



Evaluating the Reactivity Superiority of Two Different Single-Walled Carbon Nanotube Anions Using An Anhydride Electrophile

İki Farklı Tek Duvarlı Karbon Nanotüp Anyonunun Reaktivite Üstünlüğünün Bir Anhidrit Elektrofil Kullanarak Değerlendirilmesi

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ABSTRACT

Reductive chemistries have widely been used to functionalize single-walled carbon nanotubes (SWCNTs). However, the reactivity of negatively charged SWCNTs (NC-SWCNTs), prepared by different reductive chemistries, to the same electrophilic reagent has not been evaluated. Here in, the first example of the reactivity comparison of two different NC-SWCNTs towards 3-nitrophthalic anhydride is presented, and two novel functionalized SWCNTs are synthesized and characterized. The NC-SWCNTs, that are denoted as [(nBu—SWCNT)ⁿ•Li_n⁺] and [SWCNTⁿ•Li_n⁺], are prepared via n-butyl lithium and lithium naphthalenide addition, respectively, and are reacted by 3-nitrophthalic anhydride under dry conditions. The resulting functionalized SWCNTs are characterized by Raman, UV-vis-NIR, TGA-MS, XPS, and TEM. The reactivity of [(nBu—SWCNT)ⁿ•Li_n⁺] towards electrophilic 3-nitrophthalic anhydride is found to be higher than [SWCNTⁿ•Li_n⁺]. This is probably due to the high nucleophilic character of [(nBu—SWCNT)ⁿ•Li_n⁺] which bears lone pair electrons and electron-donating butyl groups.

Keywords

Single-walled carbon nanotube, reduction, surface functionalization, reactivity.

ÖZ

İndirgenme kimyası tek duvarlı karbon nanotüpleri (TDKNT'ler) işlevselleştirmek için yaygın olarak kullanılmaktadır. Bugüne kadar, farklı indirgeyici kimyasallar tarafından hazırlanan negatif yüklü TDKNT'lerin (NY-TDKNT) elektrofilik reaktiflere karşı reaktivitesi değerlendirilmemiştir. Burada, iki farklı NY-TDKNT'nin 3-nitroftalik anhidrid'e karşı reaktivite karşılaştırmasının ilk örneği sunulmuştur ve iki yeni işlevselleştirilmiş TDKNT sentezlenmiş ve karakterize edilmiştir. Sırasıyla n-bütilliyum ve lityum naftalinit ilavesiyle hazırlanmış olan NY-TDKNT'ler ([[(nBu—TDKNT)ⁿ•Li_n⁺] ve [TDKNTⁿ•Li_n⁺]) kuru koşullar altında 3-nitroftalik anhidrit ile reaksiyona tabi tutulmuşlardır. Elde edilen işlevselleştirilmiş TDKNT'ler Raman, UV-vis-NIR, TGA-MS ve TEM ile karakterize edilmiştir. [(nBu—TDKNT)ⁿ•Li_n⁺]nin 3-nitroftalik anhidrit elektrophile karşı reaktivitesinin [(nBu—TDKNT)ⁿ•Li_n⁺]den daha yüksek olduğu bulunmuştur. Bu muhtemelen yalnız bir elektron çifti ve elektron veren bütilliyum grupları taşıyan [(nBu—TDKNT)ⁿ•Li_n⁺]nin yüksek nükleofilik karakterinden kaynaklanmaktadır.

Anahtar Kelimeler

Tek duvarlı karbon nanotüp, indirgenme, yüzey işlevselleştirme, reaktivite.

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INTRODUCTION

The covalent surface modification has extensively been used to change the properties of SWCNTs for more than a decade. The presence of a wide range of synthetic methods, along with a large number of chemical protocols, has resulted in the preparation of many functionalized nanotubes [1–3]. Organolithium compounds including *n*-butyllithium (*n*-BuLi), *sec*-butyllithium (*sec*-BuLi), *t*-butyllithium (*t*-BuLi) and *n*-methylolithium (*n*-MeLi) have gained a particular interest to generate negatively charged SWCNT intermediates ($[\text{SWCNT}^{n-} \cdot \text{Li}_n^+]$). These intermediates are later used to introduce new functional moieties or macromolecular chains on carbon nanotube sidewalls. Reductive alkylation of SWCNTs followed by the addition of electrophiles has been carried out to introduce formyl [4], carbonyl [5,6], alkyl [7], and aryl [8] groups on SWCNT surface. Furthermore, the SWCNT carbanions generated by alkyl lithium reagents have also been used to prepare polystyrene [9] and polypropylene [10] grafted SWCNT nanocomposites.

Chen and colleagues have shown that the treatment of SWCNTs with *sec*-butyl lithium and then with carbon dioxide affords both alkyl- and carboxyl-modified SWCNTs [11]. Pekker et al. have reported that it was possible to produce carbanionic SWNTs using metallic lithium or sodium in the presence of methanolic ammonia [12]. Similarly, Penicaud and co-workers [13] showed that lithium/sodium naphthalene could be used to produce negatively charged SWNT intermediates which can be easily alkylated with alkyl halides. Roubeau and co-workers have shown the use of methylolithium in THF solvent under an inert atmosphere to generate carbanionic SWCNTs which can react with several alkyl halides to prepare alkyl-SWCNTs [14]. Very recently, Bayazit et al. have reported that gold nanoparticles can be evenly decorated on SWCNT surface via the reduction of a highly stable gold complex, which is called chloro(triphenylphosphine) gold(I), by SWCNT anions [15].

In this study, the chemical reactivity of two different negatively charged SWCNTs (NC-SWCNTs), prepared by *n*-butyl lithium and lithium naphthalene addition to SWCNTs, towards 3-nitrophthalic anhydride is evaluated for the first time. Further, two novel functionalized SWCNTs have been synthesized and characterized. Results are believed to be useful for the development of carbon nanotube- and graphene-based new or existing technologies. Results are believed to aid the development

of carbon nanotube- and graphene-based new or existing technologies [3,16] with improved properties.

MATERIALS and METHODS

Material Preparation

As-received dry SWCNT (15 mg, 1.25 mmol) is weighed in a Schlenk flask and 50 mL of anhydrous THF is cannulated to a reaction vessel under nitrogen. The resulting mixture is ultrasonicated for 15 min using Ultrawave U50 (30–40 kHz). 5 mmol of *n*-butyllithium (1.6 M in hexane, Sigma-Aldrich) is slowly added to the prepared dispersion of SWCNTs over 30 min. The resulting solution is further mixed for 30 min, ultrasonicated for 30 min and stirred for 24 h at room temperature to prepare $[(n\text{Bu-SWCNT}^{n-}) \cdot \text{Li}_n^+]$. Dry 3-nitrophthalic anhydride ($\text{C}_8\text{H}_3\text{NO}_5$) (1.5 g, 8 mmol) is then added to THF solution (50 mL), which contains the $[(n\text{Bu-SWCNT}^{n-}) \cdot \text{Li}_n^+]$ (15 mg), under nitrogen flow, and the reaction medium is kept at room temperature overnight. Unreacted $\text{C}_8\text{H}_3\text{NO}_5$ is removed by cannula filtration under nitrogen and the remaining solid is re-sonicated and cannula filtered using anhydrous THF (2×40 mL). Methanol (50 mL) is then added to Schlenk flask and the unreacted $[(n\text{Bu-SWCNT}^{n-}) \cdot \text{Li}_n^+]$ is neutralized by stirring the reaction mixture for an additional 1 h. The functionalized SWCNTs [*n*Bu-SWCNTs-NBA] (2) were isolated following the literature procedure [15]. The functionalized SWCNTs [*n*Bu-SWCNTs] (1) are also prepared in anhydrous THF by quenching the $[(n\text{Bu-SWCNT}^{n-}) \cdot \text{Li}_n^+]$ with MeOH in Schlenk flask under nitrogen, and isolated by re-dispersing and filtering using the above-described procedure for (2).

The $[\text{SWCNT}^{n-} \cdot \text{Li}_n^+]$ was synthesized by using fresh Li/naphthalene solution (1 mg mL^{-1}) prepared in freeze-dried THF. In a typical experiment, 15 mg of SWCNT (1.25 mmol) were reduced in anhydrous THF (50 mL) by Li/naphthalene solution (5 mmol) under nitrogen and then reacted by dry 3-nitrophthalic anhydride ($\text{C}_8\text{H}_3\text{NO}_5$) (1.5 g, 8 mmol) to yield [SWCNTs-NBA] (3). Formed SWCNTs are isolated by re-dispersing and filtering following the above-described procedure for (2).

Characterization

A Jobin Yvon Horiba LabRAM spectrometer (He/Ne laser, 632.8 nm, 1.96 eV) was used for Raman analysis. Measurements were carried out on powder specimens on various regions and were calibrated

to the Si-line at 520 cm^{-1} . A Perkin–Elmer Lambda 900 spectrometer was used for the UV–vis–NIR absorption spectra. Measurements were obtained in *N,N*-dimethylformamide (*ca.* 0.04 mg mL^{-1}). Thermogravimetric analysis–mass spectrometry analysis of SWCNTs (1–3 mg) was performed using a Perkin–Elmer Pyris I-Hiden HPR20 mass spectrometer. Measurements were carried out as described in the previous literature [4]. XPS spectra were recorded by RM using a Thermo Scientific K-Alpha instrument using focused ($400\text{ }\mu\text{m}$ spot) monochromatic Al- K_{α} radiation at a pass energy of 40 eV and processed using CasaXPS. Jeol JEM-1010 instrument was used for transmission electron microscopy images. TEM images were recorded over the carbon-coated copper grids using the stable solutions of functionalized SWCNTs in ethanol.

RESULTS and DISCUSSION

First, as-received dry SWCNTs are reacted with *n*-BuLi or lithium naphthalene in de-oxygenated THF solvent to form the NC-SWCNTs ($[(n\text{Bu-SWCNT})^{\ominus}\cdot\text{Li}_n^{\oplus}]$ and $[\text{SWCNT}^{\ominus}\cdot\text{Li}_n^{\oplus}]$) then the formed SWCNT carbanions

react with 3-nitrophthalic anhydride under an inert atmosphere to yield 3-nitrobenzoic acid (NBA) modified single-walled carbon nanotubes ($[\text{nBu-SWCNTs-NBA}]$ and $[\text{SWCNTs-NBA}]$, respectively). Figure 1 shows the synthetic strategy leading to the formation of $[\text{nBu-SWCNTs}]$ (1), $[\text{nBu-SWCNTs-NBA}]$ (2) and $[\text{SWCNTs-NBA}]$ (3). The NC-SWCNTs are synthesized following a modified literature procedure [4,13,15]. Characterization of the functionalized SWCNTs (1-3) was performed by Raman spectroscopy, ultraviolet-visible-near infrared (UV-vis- NIR) spectroscopy, thermogravimetric analysis coupled with mass spectrometry (TGA-MS), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM).

Alteration in the intensity of the radial breathing modes (RBMs) of SWCNTs can be attributed to the selectivity towards metallic and semiconducting SWCNTs as a consequence of covalent surface functionalization [17]. The RBMs displayed substantial differences between the covalently functionalized (1-3) and unfunctionalized SWCNTs (Figure 2, Inset). Four main peaks at ~ 190 , 200, 210 and 250 cm^{-1} can be acquired from the spectrum of

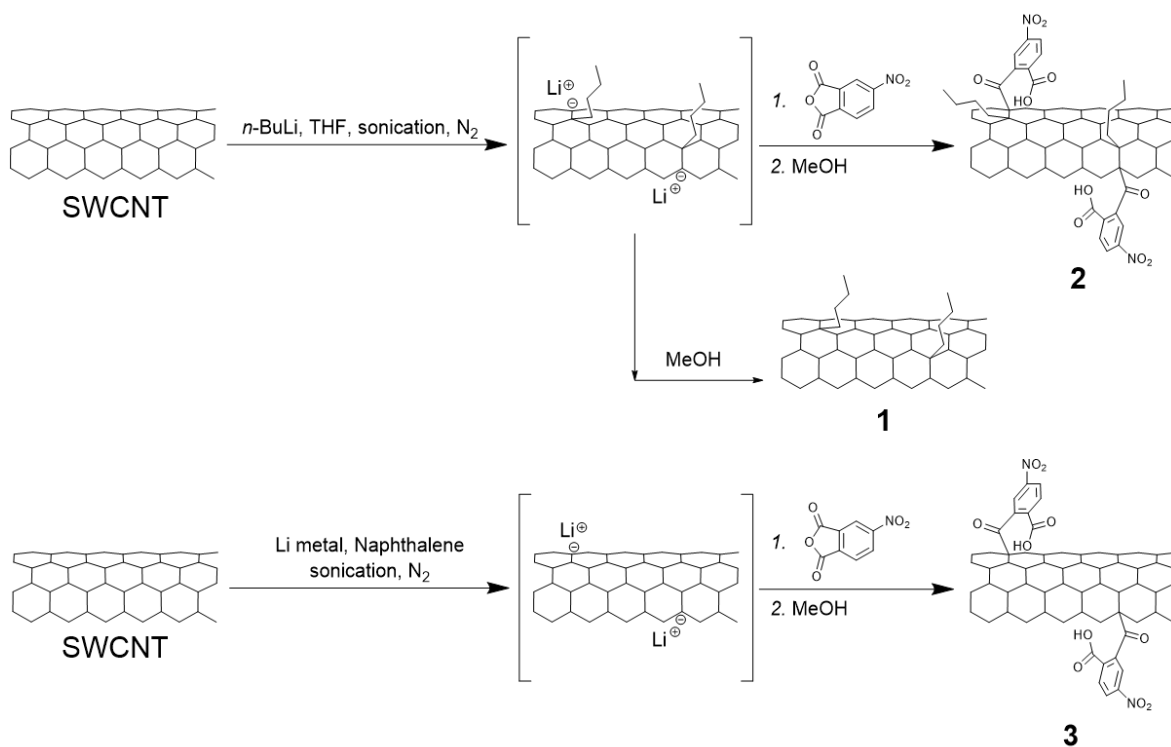


Figure 1. (a) Preparation of the NC-SWCNTs by *n*-BuLi addition and their direct discharging via MeOH to yield (1) and reaction with 3-nitrophthalic anhydride to yield (2). (b) Preparation of the NC-SWCNTs by lithium naphthalene and their reaction with 3-nitrophthalic anhydride to yield (3).

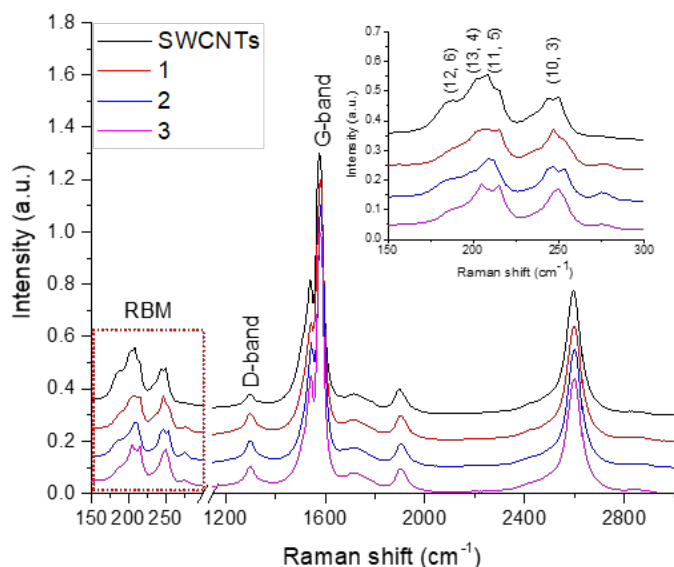


Figure 2. Raman spectra (632.8 nm, 1.96 eV) of unfunctionalized SWCNTs, [nBu-SWCNTs] (1), [nBu-SWCNTs-NBA] (2) and [SWCNTs-NBA] (3). All data are normalized and offset at the G-band. Dotted-rectangle shows the Radial Breathing Modes (RBMs) of corresponding SWCNTs. The inset shows the enlarged region of the RBMs.

unfunctionalized SWCNTs. These peaks are attributed to (12,6), (13,4), (11,5) and (10,3) SWCNTs with diameters of 1.266, 1.198, 1.125 and 0.941 nm, respectively [4]. Consistent with the literature [18], the peaks at ~ 190 , 200 and 210 cm^{-1} are metallic and the one at 250 cm^{-1} semiconducting. The unchanged semiconducting band at ~ 250 cm^{-1} in the spectra of unfunctionalized and functionalized (1-3) SWCNTs can be designated as a reference band. When the spectra were normalized at ~ 250 cm^{-1} one can see that there was a notable reduction in the intensity of the band related to (11,5) SWCNTs

at ~ 210 cm^{-1} . Agreeing with the previous studies [18, 19], noteworthy change in the metallic band intensity shows that the n-butyllithium addition to SWCNTs was mainly selective to metallic SWCNTs.

Optical absorption spectra of the SWCNTs in the UV-vis-NIR region show the transitions between the electronic densities of state in SWCNTs and these transitions appear as absorption bands [20]. The metallic transitions (M_{11}), two semiconducting transitions (S_{22} and S_{11}) are observed in 400-600, 600-900 and 900-1400 nm

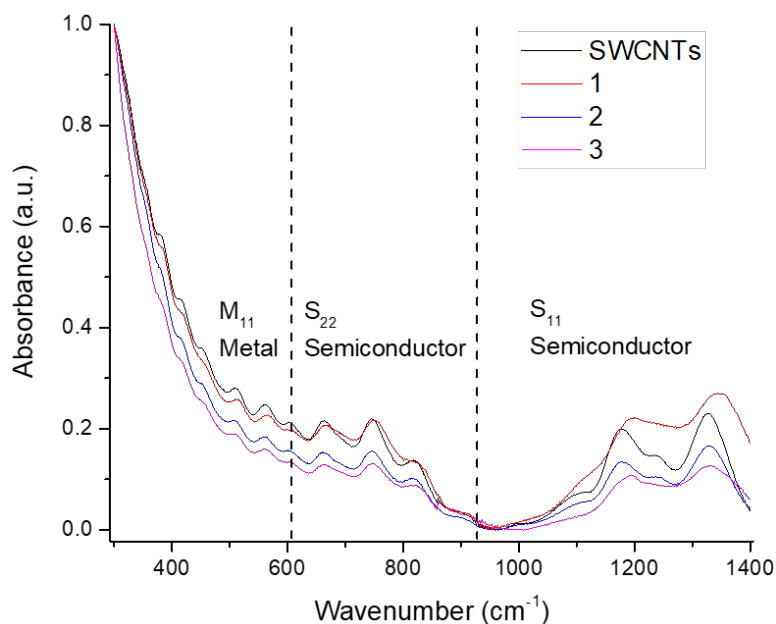


Figure 3. UV-vis-NIR spectra of the unfunctionalized SWCNTs, [nBu-SWCNTs] (1), [nBu-SWCNTs-NBA] (2) and [SWCNTs-NBA] (3). Dashed-lines separate the regions (M_{11} , S_{22} , and S_{11}) for the corresponding electronic transitions.

regions, respectively [21]. Figure 3 displays the electronic spectrum of the unfunctionalized and functionalized (1-3) SWCNTs. It has been reported that the covalent surface functionalization suppresses the electronic transition bands [20]. Furthermore, the functionalization of SWCNTs by alkyl lithium compounds is known to be selective for metallic SWCNTs over semiconducting ones [22]. Similar findings were obtained by the work here using UV-vis-NIR spectroscopy. For modified SWNTs (1-3), the electronic bands at ca. 500 nm (M_{11}), 750-800 nm (S_{22}) and 1200 nm (S_{11}) were suppressed when compared with the unfunctionalized SWCNTs as a measure of covalent addition.

Thermogravimetric analysis of the SWCNTs recorded under inert atmosphere between 100 and 900°C shows a weight loss attributable to amorphous carbon, groups produced by covalent surface modification, and low molecular-weight graphitic particles. Thus the degree of functionalization can be estimated from TGA data while heating. Furthermore, TGA coupled with gas phase mass spectrometry (MS) can identify the groups fragmented during the heating process.

Figure 4 shows the released mass fragmentations of the functionalized SWCNTs (1-3) during the heating of

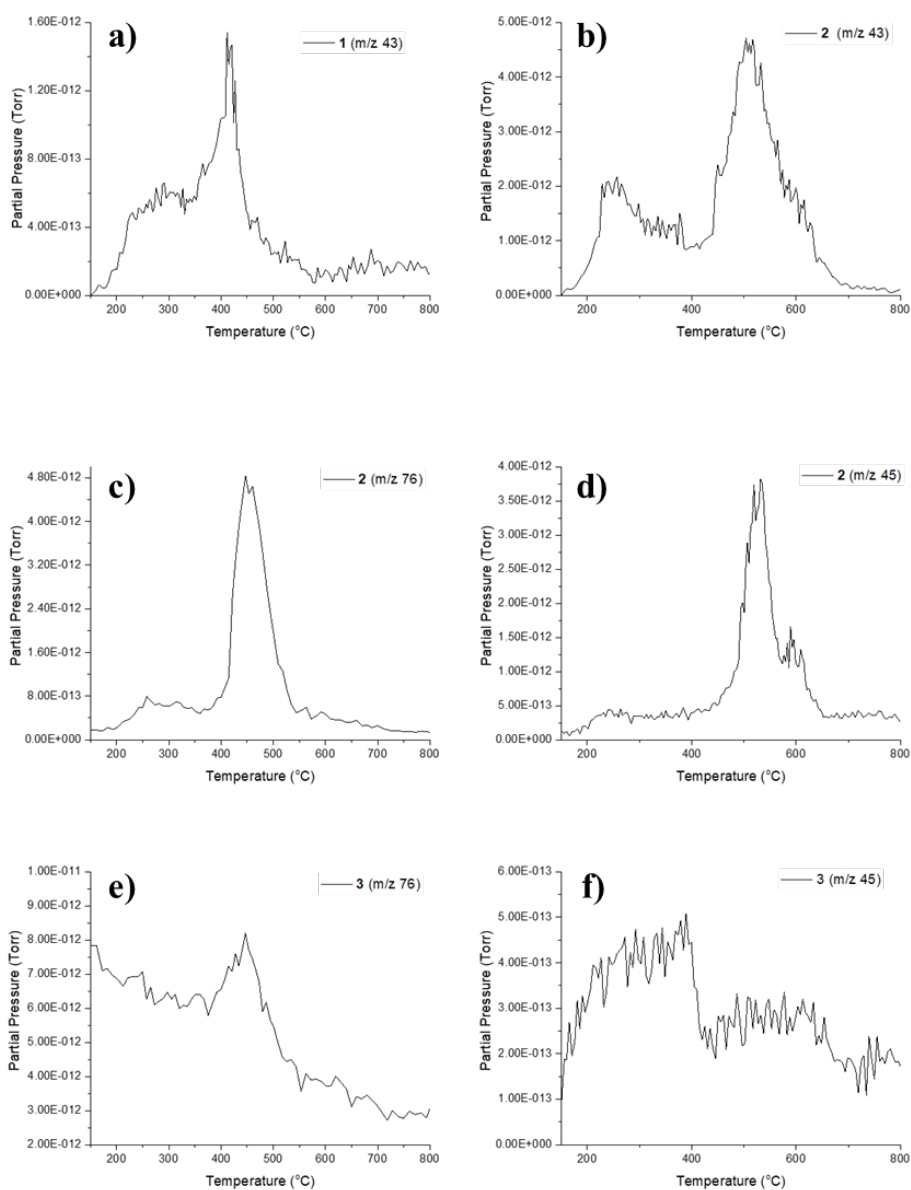


Figure 4. Mass trace of propyl (C_3H_7 , 43 amu) fragment released during the decomposition of 1 (a) and 2 (b). Mass trace of phenyl (C_6H_5 , 76 amu) and carboxylic acid (CO_2H , 45 amu) fragment during the decomposition of 2 (c and d) and 3 (e and f), respectively.

SWCNT samples by $10^{\circ}\text{C min}^{-1}$ to 900°C . Figure 4 shows the released mass fragmentations of the functionalized SWCNTs (1-3) during the heating of samples by $10^{\circ}\text{C min}^{-1}$ to 900°C . In agreement with the previous studies [4, 15], mass fragment at $\sim 200\text{--}600^{\circ}\text{C}$ for the modified SWCNTs (1 and 2) in Figure 4a-b corresponds to the propyl groups (C_3H_7 , 43 amu). However, no propyl group (C_3H_7 , 43 amu) fragment was observed during the heating of (3), indicating that fragment in Figure 4a-b was related to the covalently added n-butyl groups on SWCNTs surface. Furthermore, the functionalized SWCNTs (2 (Figure 4c-d) and 3 (Figure 4e-f)) fragmented into phenyl (C_6H_5 , 76 amu, at $\sim 400\text{--}500^{\circ}\text{C}$) and carboxylic acid (CO_2H , 45 amu, at $400\text{--}650^{\circ}\text{C}$) groups upon heating and these fragments confirm the presence of covalently attached NBA groups on functionalized SWCNT surface.

The degree of surface modification was estimated by thermogravimetric analysis under nitrogen. TGA of the functionalized SWCNTs (1-3) showed a mass loss of ~ 20.6 , 33.0 and 21.9% , respectively, at 800°C compared to $\sim 9.3\%$ for unfunctionalized SWCNTs, Figure 5. Calculations showed the existence of ~ 1 butyl group per 37 (2.68 atomic%) C-atoms for (1), ~ 1 NBA group per 67 (1.49 atomic%) C-atoms for (2) and ~ 1 NBA group per 112 (0.89 atomic%) C-atoms for (3). Complementary X-ray photoelectron spectroscopy (XPS) was performed for the percentage elemental composition analysis of nitrogen atoms in the functionalized SWCNTs (2 and 3) to further confirm the surface modification. In agreement with TGA data, XPS survey spectra showed the presence of 1.73% (1.49 N% by TGA) and 0.74% (0.89 N% by TGA) nitrogen atom in [nBu-SWCNTs-NBA] (2) and [SWCNTs-NBA] (3),

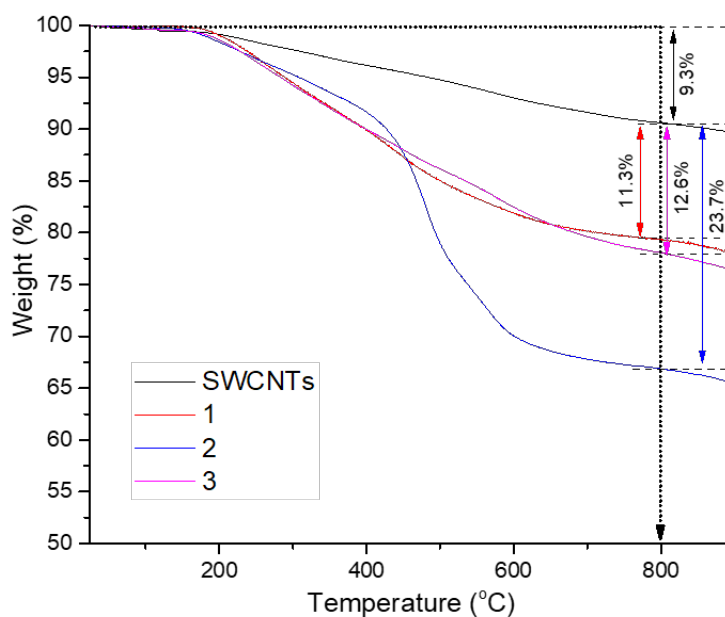


Figure 5. TGA data ($10^{\circ}\text{C min}^{-1}$) of the unfunctionalized SWCNTs, [nBu-SWCNTs] (1), [nBu-SWCNTs-NBA] (2) and [SWCNTs-NBA] (3).

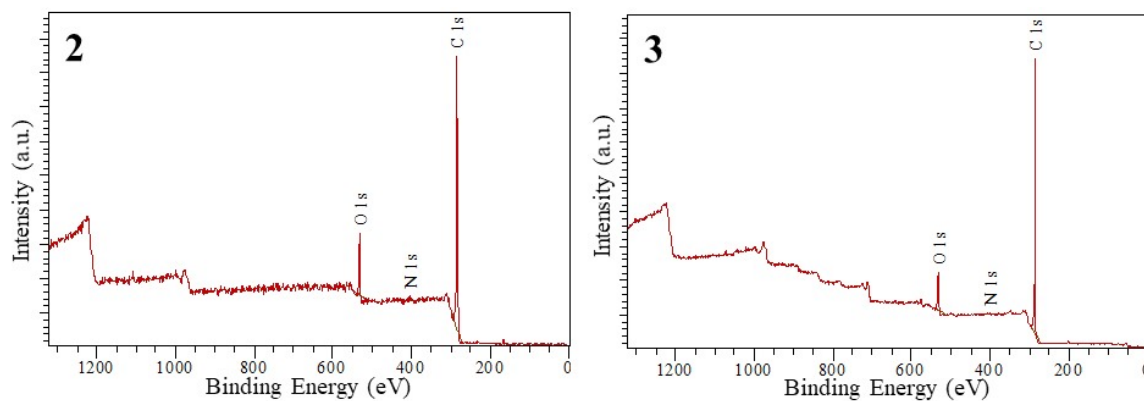


Figure 6. XPS survey spectra of [nBu-SWCNTs-NBA] (2) and [SWCNTs-NBA] (3).

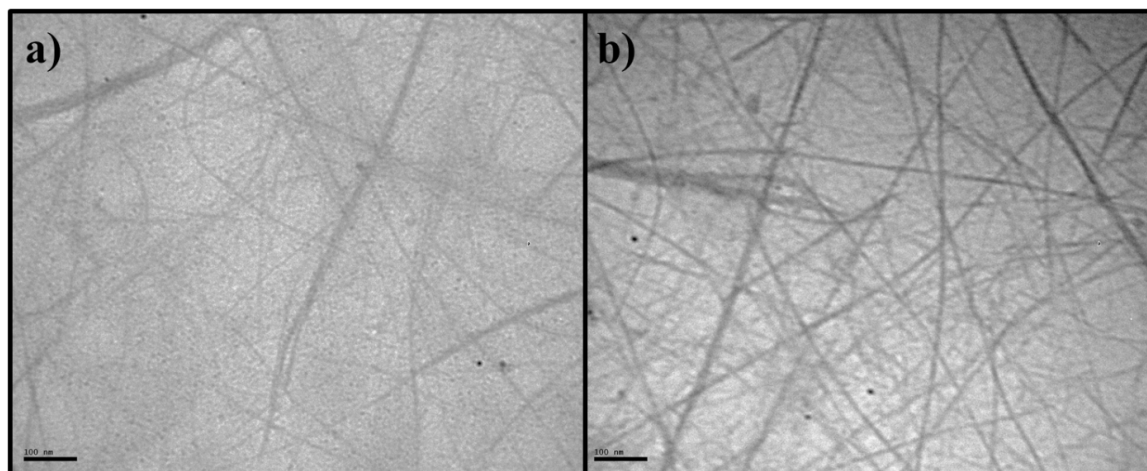


Figure 7. TEM images of (a) [nBu-SWCNTs-NBA] (2) and (b) [SWCNTs-NBA] (3).

respectively (Figure 6). TGA and XPS results revealed that the NC-SWCNTs prepared via *n*-butyl lithium [(nBu—SWCNTⁿ)⁻•Li_n⁺] are more reactive towards 3-nitrophthalic anhydride electrophile than that of the one prepared via lithium naphthalene [SWCNTⁿ•Li_n⁺]. This may be related to high nucleophilic character of [(nBu—SWCNTⁿ)⁻•Li_n⁺], induced by the presence of electron donating alkyl groups and a lone pair electrons on SWCNTs surface. However, it is worth pointing out that total negative charge produced on [(nBu—SWCNTⁿ)⁻•Li_n⁺] are not 100% utilized for further functionalization, probably due to the steric effect of the butyl groups.

TEM analysis further confirmed the higher reactivity of the NC-SWCNTs [(nBu—SWCNTⁿ)⁻•Li_n⁺], prepared via *n*-butyl lithium, to 3-nitrophthalic anhydride electrophile, compared with the NC-SWCNTs [SWCNTⁿ•Li_n⁺] prepared via Li-naphthalene. TEM image of the stable dispersion of the [nBu-SWCNTs-NBA] (2) showed enhanced nanotube homogeneity, as a result of the higher degree of functionalization, compared with TEM image of the stable dispersion of the [SWCNTs-NBA] (3), Figure 7.

CONCLUSION

For the first time, the NC-SWCNTs were shown to be highly reactive towards a phthalic anhydride electrophile, and two novel functionalized SWCNTs were prepared and characterized. Among the NC-SWCNTs, the one prepared by using *n*-butyl lithium exhibited higher chemical reactivity towards 3-nitrophthalic anhydride, when compared with the one prepared by Li-naphthalene. The degree of negative charge utilization

for *n*-butyl lithium based SWCNT carbanions (~100% higher than Li/naphthalene based SWCNT carbanions) was found to be high enough to carry out additional surface modifications. This can facilitate de-bundling of the SWCNTs and increase the processability of them in common organic solvents. These findings can be extended for the effective surface modification of other sp²-hybridized carbon frameworks such as graphene.

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