

First comparative emission assay of single-wall carbon nanotubes—solutions and dispersions

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A variety of single-wall carbon nanotube samples were tested in steady-state and time-resolved emission experiments, where it was found that chemical functionalization and different degrees of oxidation affect the emission behavior.

Single-wall carbon nanotubes (SWNT) are currently obtaining considerable attention, owing to their unique strength properties, ballistic transport, *etc.*^{1,2} Notably, the tubular structure and the thermal/electrical conductivity of SWNTs open promising scenarios for these “molecular wires” as integrative components in the design of electro- and photoactive ensembles.³ However, considerable difficulties must be overcome in processing and handling SWNTs. In order to investigate their properties and to realize their full potential, recent protocols regarding the chemical modification of SWNTs have emerged, especially to control the inherent insolubility of SWNTs.⁴

An important structural consideration is the fact that SWNTs disperse in solution as large and agglomerated bundles because strong van der Waals attractions between individual SWNTs render their cohesive energies significantly greater than their solvation energies.⁵ If, indeed, the affinity of SWNTs bundles towards solvation is low, then the resulting dispersions become only kinetically stable. This is found, for example, to be the case for shortened SWNTs that are neither functionalized nor dispersed with the help of surfactant capping. Chemical functionalization of SWNTs, although successful in terms of solubilization, exerts an impact on their electronic structure and physical property.⁶

Here, we compare the solution properties of SWNTs—by means of steady-state and time-resolved emission techniques—produced by various techniques (*i.e.*, *laser ablation*, *arc discharge* and *HIPco*) with those of chemically-modified SWNT materials (*i.e.*, strongly functionalized both at end-caps and on side-walls).[†]

Upon excitation with visible light, all dispersions/solutions of SWNTs reveal distinct sets of emission spectra. Upon variation of the excitation light, a wavelength progression of the emissive features was seen in most cases. In particular, a red-shift of the excitation wavelength, for instance, from 300 nm to 500 nm led to parallel red-shifts of the emission features. This effect can be as large as 100 nm and depends strongly on the SWNT material. In general, this phenomenon was observed regardless of the class of SWNT—*arc*-SWNT, *HIPco*-SWNT and *laser*-SWNT and regardless of the medium.

In terms of emission shifts, the most striking picture emerges from the heavily oxidized *arc*-SWNTs. Broad emission bands characteristically shift upon varying the excitation wavelength—reminiscent of earlier observations by Sun and co-workers.^{7a} To substantiate this observation, the excitation spectrum of each emission maximum was recorded in a separate set-up. This led to good agreement between excitation maximum and initial excitation wavelength (not shown). Also time-resolved lifetime measurements, which yielded radiative values of the order of ~2 ns, confirm the nature of the emission.

Our finding can be rationalized on the following grounds: Raman spectra of *arc*-SWNTs show in comparison to *HIPco*-

SWNT and *laser*-SWNT the broadest resonance for the radial-breathing modes—a feature that is directly related to the SWNT diameter. It is safe to assume that these broader transitions prompt to wider diameter distributions. Besides the Raman radial-breathing modes, the visible and NIR transitions in the absorption spectrum, referring to the different van Hove singularities in semiconducting SWNTs, emerged as another sensitive marker for the SWNT diameter.⁸ Larger diameters lead to less energetic transitions across the electronic band gap. This consideration is further supported by a theoretical treatment, which showed that SWNT sections may be viewed as a chain of aromatic “molecules” with each “molecular unit” consisting of $(4n + 2)$ sp^2 -bonded carbon atoms.⁹ Large energy gaps were concluded for short tubes, whereas for tubes of intermediate lengths, the energy gap decreases as a function of SWNT length.

An alternative rationale can be gained from the fact that several quantum wells, quantum dots and metal-oxide surfaces exhibit broad emission bands corresponding to a high defect concentration by emission of trapped carriers.^{10,11} Regardless of the diameter, the oxidized *arc*-SWNTs are readily soluble in aqueous solutions, without the necessity of an additional aid, such as excessive bath- or horn-sonication. The latter fact suggests the presence of a considerable number of defects—such as shallow and deep trapping sites for charge carriers—in the region of the end-caps and on the side-wall.

It is, however, rather difficult to ascribe our finding exclusively to (i) the change of diameter of the SWNT/the size of the bundles and/or (ii) the structure/defects on the SWNT's surface.¹² Mainly, the poor control over these variables and the lack of unambiguous proof prevents a definitive answer. But a comparison between pristine *laser*-SWNT and the triethyleneglycol (TEG) derivatized analogs, TEG-*laser*-SWNT—obtained via a recently described procedure—allows a more general trend to be identified: *surface chemistry with SWNT clearly broadens the wavelength distribution (vide infra)*.

Among all samples examined, the pristine *laser*-SWNT shows the narrowest distribution. In fact, variation of the excitation frequency between 320 nm and 460 nm led to a red-shift of only 4 nm (!)—see Fig. 1. This observation is in line with the sharp radial-breathing mode—around 170 cm^{-1} upon 457 nm excitation—found in Raman spectroscopy.¹³ Please note that the lack of chemical functionalization avoids the modification of the SWNT surface. The emission decay of the 520 nm maximum—Fig. 2—is best fitted by a single exponential decay function from which a lifetime of 2.3 ns is derived.

The situation changed dramatically for the TEG-*laser*-SWNT, which (i) gives rise to notable shifts (*i.e.*, 40 nm) and (ii) higher quantum yields (*i.e.*, 10 times stronger—0.4%). We emphasize that in this case an extensive chemical modification of SWNTs has been carried out with the raw *laser*-SWNT material. What is interesting to note is that the quantum yields of the high energetic maxima are lower than those of the low energetic maxima. The differences are as large as 30%. The half-width of the emission bands remains exactly the same as

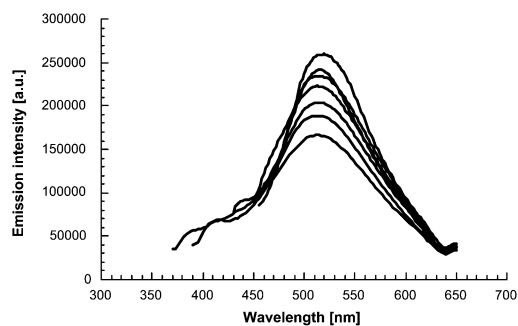


Fig. 1 Emission spectra of aqueous suspensions of *laser*-SWNT with excitation wavelengths of 340, 360, 380, 400, 420, 440 and 460 nm (bottom to top). The emission quantum yield is 0.04. The solutions exhibited absorbances of ~ 0.4 at the excitation wavelengths; ZnTPP was used as standard.

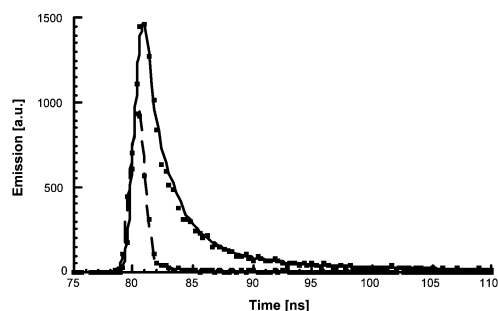


Fig. 2 Time-resolved emission decay of an aqueous suspension of *laser*-SWNT (solid line), following the emission at the 520 nm maximum—laser scatterer (dashed line).

that determined prior to the functionalization. This comparison confirms that SWNT-functionalization has an impact on the emissive features.

Parallel to the energetic shift is the fact that the emission lifetime, as another sensitive variable, changed similarly. In contrast to the steady-state experiments, this assay allows the contributions from the discrete levels to be investigated, without, however, changing the excitation wavelength. We examined several representative wavelengths (*i.e.*, 400, 450, 500, 550 and 600 nm) following a short 337 nm laser pulse. As expected, the emission-time profiles—recorded at different wavelengths between 400 and 600 nm—cannot be fitted strictly to a single exponential decay. Instead a polyexponential fit was applied, in which the major component gives rise to an interesting trend. In general, the lifetimes steadily increase from 400 to 600 nm, starting with a value of 3.7 ns (*i.e.*, τ_{emission} 400 nm). Appreciably longer values are seen at the long wavelength probe (*i.e.*, τ_{emission} 600 nm), giving a value of 5.2 ns.¹⁴

Also in the oxidized-*laser*-SWNT similar changes of the emission wavelength were discernable. The actual magnitude depends mainly on the experimental conditions, that is, the sample preparation. For instance, the effects were stronger upon treating SWNTs with 14.3 M HNO₃ than with 2.6 M HNO₃, which led to shifts of 33 nm and 18 nm, respectively. In other words stronger oxidative treatment gave stronger impacts on the shift of the emission maximum. Interestingly, in comparison to *laser*-SWNT the oxidized *laser*-SWNT are the weaker emitter (*i.e.*, $\sim 20\%$). In the Raman spectra of the oxidized-*laser*-SWNT, clear up-shifts of the critical radial-breathing modes are seen relative to those of *laser*-SWNT, suggesting substantial perturbations in the inter-tube interactions.¹³

An alternative way to affect the nature of SWNTs is sonication of their suspensions. In this context, the best-explored and understood phenomenon is the cutting of individual SWNTs. In fact, subjecting an aqueous suspension of *laser*-SWNT to 5 minutes of horn-sonication brings about

notable effects in their emission features: shifts of around 10 nm are found. On the other hand, the lifetime is 2.3 ns, similar to that in *laser*-SWNT.

In summary, we found that in controlling the degree of SWNT chemical modification, that is, functionalization, oxidative treatment or cutting, defect states dominate the optical properties. Higher degrees of surface modification augment the observed effects. A likely rationale is that SWNT chemistry leads to the incorporation of shallow acceptor levels into their band structure. The emission energy reveals a distribution of such traps to varying depths on the surface of the SWNTs.

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Notes and references

† *HIPco*-SWNT was received from Tubes@Rice (Houston, USA). For details on *laser*-SWNT and oxidized-*laser*-SWNT, see A. A. Mamedov, N. A. Kotov, M. Prato, D. M. Guldi, J. P. Wicksted and A. Hirsch, *Nature Mater.*, 2002, **1**, 190. Arc-discharge-SWNT and oxidized arc-discharge-SWNT were prepared according to: M. Holzinger, A. Hirsch, P. Bernier, G. S. Duesberg and M. Burghard, *Appl. Phys. A*, 2000, **70**, 599. The TEG-functionalized *HIPco*- and *laser*-SWNT were prepared according to ref. 4b.

- Special issue on Carbon Nanotubes: *Acc. Chem. Res.*, 2002, **35**, 997.
- Carbon Nanotubes: Synthesis, Properties and Applications*, eds. M. Dresselhaus, G. Dresselhaus and Ph. Avouris, Springer-Verlag, Berlin, 2001.
- H. Ago, K. Petritsch, M. S. P. Shaffer, A. H. Windle and R. H. Friend, *Adv. Mater.*, 1999, **11**, 1281.
- (a) M. Holzinger, O. Vostrowsky, A. Hirsch, F. Hennrich, M. Kappes, R. Weis and F. Jellen, *Angew. Chem., Int. Ed.*, 2001, **40**, 4002; (b) V. Georgakilas, K. Kordatos, M. Prato, M. D. M. Guldi, M. Holzinger and A. Hirsch, *J. Am. Chem. Soc.*, 2002, **124**, 760; (c) J. L. Bahr and J. M. Tour, *J. Mater. Chem.*, 2002, **12**, 1952.
- S. Reich, C. Thomsen and P. Ordejón, *Phys. Rev. B*, 2002, **65**, 155411.
- (a) J. L. Bahr, J. Yang, D. V. Kosynkin, M. J. Bronikowski, R. E. Smalley and J. M. Tour, *J. Am. Chem. Soc.*, 2001, **123**, 6536; (b) M. A. Hamon, M. E. Itkis, S. Niyogi, T. Alvarez, C. Kuper, M. Menon and R. C. Haddon, *J. Am. Chem. Soc.*, 2001, **123**, 11292; (c) C. A. Dyke and J. M. Tour, *J. Am. Chem. Soc.*, 2003, **125**, 1156.
- (a) J. E. Riggs, Z. Guo, D. L. Carroll and Y.-P. Sun, *J. Am. Chem. Soc.*, 2000, **122**, 5879; (b) Y. Sun, S. R. Wilson and D. I. Schuster, *J. Am. Chem. Soc.*, 2001, **123**, 5348; M. Álvaro, P. Atienzar, J. L. Bourdelande and H. García, *Chem. Commun.*, 2002, 3004.
- (a) M. J. O’Connell, S. M. Bachilo, C. B. Huffman, V. C. Moore, M. S. Strano, E. H. Haroz, K. L. Rialon, P. J. Boul, W. H. Noon, C. Kittrell, J. Ma, R. H. Hauge, R. B. Weisman and R. E. Smalley, *Science*, 2002, **297**, 593; (b) S. M. Bachilo, M. S. Strano, C. Kittrell, R. H. Hauge, R. E. Smalley and R. B. Weisman, *Science*, 2002, **298**, 2361.
- L. Liu, C. S. Jayanthi and S. Y. Wu, *Chem. Phys. Lett.*, 2002, **357**, 91.
- (a) J. F. Chen, P. Y. Wang, C. Y. Tsai, J. S. Wang and N. C. Chen, *Appl. Phys. Lett.*, 1999, **75**, 2461; (b) N. S. Andreev, A. V. Emeline, V. A. Khudnev, S. A. Polikhova, V. K. Ryabchuk and N. Serpone, *Chem. Phys. Lett.*, 2000, **325**, 288.
- C. Burda, S. Link, M. Mohamed and M. El-Sayed, *J. Phys. Chem. B*, 2001, **105**, 12286.
- Remaining catalyst particle in functionalized *HIPco*-SWNT is $< 0.4\%$ iron: V. Georgakilas, D. Voulgaris, E. Vázquez, M. Prato, D. M. Guldi, A. Kukovec and H. Kuzmany, *J. Am. Chem. Soc.*, 2002, **124**, 14318.
- M. Holzinger, Ph.D. Thesis, Universität Erlangen, 2002.
- The value at the 600 nm wavelength in a dichloromethane solution is 6.0 ns. This supports the existing interactions between the solvent and the photoexcited TEG-*laser*-SWNTs.