Reductive Alkylation and Arylation of Single-walled Carbon Nanotubes in Ethylenediamine via Benkeser Reaction

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Single-walled carbon nanotubes (SWNTs) were functionalized with alkyl and aryl groups using lithium in ethylenediamine under moderate conditions. This Benkeser reaction was convenient and scalable because no liquid ammonia was used. Raman, infrared spectra, scanning electron microscopy, transmission electron microscopy, and thermogravimetric analysis as well as UV–vis–NIR spectra were used to characterize the functionalized SWNTs.

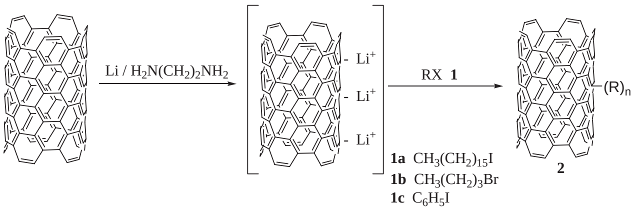
Since the discovery of multiwalled carbon nanotubes (MWNTs) in 1991 and single-walled carbon nanotubes (SWNTs) in 1993, carbon nanotubes (CNTs) have attracted a great interest owing to their remarkable electronic, thermal and mechanical properties, which make them attractive candidates in diverse nanotechnological applications.[1,2] However, further development of CNTs is hampered by their poor solubility and difficult manipulation in solvent. It is well-known that chemical modifications on the surface of CNTs can significantly overcome these problems and for this reason, investigations on superficial modification of CNTs have been an intense focus of attention.[3]

Recently, Billups et al.[4] and Tour et al.[5] reported reductive alkylation and arylation reactions of CNTs with lithium and halides in liquid ammonia. The method can highly debundle and functionalize CNTs to obtain the corresponding alkyl- or aryl-substituted CNTs with favorable solubility and dispersion in organic solvents or in water. However, the Billups condition is similar to the Birch reduction[6] that requires low temperature and a long period of waiting for liquid ammonia to evaporate. This makes the process inconvenient. The Benkeser reaction[7] can minimize some of these problems by using alkylamines with low molecular weight to replace liquid ammonia as the solvent. Additionally, it can be performed on a large scale. Functionalization of CNTs on a large scale by a convenient way is still an important challenge for researchers. In this paper, we report the reductive alkylation and arylation of SWNTs in ethylenediamine which undergoes a convenient, scalable, and moderate process (see Experimental in the Supporting Information).[10]

Scheme 1 shows the procedure of our functionalization reaction. SWNTs are lithiated by dissolving lithium in ethylenediamine to form a carbanion compound which then reacts with the halides through radical addition.[4c]

Direct evidence for the sidewall covalent functionalization of CNTs is obtained from Raman spectroscopy, which is considered a promising method to characterize functionalized carbon nanotubes.[8]

Figure 1 shows the Raman spectra of the SWNTs. The pristine SWNTs exhibit typical Raman spectra of carbon nanotubes: the weak D band at 1344 cm^{-1}, strong G band at 1586 cm^{-1}, and the radial breathing mode at 167–265 cm^{-1}, respectively. As expected, the D bands are intensified compared to G bands after alkylation or arylation in ethylenediamine, which indicates that the functionalization route introduces much more defects in the sp^2 network of SWNTs. As shown in Table 1, the D to G band intensity ratios (I_D/I_G) for pristine SWNTs, **2c**, **2b**, and **2a** are 0.24, 0.54, 0.61, and 0.75, respectively, which show an increasing degree of functionalization that is in sharp contrast with the trend observed by the following TG analysis. The existence of RBM regions at 160–267 cm^{-1} in the functionalized tubes suggests that the tubular structure of SWNTs is preserved.



Scheme 1. Proposed reaction route of reductive alkylation or arylation of SWNTs in ethylenediamine.

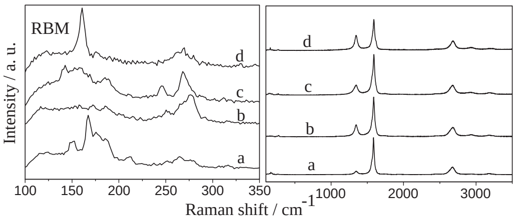


Figure 1. Raman spectra of pristine SWNTs (a), **2c** (b), **2b** (c), and **2a** (d).

Table 1. Raman D/G, TGA-determined weight loss of pristine SWNTs, **2a**, **2b**, and **2c**

Compound	Raman I_D/I_G[a]	% TGA wt loss[b]
Pristine SWNTs	0.24	2
2c	0.54	11
2b	0.61	13
2a	0.75	44

[a]Representative Raman (532 nm excitation) D/G values averaged over three scans per sample. [b]TGA weight loss was obtained by ramping at 10 °C min^{-1} from room temperature to 800 °C in nitrogen–air atmosphere.

The alkylation and arylation of SWNTs are confirmed by FT-IR spectra. As shown in Figure 2, **2a** exhibits strong C–H stretching vibrations at 2850, 2920 cm^{-1} associated with a peak of C–H deformation mode at 1464 cm^{-1}. **2b** shows similar C–H modes as **2a** with weak absorptions due to the comparatively low degree of functionalization and smaller content of methylene groups. These bands are not found in pristine SWNTs, suggest-

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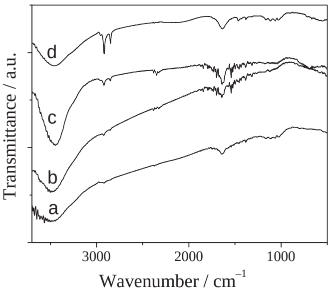

Figure 2. IR spectra of pristine SWNTs (a), **2c** (b), **2b** (c), and **2a** (d).

ing that the alkyl groups are attached to the SWNTs in **2a** and **2b**. The weak peaks at 3010 and 3030 cm^{-1} (see Figure S1 in the Supporting Information) in the spectrum of **2c** characterize the aromatic C–H stretching modes of phenyl groups attached to the SWNTs. The bands centered at 1634 and 1544 cm^{-1} are assigned to C=C stretching modes of SWNTs.

The morphology of the SWNTs was observed by SEM and TEM (see Figure S3 in the Supporting Information). Bundles of tubes are clearly seen from the images, suggesting that the structural integrity of SWNTs is retained. HRTEM images (see Figure S4 in the Supporting Information) reveal a representative morphology of roughened sidewalls which can be attributed to the high degree of functionalization.[9]

UV–vis–NIR spectra of pristine and functionalized SWNTs were measured in *N*,*N*-dimethylformamide (DMF) (see Figure S5 in the Supporting Information). Our pristine SWNTs show typical van Hove singularities in the absorption spectra but they are lost in **2a**, **2b**, and **2c**, which provides further evidence for the sidewall covalent functionalization.[3j,9] The functionalized tubes also exhibit improved solubilities in general solvents (see Figure S6 in the Supporting Information).

The thermostability of functionalized SWNTs and the functionalized degree was investigated by thermogravimetric analysis (TGA) (see Figure S2 in the Supporting Information). The pristine SWNTs are thermally stable below 550 °C. In contrast, the alkyl- and aryl-functionalized **2a**, **2b**, and **2c** show much lower decomposition temperature. Two main weight loss regions can be seen from the curves of functionalized SWNTs: the first region in the range of 200–400 °C is ascribed to the decomposition of the covalently functionalized groups. The second region at about 600 °C is attributed to the decomposition of SWNTs framework. The weak loss below 200 °C may be due to the adsorbed molecules and moisture. A rough estimation (after subtracting the contribution of the pristine SWNTs shown in Table 1) for the weight loss resulting from the functionalized groups for **2c**, **2b**, and **2a** is 9%, 11%, 42%, respectively, which shows the same trend as observed by Raman spectra.

In conclusion, successful reductive alkylation and arylation of SWNTs were developed by treating SWNTs with lithium in ethylenediamine under moderate conditions. This process is convenient, scalable owing to the avoidance of the troublesome handling procedure resulting from the liquid ammonia. The high degree of functionalization was confirmed by Raman, IR, HRTEM imaging, and TG analyses. Testing of this reductive method in other aliphatic amines, such as propylamine, diethylenetriamine, and the reductive reaction of MWNTs and its use in polymers is underway in our laboratory.

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10 Supporting information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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