Purity Assessment of As-Produced Single Wall Carbon Nanotube Soot

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Introduction

The unique electrical, optical, and mechanical properties inherent to single wall carbon nanotubes (SWNTs) have garnered tremendous efforts in basic science and applied research [1]. Further development of SWNT-based applications is expected to require material standardization, specifically in the area of electronic type and degree of purity. Although a variety of experimental methods have been employed in the fabrication of SWNTs (typically arc-discharge, chemical vapor deposition, and pulsed laser vaporization), each technique produces SWNTs with differing distributions of electronic types and relative amounts of synthesis by-products [1]. In general, these by-products can be a significant component of the as-produced materials or raw SWNT "soot." By-products such as secondary graphitic and non-graphitic carbon phases, metal catalysts, fullerenes, and carbonaceous coatings on the SWNTs may not only dominate the physical characteristics of the raw soot, but they also pose significant challenges in subsequent purification [2,3].

Techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV-Vis-NIR spectroscopy, thermogravimetric analysis (TGA), and Raman spectroscopy have been employed to estimate the “purity” of a given SWNT-containing sample [2,3]. Recently, attempts to more accurately quantify the “purity” have been proposed via UV-Vis-NIR spectroscopy on SWNT-DMF dispersions and Raman spectroscopy on constructed samples [4]. The optical absorption study showed that the degree of SWNTs present in a sample can be directly related to the absorbance of the electronic transition corresponding to the semiconducting peak at the energy of the 2^{nd} Van Hove singularity. In addition, others have proposed a relationship between the Raman tangential mode shift and laser power density as another means to quantify the relative SWNT fraction in a carbon-containing sample [5]. Ultimately, the definition of purity is application-specific where some may require single chirality (n,m) SWNTs and others desire type-pure (semiconducting or metallic). In this paper, “purity” is investigated in relation to the total mass fraction of SWNTs (w_{SWNTs}) contained within the carbonaceous component of the sample.

SWNTs produced by the pulse laser vaporization process were analyzed using solvent dispersions in N,N-dimethylacetamide (DMA) as recently reported [6]. Production of stable SWNT-DMA dispersions without the use of surfactants or functionalization strategies emerges as an extremely attractive technique for probing the electronic properties of SWNTs. The results from UV-Vis-NIR spectroscopy of SWNT-DMA dispersions have shown highly resolved spectra, enabling the subsequent

deconvolution of the peaks corresponding to both the semiconducting and metallic SWNT types. This technique has been used to estimate w_{SWNTs} for a constructed sample set comprising purified SWNTs and nanostructured carbon to within 1% of the designed values. An extension of this approach is expected to accurately quantify w_{SWNTs} in any raw soot and serve as an experimental guide during the purification process.

Experimental

SWNTs were synthesized using the pulse laser vaporization technique, employing an Alexandrite laser (755 nm). The laser pulse was rastered over the surface of a graphite (1-2 micron) target doped with 2% w/w Ni (submicron) and 2% w/w Co (< 2 micron), at an average power density of 100 W/cm^2. The reaction furnace temperature was held at 1150°C, with a chamber pressure of 700 torr under 100 sccm flowing $Ar_{(g)}$. The as-produced SWNT soot was collected from the condensed region on the quartz tube at the rear of the furnace. Synthesis of a representative nanostructured carbon (NC) component in the raw soot was performed by laser vaporization at the described conditions for an undoped graphite target, devoid of SWNTs detectable by SEM, Raman or optical absorption spectroscopies [6].

Analysis of SWNTs was performed by scanning electron microscopy (SEM), Raman spectroscopy, and thermogravimetric analysis (TGA). The SEM was operated at 2kV using a Hitachi S-900, with samples applied directly to the brass stub using silver paint. Raman spectroscopy was performed at room temperature using a JY-Horiba Labram spectrophotometer from 50 – 2800 cm^{-1} using an incident beam attenuation filter, with excitation energies of 1.96 and 2.54 eV. These energies have been shown to probe the metallic and semiconducting laser-generated SWNTs, respectively, over the range of diameters used in this study [7]. Thermogravimetric analysis (TGA) was conducted using a TA Instruments 2950. Samples were placed in the platinum pan balance in quantities of ~1 mg and ramped at 5ºC/min from room temperature up to 950ºC under air at a gas flow rate of 60 sccm and $N_{2(g)}$ balance purge at a gas flow rate of 40 sccm [6].

Purification of SWNT soot was performed using a modification of a previously reported procedure [2]. Approximately 50 mg of raw SWNT soot was brought to reflux at 125 ºC in 3M nitric acid for 16 hours, and then filtered over a 1 μm PTFE membrane filter with copious amounts of water. The filter paper was rinsed consecutively with acetone, ethanol, 2.5 M NaOH, and H_2O until filtrate became colorless after each step. The membrane filter was dried at 70°C in vacuo to release the resulting SWNT paper from the filter paper. The SWNT paper was thermally oxidized in air at 550°C for 1 minute in a Thermolyne 1300 furnace. Finally, a 6M Hydrochloric acid wash for 60 minutes using magnetic stirring, with similar filtering steps and thermal oxidation at 550°C for 20 minutes completed the purification [6].

UV-Vis-NIR spectra were obtained on stable dispersions of SWNTs in N,N-dimethylacetamide (DMA)using a Perkin Elmer Lambda 900 spectrophotometer. The dispersions were analyzed after ultrasonication, centrifugation, and decantation. Sample handling for dispersion solutions involved the use of 1 cm quartz cuvettes, while dry SWNT samples were air sprayed from a 0.1 mg/mL acetone solution onto 1 in^2

quartz slides. The instrument scanned over a wavelength range of 300-1600 nm at a data interval of 1 nm. The electronic transitions probed in this optical absorption analysis are $^{S}E_{22}$, $^{M}E_{11}$, and $^{S}E_{33}$, due to the absorption windows of the alkyl amide solvents [6].

Results and Discussion

The relationship between optical absorption spectroscopy and solute concentration has been well established using Beer's Law and has recently been applied to SWNT purity assessment [6]. In our previous work on SWNT-solvent dispersions, the ability to form stable dispersions of both raw and purified SWNTs was demonstrated and the corresponding optical absorption spectra were easily obtained (Figure 1). Additionally, the extinction coefficients (ε) for nanostructured carbon (NC), raw SWNT soot, and purified SWNTs were calculated. These values for an established diameter distribution (~1.2 - 1.4 nm) and metallic to semiconducting ratio, can be used to calculate w_{SWNTs} in a SWNT-containing sample, using Equation 1:

$$w_{SWNTs} = \frac{\zeta}{1+\zeta} \qquad \text{where} \qquad \zeta = \frac{(A_{M_{E_{11}}} \cdot \varepsilon_{NC_{S_{E_{22}}}} - A_{S_{E_{22}}} \cdot \varepsilon_{NC_{M_{E_{11}}}})}{(A_{S_{E_{22}}} \cdot \varepsilon_{M_{E_{11}}} - A_{M_{E_{11}}} \cdot \varepsilon_{S_{E_{22}}})} \qquad (1)$$

This expression is derived from the ratio of absorption maxima (A) for the semiconducting ($^{S}E_{22}$) and metallic ($^{M}E_{11}$) peaks. The equation is valid for a fixed SWNT distribution and is dependent on the purified SWNT extinction coefficients being representative of a 100% sample. Such a reference sample is however, not yet known to be available since the techniques for assessing purity are currently under development. However, our reference sample has shown the highest degree of purity based on SEM, TEM, TGA, UV-Vis-NIR, and Raman spectroscopy.

To establish the accuracy of estimating w_{SWNTs} with Equation 1, a series of reference samples were constructed using purified laser SWNTs and NC. Shown in Figure 2 are the optical absorption data corresponding to each reference sample at a total concentration of 3 μg/mL in a DMA dispersion. Evident from the data is the general trend towards more resolved peak structure with higher SWNT content. The results as shown in column 2 of Table 1 indicate that this estimation technique, which includes the transitions from both semiconducting and metallic components, is within 3% of the designed value. This approach is in contrast to the previous report where the optical absorption analysis only considers the absorption from semiconducting SWNTs [4]. Equation 1 only provides a value for w_{SWNTs}, however, further analysis can lead to the semiconducting to metallic ratio and individual diameter concentrations.

To investigate these aspects, the removal of the SWNT π–plasmon and the NC absorbance backgrounds from the reference data is necessary. Various methods for estimating the π-plasmon contribution were investigated, two of which are shown in Figure 3. The linear fit is simple, but obviously overestimates the plasmon contribution. Due to the resonant nature of the plasmon excitation, a Lorentzian distribution was

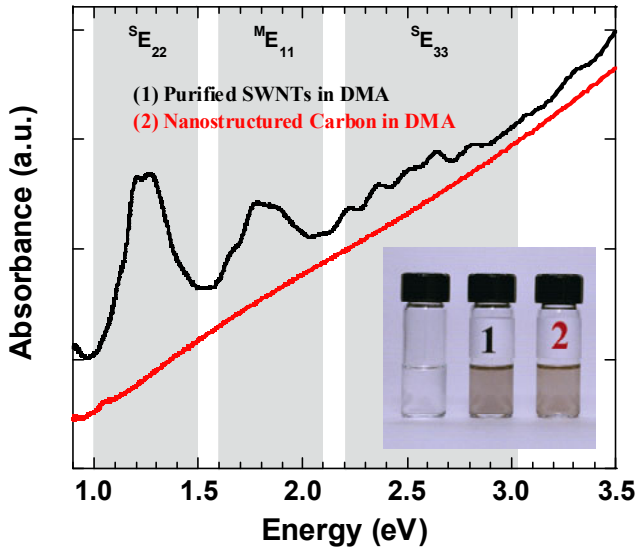

Figure 1. Optical absorption spectrum of (1) purified SWNTs in DMA and (2) NC in DMA. The inset photograph displays the actual solutions used to generate the data in the plot. The gray bands indicate the range of electronic transitions for the diameter distribution and are denoted by the symbols for semiconducting ($^{S}E_{22}$ and $^{S}E_{33}$) and metallic ($^{M}E_{11}$).

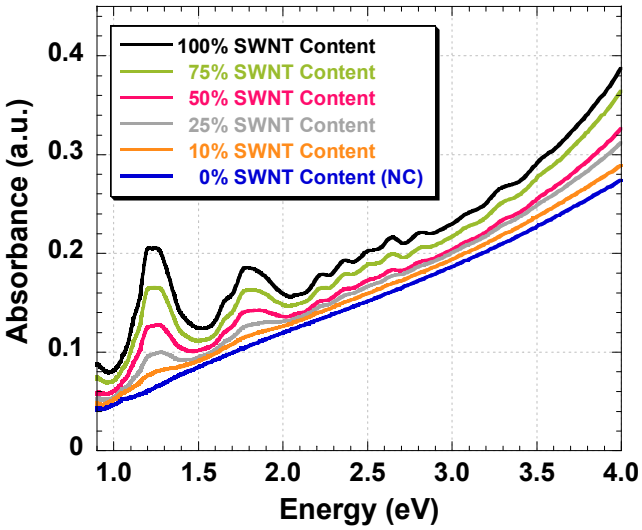

Figure 2. Optical absorption spectra of the reference sample set comprising purified SWNTs and nanostructured carbon (NC) in DMA at described percent weight levels with each solution having a total concentration of 3 μg/mL.

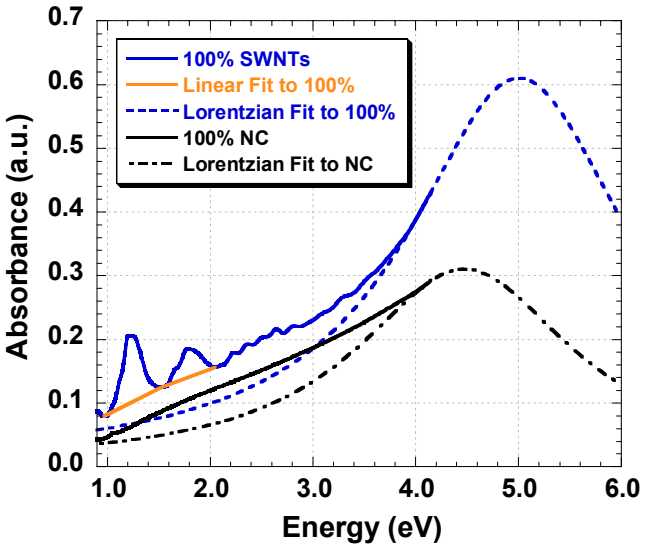

Figure 3. Optical absorption spectra of purified SWNTs and NC (solid lines) with corresponding π-plasmon Lorentzian fits (dashed lines).

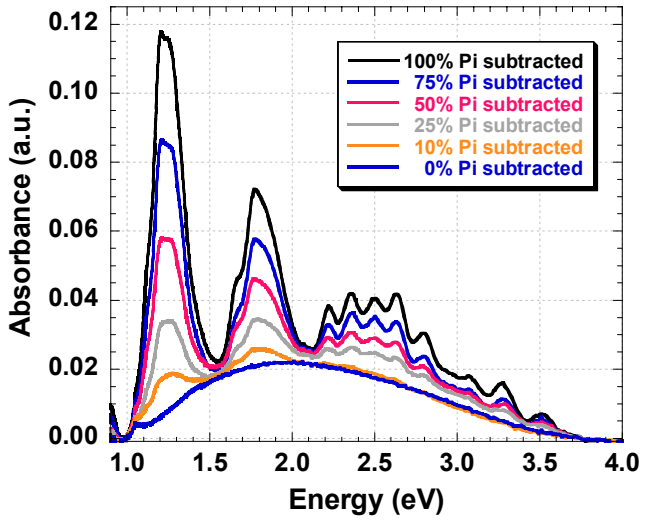

Figure 4. Optical absorption spectra of the reference sample set after π-plasmon subtraction using a Lorentzian fitting function.

utilized as the fitting function. As can be seen in Figure 3, the Lorentzian fit predicts a plasmon energy of approximately 4.5 eV for the NC and 5.0 eV for the 100% SWNT sample, this is in general agreement with the values reported in the literature of 5 – 7 eV [8-10]. Using the Lorentzian fitting function, the π-plasmon contribution was subtracted from each of the reference curves resulting in figure 4. In order to subtract out the contribution of NC in the remaining data, the weighted value of the NC curve was subtracted from each of the other curves resulting in figure 5. The curves in figure 5 have been normalized to the maximum value of the 100% reference sample. The

values of the peak amplitudes for the other samples relative to the 100% values, for both the $^{S}E_{22}$ and $^{M}E_{11}$ peaks, are given in columns 3 and 4 of Table 1. It is clear that these fractions yield very good agreement with the designed mass fractions for these samples with a standard deviation of 1%. This suggests that there are no more contributions to the absorption to be considered. The fully subtracted data enhance the fine structure for the higher energy transitions associated with $^{S}E_{33}$ and $^{M}E_{22}$, which may allow for the determination of individual diameter concentrations. Also, given values for the extinction coefficients for phase-pure semiconducting and metallic SWNTs, the semiconducting to metallic mass ratio can be determined from this data.

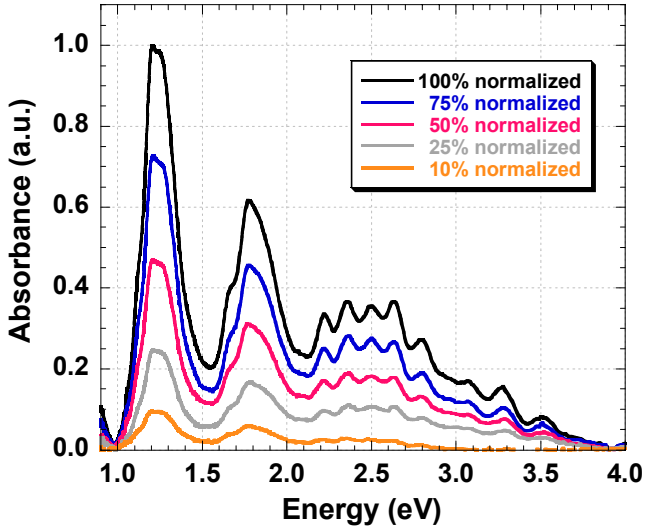

Figure 5. Optical absorption spectra of the reference sample set from Figure 4 which has been corrected for the NC absorbance contribution and normalized.

Table 1. Overview of purity assessment techniques for the constructed reference samples based on Equation (1) and the deconvolution shown in Figure 5.

	Assessment Technique		
Designed w_{SWNTS}	Equation (1)	Subtracted 1.27 eV	Subtracted 1.77 eV
100%	95%	100%	100%
75%	73%	72%	74%
50%	47%	47%	50%
25%	25%	25%	27%
10%	12%	9%	10%
St. Dev.	3%	1%	1%

Conclusions

The use of SWNT-DMA dispersions in optical absorption spectroscopy has been shown to enable the accurate determine of SWNT purity, as defined by the mass fraction, w_{SWNTs}, of the carbonaceous content. Two methods have been employed to assess w_{SWNTs}, the ratio of absorption maxima for $^{S}E_{22}$ and $^{M}E_{11}$, and the non-linear regression modeling of the π-plasmon. These techniques have been applied to a reference sample set, yielding verifiable agreement to within 3% of the designed value. An extension of this analysis can lead to the semiconducting to metallic ratio and individual diameter concentrations for a given SWNT sample. Correlation of the optical absorption spectra with equivalent data from Raman spectroscopy will allow for refinement in diameter distribution analysis. Combination of the optical absorption spectra with TGA profiles for SWNT-containing samples should lead to a more thorough understanding of the decomposition dynamics.

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