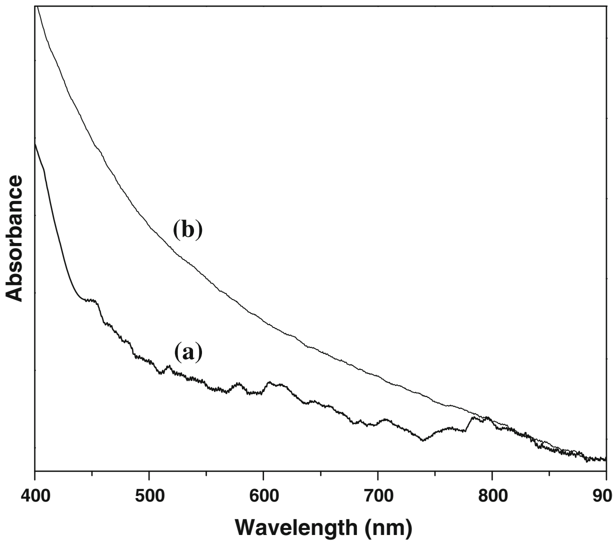

Fig. 2 Ultraviolet–visible spectra of single-walled carbon nanotubes in dimethylformamide (1 mg/L): (*a*) pristine single-walled carbon nanotubes and (*b*) functionalized single-walled carbon nanotubes

Mass Spectrometer operating in an electron impact ionization mode. The images of transmission electron microscopy (TEM) were recorded on a JEOL JEM-3010 electron microscope operating at 300 kV. First, the samples were dispersed in acetone and then cast on a Cu grid followed by drying in air at room temperature (Fig. 2)

Results and discussion

The evidence for modification of SWCNTs came from the UV–visible spectra. In the UV spectra, the curve (a) and curve (b) were compared to show the change in characteristic signals. The curve (a) represents the pristine carbon nanotubes while the curve (b) represents modified carbon nanotubes. The van Hove singularities are the small characteristic peaks which are appeared in case of pristine carbon nanotubes as shown in the curve (a). The van Hove singularities are suppressed or lost after the introduction of functional groups on the surface of carbon nanotubes. In result, these singularities were no more in the curve (b) due to modification.

The curve (b) showed a complete loss of the van Hove singularities what indicated the covalent modification of the nanotubes [16]. In the F-SWCNTs, the introduction of sp^3-hybridized carbon atoms disrupted the extended π-network of the bare sp^2-hybridized nanotubes what exhibited the successful modification of SWCNTs [17].

Figure 3 shows the FT-IR spectral changes of the SWCNT sample caused by the modification. The two bands around 1546 and 1149 cm^{-1} are attributed to the graphitic structure of carbon nanotubes. The peak around

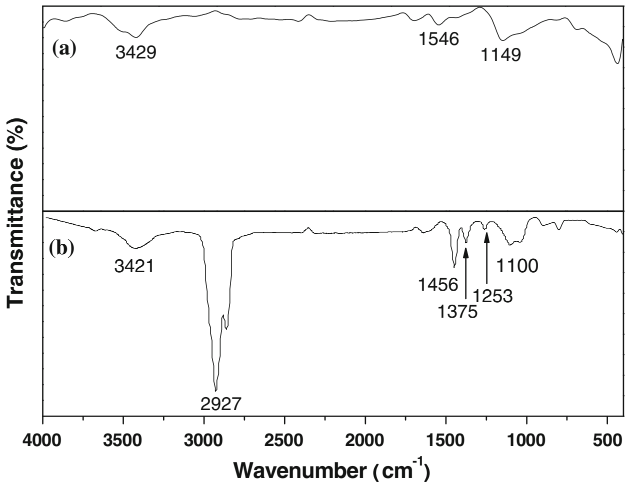

Fig. 3 Fourier transform infrared spectra of single-walled carbon nanotubes in potassium bromide: (*a*) pristine single-walled carbon nanotubes and (*b*) functionalized single-walled carbon nanotubes

3429 cm^{-1} is attributed to the stretching of some hydroxyl groups, mainly due to moisture (H–OH) contents, because there was no signal at 1100 cm^{-1} to show characteristic bending frequency of C–OH bond. There were no other obvious bands in the spectrum of pristine single-walled carbon nanotubes (p-SWCNTs), indicating that the p-SWCNTs contain no functional groups.

The F-SWCNTs clearly showed the characteristic stretching vibration of O–H at 3421 cm^{-1}, and relevant band at 1100 cm^{-1} indicated the bending frequency of C–OH bond of hydroxyl group. It can be inferred from peak value that the OH group is tertiary in nature. Because, the secondary nature of OH group has converted to tertiary by making the bond between $(CH_3)_2C^*OH$ and carbon atom of the nanotube [18]. Furthermore, the peaks at 2927 and 2858 cm^{-1} were attributed to the asymmetric and symmetric stretching modes of sp^3-hybridized C–H bond, respectively. The deformation band (1250–1470 cm^{-1}) belonged to asymmetric and symmetric bending frequencies of C–H bond. The two characteristic graphitic bands of p-SWCNTs have been suppressed after modification (Fig. 3a) due to the conversion of sp^2-hybridized carbon atoms to sp^3-hybridized in the framework of SWCNTs. These results indicated the modification of carbon nanotubes due to the conversion of surface atoms and the nature of functional groups as well.

Direct evidence for covalent modification was found in the Raman spectra of F-SWCNTs shown in Fig. 4. The p-SWCNTs exhibited two strong bands: a diameter-dependent radial breathing mode (R band) at ~216 cm^{-1} depending on the diameter of nanotubes and a tangential mode (G band) at ~1586 cm^{-1} depending on the graphitic nature of nanotubes. The weak band centered at ~1323 cm^{-1}, the disorder mode (D band), is attributed to

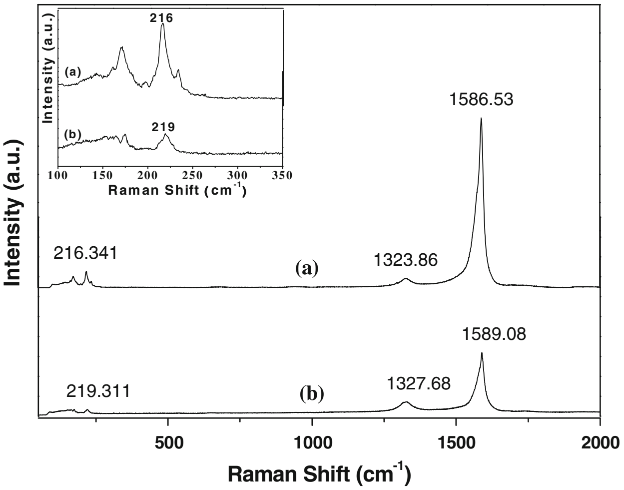

Fig. 4 Raman spectra of single-walled carbon nanotubes: (*a*) pristine single-walled carbon nanotubes and (*b*) functionalized single-walled carbon nanotubes. *Inset*: expanded view of the radial breathing mode

sp^3-hybridized carbon in the hexagonal frame work of the nanotube walls.

In the case of F-SWCNTs, the radial breathing modes suppressed and shifted at ~219 cm^{-1} by the introduction of the 2-propanol-2-yl substituents. Raman spectra exhibited that the peak intensity of the D band in F-SWCNTs increased in comparison with p-SWCNTs showing the presence of scattering defects on the sidewall of F-SWCNTs due to covalent modification [11]. Another very interesting feature is that the maximum of G band was shifted to higher frequency for modified material. It shifted about 3 cm^{-1} to higher frequency from ~1586 to ~1589 cm^{-1}, a disorder peak with higher intensity than the tangential mode. Resolution of Raman spectrometer is 0.3 to 1 cm^{-1} so that the shift value is appreciable. The intensity ratio of the tangential mode to the disorder mode (I_G/I_D) decreased from 16.4 for p-SWCNTs to 4.45 for F-SWCNTs. As expected, the introduction of covalently bound moieties (i.e., 2-propanol-2-yl groups in this study) to the SWCNT framework will inevitably change the sp^2-hybridized carbons into sp^3-hybridized. The significant increase in the sp^3 population revealed by the Raman spectra indicated the appreciable percentage of 2-propanol-2-yl groups introduced onto the carbon nanotubes.

Further evidence for modification of SWCNTs obtained from ^{1}H-NMR (600 MHz, deuterated chloroform) spectrum of F-SWCNTs.

Figure 5 showed that the characteristic resonance bands of protons centered at $\delta = 1.2$ ppm and at $\delta = 3.9$ ppm due to the methyl groups and tertiary hydroxyl groups of 2-propanol-2-yl radicals, respectively. Moreover, the ratio of methylic protons to hydroxylic protons is 6:1, respectively, which describes the arrangement of protons in the functional group. These characteristic values explained the chemical structure of the functional group. ^{1}H-NMR studies are in good agreement with FT-IR studies about the nature of functional groups.

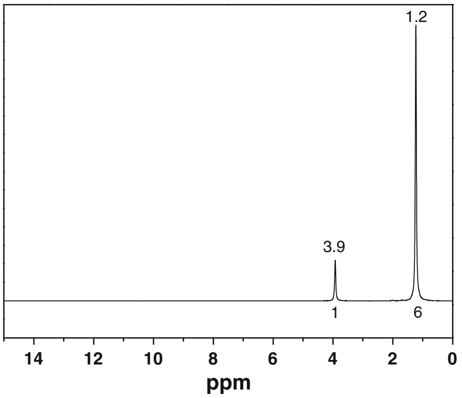

Fig. 5 Proton nuclear magnetic resonance chemical shifts of functionalized single-walled carbon nanotubes in deuterated chloroform ($CDCl_3$)

TGA gave useful information about F-SWCNTs, because most functional moieties on SWCNTs are thermally unstable, i.e., most of the organic functional groups are decomposed before the onset of SWCNT weight loss [19, 20].

Figure 6 showed the TGA data of SWCNTs before and after the modification. The percentage weight loss curves indicated that the overall weight loss, during the process, was 9% for p-SWCNTs and about 25% for F-SWCNTs. The weight loss of p-SWCNTs is due to degassing and the evaporation of residual solvent. Excluding this part of weight loss, there was net weight loss of 16% for F-SWCNTs, revealing the decomposition of the functional groups on the carbon nanotubes. The percentage weight loss was not so high, it is meant that the large number of functional groups has not introduced (mild

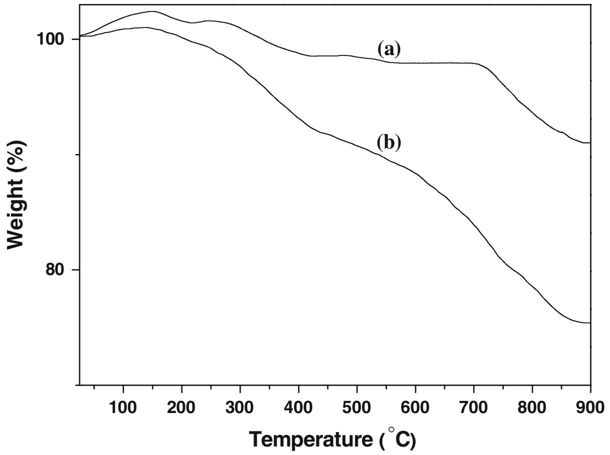

Fig. 6 Thermal gravimetric analysis of single-walled carbon nanotubes: (*a*) pristine single-walled carbon nanotubes and (*b*) functionalized single-walled carbon nanotubes

functionalization) which could cut the size of carbon nanotubes or make some structural defects. Thus, the method is very efficient to introduce functional groups onto the surface of SWCNTs.

Further evidence for covalent modification of SWCNTs has been provided by TGA–MS (thermal gravimetric analysis–mass spectrometry) in the 20–900 °C range with online monitoring of volatile products by mass spectrometer operating in an electron impact ionization mode.

In the Fig. 7, the TGA–MS data illustrated the evolution of detached 2-propanol-2-yl groups at about 400 °C is shown by a major peak (a) at *m*/*z* 59. On the other hand, the curve (b) resulted in a base line at *m*/*z* 165, it is meant that there was no ion detected by mass spectrometer like $HOCH_2CH_2OC_6H_4C^+O$. Therefore, it is obvious that $HOCH_2CH_2OC_6H_4C^*O$ radicals had no contribution in functionalization. It is concluded that the modification was solely due to 2-propanol-2-yl radicals, which were

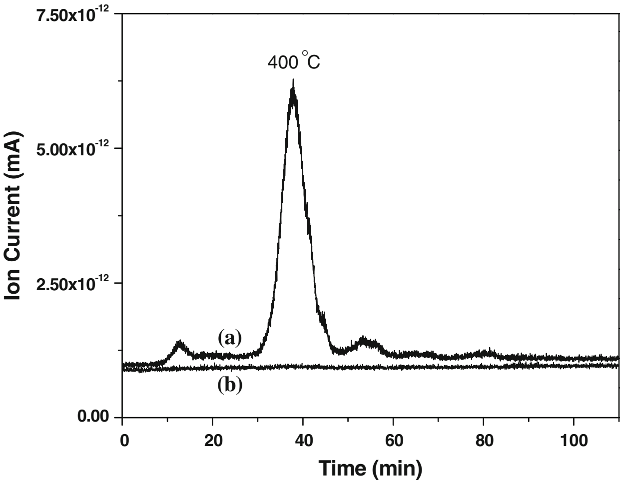

Fig. 7 Thermal gravimetric analysis–mass spectrogram of the functionalized single-walled carbon nanotubes: ion current versus time plot for *m*/*z* ions (*a*) 59 $(CH_3)_2C^+OH$ and (*b*) 165 $HOCH_2CH_2OC_6H_4C^+O$

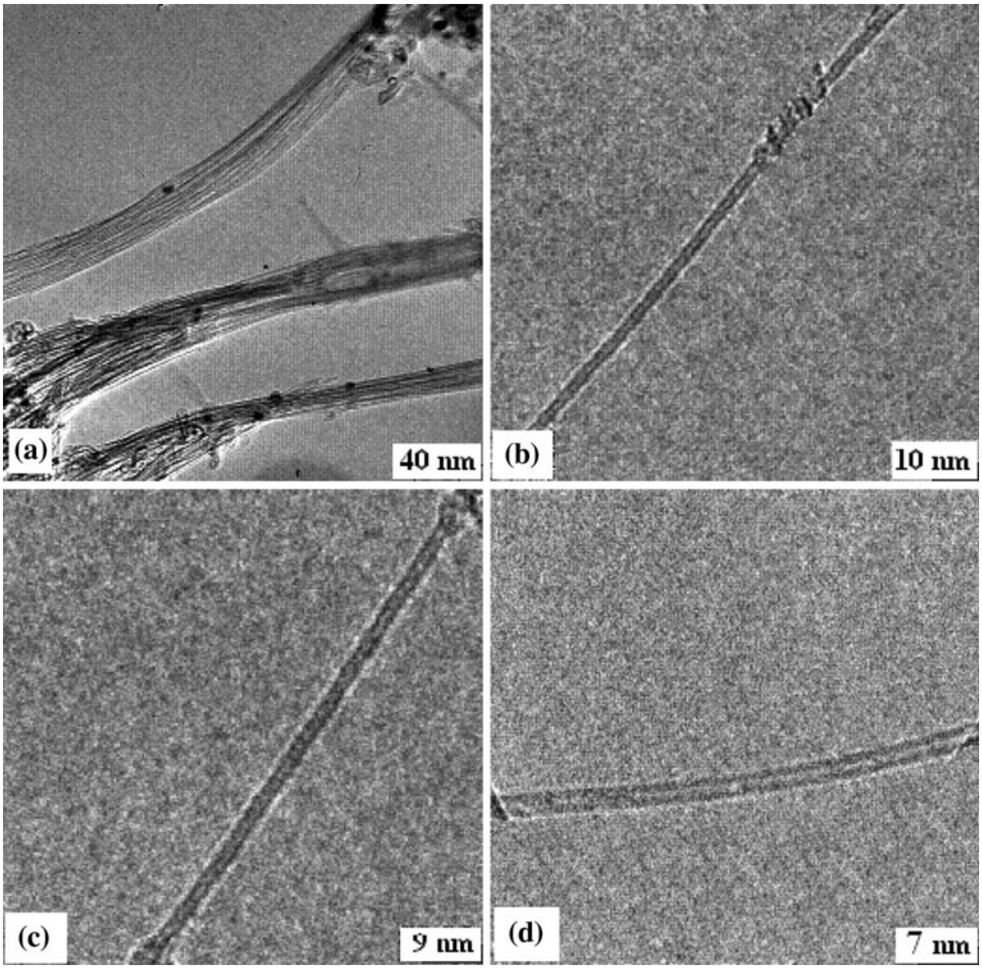

Fig. 8 Transmission electron microscopic images of single-walled carbon nanotubes: **a** pristine single-walled carbon nanotubes, **b–d** functionalized single-walled carbon nanotubes. Samples for TEM imaging were loaded by placing one drop of single-walled carbon nanotubes (dispersed in acetone) on a copper grid and dried in air

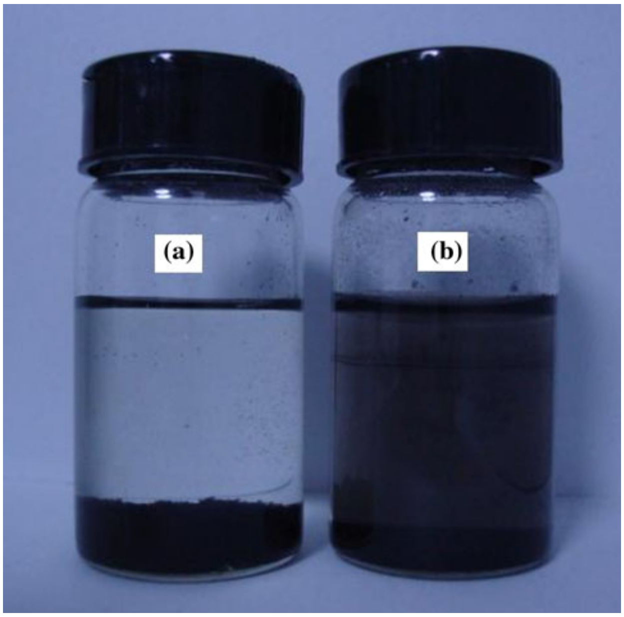

Fig. 9 Single-walled carbon nanotubes solutions in dimethyl formamide (79.2 mg/L) after 24 h: (*a*) pristine single-walled carbon nanotubes and (*b*) functionalized single-walled carbon nanotubes

Table 1 Room temperature dispersibility data (mg/L) for pristine single-walled carbon nanotubes and functionalized single-walled carbon nanotubes in different solvents

Solvent	p-SWCNTs	F-SWCNTs
Dimethylformamide	7.2	79.2
Isopropyl alcohol	Indispersible	11.2
Tetrahydrofuran	4.9	53.9
Carbon disulfide	2.6	28.6

originated from the surface of F-SWCNTs, and detected by mass spectrometer.

Transmission electron microscopic images of p-SWCNTs and F-SWCNTs are compared in Fig. 8. The p-SWCNTs seemed to be like a bundle or a rope of SWCNTs. On the other hand, the modified SWCNTs have dissociated that directs them to disperse and behave individually. Because, the modification has prevented SWCNTs to aggregate due to hindrance of functional groups present on the surface of modified SWCNTs and enhanced their discreteness. Therefore, F-SWCNTs also showed high and facile dispersion in solvents than p-SWCNTs.

The TEM images revealed that the sidewall modification with HPHMP neither cut the size of carbon nanotubes nor create the defects on the surface of SWCNTs, which could happen in the case of heavy and harsh modification. Thus, it can be concluded that the functionalization was mild rather than severe, which could cut the SWCNTs into shorter ones.

As a result of this modification, the dispersibility of F-SWCNTs was improved significantly, and they were easily dispersed in dimethylformamide (Fig. 9). The dispersibility of F-SWCNTs in dimethylformamide was about 79.2 mg/L determined as described [21], about 11 times larger than that of p-SWCNTs (7.2 mg/L). The room temperature dispersibility data of F-SWCNTs and SWCNTs were shown in Table 1.

As the data showed that F-SWCNTs are more dispersible in common organic solvents such as isopropyl alcohol, tetrahydrofuran, and carbon disulphide than p-SWCNTs. It is very interesting that the dispersibility of the F-SWCNTs increased nearly 11 times that of the p-SWCNTs in THF and CS_2. It can be concluded that modification improved the dispersibility of nanotubes by dispersing their bundles. Therefore, the dispersion of SWCNTs is expected to facilitate their chemical manipulation, characterization, properties investigation, and wide application.

Based on the data from above experiments, we proposed the route of modification of SWCNTs using our method as follows (Fig. 10): photolysis of HPHMP generated the 2-propanol-2-yl and derivative benzoyl radicals in the presence of SWCNTs in acetone. Mechanistically, 2-propanol-2-yl radicals with high reactivity than derivative benzoyl radicals attacked on the surface of SWCNTs, which were activated by photoelectrons emitted by UV light source to form F-SWCNTs.

According to TGA–MS results, it can be explained that the relatively stable derivative benzoyl radicals may have

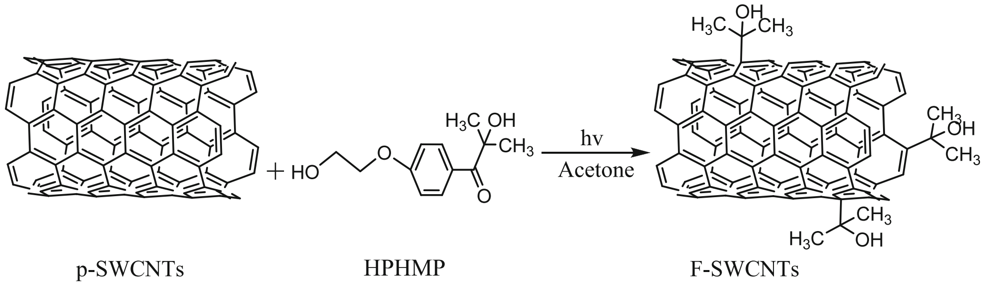

Fig. 10 Illustration of chemical modification of single-walled carbon nanotubes by HPHMP photoinitiator

joined together to form benzyl derivative. In the meanwhile, the 2-propanol-2-yl radicals were introduced onto the surface of SWCNTs with relatively higher rate constant than derivative benzoyl radicals [22] and modified the nanotubes as illustrated above.

Conclusions

A new, simple, and photoinduced method for modification of SWCNTs with HPHMP was presented. 2-propanol-2-yl functional groups were introduced to the SWCNTs through covalent bonds. The modification unbundled the SWCNTs and enhanced their dispersion in organic solvents as well. These organic functional groups may allow us to chemically join SWCNTs with other materials. This new way of modification will help to modify the SWCNTs by using different kinds of photoinitiators. It will also assist to further modify the already attached functional moieties into several derivatives. Ease in dispersion makes modified SWCNTs useful in wide range of application to improve the physical and chemical properties of materials. These results represent a new way for covalent chemical modification of SWCNTs.

References

1. Iijima S (1991) Nature 354:56
2. Nishikawa M et al (2009) J Mater Sci 44(1):339. doi:10.1007/s10853-008-3127-7
3. Chen RJ, Zhang Y, Wang D (2001) J Am Chem Soc 123:3838
4. Barthos R, Méhn D, Demortier A (2005) Carbon 43:321
5. Wang Y, Iqbal Z, Mitra S (2005) Carbon 43(5):1015
6. Marcux PR, Schreiber J, Batail P (2002) Phys Chem Chem Phys 4:2278
7. Hu H, Zhao B, Hamon MA (2003) J Am Chem Soc 125:14893
8. Mickelson ET, Huffman CB, Rinzler AG (1998) Chem Phys Lett 296:188
9. Tasis D, Tagmatarchis N, Bianco A (2006) Chem Rev 106:1105
10. Liu M, Yang Y, Zhu T (2007) J Phys Chem 111(6C):2379
11. Nakamura T, Ishihara M (2004) Diam Relat Mater 13(11–12):1971
12. Nakamura T, Ohana T, Ishihara M (2008) Diam Relat Mater 17(4–5):559
13. Kovtyukhova NI, Mallouk TE, Pan L (2003) J Am Chem Soc 125:9761
14. Larsen RM (2009) J Mater Sci 44(3):799. doi:10.1007/s10853-008-3155-3
15. Najafi E, Kim J, Han S (2006) Colloids Surf 284(A):373
16. Umek P, Seo J, Hernadi K (2003) Chem Mater 15(25):4751
17. Wu W, Zhang S, Li Y (2003) Macromolecules 36(17):6286
18. Pavia D, Lampman G et al (2009) Introduction to spectroscopy. Cole Pub Co. Ltd, Florence
19. Liu M, Yang Y, Zhu T (2005) Carbon 43(7):1470
20. Ahmad MN, Xie JY, Ma YH, Yang WT (2010) New Carbon Mater 25(2):134
21. Peng H, Alemany L, Margrave J (2003) J Am Chem Soc 125(49):15174
22. Vacek K, Geimer J (1999) J Chem Soc Perk Trans 2(11):2469