

In situ Raman studies on lithiated single-wall carbon nanotubes in liquid ammonia

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Abstract

The charge transfer induced lithiation of single-wall carbon nanotubes (SWNTs) was investigated by in situ monitoring by Raman spectroscopy as lithium was added incrementally to a dispersion of SWNTs in liquid ammonia. Charge transfer from liquid ammonia solvated lithium to the SWNTs led to intercalation of lithium into the SWNT ropes, as well as to the semi-covalent lithiation of the SWNTs. Raman spectra of the SWNTs recorded as lithium was added showed a ~ 30 wavenumber downshift of the G band (1594 cm^{-1}) with the concomitant appearance of a new peak at 1350 cm^{-1} that was assigned as the signature of the lithiated SWNTs. Addition of 1-iodododecane to the lithiated SWNTs resulted in the covalent attachment of dodecyl groups. The intercalation of lithium throughout the SWNT ropes led to complete dodecylation of all individual SWNTs.

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1. Introduction

Many of the applications that have been proposed for single-wall carbon nanotubes (SWNTs) will require individually dispersed SWNTs in either organic or aqueous solution [1–5]. Covalent sidewall derivatization by organic functional groups provides a convenient way to prepare individual SWNTs [1,6]. A new functionalization reaction described recently by Liang et al. [7] yields functionalized SWNTs that are soluble as individuals in chloroform. The salient feature of this functionalization reaction involves the reaction of SWNTs that have been reduced by lithium in liquid ammonia with alkyl halides to yield nanotubes functionalized by alkyl groups. The lithium–liquid ammonia system has also been used by

Pekker et al. [8] to hydrogenate SWNTs. Electron transfer from the ammonia solvated lithium to the SWNTs is an important initial step that accounts for the structural and reactivity changes of the SWNTs.

Similar charge transfer experiments by alkali metals have been studied [9–19] by vapor phase [9,17–19] and/or electrochemical doping [11–16]. Raman spectroscopy has been used to investigate these doping experiments, since Raman vibrations are sensitive to changes in both the structural and electronic properties of SWNTs. Electron transfer from alkali dopants to SWNTs was proven by Raman scattering [18], which showed a downshift (softening) and broadening of the tangential modes (TM or G band) at $\sim 1593\text{ cm}^{-1}$, along with the appearance of the broad, asymmetric Breit–Wigner–Fano (BWF) peak that is caused by interference scattering between multi-phonon continuum and the highest-frequency nanotube phonons that have been softened. However, different interpretations have been proposed

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on diverse Raman observations of alkali doped SWNTs and many phenomena have not been understood clearly. We report here the results of an in situ Raman investigation on lithiation of SWNTs in liquid ammonia and the reaction of the lithiated SWNTs with 1-iodododecane.

2. Experimental

The SWNTs used in this study were produced by the HiPco process and purified to remove the metal catalyst and the non-SWNT carbon species. The glass vessel that was used for the measurements was equipped with a specially designed quartz tube that could be immersed into liquid ammonia for in situ Raman measurements. A Teflon coated magnetic stirring bar was used to maintain a uniform dispersion of SWNTs in the liquid ammonia. The apparatus was then evacuated using a vacuum pump, flame dried, and purged with dry argon. An atmosphere of argon was used to ensure a moisture and oxygen free system. ~ 50 mg (4.2 mmol) of purified SWNT powder was dried in a vacuum oven overnight and introduced into the reaction system. Hundred milliliters of ammonia was then condensed into the glass reactor equipped with a dry ice condenser and cooled to -78 °C by an acetone-dry ice bath. The temperature of the system was kept at -78 °C as 40.7 mg (5.9 mmol) of lithium (Li to C ratio of 1.40) was added in 1–5 mg increments as the Raman spectrum was monitored. 1.5 mL (~ 6.1 mmol) of 1-iodododecane was then added and the acetone-dry ice bath was removed. The reaction was maintained at -33 °C for ~ 2.5 h. At this point, the Raman spectra did not change.

A Kaiser Process Raman spectrometer (Kaiser Optical, Inc.) with a 785 nm excitation laser (laser power density 40 W/cm 2) was used to monitor Raman spectra. The Raman probe with a $10\times$ objective was focused downward into the liquid ammonia through a quartz window. Spectra were taken at 3 min intervals. Care was taken to minimize the laser-induced deposition of SWNTs onto the quartz window.

3. Results and discussion

The Raman spectrum recorded in liquid ammonia of undoped SWNTs is shown in Fig. 1a. The tangential mode (G band) appears as a strong peak at 1594 cm $^{-1}$ along with a shoulder at 1563 cm $^{-1}$. The radial breathing modes (RBM) appear as three peaks at 210, 234, and 269 cm $^{-1}$. The disorder mode (D band) at 1296 cm $^{-1}$ is widely used as a measure of sidewall covalent derivatization. The low intensity indicates a low level of initial sidewall functionalization (defects) of the purified SWNTs that were used in this study. The N–H stretching modes of NH_3 appear as the strong

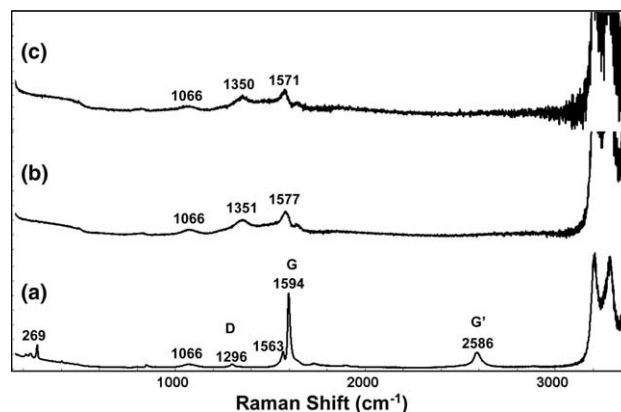


Fig. 1. In situ Raman spectra of SWNTs in liquid ammonia. (a) Before Li addition; (b) after first Li addition (Li/C ratio 0.18. Raman intensity is scaled up by a factor of 4 for clarity); (c) after second Li addition (Li/C ratio 0.31. Raman intensity is scaled up by a factor of 16 for clarity).

triplet at 3180 – 3400 cm $^{-1}$. Two weaker vibration modes at 1066 and 1640 cm $^{-1}$ (superimposed on the SWNT G band) are also assigned to NH_3 .

The dark blue color resulting from solvated electrons appeared as lithium (0.76 mmol, Li/C ratio of 0.18) was added to the liquid ammonia. A controlled experiment demonstrated that the blue color could be sustained for several hours with liquid ammonia only (without SWNTs), confirming that the system was free of air, moisture or other oxidants. The disappearance of the blue color when lithium is added to a dispersion of SWNTs in liquid ammonia is an indication that electrons are transferred efficiently from solution to the SWNTs. The reduced SWNTs were observed visually to disperse more readily as the size of the SWNT aggregates decreased.

The Raman spectrum was observed to change *dramatically* as the lithium was added. The spectrum presented in Fig. 1b was recorded 1 min after the first addition of lithium. The RBM disappeared and the resulting broadened G band decreased in intensity and downshifted ~ 17 cm $^{-1}$. A broad new peak appeared at ~ 1350 cm $^{-1}$. The G band was observed to downshift an additional 6 cm $^{-1}$ 1 min after the second addition of lithium (0.55 mmol, Li/C ratio of 0.31) as illustrated in Fig. 1c. The peak at 1350 cm $^{-1}$ did not change and the overall Raman intensity decreased as additional lithium was added.

The effects of doping on the Raman spectra of SWNTs have been observed previously [18]. Doping with bromine was shown to result in an upshift of the RBM by as much as 74 cm $^{-1}$, whereas doping with K or Rb caused the disappearance of the RBM from the detectable range. The G band shift for alkali metal doped SWNT ropes is the result of a complicated process, since the various modes within the unresolved G band can experience different shifts upon electron

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