

Research Letter

Apparent Enhanced Solubility of Single-Wall Carbon Nanotubes in a Deuterated Acid Mixture

T. Ramanathan,¹ Frank T. Fisher,² Rodney S. Ruoff,³ and L. Catherine Brinson^{1,4}

¹ Department of Mechanical Engineering, Northwestern University, Evanston, IL 60208, USA

² Department of Mechanical Engineering, Stevens Institute of Technology, Hoboken, NJ 07030, USA

³ Department of Mechanical Engineering, The University of Texas at Austin, Austin, TX 78712, USA

⁴ Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA

Correspondence should be addressed to Frank T. Fisher, ffisher@stevens.edu

Received 8 January 2008; Accepted 17 March 2008

Recommended by Valery N. Khabashesku

An apparent enhanced solubility of single-wall carbon nanotubes (SWNTs) in the deuterated form of the standard 3 : 1 sulfuric (H_2SO_4) to nitric (HNO_3) acid mixture treatment is reported and attributed to the stronger interaction of deuterium bonds with the single-wall carbon nanotube surface. UV-Visible spectroscopy was used to characterize the apparent enhanced solubility of the SWNTs treated in deuterated forms of the acid mixture in comparison to the standard acid mix, while FTIR was used to analyze the nature of the functional groups generated on the SWNTs as a result of the different acid treatments. The apparent enhanced solubility reported here is consistent with the limited number of computational and experimental results published in the literature regarding the interaction of carbon nanotubes with deuterated solvents; however, a detailed understanding of the underlying mechanism responsible for this observation is currently lacking. The apparent increased solubility observed here could potentially be utilized in many applications where carbon nanotube dispersion is required.

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1. INTRODUCTION

Owing to their excellent electrical and mechanical properties, single-wall carbon nanotubes (SWNTs) have been an area of intense research since their discovery in 1991 [1] and a variety of potential applications have been proposed [2, 3]. Many of these applications will likely require chemical modification (functionalization) of the nanotube surface to facilitate their integration into more complex assemblies, and thus solubilization of SWNTs in a variety of solvent systems has been a considerable research pursuit [4]. One common functionalization technique is treatment of the SWNTs in a 3 : 1 acid mixture of concentrated sulfuric and nitric acid (which we will refer to as the *H-acid mixture*), which creates defects on the nanotube surface from which carboxylic acid groups are attached [5, 6]. The solubility of the nanotubes after this standard acid treatment is typically much greater than that for the pristine nanotubes. However, we have recently observed that a similar treatment with the deuterated forms of this acid mixture (3 : 1 ratio of D_2SO_4 : DNO_3 ,

which we will refer to as the *D-acid mixture*) results in an apparent significant enhancement in the solubility of the SWNTs. This solubility enhancement is attributed to the strong affinity for deuterium interactions with the nanotube surface.

2. EXPERIMENTAL

The purified (>90%) SWNTs used for this study were Buckypearls (Carbon Nanotechnologies, Inc., Houston, TX). As previously reported in the literature, the diameters of these SWNTs are in the range of 0.8–1.3 nm [7]. The surface properties of the as-received SWNTs have been studied using X-ray photoelectron spectroscopy (XPS) and the results were discussed elsewhere [8]. Deuterated forms (99% of isotopes) of sulfuric acid (D_2SO_4 : catalog number DLM-33-50 with concentration of 98% D_2SO_4 in D_2O) and nitric acid (DNO_3 : catalog number DLM-33-50 with concentration of 65% DNO_3 in D_2O) were used in this study. Additional chemicals used in the experiments were heavy water

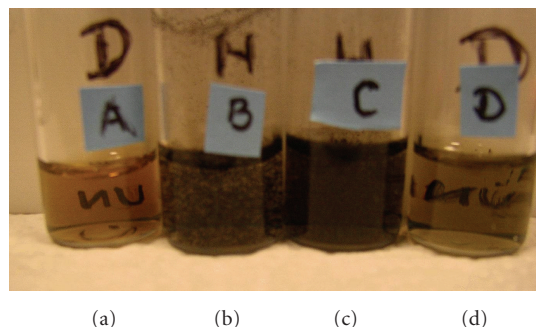


FIGURE 1: Different SWNT treatments diluted to 10% solutions. (a) D-acid mixture in D_2O ; (b) H-acid mixture in distilled water; (c) H-acid mixture in H-acid mixture; (d) D-acid mixture in D-acid mixture.

(D_2O) from Cambridge Isotope Laboratories (Andover, MA); H_2SO_4 (SA 123 with concentration of 98% H_2SO_4 in H_2O); and HNO_3 (SA 95 with concentration of 65% HNO_3 in H_2O) from Fisher Scientific (Hanover Park, IL). In this study the acids were used as received without further modification. The D-acid mixture (4 ml) was prepared in a vial with a 3 : 1 ratio of D_2SO_4 to DNO_3 to which 2 mg SWNTs (sample I) was added. A similar solution was prepared using H_2SO_4 and HNO_3 (sample II) to which 2 mg of SWNTs were added and treated as a control. In each case the vial was capped and sonicated in a bath sonicator at 350 W for 4 hours at $40^\circ C$. As described below, the apparent enhanced solubility of SWNTs in the D-acid mixture was highly reproducible and confirmed by repeating the experiment three times on three separate occasions using the procedure described above.

3. RESULTS AND DISCUSSION

After completing the sonication process, the solubility of the SWNTs was found to be significantly enhanced in the D-acid mixture compared to the solubility obtained from the standard (undeuterated acid) H-acid mixture. This observed apparent enhancement of the solubility of SWNTs in the D-acid mixture was highly reproducible and confirmed by repeating the experiment three times. For further characterization of the enhanced solubility of the D-acid mixture, the concentrated sample I was diluted to 10% solution using heavy water and the D-acid mixture, while sample II was diluted in a similar manner using both distilled water and the H-acid mixture. A photograph of the resulting solutions is shown in Figure 1, where vials A and D contain the D-acid mixture treated SWNTs (sample I) in heavy water (vial A) and in the D-acid mixture (vial D); vials B and C (sample II) contain the H-acid mixture-treated nanotubes in distilled water (vial B) and in the H-acid mixture (vial C). It is clear that vials A and D (sample I) are more transparent when compared to the corresponding vials containing sample II. Also noticeable is the lack of discernible aggregates in the vials prepared using sample I.

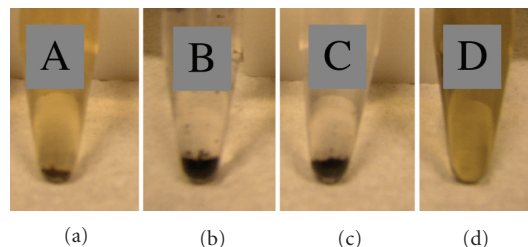


FIGURE 2: Precipitate after centrifugation for different SWNT treatments dispersed in solution. (a) D-acid mixture in D_2O ; (b) H-acid mixture in distilled water; (c) H-acid mixture in H-acid mixture; (d) D-acid mixture in D-acid mixture.

Each of the 10% solutions shown in Figure 1 was then centrifuged (IEC Medispin, Needham Heights, MA) at 12000 rpm for 30 minutes. Significant SWNT precipitation collected at the bottom of the centrifuge microtubes (0.6 ml, SciMart, St. Louis, MO) for the H-acid mixture-treated solutions (Vials B and C) as shown in Figure 2. However, for the case of SWNTs treated with the D-acid mixture significantly less precipitate was found for the solution diluted in D_2O (Vial A), and no precipitate is observed for the solution diluted in the deuterated acid mixture (Vial D). Figures 1 and 2 demonstrate the apparent increased solubilization of SWNTs treated with the D-acid mixture.

Further confirmation of this apparent increased solubility was sought via analysis of the UV-Visible spectra for sample I (Figure 3(a)) and sample II (Figure 3(b)) using a double-beam UV-Vis-NIR spectrophotometer (Cary 500, Varian, Palo Alto, CA). Figure 3(a) shows the UV-Vis spectra obtained for the 10% solution of sample I in the D-acid mixture (Figure 1, Vial D), the supernatant after the centrifuge step (Figure 2, Vial D), and the pure D-acid mixture; corresponding data is shown for the H-acid mixture-treated SWNTs (sample II) in Figure 3(b). Figure 3(a) shows strong absorption between 325 and 400 nm for both the 10% solution and supernatant for the case of the D-acid mixture treatment, with no noticeable absorption for the pure D-acid mixture. However, for the case of sample II (Figure 3(b)), only a weak peak is shown within this wavelength range for the 10% solution in the H-acid mixture, with no detectable absorption observed for the supernatant. This demonstrates that after sonication, the D-acid mixture-treated SWNTs are very finely dispersed [9]. For comparison, the dispersion of sample II is not as fine, such that the conglomeration of the SWNTs within the H-acid solution is reflected by the poor absorption of these samples.

Finally, FTIR spectra (BIO-RAD FTIR FTS 60, Hercules, CA) were collected for the sample I precipitate diluted in D_2O and the sample II precipitate diluted in distilled water after each sample was rinsed well with D_2O and distilled water, respectively, and centrifuged at 12000 rpm for 30 minutes. The precipitates were collected and dried at $80^\circ C$ under vacuum overnight prior to the FTIR analysis. For FTIR, the SWNT samples were grounded well with KBr and the sample was made into a pellet form using a

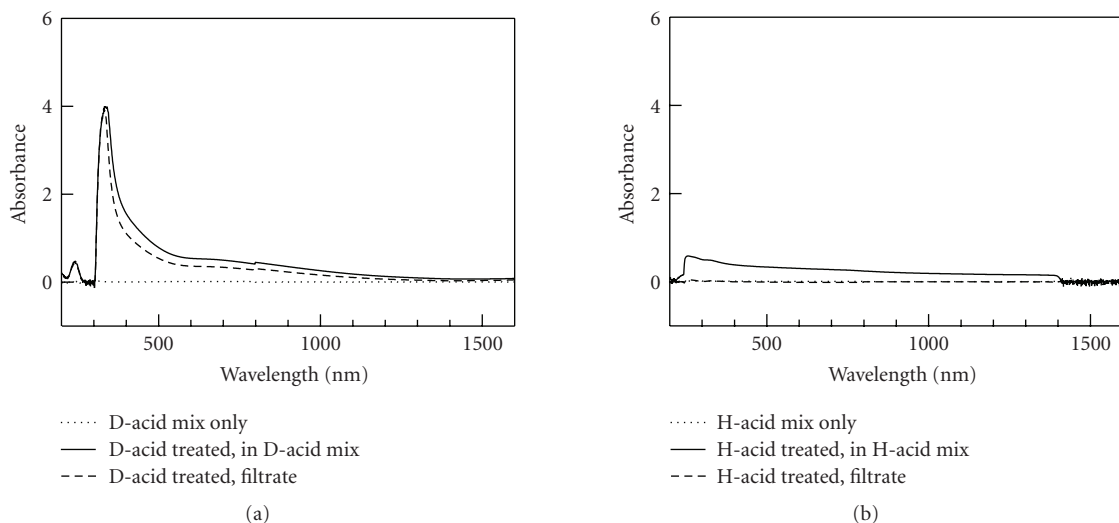


FIGURE 3: UV-Vis spectrum of (a) D-acid mixture sample, (b) H-acid mixture sample.

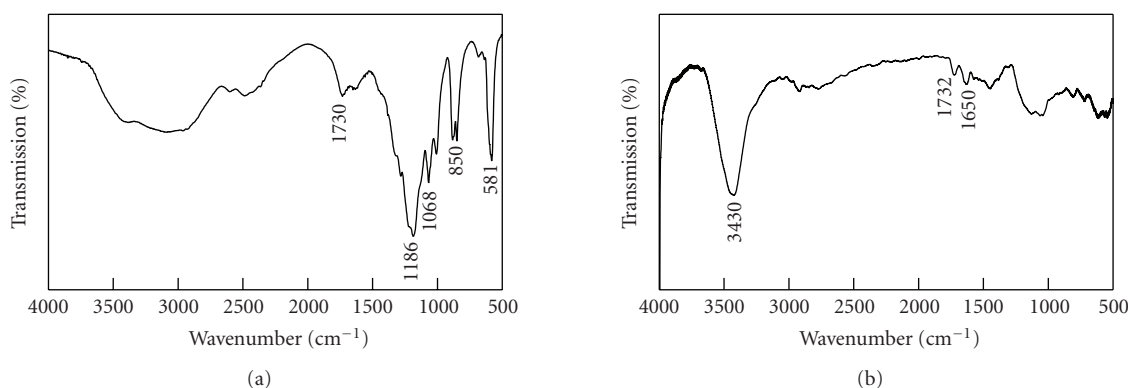


FIGURE 4: FTIR spectra of (a) D-acid mixture sample, (b) H-acid mixture sample.

hydraulic press. The FTIR spectrum was recorded using these pellets. The FTIR spectrum for the D-acid mixture-treated sample I precipitate (Figure 4(a)) displays bands at $\sim 1732\text{ cm}^{-1}$ that may be due to the presence of C=O from carboxylic acid groups, various bands between 1000 and 1185 cm^{-1} consistent with C–O–C bonds and C–O stretching frequencies, and bands between 400 and 900 cm^{-1} which likely represent aromatic rings [10]. The intermediate bands between 1000 and 1185 cm^{-1} are also in the range of the C–D bending mode [11]. For the H-acid samples shown in Figure 4(b), the band at 3430 cm^{-1} represents the stretching frequency of –O–H groups, while the bands at 1732 and 1650 cm^{-1} are attributed to the C=O bonds in saturated and aromatic carboxylic acid. As expected, when sample I was diluted with D_2O , the –O–H stretching was not present at $\sim 3400\text{ cm}^{-1}$.

The strong presence of C–O, C–O–C and aromatic carbon in the sample I spectra may be caused by a larger number of defects on the nanotube sidewall resulting from the stronger interaction of heavy water (D_2O) in the D-acid

mixture with the SWNTs. Such a hypothesis is consistent with *ab initio* results discussed in the literature which suggest that a D-bond is stronger than an H-bond based on their respective binding energies [12]. In addition, a recent computational study of water and single-layer graphite found sufficiently large binding energies that are believed to be important in the interaction of water with carbon nanotubes [13, 14]. We hypothesize that water (D_2O and H_2O , resp.) in the D-acid and H-acid mixtures interacts with the carbon nanotube walls. In the case of the D-acid mixture, a combination of the higher binding energy of (i) DOD in D-acid mixture and (ii) further dilution of the concentrated solution into heavy water and D-acid mixture (also containing D_2O) results in a stronger interaction with the SWNTs, resulting in the apparent increased solubility for the D-acid treatment observed here. Other researchers have also reported that strong C–D interactions are responsible for deuterium attachment to carbon nanotubes [11]. Thus our preliminary conclusion is that the apparent enhanced solubility of the SWNTs subjected to the D-acid treatment

is due to stronger interaction of D₂O with the SWNTs in comparison to H₂O available in the H-acid treatment.

In summary, we have found that the treatment of as-received single-wall carbon nanotubes with the deuterated form of the 3 : 1 sulfuric to nitric acid treatment results in an apparent solubility enhancement of the nanotubes. This observation is consistent with the limited number of computational and experimental results published in the literature regarding the interaction of carbon nanotubes with deuterated solvents; however, a detailed understanding of the underlying mechanism responsible for this observation is currently lacking. This reported experimental observation regarding the interaction of carbon nanotubes with different forms of chemical treatments should be further investigated both experimentally and theoretically. In particular, at the moment one cannot rule out the possibility that the D-acid treatment results in significantly greater levels of damage to the structure of the SWNT, which in effect could lead to fragments of oxygenated polyaromatic hydrocarbons having similar UV-Vis and IR spectra as the oxidized SWNTs. In any case, the apparent increased solubility of the D-acid treated SWNTs (or, alternatively, the large-scale structural damage resulting from the D-acid treatment) is of both scientific and technological interest. The increased solubility observed here could be utilized in many applications where carbon nanotube dispersion is required.

ACKNOWLEDGMENTS

We gratefully acknowledge comments by Sasha Stankovich and the grant support from the NASA University Research, Engineering and Technology Institute on Bio Inspired Materials (BIMat) under Award no. NCC-1-02037. The useful comments from an anonymous reviewer on an earlier version of this manuscript are also appreciated.

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