

Inverted Spectra of Single-Wall Carbon Nanotube Films

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We present absolute measurements of reflectance and absorbance for a purified single wall carbon nanotube (SWCNT) film. The absorbance spectrum of a SWCNT-laminated pyroelectric detector for wavelengths 0.6–2 μm is inverted when compared to absorbance data in the literature, which is typically inferred by reciprocity from transmissivity measured by a spectrophotometer. This surprising behavior has been corroborated by diffuse reflectance measurements and suggests that reflectance dominates absorption for wavelengths near excitonic transitions.

Introduction

In the literature, we commonly see absorbance for single wall carbon nanotubes (SWCNTs) in solution based on transmittance from spectrophotometer-based measurements. This is presented in terms of arbitrary units (AU) and sometimes with an estimate of the optical density.^{1,2} This strategy has been repeated for various types of carbon nanotubes and widely adopted. The absorbance is fairly assumed to be complementary to the transmittance, while the reflectance is neglected and the spectrum is characterized by local maxima (peaks) near the excitonic transitions. Only in certain instances (see for example, Barnes, et al.,³ Wang, et al.⁴) is reflectance addressed, much less explicitly accounted for. In the past, the spectral responsivity of a pyroelectric detector coated with a single wall carbon nanotube (SWCNT) sample has been documented as a means to determine the absolute absorbance of bulk SWCNT samples.⁵ We have been forced to question the absorbance results because our spectra are characterized by local minima (dips) where others show peaks. In the present work, we document diffuse reflectance and specular absorbance of a SWCNT film and assert that the appearance of spectral features is dominated by reflectance rather than absorbance. We begin by describing the preparation of the SWCNT material followed by a description of the pyroelectric detector operation and measurements.

The SWCNTs were synthesized by a laser vaporization method similar to that reported previously.⁶ The SWCNTs were purified by oxidation of the raw soot in flowing CO_2 at 800 °C for 1 h, followed by a reflux in 3 M HNO_3 for 16 h. The solution was then filtered, and the filtrand was washed and dried at 50 °C for 30 min. During this drying process the SWCNTs separated from the filter, producing a free-standing “bucky paper” or film. The film was further oxidized in air at 550 °C for 30 min. The material purity was greater than 97% by weight as determined by thermogravimetric analysis.

Raman spectroscopy with laser excitation (E_{laser}) at 2.54 eV was employed to analyze the disorder induced D-band at $\sim 1350 \text{ cm}^{-1}$. The full width at half-maximum (fwhm) of the D-band

was $\sim 18.7 \text{ cm}^{-1}$, and the D/G ratio was 0.011. The frequencies of the radial breathing modes indicated that the resonant diameter distribution was in the range of 1.3–1.5 nm. Therefore, the fwhm of the D-band for the purified sample is consistent with material that is substantially free of non-nanotube carbon impurities.⁷ Raman spectra taken with $E_{\text{laser}} = 1.96 \text{ eV}$ indicated a broader resonant diameter range of approximately 1.2–1.7 nm.

We have completed several additional measurements of the same SWCNT material and the measurement results are the emphasis of this work: (1) specular absorbance of the laminated detector (2) diffuse reflectance of the same detector, (3) transmittance of the sample in solution, and (4) transmittance of a semitransparent film (semifilm) sample on a quartz slide. The specular absorbance was determined by measuring the spectral responsivity of the SWCNT laminated pyroelectric detector. The diffuse reflectance of the bucky paper sample was measured *in situ* on the detector. A semitransparent film sample was prepared from a chloroform dispersion that was sonicated for 1 min using an ultrasonication microtip, followed by 15 min in an ultrasonication bath, and then deposited on a quartz substrate by airbrush. A solution phase sample was prepared by sonicating 0.1 mg/mL purified SWCNTs in DMF with a microtip for 1 min, followed by 15 min in a sonication bath. This solution was then diluted to 0.025 mg/mL and placed in a sonication bath for 5 min. The optical absorption spectra of purified SWCNT samples were measured by a Perkin-Elmer Lambda 19 spectrophotometer. [Note: The description of commercial products is given for completeness and does not represent an endorsement by NIST.]

The pyroelectric detector to which the SWCNTs were applied was prepared from a z-cut LiTaO_3 plate 12 mm in diameter and 60 μm thick. The electrodes centered on the back side of the LiTaO_3 plate were 10 mm in diameter and consisted of 50 nm of gold on top of 25 nm of chromium. The front electrode, to which the SWCNTs were applied, was 25 nm of chromium. The back electrode was connected to the signal input of a current amplifier with 10^{-10} A/V sensitivity, and the front electrode was connected to ground. The optical input to the detector was modulated at 8 Hz and measured with a lock-in detection scheme.⁸ A SWCNT film approximately 4 mm \times 8 mm square with an average thickness of 10 μm (see Figure 1a), was placed

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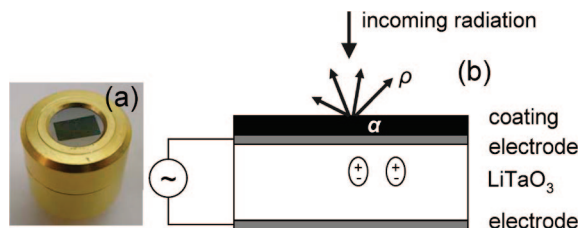


Figure 1. (a) Photo and (b) schematic diagram of pyroelectric detector with coating absorbance, α , and reflectance, ρ .

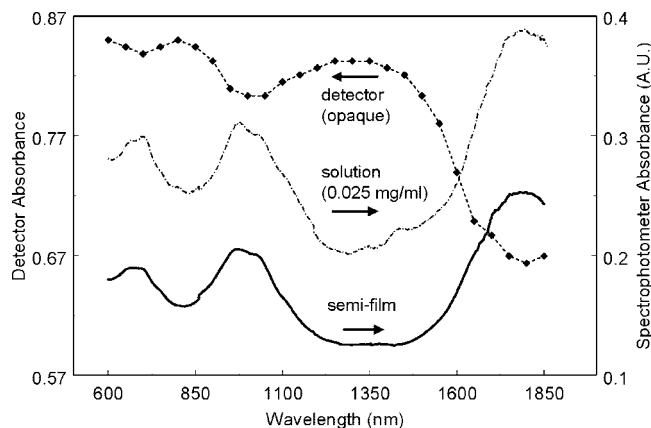


Figure 2. Absorbance determined by detector responsivity (\blacklozenge) and spectrophotometer transmittance of the solution sample ($- \bullet -$) and semifilm ($-$).

on the front with a drop of chloroform to facilitate adhesion. The film then remained laminated to the detector after the chloroform evaporated. A photo of the laminated detector and a schematic representation is shown in Figure 1.

Although the principles of the pyroelectric detector method are well-known, it is important to emphasize that the spectral responsivity of the pyroelectric detector is proportional to the absorbance, α , of the coating. The current, i , generated by the detector may be expressed as

$$i = \alpha p \frac{A}{h} \int_0^h \frac{d\theta}{dt} dz \quad (1)$$

where p is the pyroelectric coefficient, A is the area of optical probe, h is the thickness, and $d\theta/dt$ is the change in detector temperature with respect to time. The pyroelectric coefficient may be considered a scalar if it is assumed to be constant and isotropic relative to the orientation of the spontaneous polarization (z -axis of the crystal), which is perpendicular to the detector faces.⁹ Therefore, knowledge of the absolute spectral responsivity in units of A/W , is a means to measure α .

The measurement system for the spectral responsivity consists of a lamp source, a grating monochromator, and a NIST transfer-standard detector.¹⁰ The method of direct substitution provides absolute spectral responsivity relative to the NIST standard at 10 nm wavelength increments from 600 nm – 2000 nm with a relative expanded uncertainty of 1.24%. For this work, the beam exiting the monochromator was focused on the film to a beam size of approximately 2 mm \times 2 mm, normal to the plane of the detector surface, with a bandwidth of 10 nm or less. Since the detector responsivity is measured in absolute terms, the absorbance may be calculated from eq 1. The absorbance based on the responsivity measurement results are plotted in Figure 2 opposite the absorbance of the cuvette sample and semifilm that was measured with the spectrophotometer.

The spectral diffuse reflectance of the SWCNT film, while situated on the detector, was measured with the Measurement

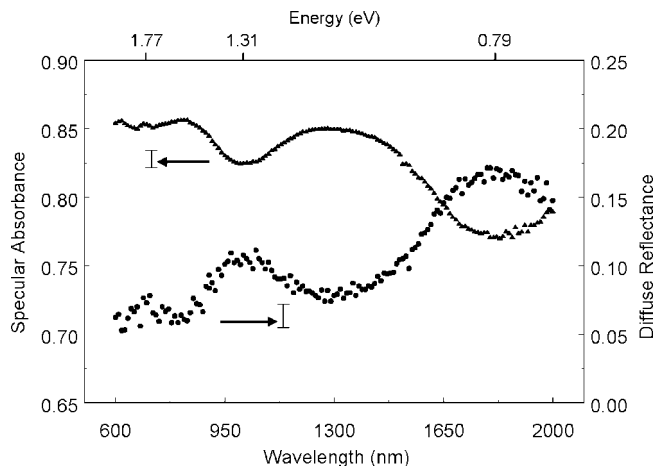


Figure 3. Specular absorbance (\blacktriangle) and diffuse reflectance (\bullet) for the SWCNT sample. The uncertainty is indicated with sample error bars.

Standards Laboratory (MSL) spectrophotometer. This system is configured around a monochromator of 1 m focal length, equipped with a prism predisperser, and has a numerical aperture of $f/8.7$. The exit beam of the monochromator was collimated by a 10° off-axis parabolic mirror with a focal length of 190 mm. A second parabolic mirror of 350 mm focal length produced a 4 mm by 3 mm image at the sample port of an integrating sphere lined with pressed halon. The sample was measured against an MSL working standard of pressed halon from 600 to 2000 nm in increments of 10 nm with a 0.3 nm bandwidth. The total estimated relative uncertainty of the reflectance measurement varies with wavelength; 0.002 at wavelengths less than 1100 nm and 0.005 from 1100 to 1800 nm ($k = 2$). The measurement results are plotted in Figure 3, opposite those of responsivity.

From the theory of an effective media,¹¹ reflectance may depend on anisotropy and topology of the SWCNT preparation if the percolation threshold is on the order of the wavelength being absorbed. At the extreme, SWCNTs in bulk become a porous and efficient absorber (fluffy) and the reflectance is small and spectrally uniform.¹² In contrast, our films constitute a dense mat with a specular (visibly shiny) appearance. In earlier work⁵ we concluded that the detector spectral responsivity from 600–2000 nm is proportional to the α of the SWCNT film. This is still true, but at wavelengths where we expect to see the absorbance characterized by peaks due to the thermalization of photons, we see dips. The responsivity result is dominated by the reflection of photons and thus α , is inverted ($1 - \alpha$) compared to that which we typically see in the literature obtained by transmission data.¹³ The diffuse reflectance measurement results opposite the absorbance in Figure 3 corroborate the observation of dips rather than peaks. We clearly observe variations near 700 nm, 950 and 1750 nm that correlate with regions where we expect characteristic excitonic transitions. In Figure 4 we compare with the calculated detector reflectance the diffuse reflectance that was measured explicitly. The two sets of values differ by between 0.05 and 0.1, which is plotted opposite the reflectance in Figure 4. The difference is monotonic within the uncertainty of the two measurements, thus the two independent measurements depict the same relative wavelength-dependent reflectance.

There are several possible explanations that may individually or collectively account for the difference in Figure 4. First, there is the likelihood of *nonequivalence*.¹⁴ In this scenario, photons absorbed by the film are thermalized, but rather than being

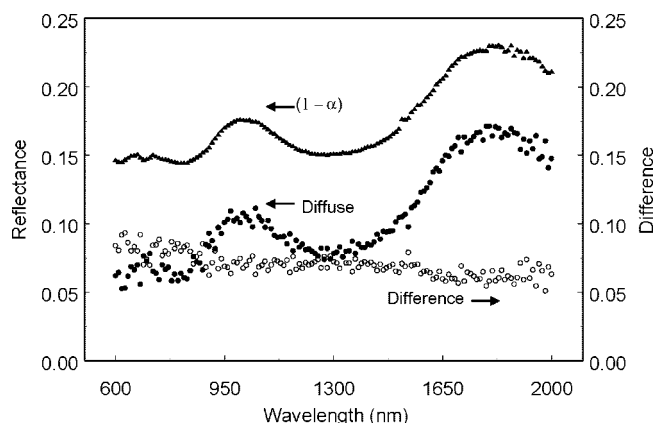


Figure 4. Comparison of calculated reflectance (▲), diffuse reflectance (●) and their difference (○) as a function of wavelength.

absorbed by the detector substrate, are reradiated as blackbody emission from the film. Scanning electron microscope images indicate that the film is a mat of intertwined bundles. Heat can be dissipated laterally along the bundles and diffused rather than being transferred toward the detector. Second, it is possible that the average film thickness is less than we measured and the detector's bucky paper coating is not completely opaque. The light transmitted on the first pass, however, will be substantially reflected or absorbed by the underlying chromium electrode and absorbed by the film on the second pass. Third, there is the possibility of fluorescence. We expect fluorescence to account for very little of the difference because it is considered to be an inefficient process under ideal circumstances and is substantially quenched (and thus thermalized) in the presence of bundles and metallic tubes.¹⁵

So far we have presented and discussed absorbance and reflectance using our own detector-based absorbance and reflectance techniques as well as the more conventional technique of measuring transmittance using a commercial spectrophotometer and inferring the optical density. The critical finding is that the reflectance of an opaque film is comparable to what is considered to be absorbance measured by a spectrophotometer. Pekker et. al, recognized the significance of scatterers in transmittance of SWCNT spectra. He notes that "Optical density is proportional to the absorption coefficient α only when reflection can be neglected."¹⁶ Determination of optical density is a critical procedure in the process of determining the purity of SWCNTs described by Zhao et al.¹⁷ Zhao et. al, concluded that, for a range of concentrations an absolute molar extinction coefficient can be determined. However, a significant portion of bulk SWCNTs typically contains scatterers (reflectors) such as metal catalyst and metallic SWCNTs.¹⁷ This is a fundamental challenge that must be recognized in order to make a correct assessment of the dielectric function of SWCNTs. Our results

illustrate that absorbance can be determined from opaque samples independent of the concentration and without the need for solvent subtraction and, following Zhao et. al and Pekker et. al, reveal important spectral features.^{16,17}

The significance of the measurement results is that spectral features near the excitonic transitions are dominated by relatively higher reflectance than by higher absorbance. From the standpoint of realizing the hope of SWCNT detector coatings, photovoltaic or photoconductor materials, or inferring other properties such as emissivity, it should be known that the absorbance in bulk is potentially different from that implied by spectrophotometer-based measurements of SWCNTs in suspension.

In light of the present work, we have begun to investigate responsivity and reflectance measurements spectrally near the pi-plasmon resonance of SWCNT films (UV) as well as farther into the infrared following the theoretical work of Pekkar et al.¹⁶ In the future we plan to present these results compared to spectrophotometer-based measurements and further investigate their validity for the basis of future documentary standards.

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