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COMMUNICATION

Improving the Degree of Functionalization and Solubility of Single-Walled Carbon Nanotubes via Covalent Multiple Functionalization

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Abstract The synthesis of covalent multi-functionalized single-walled carbon nanotubes (SWNT) via the combination of two diazonium salt addition reactions with tetrabutylammonium hydroxide to form carbon nanotube salts was carried out. The formation of carbon nanotube salts allows SWNT to be easily dissolved in common solvents, which increases the processing capability of the SWNT. The dissolutions of some of the obtained products can be increased three-fold through multi-functionalization. Thus tetrabutylammonium cation plays an extraordinarily important role; i.e., balancing the charges on the functionalized SWNT surface and de-bundling of the functionalized SWNT. This approach provides a useful way of preparing some SWNT-containing biomaterials. The multi-functionalized SWNT were confirmed by standard techniques used for carbon nanotube characterization.

Keywords Single-wall carbon nanotubes · Covalent multi-functionalization · Carbon nanotubes solubility · Arene radical addition reaction

1 Introduction

Single-walled carbon nanotubes (SWNT) are unique nanomaterials with remarkable mechanical strength, chirality-dependent conductivity, thermostability and chemical resistance [1–7]. Various potential applications, such as chemical and biochemical sensors [8–11], in drug delivery systems [11–14], in crystals [15], for hydrogen sorption [16–18] and in nanoelectronic and optoelectronic devices [19–29] have been widely explored. However, SWNT are difficult to process because they are immiscible with most media due to the strong van der Waals and π-π interactions between the SWNT, which cause SWNT to form tight bundles. To explore the unique properties of SWNT and understand their chemistry, some developments in enhancing their dispersion or solubilization in organic and aqueous media have been achieved [30–33]. Therefore, selective functionalization approaches are still highly desirable to enable new protocols that are simple to execute and easy to scale up.

Diazonium salt chemistry is a well-known foundation for the remarkably efficient functionalization of carbon nanotubes [34–37]. Formation of diazonium salts in situ from aniline precursors is a method that avoids the direct use and long-term storage of diazonium compounds, thereby avoiding their potential experimental hazard [38–41]. Additionally, water can be substituted for any organic solvent previously used in the diazonium-based processes. Price and Tour [38] have described a synthetic route to obtain functionalized SWNT 'on water' in the presence of a substituted aniline and an oxidizing species.

The present work aims to optimize a multiple functionalization approach, improve the degree of functionalization and enhance the solubility of SWNT in common organic solvents. To achieve these objectives, a new

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synthetic strategy was developed for the synthesis of multifunctionalized and non-oxidized SWNT. Experimental results show a significant decrease in the van Hove singularities for multi-functionalized SWNT compared to mono-functionalized SWNT. Consequently, the dissolution and degree of functionalization of SWNT are conspicuously increased. To increase the solubility of SWNT in common organic solvents, the foregoing products were reacted with the base, tetrabutylammonium hydroxide, (Bu_4NOH), which contains a large cationic group. By this procedure, multifunctional SWNT with a variety of groups that can be customized to fit a desired application are possible (Scheme 1). The multi-functional SWNT were characterized by Raman, Fourier transforms infrared (FTIR), UV–Vis spectroscopies, thermogravimetric analysis (TGA), and transmission electron microscopy (TEM).

2 Experimental Sections

2.1 Measurement and Techniques

Raman spectra were performed on a Lab RAM HR 800 UV Raman spectrometer with a 632.8 nm exciting lines. UV–Vis spectra were recorded on a Varian Cary 5000 spectrophotometer. FTIR spectra were obtained with a Nicolet MAGMAIR 860 spectrometer; all samples were prepared as KBr pellets. Thermogravimetric analyses were carried out with a TGA Q500 TA Instruments at 10 °C/min in an air flow (20 mL/min). For TEM analyses, a small amount of the functionalized SWNT was suspended in dimethylformamide (DMF) and a drop of the suspension was placed on a copper grid. After air-drying, the sample was investigated with a TEM Philips EM 208 (accelerating voltage of 100 kV). HR-TEM images were obtained on a JEM-2100F STEM/EDS high resolution transmission electron microscope.

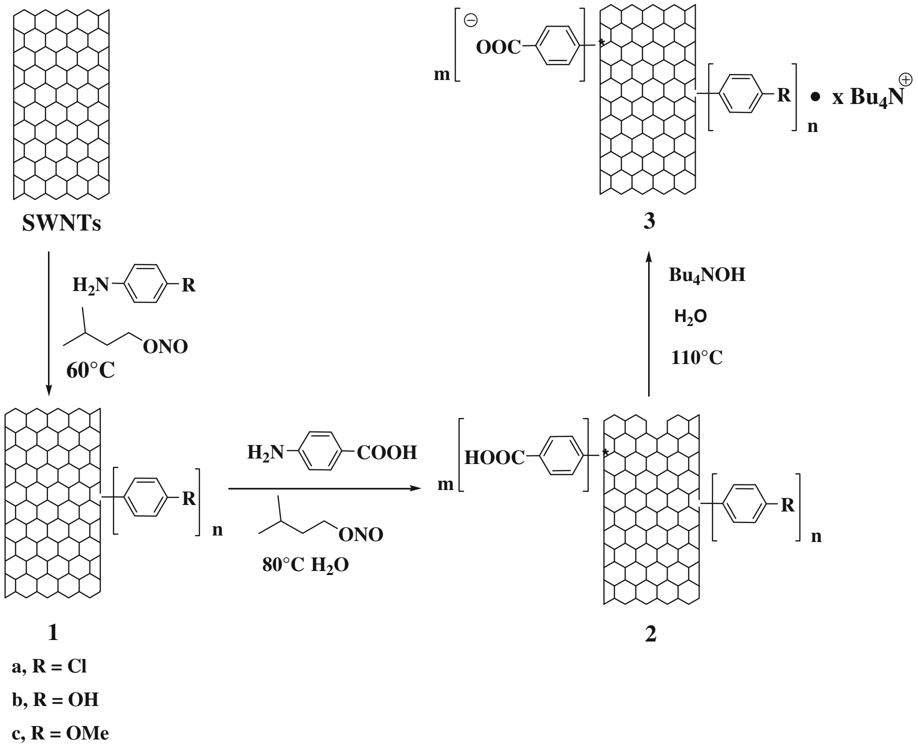
2.2 Materials

SWNT (diameter: 1–2 nm, purity 90 %) were supplied by Chengdu Organic Chemicals (Chinese Academy of Sciences) and used without further purification. All other reagents and solvents were purchased from commercial suppliers and used as received.

2.3 Preparation of first functionalized SWNT (**1a–1c**)

The first sidewall functionalized SWNT was conducted according to a previously reported procedure [39]. Raw SWNT (24 mg, 2 mmol of carbon), 4-substituted aniline (2 equiv/mol of carbon) and tetrahydrofuran (THF) (20 mL) were mixed in a flask. After sonication for 20-min at room temperature, the solvent was evaporated under reduced pressure. The flask was equipped with a reflux condenser and a magnetic stirring bar. After cautious and slow addition of isoamyl nitrite (4.8 equiv/mol of carbon) with a syringe, the mixture was stirred and heated to 60 °C; vigorous stirring was continued at this temperature for 6-h.

Scheme 1 Synthesis of the covalent multifunctionalization of single-wall carbon nanotubes (SWNT) and their salts on carbon nanotubes



After cooling and dilution of the resulting paste with DMF, the suspension was centrifuged and filtered through a poly(tetrafluoroethylene) (PTFE) (450 nm pore diameter) membrane. The collected solid was washed with DMF until the filtrate was colorless. The product was dispersed in DMF (30 mL) through sonication for 10-min to remove the remaining unreacted organic materials, followed by filtration and washing with DMF (100 mL). The residual solids were washed with diethyl ether (50 mL) and dried in a vacuum oven at 50 °C for 10-h to yield the first sidewall functionalized SWNT. The loss of the van Hove singularities were confirmed by UV/vis absorption spectroscopy of the nanotubes dispersed in DMF; this is indicative of covalent functionalization. The TGA weight losses, degree of functionalization and ratio of Raman D- to-G-band intensities for **1a**–**1c** are listed in Table 1.

2.4 Preparation of Double Functionalized SWNT (2a–2c)

The second functionalization was carried out using the previously described method [38]. In a typical experiment, **1a**–**1d** (20 mg) and deionized water (50 mL) were added to a 100 mL round-bottom flask. The mixture was vigorously stirred for 30-min. The reaction flask was heated to 80 °C in an oil bath. *p*-Aminobenzoic acid (0.46 mg) and isoamyl nitrite (5 mL) were added. The mixture was stirred vigorously at 80 °C for 24-h. After the mixture was cooled to room temperature, the suspension was centrifugated and filtered through a PTFE (450 nm pore diameter) membrane. The filter cake was washed with deionized water, DMF and acetone until the filtrate was clear. Characterizations of **2a**–**2c** was performed as mentioned above (Table 1).

2.5 Preparation of the Salt-Functionalized SWNT (3a–3c)

2a–**2d** (15 mg), NBu_4OH (10 %) (5 mL) and deionized water (50 mL) were added to a 100 mL round-bottom flask. After sonication for 10-min at room temperature, the reaction flask was heated to 110 °C in an oil bath for 20-h. After cooling to room temperature, the mixture was centrifuged and filtered through a PTFE (220 nm pore diameter) membrane. The filter cake was washed with deionized water until the filtrate was neutral. The residual solids were washed with acetone (50 mL) and dried overnight in a vacuum oven at 50 °C.

Table 1 Comparison of functionalized products

Products	TGA wt (%)	Raman D/G ratio	Functional group coverage
1a	18	0.32	43
1b	24	0.25	25
1c	19	0.20	38
2a	26	0.48	27
2b	31	0.34	20
2c	26	0.30	26

3 Results and Discussion

In the first approach, purified SWNT is functionalized through arene radical addition reactions. However, under solvent-free conditions, a small amount of reagent is used. The reaction is heterogeneous and results in unequal functionalization. In the present experiment, the dosage of isoamyl nitrate exceeded those previously reported under solvent-free conditions [39]. Therefore, isoamyl nitrite acts not only as a reagent but also as a solvent. Subsequently, the functionalized SWNT were subjected to diazonium salt reaction 'on water' to introduce other functional groups onto the same SWNT. The method described here provides SWNT with improved degree of functionalization. After the second step of functionalization, carboxyl groups reacted with Bu_4NOH to form carbon nanotube salts. The multi-functionalized SWNT were characterized using Raman, FT-IR, UV–Vis spectroscopy, TGA, TEM, and HR-TEM.

The Raman spectrum of the pristine SWNT starting material (Fig. 1) shows a minimal disorder mode (D-band) with very low intensity at 1,324 cm^{-1}. The spectra of the functionalized products **1a** and **2a** exhibit an increased intensity in the D-band corresponding to the functionalization

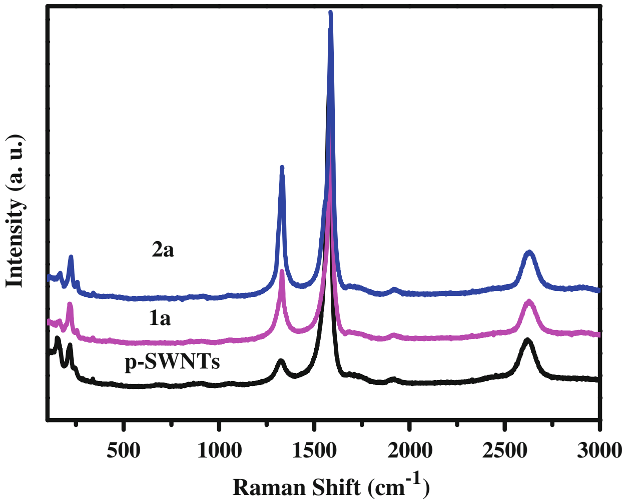


Fig. 1 Raman spectra (632.8 nm excitation) of pristine SWNT (p-SWNT), **1a**, and **2a**

of SWNT (Fig. 1a, b). This finding is an expected result for the introduction of covalently bonded moieties to the nanotube framework wherein significant amounts of carbon are converted from sp^2 to sp^3 hybridization. The other functionalized samples, **1b**–**2b** and **1c**–**2c**, exhibit similar the Raman spectral features. If the intensity of the D-band is divided by the intensity of the tangential mode (G-band) (at ~1,600 cm^{-1}), the ratio provides a good indication of the relative degree of functionalization [41]. The resonance Raman enhancement shown in the pristine SWNT spectrum is markedly suppressed in the functionalized product. The disorder-induced D-band peak at ~1,320 cm^{-1} was greatly enhanced whereas the G-band characteristics remained present at ~1,580 cm^{-1}. The functional group coverage obtained via TGA and the D/G ratios are given in Table 1. The results suggest different degrees of functionalization. The amount of functional groups was estimated by the reported approach [42]. The weight loss was estimated using the following calculation: e.g., for **1a**, the amount of functional group is (82 %/12)/(18 %/112.56) = 42.7; This means that there is 1 group/~43 carbon atoms. No quantitative relationship was found between the D/G ratio and the degree of functionalization calculated from the TGA data [41]. However, a qualitative and consistent trend is clearly observed that the D/G ratio increases with the increased weight loss.

UV–Vis spectra were recorded in DMF solution in the double-beam mode. The absorption spectrum of the pristine SWNT shows characteristic van Hove singularities (Fig. 2). By contrast, the spectrum of the functionalized SWNT shows the dramatic decrease in the van Hove transitions. This result is consistent with covalent functionalization of SWNT [41]. The spectrum also confirms an increase in the degree of functionalization and, accordingly, a dramatic decrease in the van Hove singularities for **2a** relative to **1a**. The loss of structure in the absorption spectrum is indicative of significant electronic perturbation of the nanotubes and disruption of the extended π network [34]. The different UV–Vis spectra and Raman spectra seem to suggest differences in the degrees of functionalization of SWNT. However, in these cases, after the second step, the overall degrees of functionalization of SWNT have clearly increased. Therefore, in agreement with previous results [37], this study confirms that the arene radical addition introduces defects that perturb the intrinsic periodicity of the conjugated nanotube π-system. Other products, **1b**–**2b** and **1c**–**2c**, exhibit similar spectral features to **1a**–**2a**. This effect is consistent with covalent functionalization rather than simple adsorption onto the nanotube walls or end-caps [42–43].

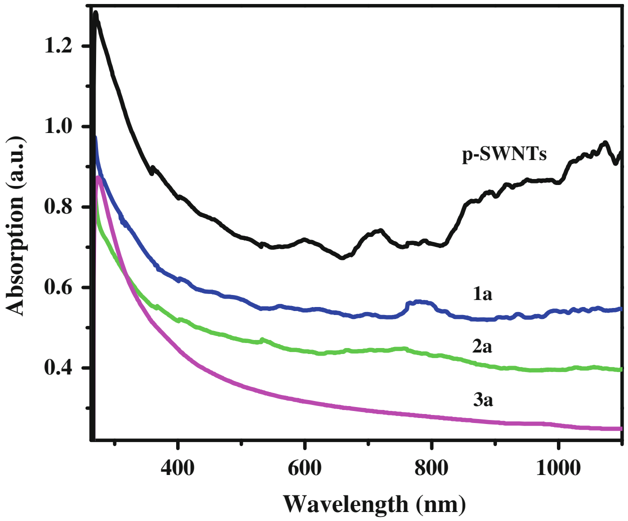


Fig. 2 Absorption spectra in DMF of pristine SWNT (p-SWNT), **1a**, **2a**, and **3a**

TEM characterization provides direct evidence for the presence of functionalized SWNT. TEM images of **1a**, **2a** and **3a** are shown in Fig. 3. The images show that small bundles of nanotubes appear throughout the scanned areas. A comparison of these images with those of the raw material illustrates that de-bundling has occurred, providing evidence for the success of the functionalization. Without the functional groups present, the SWNT would re-bundle because of 0.5 eV/nm inter-tube attractive forces [38].

The functionalized group moieties attached to the nanotubes can be removed by heating in air. The TGA results provide a quantitative estimate of the degree of functionalization. The crude SWNT are thermally stable below 600 °C (Fig. 4). By contrast, the functionalized SWNT decompose at a lower temperature with two main weight loss regions; for **3a**, the first occurs below 300 °C and may be attributed to the decomposition of the tetrabutylammonium compound. For **1a** or **2a**, the first weight loss occurs at ~450 °C and is attributed to the decomposition of the covalently functional groups. Significant weight reduction in the second regions (at ~550 °C) is attributed to the decomposition of SWNT.

The FT-IR spectrum of **2a** (Fig. 5) shows the appearance of a carboxylic acid group and provides additional support for successful functionalization; i.e., the C=O stretch of the carboxylic acid group appears at 1,654 and 1,537 cm^{-1}. When the carboxylic acid groups react with Bu_4NOH, the C=O stretch frequency features of carboxyl shift to 1,631 and 1,592 cm^{-1}, respectively. Also, the appearance of C–H stretch (2962, 2876 cm^{-1}) and the C–N stretch (1348, 882 cm^{-1}) provide additional support for the introduction of Bu_4N^+ in **3a**.

After reaction, the solubility of each functionalized materials was evaluated using the extinction coefficients

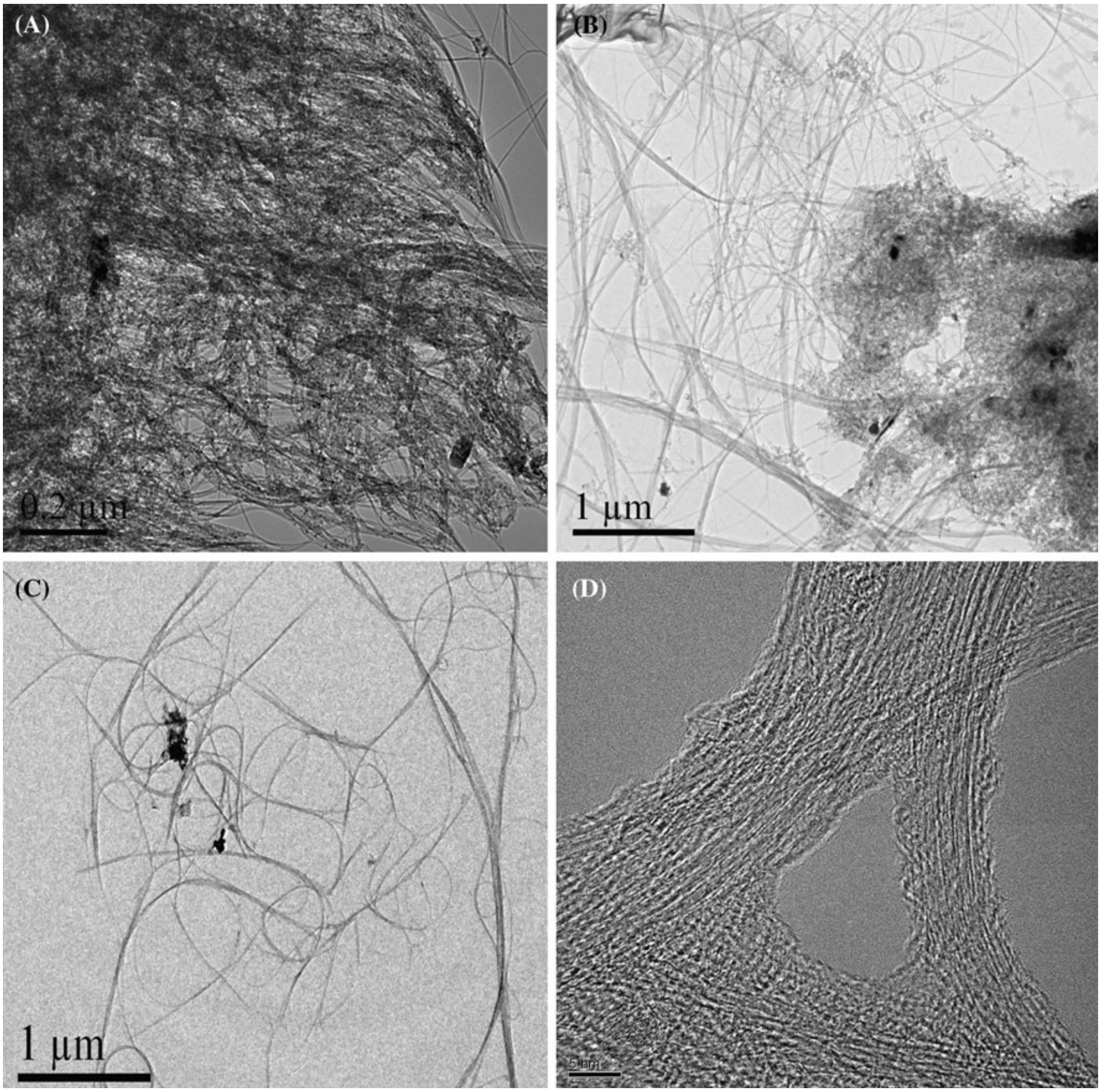


Fig. 3 TEM image of SWNT (**a**) **2a** (**b**), and **3a** (**c**), HR-TEM image of **3a** (**d**)

calculated for each material at 540 nm in organic solvents with a solvent reference. The dissolution of double-functionalized products is greater than the single-functionalized products (Table 2). Thus, when the functionalized SWNT react with Bu_4NOH, dissolution significantly increases. This increase is caused mainly by the presence of tetrabutylammonium cations, which balance the charges on the functionalized SWNT surface; i.e., the larger cation efficiently de-bundles the functionalized SWNT and destroys part of the strong van der Waals and π–π interactions, which causes de-bundling. Finally, all the products were dispersed in organic solvents to form a stable dispersion (Fig. 6).

To conduct a further study on covalent multi-functionalization, the reaction sequence was changed. The arene radical addition of *p*-aminobenzoic acid was performed first followed the 4-substituted aniline. In this case, the Raman spectrum shows an increase in the D/G ratio when the arene radical addition of *p*-aminobenzoic acid is performed. Unfortunately, the same ratio does not conspicuously increase after the second reaction. This finding indicates that once the radical addition of *p*-aminobenzoic acid is carried out, the double functionalization proceeds to a much lesser extent. This may be due to the electronic effect of carboxyl groups and the distribution of surface charges on SWNT.

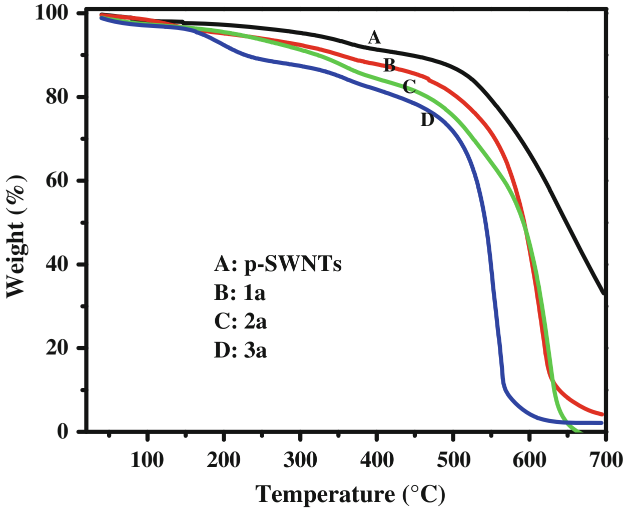


Fig. 4 TG curves of pristine SWNT (p-SWNT) (*a*), **1a** (*b*), **2a** (*c*), and **3a** (*d*)

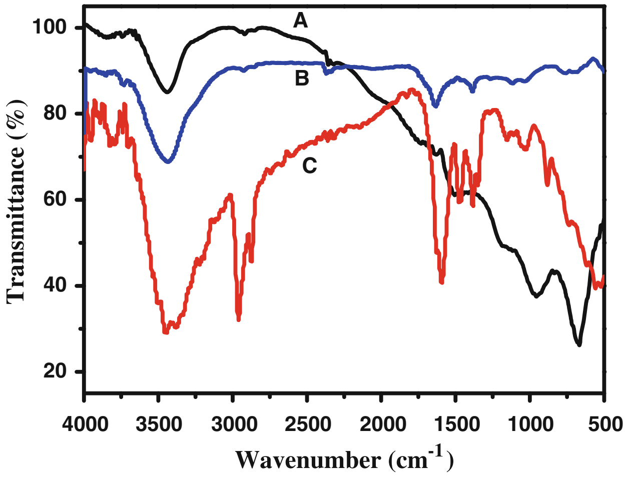


Fig. 5 FT-IR of p-SWNT (*A*), **2a** (*B*), and **3a** (*C*)

Table 2 Dissolution of functionalized nanotubes in common organic solvents (mg mL^{-1})

	DMF	$CHCl_3$	CH_2Cl_2	MeOH	THF
1a	0.87	0.58	0.35	0.13	0.15
1b	0.66	0.31	0.21	0.17	0.13
1c	0.53	0.33	0.15	0.13	0.14
2a	1.35	0.48	0.40	0.10	0.25
2b	1.04	0.42	0.27	0.24	0.12
2c	0.76	0.42	0.27	0.15	0.22
3a	1.85	1.04	0.60	0.23	0.37
3b	1.98	0.82	0.52	0.36	0.25
3c	1.03	0.67	0.39	0.38	0.30

Fig. 6 Covalent multifunctional SWNT dissolution in DMF after sonication; from left to right: p-SWNT, **1a**, **2a**, **3a**

4 Conclusion

To increase the dissolution of SWNT in common organic solvents for practical use, the synthesis of covalent multi-functionalized SWNT by two different diazonium salt addition reactions is described. The formation of SWNT salts through tetrabutylammonium hydroxide further enhances the dispersion capability of SWNT in common solvents. Multiple-functionalized processes are realized to enhance the dispersion of SWNT. The dissolution of the carbon nanotube derivatives gradually increases with the functionalization. For samples **1b–3b**, the dissolution increases approximately three-fold by multi-functionalization. This new approach to carbon nanotube derivatization paves the way for chemical and biomedical applications of SWNT.

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