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# Variation of single wall carbon nanotube dispersion properties with alkyl amide and halogenated aromatic solvents

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## ABSTRACT

Organic solvents from the alkyl amide and halogenated aromatic classes have been analyzed as dispersion agents for high purity single wall carbon nanotubes (SWCNTs). The resulting dispersions from two novel SWCNT solvents, N,N,N′,N′-tetramethylmalonamide (TMMA) and 1-chloronaphthalene (1-CLN), have been compared to the well-established solvents, N,N-dimethylacetamide (DMA) and 1,2-dichlorobenzene (DCB). Optical absorption spectroscopy on a series of high purity SWCNT concentrations was used to obtain solvent-dependent dispersion limits, extinction coefficients, and dispersion stability. The variation in SWCNT optoelectronic properties was measured for each solvent dispersion as a function of ultrasonication time and the results demonstrate that under conventional ultrasonication times the halogenated aromatic solvents (DCB and 1-CLN) can significantly affect the SWCNT optical absorption. A post-dispersion analysis was performed on samples, after removal of the solvents, by Raman spectroscopy to monitor structural changes in the SWCNTs. The spectroscopy results for the halogenated aromatic solvents are consistent with formation of a sonopolymer and subsequent interaction with the SWCNTs. In comparison, the alkyl amide solvents (DMA and TMMA) show similar dispersion limits with no significant change in absorbance as a function of ultrasonication, and can easily be removed without affecting the SWCNTs.

## 1. Introduction

Because of their unique electrical, optical, and mechanical properties; single wall carbon nanotubes (SWCNTs) are being evaluated for a variety of applications such as lithium ion batteries, organic solar cells, and polymeric actuators [1–3]. The opportunity to capitalize on these properties in functional devices depends on the successful characterization and manipulation of SWCNTs from synthesis through purification. This is usually performed with stable solution-phase SWCNT dispersions, where the dispersing media needs to overcome the nanotube sidewall interaction from bundling ($\sim 1\,\mathrm{eV\,nm^{-1}}$) [4]. A stable dispersion is accomplished when the SWCNT-dispersing media interaction energy is more favorable compared to the media–media or nanotube–nanotube interaction [5]. The ability to effectively disperse and individualize SWCNTs for optical spectroscopy studies has been demonstrated successfully with dispersing agents like polymers, ionic surfactants, and most recently with bile salts [6–8]. However, the SWCNT surface can become inhibited for further chemical modification by the dispersing agent and subsequent removal of the agent can alter the physical structure of the SWCNTs [9]. An alternative to surfactant dispersions that has received considerable attention is the use of organic solvents. One potential advantage of this approach is the ability to simply remove the solvent through evaporation. In addition, the dispersions can be used in processing steps for applications such as organic coupling reactions, polymer encapsulation, and composite fabrication [10].

Two classes of organic compounds have emerged for dispersal of SWCNTs, namely alkyl amides and halogenated aromatics. Of the extensively studied solvents from each class, N,N-dimethylacetamide (DMA) and 1,2-dichlorobenzene (DCB) have demonstrated the highest dispersion limits and potential utility [11,12]. SWCNT–DCB interactions have been associated with electronic properties such as strong π–π and hydrophobic interactions as well as a weak dipole–dipole relationship [13,14]. Others have observed DCB to polymerize with ultrasonication and concluded that a sonopolymer wrapping of SWCNTs is the primary mechanism of dispersion [15]. In the case of alkyl amide solvents, effective SWCNT dispersion has been attributed to the dipolar resonance structures from the lone pair electrons on the amide nitrogen which can promote an induced dipole–dipole interaction [11,13]. The alkyl amide solvents, which have the largest contribution from dipolar

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resonance structures, within favorable SWCNT steric constraints for $\pi$-orbital overlap, are predicted to have the highest dispersion limit; as was reported recently for DMA [11].

The reports on SWCNT–solvent relationships and dispersion limits will vary with SWCNT synthesis method (i.e., HiPco, laser, arc, etc.) due to the variation in SWCNT properties such as purity, defect density, chirality, and diameter distributions [16]. The formation of stable solutions in both classes of organic solvents defines a set of structural and electronic properties that act favorably with SWCNTs, but whether these attributes are specific to a solvent or class of solvents is not particularly clear. A systematic comparison of these classes of solvents on the same sample of high purity SWCNTs is necessary to elucidate any differences in dispersion properties and SWCNT–solvent interaction.

## 2. Experimental

### 2.1. Overview

The variation in SWCNT dispersion properties (i.e., dispersion limit ($D_L$), extinction coefficients, and dispersion stability) has been examined to investigate the nature of organic solvent interaction and to evaluate whether a unique mechanism exists within the solvent classes. In addition to a direct comparison of the solvent effects on the dispersion of high purity SWCNTs in DCB and DMA, a new solvent from each class (1-chloronapthalene (1-CLN) for the halogenated aromatics and N,N,N′,N′-tetramethylmalonamide (TMMA) for the alkyl amides) has been included. Using optical absorption and Raman spectroscopy, the effects of solvent structure and ultrasonication time were measured for dispersions containing equivalent concentrations of high purity SWCNTs.

### 2.2. SWCNT synthesis and purification

The SWCNT materials were synthesized by laser vaporization using a pulsed alexandrite laser as described previously [17]. The reaction furnace temperature was maintained at 1150 °C, with a chamber pressure of 760 Torr under 200 sccm flowing Ar. The target was pressed at 2500 psi and contained 94% (w/w) graphite (1–2 μm), 3% (w/w) Ni (submicron), and 3% (w/w) Co (1–2 μm). The raw SWCNT soot was purified by acid reflux at 120 °C for 14 h as described previously [17]. The reflux solution was filtered over a 1 μm PTFE membrane filter with excess distilled $H_2O$ to form a SWCNT paper. The acid filtrate was discarded and subsequently washed (3×) with acetone and distilled $H_2O$ until the filtrate was clear removed functionalized carbon impurities. The resulting paper from acid reflux was ultimately purified with a final oxidation in air at 550 °C for 30 min; the appropriate conditions of time and temperature were found using thermal oxidation profiling (TOP) [18].

### 2.3. Optical absorption

Initial dispersions of SWCNTs were prepared for each of the four solvents at 25 $\mu g\,mL^{-1}$ using bath ultrasonication (40 kHz) at 40 °C. A concentration series for each solvent was prepared by serial dilution with the pure solvents to obtain concentrations of 12.5, 6.25, 3.13, 1.56, 0.78, and 0.39 $\mu g\,mL^{-1}$. The DMA (≥99%, Aldrich) and TMMA (>97%, TCI) dispersions were ultrasonicated for 30 min after each dilution. The DCB (99%, Aldrich) and 1-CLN (90%, Aldrich) dispersions were ultrasonicated for 5 min and each subsequent dilution was ultrasonicated for 1 min. UV–vis-NIR spectra were obtained for each SWCNT–solvent dispersion using a PerkinElmer Lambda 900 spectrophotometer in a 1 cm cuvette [11]. The ultrasonication-induced effects on both the pure solvents and the SWCNT–solvent dispersions (for a stable concentration below the determined $D_L$) were measured by optical absorption after ultrasonication at 5 min increments. Dispersion stability was evaluated by measuring time-dependent absorption measurements on SWCNT–solvent dispersions (at a concentration below the determined $D_L$) in 15 min increments until the absorbance decreased below 95% of the original peak maximum intensity at 1.27 eV, corresponding to absorption from the secondary set of semiconducting transitions ($^SE_{22}$).

### 2.4. Raman spectroscopy and atomic force microscopy

Raman spectroscopy was performed at room temperature using a JY-Horiba Labram spectrophotometer from 100 to 3000 $cm^{-1}$ with excitation energy of 1.96 eV (He/Ne laser). The Raman samples were prepared by ultrasonicating SWCNTs for 30 min at a concentration of 25 $\mu g\,mL^{-1}$ in each solvent. The semi-dispersed solutions were decanted onto a glass slide at 50 °C, and compared to the initial purified SWCNT paper. Atomic force microscopy (AFM) was performed using a Veeco Multimode SPM in contact mode. Samples were prepared from a 3.13 $\mu g\,mL^{-1}$ dispersion of SWCNTs in each solvent, which were ultrasonicated for 30 min. A drop of each solution was decanted on a cleaved mica surface at 80 °C.

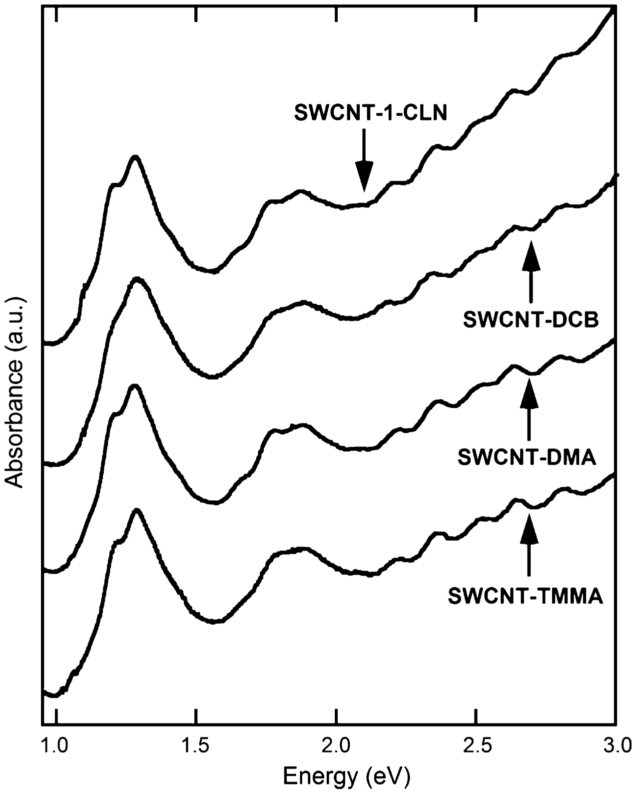

**Fig. 1.** Optical absorption overlay of normalized absorbance ($^SE_{22}$ peak) versus energy for 3.13 $\mu g\,mL^{-1}$ of purified SWCNTs in each of the four solvents.

## 3. Results

### 3.1. Optical absorption analysis

The SWCNT material used in the current study was purified to at least the equivalent of the "100%" reference standard from previous work and a concentration series was prepared by serial dilution of a 25 $\mu g\,mL^{-1}$ stock dispersion for each solvent series [11,18]. The ultrasonication time was kept to a minimum based upon previous work for DCB [15]. Optical absorption spectroscopy was performed on the concentration series for each solvent. Representative optical absorption spectra for each of the SWCNT–solvent dispersions at a concentration of 3.13 $\mu g\,mL^{-1}$, which is below the $D_L$ for each solvent, are shown in Fig. 1 (data offset in the figure for clarity). The well-resolved absorption peaks show no major shifts between solvents and are consistent with the electronic transitions between allowed states within the dimensionally confined density of states for purified laser SWCNTs. The prominent peaks at 1.27 eV are due to the absorption from the second set of transitions for semiconducting SWCNT chiralities and the peak at 1.86 eV originates predominantly from metallic-type SWCNT absorption [19]. Each SWCNT–solvent dispersion shows comparable peak intensities with the FWHM exhibiting subtle broadening for the DCB dispersion.

The $D_L$ for each SWCNT–solvent combination has been estimated using a Beer's Law analysis by evaluating the peak maxima value of 1.27 eV for each dispersion concentration [11]. The point at which the data deviates from a linear trendline is assigned as the $D_L$ (see values in Table 1). The spectroscopic analysis showed a correlation with the visual observation of undispersed sediment after centrifugation for the concentrations greater than the $D_L$. The variation in dispersion limit is attributed to the nature of interaction between each of the solvents with high purity laser SWCNTs. In the case of the alkyl amides, TMMA shows at least a factor of two higher