

Visible Luminescence of Carbon Nanotubes and Dependence on Functionalization

Yi Lin,[†] Bing Zhou,[†] Robert B. Martin,[†] Kevin B. Henbest,[†] Barbara A. Harruff,[†] Jason E. Riggs,[†] Zhi-Xin Guo,[†] Lawrence F. Allard,[‡] and Ya-Ping Sun^{*,†}*Department of Chemistry and Laboratory for Emerging Materials and Technology, Clemson University, Clemson, South Carolina 29634-0973, and High-Temperature Materials Laboratory, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6062**Received: June 8, 2005; In Final Form: July 4, 2005*

Strong luminescence emissions over a broad wavelength region were detected from well-dispersed carbon nanotubes in most functionalized samples, even with excitation wavelengths into the near-IR. Apparently, the better dispersion and functionalization of the nanotubes resulted in more intense luminescence emissions. These emissions may logically be attributed to the trapping of excitation energy by defect sites in the nanotube structure, which are passivated upon the appropriate functionalization of the nanotubes. Better functionalization improves not only the nanotube dispersion (thus diminishing the quenching due to intertube interactions) but also the surface passivation to make the energy trapping sites more emissive, leading to stronger luminescence emissions. Because of such high sensitivity, the visible luminescence emissions may prove valuable in the evaluation of dispersion in functionalized carbon nanotube samples and related nanocomposite materials.

The optical properties of carbon nanotubes have attracted much recent attention.^{1–3} For example, there have been extensive investigations of carbon nanotubes as optical limiters for attenuating pulsed laser irradiation.^{2,3} The electronic absorption features of single-walled carbon nanotubes (SWNTs) in particular have been recognized as being characteristic and specific in the structural identification from different production methods and the probing of various effects (such as surface doping).^{4–10} The study of photoexcited states and emission properties of carbon nanotubes has also advanced significantly. The report in 2000 by Riggs, et al. that carbon nanotubes in solution are luminescent in the visible^{11,12} has subsequently been confirmed by results from other research groups.^{14–17} The more recent discovery of band-gap fluorescence in the near-IR from well-dispersed semiconducting SWNTs has generated much excitement.^{18,19} In comparison, relatively less attention has been paid to the investigation of the strong visible luminescence toward a mechanistic elucidation. However, the visible luminescence represents an important property of carbon nanotubes, at least under most experimental conditions.²⁰ It can be very strong, associated with a broad range of excitation wavelengths including those for Raman measurements (often with overwhelming interferences^{21–24}). As reported here the luminescence is in fact dependent on not only the dispersion but also the surface passivation of carbon nanotubes, and thus may potentially serve as a sensitive tool in the evaluation of nanotube functionalization.

SWNT samples available commercially (Carbon Solutions, Inc.) and produced in house by using the arc-discharge method were used after purification. The purification was based on several variations of the oxidative acid (HNO₃) treatment, including the use of microwave irradiation and/or cross-flow filtration as additional steps in the purification procedure.^{22–25}

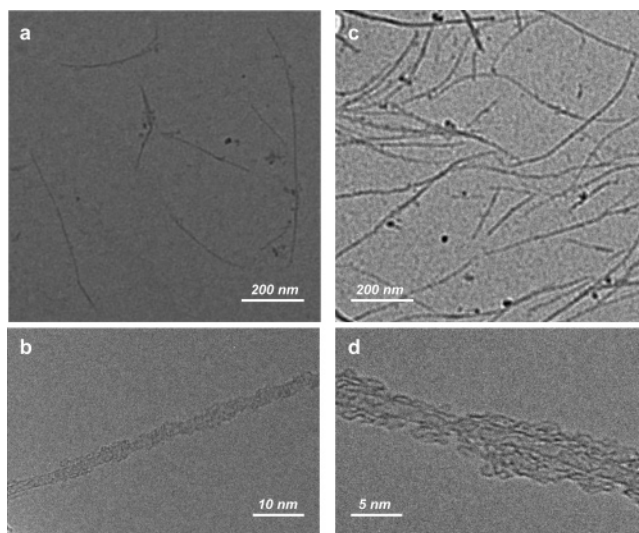


Figure 1. Representative TEM images of PEG_{1500N}-SWNT (a,b) and PPEI-EI-SWNT (c,d) samples.

No critical difference was found in the observed luminescence emission results with respect to the different sample sources and purification schemes.

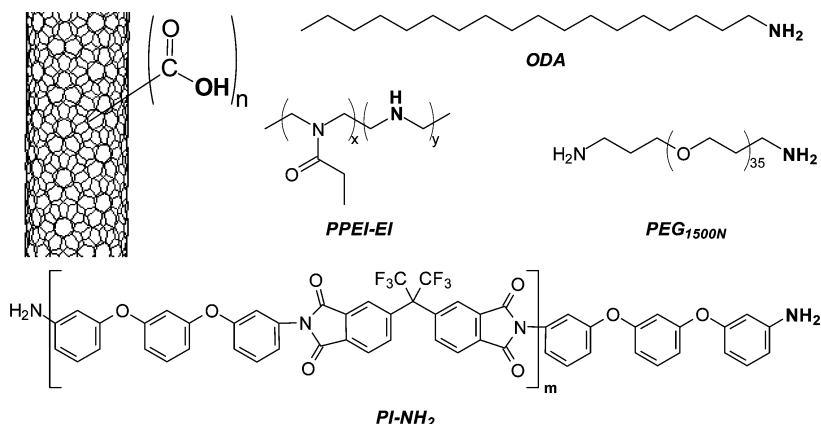
The purified SWNTs were functionalized (by targeting the nanotube-bound carboxylic acids at defect sites) with a number of polymeric and oligomeric compounds, in particular (Scheme 1) poly(propionylethylenimine-*co*-ethylenimine) (PPEI-EI-SWNT),^{11,22} an amine-terminated oligomeric polyimide (PI-NH₂-SWNT),²³ diamine-terminated poly(ethylene glycol) (PEG_{1500N}-SWNT),²⁴ and octadecylamine (ODA-SWNT).²⁶ Experimental details on the synthesis and characterization of these solubilized nanotube samples are already available in the quoted publications. Results from the characterization of the samples are consistent with the functionalization of SWNTs. Some electron microscopy images of the samples are shown in Figure 1, which suggest that the functionalized SWNTs are well-dispersed.

* Corresponding author.

[†] Clemson University.

[‡] Oak Ridge National Laboratory.

SCHEME 1



All of the functionalized SWNTs are soluble in common organic solvents, some also in water (PPEI-EI-SWNT and PEG_{1500N}-SWNT), to form optically transparent solutions. The electronic absorption spectra of these samples exhibit the characteristic transitions associated with the van Hove singularity pairs in semiconducting SWNTs (Figure 2). The solid-state and

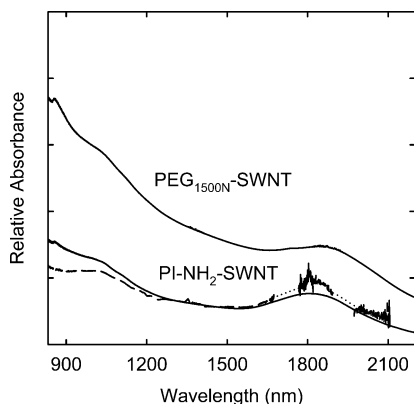


Figure 2. Absorption spectra of PEG_{1500N}-SWNT in the solid-state (—) and PI-NH₂-SWNT in DMF solution (---, the dotted line region subject to overwhelming solvent background) and the solid-state (—).

solution-phase spectra are generally similar, except that the overwhelming background of most solvents makes a clear identification of the S₁₁ band profile in solution nearly impossible (Figure 2).

The band-gap fluorescence of semiconducting SWNTs in the near-IR is very sensitive to surface chemistry and often attenuated upon doping and/or functionalization, as already known in the literature.^{18,19,27} On the other hand, the functionalized nanotubes do show significant emission in the visible when excited at shorter wavelengths. The luminescence emission spectra shown in Figure 3 are representative of those from most functionalized and solubilized carbon nanotubes in solution or in thin films and other transparent polymeric matrices. The emission intensities and quantum yields can be very high, with yields of 4.5% and 3% for the spectra of PPEI-EI-SWNT and PEG_{1500N}-SWNT, respectively, shown in Figure 3. The luminescence decays are mostly nonexponential but generally fast, on the order of a few nanoseconds.^{11,14} The decay results suggest inhomogeneity in the emitting species and/or the excited states responsible for the observed emissions. Consistent with the presence of significant inhomogeneity is the excitation wavelength dependence, with the observed emission spectra progressively moving toward the red with longer excitation wavelengths (Figure 3).

Mechanistically, it has been proposed that the luminescence emission might be due to the presence of defects in the nanotube structure which act as trapping sites for the excitation energy.^{11,14} In fact, there is evidence suggesting that the defect-derived emission is opposite to the band-gap fluorescence, namely that the latter is diminished in SWNTs that are acid-treated or subject to other defect-producing procedures, whereas the former becomes more pronounced.^{19,28} However, a necessary condition shared by both kinds of emissions is that the nanotubes must be well-dispersed (better at the individual nanotube level) to avoid the quenching of intertube interactions in bundled SWNTs. This was demonstrated well in a comparison of the visible luminescence emissions between purified nanotubes dispersed with the aid of polymers in a stable suspension and functionalized nanotubes in solution. While the two samples appeared indistinguishable (Figure 4) and were of similar absorption spectra and optical densities at the excitation wavelength, the observed luminescence emission intensities were very different. As compared in Figure 4, the solution of functionalized SWNTs was considerably more luminescent. This was due to the fact that more SWNTs were dispersed at individual nanotube level in the functionalized sample. A related observation was that the Raman characterization of SWNTs in the functionalized sample was practically impossible because of the overwhelming luminescence interference (even 1,064 nm excitation in FT-Raman), while the same characterization of the polymer-dispersed nanotube sample was rather straightforward.²³

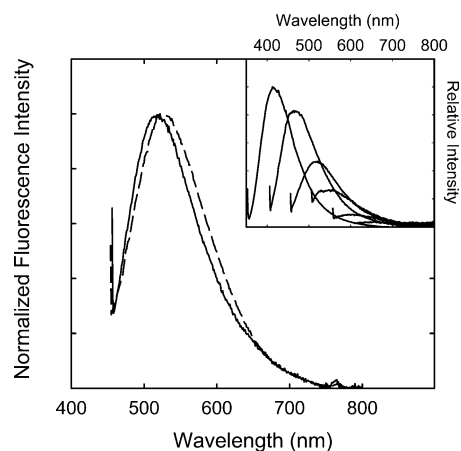


Figure 3. Luminescence emission spectra (normalized, 450 nm excitation) of PPEI-EI-SWNT (—) and PEG_{1500N}-SWNT (---) in aqueous solution. Inset: the spectra of PPEI-EI-SWNT excited at 350, 400, 450, 500, 550, 600 nm (intensities shown in relative quantum yields).

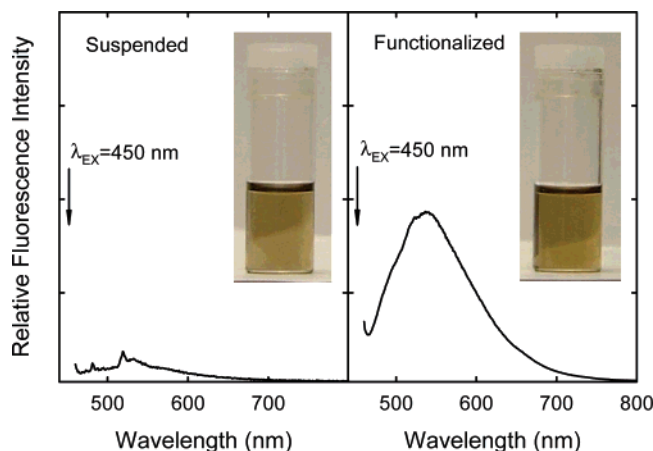


Figure 4. Luminescence emission spectra from SWNTs dispersed with the aid of polyimide in DMF (left) and the polyimide-functionalized SWNTs (PI-NH₂-SWNT) in DMF solution (right). The nanotube and polymer contents in the two samples were comparable.

The dispersion of nanotubes in solubilized samples is determined by how well the nanotubes are functionalized. As a result, stronger luminescence emission is generally associated with better functionalized nanotubes. For example, the observed emission intensities increased when a functionalized SWNT sample was subject to repeats of the same functionalization reaction for improved dispersion (presumably more at the individual nanotube level) and solubilization. Conversely, even a partial removal of functional groups from the functionalized nanotubes via hydrolysis (chemical defunctionalization^{21,29}) resulted in a substantial reduction in observed luminescence emission intensities. In fact, the defunctionalization (often making the nanotubes insoluble again) has been effective in the elimination of the overwhelming luminescence interference found in the Raman characterization of solubilized carbon nanotube samples.^{21–24} It seems that the role of functional groups on the nanotube surface may go beyond just keeping the nanotubes dispersed. The functionalization may also provide passivation of the defect sites to make the trapping of excitation energy more efficient and/or the energy traps more emissive. In better functionalized nanotube samples, there are more individually dispersed nanotubes and thus less intertube quenching and more effective passivation of the defects for higher luminescence emission yields. The opposite applies in the defunctionalization of functionalized nanotubes.

The dependence of luminescence emission from nanotubes on their functionalization was also observed in chromatography-fractionated samples. As first reported by Haddon and co-workers,³⁰ the octadecylamine-functionalized SWNTs (ODA-SWNT) could be fractionated in size-exclusion chromatography (SEC). As shown in Figure 5, the first SEC fraction was visible to the UV-vis detector (325 nm), but hardly so to the fluorescence detector (400 nm excitation and 450 nm detection). Because of the expected larger sizes of the underlying species, this fraction has often been considered as containing mostly SWNTs and less contaminated with other carbonaceous impurities. In this work, the first fraction (indicated by the rectangle in Figure 5) was collected and confirmed to be essentially nonfluorescent.³¹ However, when the collected sample was mixed with PPEI-EI polymer (molecular weight $M_w \sim 200\,000$) to be subject to the typical experimental conditions for the nanotube functionalization (carbodiimide-activated amidation),^{22b,c} the resulting sample became as luminescent (Figure 5) as the separately functionalized sample PPEI-EI-SWNT (Figure 3). Thus, the first eluted were likely small bundles of SWNTs that

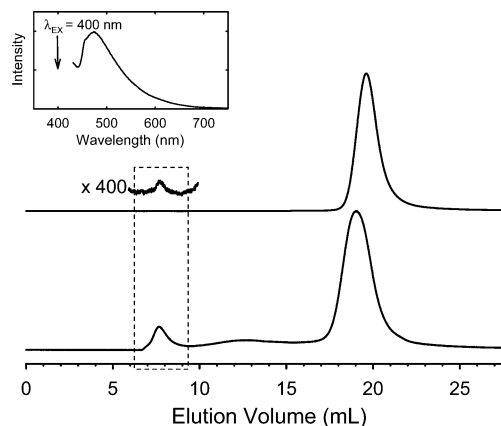


Figure 5. SEC chromatograms of ODA-SWNT from UV-vis detector (bottom) and fluorescence detector (top). Shown in the inset is the luminescence emission spectrum of the first fraction after further functionalization with PPEI-EI.

were relatively poorly functionalized, with the invisibility to the fluorescence detector being due primarily to intertube quenching effects. With the fraction collected, the subsequent functionalization with PPEI-EI yielded well-dispersed (and defect sites well-passivated) SWNTs of again strong luminescence emission in the visible.

In conclusion, there are strong luminescence emissions from well-dispersed carbon nanotubes in most functionalized samples, even with excitation wavelengths into the near-IR region. The broad luminescence emissions are logically attributed to the trapping of excitation energy by defect sites in the nanotube structure, which are passivated upon the appropriate functionalization of the nanotubes. The better the dispersion and functionalization of the nanotubes (thus better passivation), the more intense luminescence emissions. Most existing efforts have been centered on the elimination of the luminescence as interference in Raman spectroscopic characterization of functionalized carbon nanotubes. However, because of its high sensitivity to the nanotube surface passivation, the visible luminescence emission as an optical spectroscopy tool may find valuable applications in the evaluation of dispersion in functionalized carbon nanotube samples and related nanocomposite materials.

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