Functionalization of oxidized single-walled carbon nanotubes with 4-benzo-9-crown-3 ether

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Abstract. Functionalization of oxidized single-walled carbon nanotubes (SWCNTs) by a zwitterionic interaction ($COO^-NH_3^+$) between protonated amine on crown ether and an oxyanion from a carboxylic acid group on SWCNT has been described. This ionic interaction has led to a considerable increase in the solubility of SWCNTs in both organic and aqueous solvents such as ethanol, dimethyl sulphoxide, dimethylformamide, and H_2O. The highest solubility was attained in DMF and DMSO. The ionic bonded 4-benzo-9-crown-3 ether allowed the hosting of Li^+. The ionic bond of crown ether (4-(benzo-9-crown-3)) to SWCNT was identified and confirmed by infrared spectroscopy, transmission electron-microscopy, atomic force microscopy and thermogravimetric analysis methods.

Keywords. Zwitterionic interaction; carbon nanotubes; 4-benzo-9-crown-3-ether; phase transfer catalyst.

1. Introduction

The low-dimension and remarkable physical properties of single-walled carbon nanotubes (SWCNTs) render them unique material properties with a wide range of potential applications.[1,2] However, the lack of solubility in solvents presents a considerable impediment toward harnessing of their applications. The sidewall covalent functionalization of SWCNTs leads to soluble samples and opens up the possibility of attaching other molecules to nanotubes.[3–5] The establishment of nanotube chemistry will allow the combination of different materials with SWCNTs to create new class of compounds having unprecedented properties. It will also form the basis for the other processing of these systems. Kahn and co-workers have reported the ionic linkage between 18-crown-6 having amino residue and carboxyl sites on SWCNTs. They have also reported the remarkable enhancement of solubility of SWCNTs in water and other protic solvents.[6] Recently, Solubilization of both protic and aprotic organic solvents has been achieved by functionalization of SWCNTs with phase transfer catalyst.[7] Along with our previous work on functionalization of carbon nanotubes with crown ether,[8] we now describe other procedure for the functionalization of carbon nanotubes with crown ether by a zwitterionic interaction. The functionalization of carbon nanotubes can be readily dissolved in both organic and aqueous solvents.

Crown ethers are interesting because of their hydrophobic exteriors and hydrophilic cores. They are typically proper segments to make a junction with larger globular organic molecules. This can facilitate the dissolution in solvents with different polarities that are used as a phase transfer catalyst for: (i) dehydrohalogenation, addition, substitution reactions, and other organic reactions,[9] and (ii) separation of some metal cations (Li, Cu, Cd).[10] The major advantages of the SWCNTs-CE as a phase transfer catalyst support are: (i) separation of reaction mixture easily by a simple filtration, and (ii) recycling the catalyst. We exploit this procedure in an analogue fashion by ionic bond of crown ether to SWCNTs. The SWCNTs-CE was characterized by FT-IR, electron microscopy, atomic force microscopy, and also thermogravimetric analysis methods.

2. Experimental

The synthesis of benzo-9-crown-3 (**3**), 4- nitro-benzo-9-crown-3 (**4**) and 4-amino benzo-9-crown-3 (**5**) are schematically shown in scheme 1.[11]

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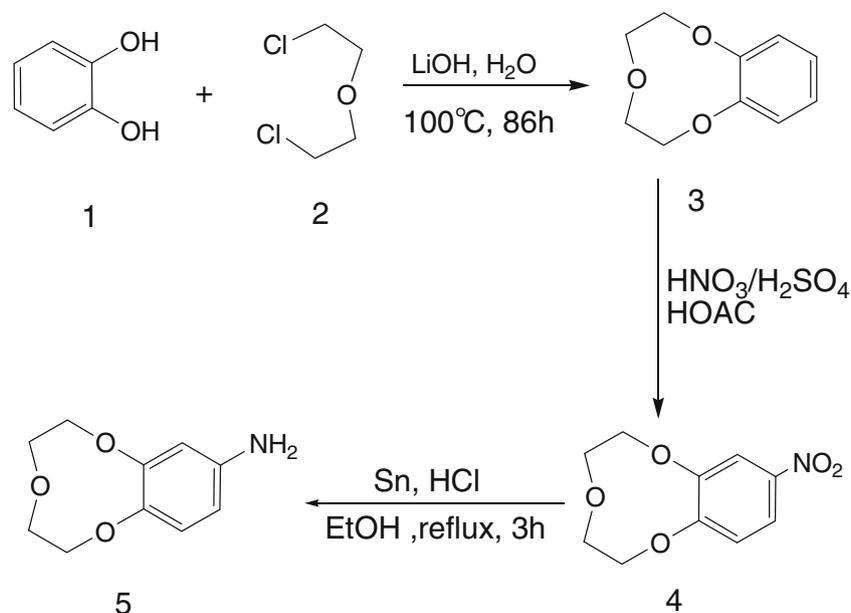
Scheme 1. Synthesis of 4-amino benzo-9-crown-3 ether (**5**).

2.1 *Synthesis of benzo-9-crown-3 (3)*

Cathecole (**1**) (1.1 g, 0.01 mol), LiOH (0.84 g, 0.02 mol) and distilled water (58 mL) were placed in a 150 mL round bottom flask. To this mixture, the bis 2-choloro ethyl ether (**2**) (1.43 g, 0.01 mol) was added drop-wise and followed by stirring for 30 min. The mixture was then refluxed for 86 h at 100°C. Addition of 5 mL of water and steam distillation produced white crystals of benzo-9-crown-3 ether (**3**) in yield of 33% (0.60 g).

2.2 *Synthesis of 4-nitro-benzo-9-crown-3 (4)*

Benzo-9-crown-3 ether (**3**) (1.8 g, 0.01 mol), dichloromethane (40 mL), glacial HOAc (28 mL) and few drops of H_2SO_4 were placed in a 200 mL round bottom flask. Then, HNO_3 (conc.) 5 mL was added drop-wise to this mixture and refluxed for 3 h. The resulting yellow reaction mixture was poured onto 35 g of crushed ice, and then sufficient amount of concentrated aqueous NaOH was added to naturalize the mixture (*p*H control). This material was extracted by dichloromethane (4×25 mL), and the combined organic extracts were dried over anhydrous Na_2SO_4 (5 g). After filtration and solvent removal in vacuum, yellow crystalline 4-nitro-benzo-9-crown-3 ether was afforded to yield 71% (1.6 g, m.p 92–94 °C).

3. Synthesis of 4-amino benzo-9-crown-3 (5)

To a mixture of 4-nitro-benzo-9-crown-3 ether (**4**), (0.23 g, 0.01 mol) and tin (0.46 g, 0.004 mol), the solution of HCl (3 mL) in absolute ethanol (5 mL) was added drop-wise and the mixture was refluxed for 3 h. When TLC monitoring indicated no further progress of the reaction, then enough aqueous KOH (conc.) was added to make the solution basic. The reaction mixture was then stirred for 30 min. The white precipitate was washed with $CHCl_3$ (4×5 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4 (1.2 g). Filtration was followed by the solvent removal in vacuum and yielded some light brown oil (1.95 g, 85%).

4. Preparation of SWCNT–COOH (6)

The SWCNTs used in this study were purchased in its pure form from Petrol Co (Close cap, average diameters of 1 to 1.7 nm and average length of 3 to 8 μm). For every 0.1 g of full length SWCNT, 50 mL mixture of 3:1 (V/V) concentrated H_2SO_4 and HNO_3 were added and the SWCNT/acid mixture was then subjected to reflux at temperature between 65 and 70°C for 30 h.

When the desired time had elapsed, the SWCNT/acid mixture was diluted with a minimum of deionized water (250 mL). The resulting diluted nanotube-acid mixture was then filtered by using a 0.45 μm polytetrafluoro-ethylene filter (PTFE—millipore) to leave a SWCNT
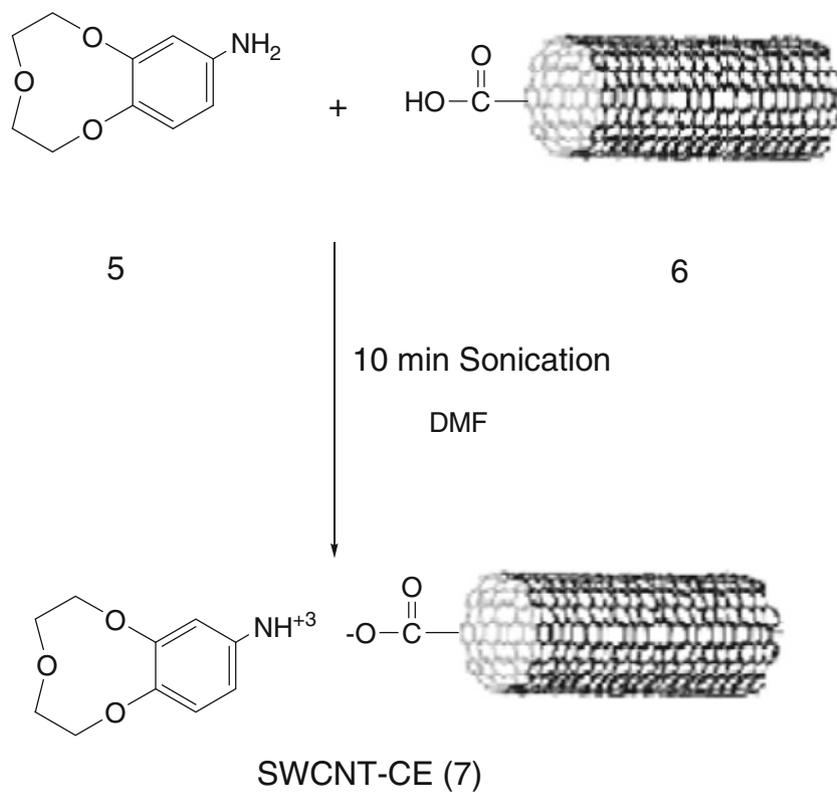
Scheme 2. Functionalization of SWCNTs-COOH with 4-amino benzo-9-crown-3 ether (**5**).
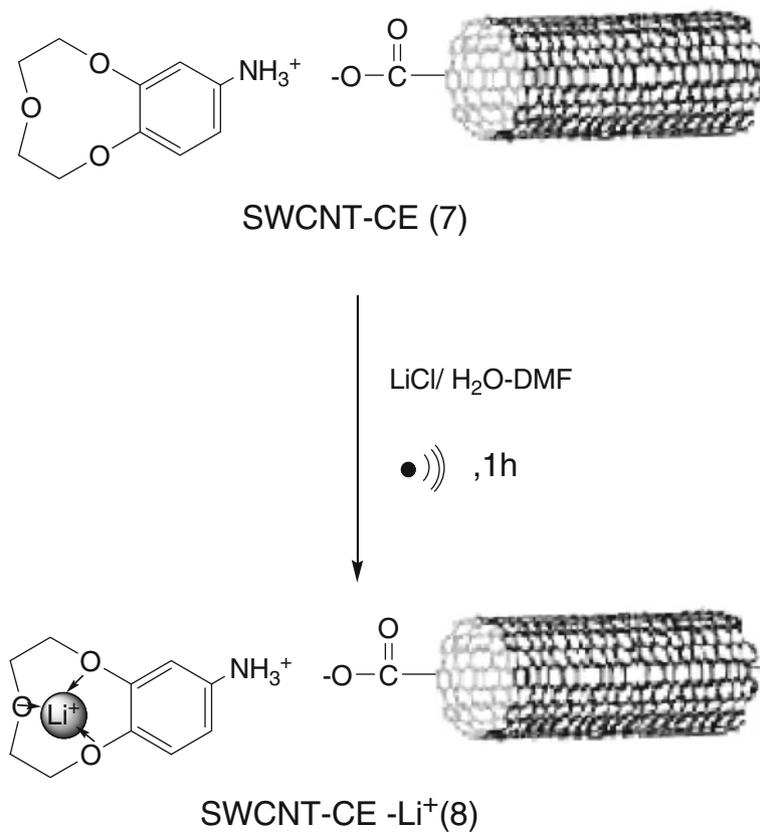
Scheme 3. Incorporation of Li^+ in SWCNT-CE.

filter cake. The nanotubes were then rinsed with water until a *p*H above 5 was obtained. Final rinsing was done by using ethanol and the resulting filter cake was suspended in a H$_2$O$_2$ (30 wt%, aq.)/H$_2$SO$_4$ (4:1) mixture. The suspension was refluxed for 2 h at 70°C to crack the SWCNTs in shorter lengths, and thereby to produce a large number of opened caps for carboxylation. Later, the resulted mixture was filtered by using a 0.45 μm polytetrafluoroethylene filter (PTFE—millipore) to separate SWCNT-COOH filter cake.[12–14] Next, concentrated HCl (12 N HCl, 2 mL) was added and briefly sonicated to remove the metal catalyst. Upon the second filtration, the precipitate was washed thoroughly with large amounts of deionized water and placed in a vacuum oven at 180°C to remove the water.
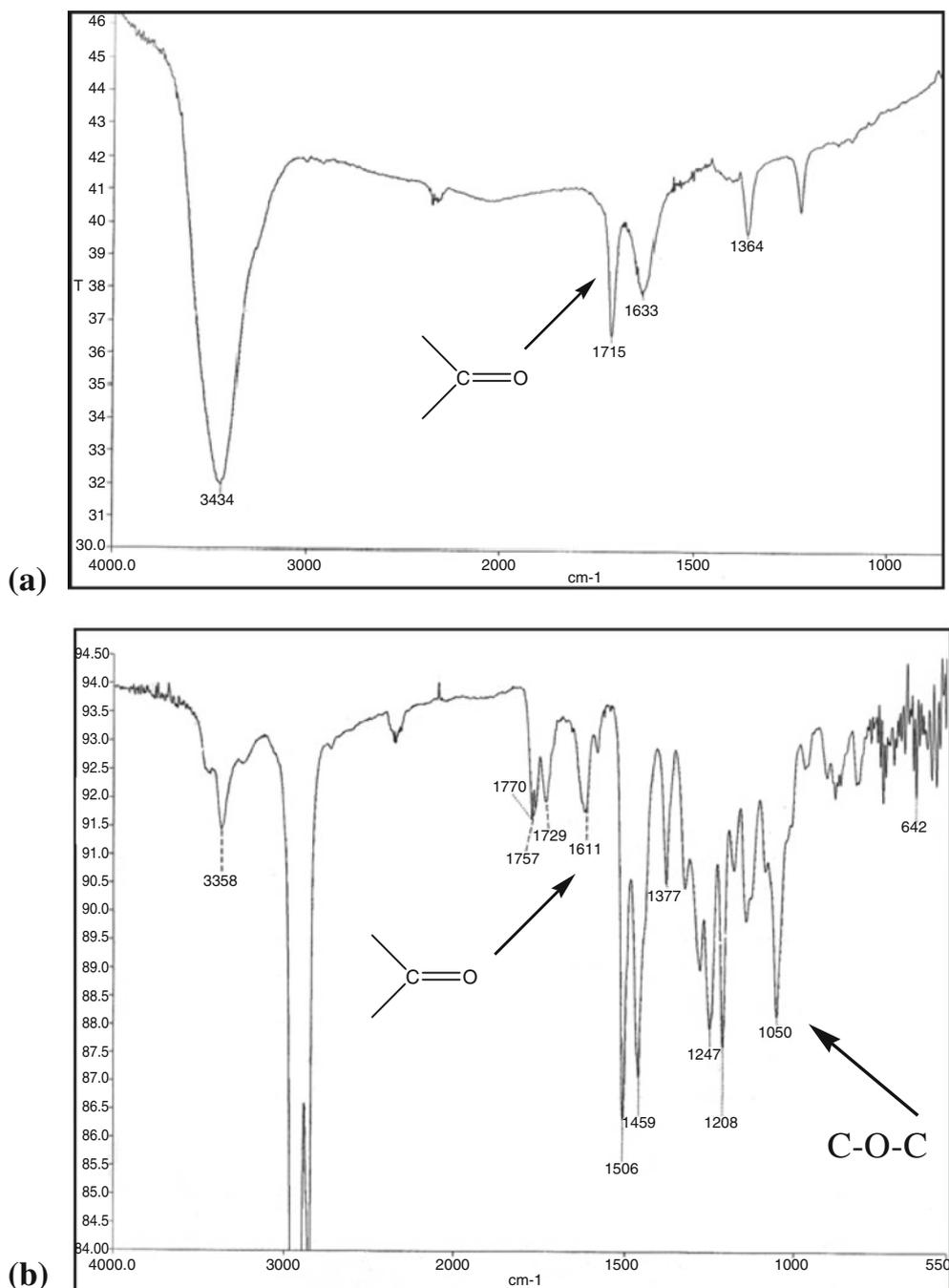

Figure 1. IR spectra of (**a**) SWCNT-COOH (**6**); (**b**) SWCNT-CE (**7**).

5. Preparation of oxidized SWCNT–CE (7)

For the production of the derivatized adduct (0.3 g) which is a black paste (**7**), 0.1 g of oxidized SWCNT (**6**) was initially mixtured with a 3:1 mass excess of 4-amino benzo-9-crown-3 (**5**). Next, 1 mL of distilled deionized water was added. The mixture was swirled and sonicated for 10 min. Then it was allowed to stand for 1 h. After that, an additional 9 mL of distilled water was made and vigorously stirred. Subsequently, the solid was separated by filtration through a PTFE (0.45 μm) membrane. The collected solid was washed with diethyl ether until the filtrate became colourless and compound of SWCNT-CE (**7**) was dried in a vacuum oven (65°C) for overnight (scheme 2).
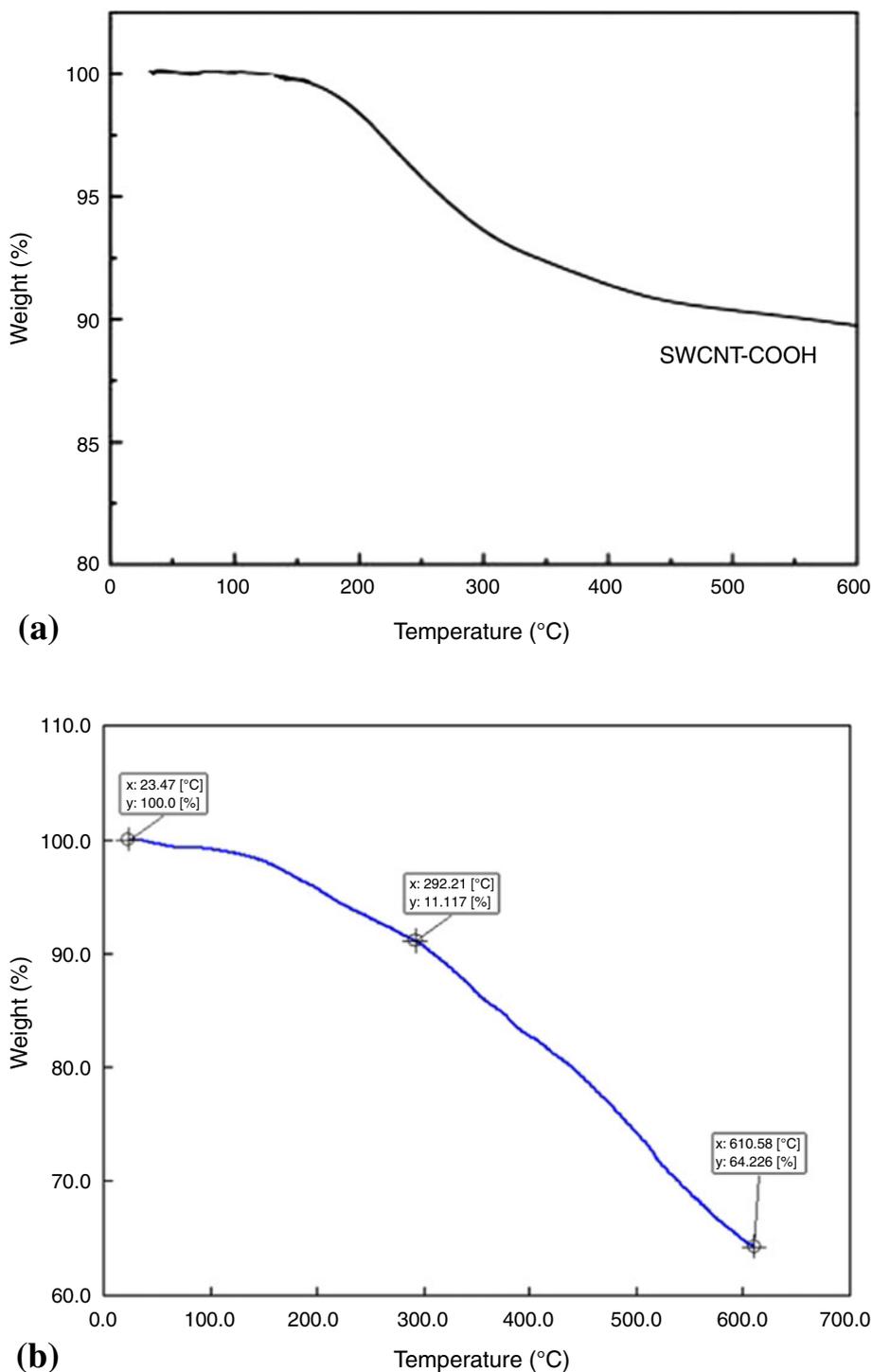
Figure 2. TGA curve of (**a**) SWCNT-COOH, and (**b**) SWCNT-CE (**7**) [Ramp, from 35°C to 605°C at 10 °C/min].

6. Preparation of SWCNT–CE-Li⁺ (8)

Solution of SWCNT–CE (**7**) in DMF was added to the solution of the Li⁺ salt (LiCl standard (4 M) in H_2O). Following a sonication for a period of time, the excess of metal salt was removed by filtration through a 0.45 µm polytetrafluoroethylene filter (PTFE—millipore). The SWCNT–CE-Li⁺ filter cake was separated and washed with distilled water (10 mL). The filtered cake was then dried in vacuum oven at 50°C for 24 h (scheme 3).

7. Characterization SWCNT-CE and SWCNT-CE-Li⁺

The SWCNT–CE (**7**) was identified by FT-IR, transmission electron microscope (TEM), atomic force microscopy (AFM), and thermogravimetric analysis (TGA). The hosted Li⁺ by **7** and formation of SWCNT-CE-Li⁺ (**8**) were also identified by ⁷Li-NMR.

7.1 *Characterization SWCNT-CE (7)*

The functionalized SWCNTs-COOH with 4-amino benzo-9-crown-3 ether (**5**) can be indicated by IR spectroscopy method. Figure 1a, is the IR spectrum of opened cap SWCNTs (SWCNT-COOH). As it is shown, there are some carboxyl functional groups on SWCNTs ($\nu_{C=O} = 1715\,cm^{-1}$). Figure 1b indicates the IR spectrum of SWCNT–CE (**7**). By comparing both spectrums, we noticed that in spectrum 1b the presence of a sharp peak at 1050 cm^{-1} in the mid-IR range is attributed to C–O–C ether bonds. Also, the IR spectrum of SWCNT-CE (figure 2b) indicates the formation of the carboxylate group: ($\nu_{C=O} = 1611\,cm^{-1}$) instead of carbonyl group ($\nu_{C=O} = 1715\,cm^{-1}$).

It is well-demonstrated that by heating the functionalized CNT in an inert atmosphere (N_2) removes the organic moieties and restores the pristine CNT structure. Therefore, TGA could be a good criterion for the degree of functionalization. Figure 2a indicates the TGA of opened cap SWCNT (SWCNT-COOH). As it is shown, there is weight loss at different tempratures. The SWCNT starts decomposing at 150°C in the air and loses the weight of its primary mass about 10% at 600°C under nitrogen (figure 2a).[15,16] While the observed weight loss from TGA of SWCNT–CE (**7**) (35°C/min to 604°C in N_2) was 36%. These results suggest a high degree (26%) of functionalization in SWCNT–CE (**7**) (figure 2b).

Transmission electron-microscopy (TEM) studies of SWCNT–CE (**7**) have been revised and revealed the
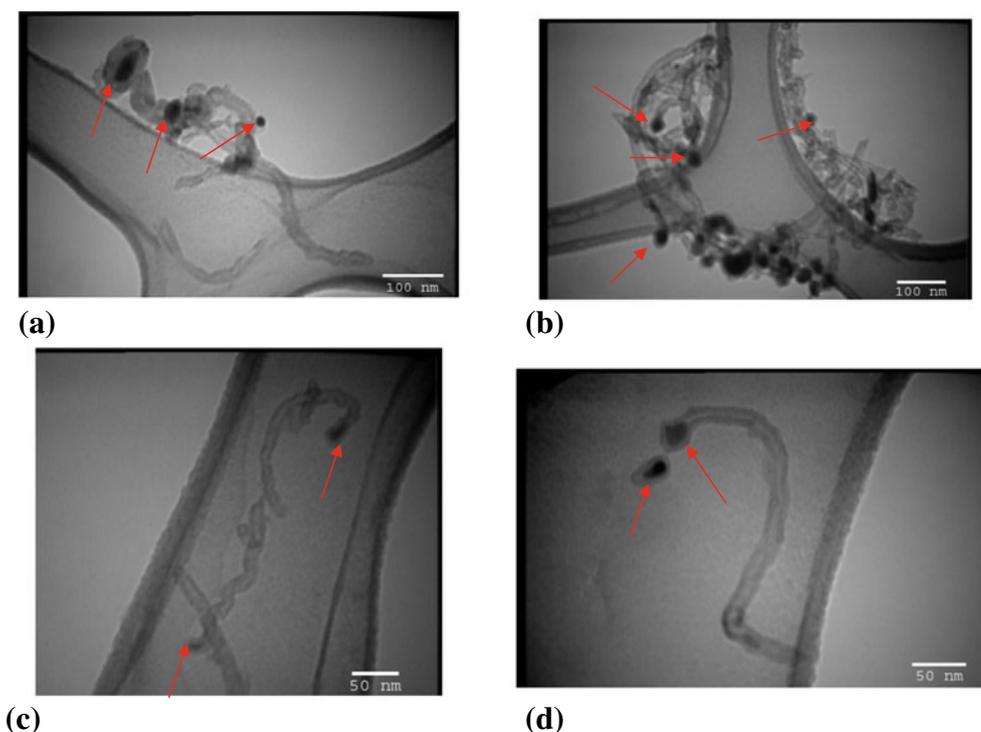
Figure 3. TEM images of SWCNT-CE (**7**).
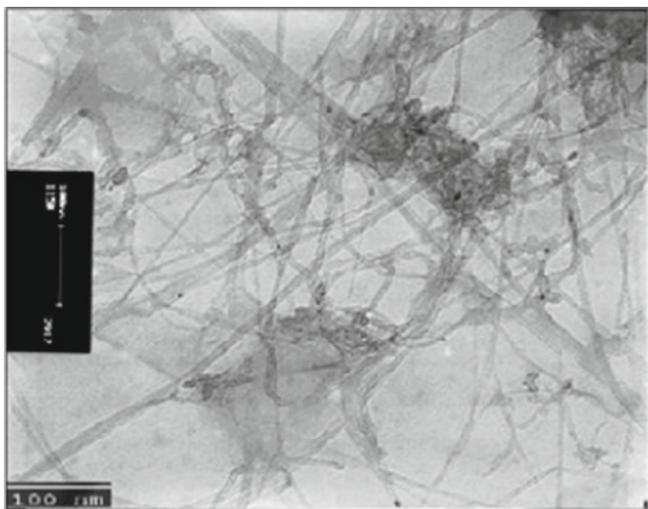
Figure 4. TEM image of pristine SWCNT.

successful grafting of crown ether to SWCNT (figures 3a–d). The bonded crown ethers are shown by arrows. The functionalization and the growth of crown ether are easily observed on the cap of SWCNTs (red arrows) in figures 3c and d.

Figures 3a and b demonstrate the TEM image of SWCNT-CE (**7**) in larger scale. As it is shown, the SWCNT-CEs (**7**) are usually observed in bamboo structure. Additionally, they have not been aggregated or aligned to form bundles. Figure 4 is related to pristine pure SWCNT in closed cap form without functionality. The average diameters of 2 to 3 nm and average length of 8 μm were measured for pristine pure SWCNT. By comparing TEM image of pristine SWCNT to those of SWCNT-CE (**7**), it is indicated that the length of SWCNT-CE (**7**) becomes shorter. It is assumed that the shortening length of SWCNT is happening during the purification and functionalization processes. Furthermore, the functionalization is mostly achieved on the surface of SWCNT, particularly on the closed cap due to activity of ends open (functionalized COOH).

SWCNT-CE (**7**) can be easily differentiated from oxidized SWCNT (**6**) by comparing AFM image of SWCNT-CE (**7**) and SWCNT-COOH (**6**). As it would be expected, the figures clearly show significant differences, especially in terms of peak heights. The height of SWCNT-COOH and SWCNT-CE were measured, giving values of 97.39 nm for SWCNT-COOH and 134.7 nm for SWCNT-CE, respectively (figures 5a and b). As it can be seen, there is a clear difference in surfaces of the bosses that aggregate with different degree of the functionalization on a SWCNT rope especially in the centre of figure 5b (high functionalization).

7.2 *Characterization of the SWCNT-CE-Li$^+$ by ^{7}Li-NMR*

To ascertain the ability of SWCNT-CE (**7**) to host Li$^+$; therefore, SWCNT-CE was immersed in a solution of lithium chloride to host the Li$^+$ in SWCNT-CE. Thus for this purpose, the ^{7}Li-NMR was applied to indicate Li$^+$ exchange (figure 6). In a solution of pure crown ether, only single ^{7}Li peak was observed, because of the fast exchange[17] between the complexed Li$^+$ and the free cation. In the same circumstance, the solution of SWCNT-CE showed a single narrow ^{7}Li peak, which is an implication of fast exchange between hosted Li$^+$ in the crown ether adducted to SWCNT and those of free Li$^+$ in solution.

The exchange of Li$^+$ between bonded CE on SWCNTs and those of free in solution are readily observed and only one ^{7}Li peak is assigned; therefore, this can be a good witness for our hypothesis: that crown ether is tethered to the SWCNT via ionic bond. SWCNT-CE (**7**) can make a complex with the Li$^+$ through its
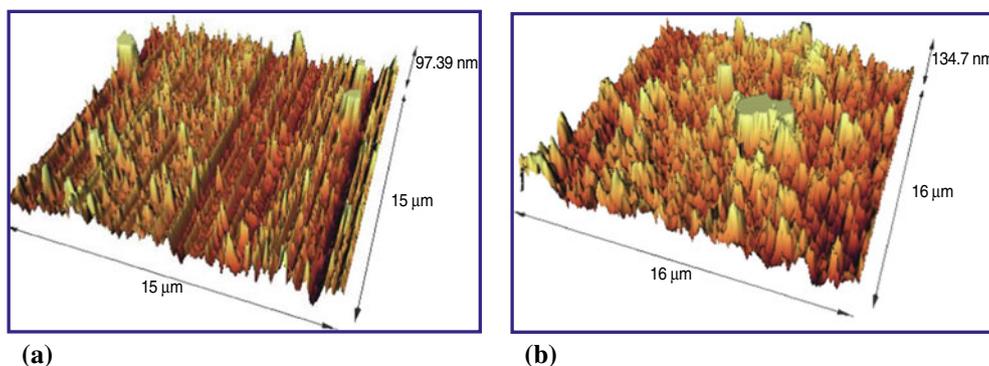
Figure 5. Typical 3D AFM images of (**a**) SWCNT-COOH, and (**b**) SWCNT-CE on mica surfaces.

CE residue. To ensure the ionic bond of crown ether to SWCNT, excess unreacted CE could be removed from the adduct by washing with diethyl ether.

We have also conducted the solubility test for SWCNT–CE (table 1). For this purpose, the remaining residue after work-up (a black powder) was used.
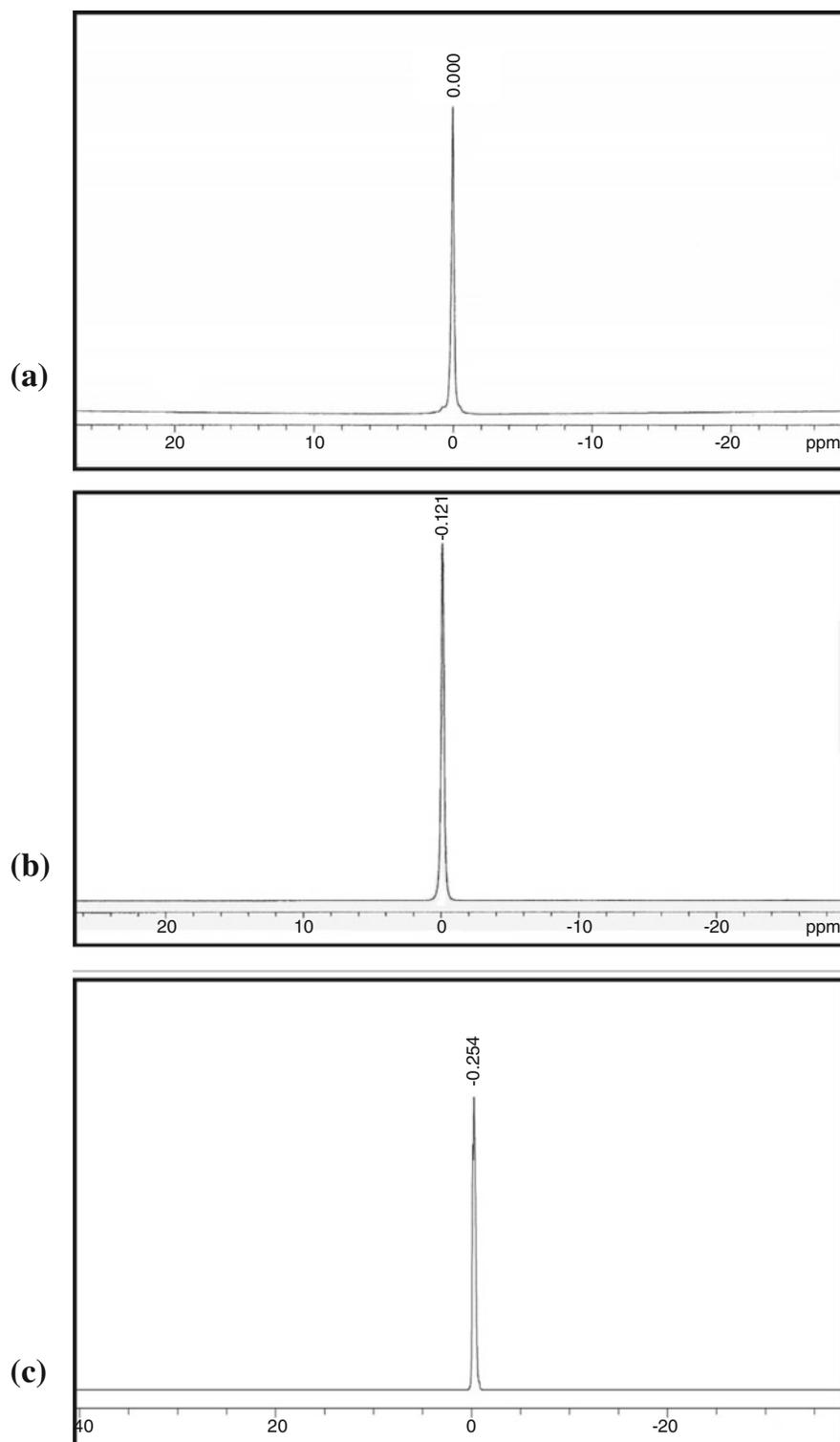
Figure 6. ^{7}Li-NMR data. (**a**) LiCl standard (4 M) in H_2O, ($\delta = 0$ ppm). (**b**) CE-Li$^+$ Complex in H_2O, ($\delta = -0.121$ ppm), and (**c**) SWCNT-CE- Li$^+$ Complex in H_2O, ($\delta = -0.254$ ppm).

Table 1. Solubility of SWCNT-CE in different solvents[a].

Solvent	Solubility (mg/ml)[b]
DMF	1
DMSO	1.1
EtOH	0.7
MeOH	0.8
H_2O	0.6
$CHCl_3$	–[c]
CH_2Cl_2	–[c]
Me_2CO	0.3
Et_2O	–[c]
n-C_6H_{14}	–[c]

[a]Values were obtained within range of $\pm 10\%$ error
[b]Values were obtained at 25°C
[c]Insoluble

This solid was soluble in DMF and DMSO and less soluble in MeOH, H_2O, EtOH, and acetone. It was also insoluble in $CHCl_3$, CH_2Cl_2, diethyl ether and hexane (table 1).

8. Conclusions

In conclusion, the adduct of 4-amino benzo-9-crown-3 ether onto SWCNTs-COOH has been explained. The functionalization was achieved by adding 4-amino benzo-9-crown-3 to SWCNTs. The ionic bond of crown ether increases the solubility of SWCNTs in both aqueous and organic solvents. SWCNT-CE can host the Li^+ through the crown ether residue bonded on its surface. The major advantages of SWCNT-CE as a phase transfer catalyst are: (i) ease of separation from reaction mixture through the simple filtration, (ii) proper carrier of Li^+ and useful source of Li^+ for catalysing the organic reactions, and (iii) ease of reusability and recycling the catalyst.

The major differences of ionic functionalization to covalent functionalization[8] are: (i) The acid–base reaction represents the simplest possible route to soluble SWNTs and can be readily scaled-up at low cost. (ii) Unlike the covalent amide bond, it seems that the presence of zwitterions (ionic functionalization) can significantly improve the solubility of SWCNT-CE in aqueous solvents. (iii) The cation in crown ether of the ionic bond of SWNT-COO^{-+}NH$_3$ of SWNTs can be readily exchanged by other organic and inorganic cations. Thus, it will be possible to adjust the solubility properties of the SWNTs and to use soluble SWNTs as versatile building blocks for advanced SWNTs-based materials via supramolecular chemistry. Furthermore, such ionic feature may allow electrostatic interactions between SWNTs and biological molecules. It can also serve as the basis for developing biocompatible SWNTs. (iv) We found that the covalent functionalization approach generally gave a much higher yield (30.4%) of SWCNT–CE than the ionic functionalization approach (26%).

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