Photoluminescence of SWNTs

Introduction

Most research into single-walled carbon nanotubes (SWNTs) has been focused on individual tubes, rather than bundles. Dr. P.H. Tan, A.C. Ferrari, and colleagues at Cambridge University, however, have been investigating the electronic properties of SWNT bundles using photoluminescence (PL) spectroscopy.[1] Excitons dominate the electronic structure of SWNTs, so the examination of excitons not only in single tubes, but also in bundles of SWNTs, is important. Using PL maps of SWNT bundles might lead to better characterization of samples of SWNTs.

Experimental method

Cobalt-molybdenum (CoMoCAT) catalytic method SWNTs were suspended in D_2O with a surfactant of sodium dodecylbenzene sulfonate (SDBS).[2] To record the PL, a HORIBA Jobin Yvon NanoLog® modular spectrofluorometer (Fig. 1) specializing in near-IR fluorescence was used.

Results and discussion

A PL map of the CoMoCAT sample is shown in Fig. 2. The left side (a) was recorded shortly after preparation; the right side (b) was scanned two months later. Assigned peaks for Fig. 2 (a) using our exclusive Nanosizer™ software are shown in Fig. 3.

Fig. 1. *NanoLog® modular spectrofluorometer.*

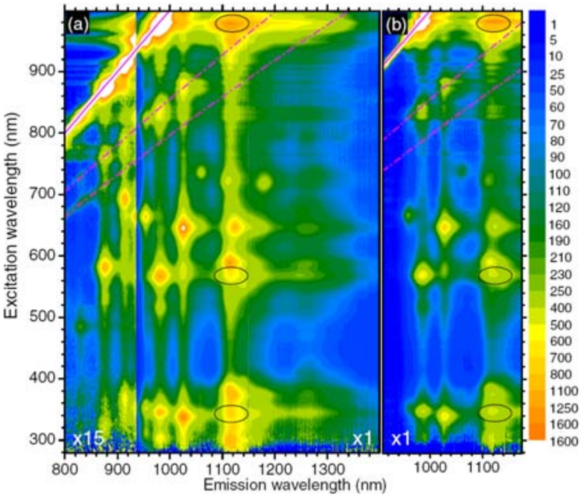

Fig. 2. *PL map for (a) as-prepared suspensions and (b) after two months. Solid lines at upper left corners are resonances with identical excitation and recombination energies. Broken lines are the range of phonon sidebands. Emission from (8,4), (7,6), and (9,4) SWNTs is circled, with excitation matching* eh_{11}, eh_{22}, eh_{33} *of (6,5).*

Ferrari and his coworkers found sixteen different SWNT species in the CoMoCAT sample, their chirality marked with the standard notation (*m*,*n*) in Fig.

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[1] P. H. Tan, *et al.*, "Photoluminescence Spectroscopy of Carbon Nanotube Bundles: Evidence for Exciton Energy Transfer", *Phys. Rev. Lett.* **99**(2007), 137402.

[2] M. J. O'Connell, *et al.*, "Band Gap Fluorescence from Individual Single-Walled Carbon Nanotubes", *Science* **297**(2002), 593.

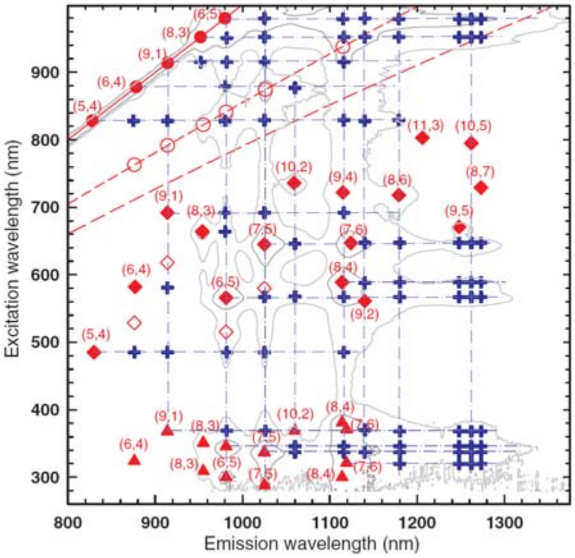

Fig. 3. *Assigned peaks of as-prepared SWNTs (Fig. 2[a]). Solid circles, diamonds, and triangles are* eh_{11} *emissions, with excitation matching the* eh_{11}*,* eh_{22}*,* eh_{33}*,* eh_{44} *transitions. Each peak is labelled with its SWNT chiral index. Open circles and diamonds are EET between semiconducting tubes. Gray contours include both exciton-related resonances and EET spectral features.*

3.[3] Certain intense peaks indicated excitons (symbolized as eh_{ii}, where i is the i^{th} electronic interband transition E_{ii}; i = 1, 2, 3, 4,...). The eh_{ii} wavelengths of most SWNTs were redshifted 3–10 nm longer than expected, indicating the presence of SWTNs bundles. Other unusual features compared with previous studies were:

- Exciton resonances' shapes were elongated horizontally and vertically;
- New peaks appeared, including (λ_{exc} = 645 nm, λ_{em} = 1265 nm) and (568 nm, 1250 nm), with intensity much greater than the (eh_{22}, eh_{11}) peaks of (10,5), (8,7), and (9,5) SWNTs;
- A strong, broad emission near (980 nm, 1118 nm) was seen.

The luminescence of the sample was examined after two months (Fig. 1[b]). Most peaks were red-shifted several nm, indicating grouping of the SWNTs into larger bundles. Though most intensities fell, certain peaks grew in strength: The (980 nm, 1118 nm) band strengthened; two peaks near (568 nm, 1118 nm) and (346 nm, 1118 nm) became more obvious, because of the weakness of the (eh_{ii}, eh_{11}) (i = 2, 3, 4) bands of (8,4) and (7,6) SWNTs, which overpowered them in the newly-made sample. These peaks do not correspond to known exciton resonances. The Cambridge team assigned them to energy-transfer between nanotubes in *bundles*, rather than between individual nanotubes.

The efficiency of exciton-exciton transfer I_A/I_D (A is acceptor, D is donor) was estimated to be

$$\frac{I_A}{I_D} = \frac{1/\tau_{DA}}{1/\tau_{rA} + 1/\tau_{rnA}} \times \frac{\tau_{rD}}{\tau_{rA}}$$

where τ_{nrD}, τ_{rD}, τ_{nrA}, and τ_{rA} are the radiative (r) and nonradiative (nr) lifetimes. For nanotube diameters 0.75–0.95 nm, the eh_{11} radiative lifetime is ~20–30 ps at room temperature, significantly shorter than the theoretical radiative lifetime (~10 ns). Therefore observed lifetimes are based on nonradiative recombinations. Thus the equation may be simplified to

$$\frac{I_A}{I_D} \approx \frac{\tau_{nrA}}{\tau_{DA}}$$

In bundles, the researchers found a large efficiency I_A/I_D. Under eh_{11} excitation of the (5,4) SWNTs, the ratio of photoluminescence intensity of all ac-

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[3] M.S. Dresselhaus and P.C. Eklund, *Adv. Phys.* **49**(6), 2000, 705–814.

ceptor tubes with emission above 900 nm [such as (6,5), (7,5), (8,4), (7,6)] to that at ~831 nm of the (5,4) donors is ≥ 75. That is, most donors transferred energy to the acceptors. In low-dimensional systems including SWNTs, the most efficient mechanisms of energy-transfer are (1) exciton tunnelling, (2) photon-exchange, and (3) Förster resonance energy-transfer (FRET). Tan, *et al.*, attributed EET in SWNT bundles to FRET, by ruling out the other mechanisms as follows:

- Exciton-tunnelling requires that the exciton wavefunctions are coupled together, with the tunnelling rate sensitive to the eh_{11} difference in energy. For the sixteen different nanotube species present in the CoMoCAT sample, diameters varied from 0.65–1.05 nm, eh_{11} varied from 0.06–0.5 eV, and chiral angle variation was from 5–26°. Exciton coupling ought to be strongly dependent on the particular donors and acceptors. Yet a scan of PL emission excited at the eh_{11} of (5,4) was quite similar to the absorption profile beyond 850 nm, with no preference for a particular (n,m). Hence exciton-tunnelling is not the major mechanism, and shape or size is not important. Rather, concentration is the crucial factor.
- Photon-exchange is a specific form of exciton-photon coupling. This energy-transfer pathway has a smaller dependence on the distance between the donor and acceptor (R_{DA}) than FRET. Thus, photon-exchange can prove important at larger distances. But the lack of major EET peaks in isolated tube solutions, when considered with the low quantum-efficiency, suggests that it is not dominant between adjacent tubes in a given bundle.
- FRET is a quite efficient EET mechanism due to resonant, near-field, dipole-dipole interactions. Biological systems, conjugated polymers, wires, and quantum dots, all exhibit FRET at short and intermediate distances. The efficiency stems from the spectral overlap between donor emission and acceptor absorption, from the R_{DA}, and the relative orientation of emission and absorption dipoles. The rate of energy-transfer is proportional to R_{DA}^{-6}. FRET efficiency in bundles is expected to be high. The overlap of emission and absorption between large- and small-gap nanotubes depends on the specific donor-acceptor couple. The fast rate of EET can allow excitons to be transferred sequentially from donor to acceptor, even when a small emission-absorption overlap is present, along intermediate-gap tubes within a bundle. SWNTs in bundles are parallel, giving a maximum dipole-orientation factor, and they have small wall-to-wall distance.
- Kiowski, *et al.*, recently reported a satellite in the photoluminescence excitation (PLE) spectra of nanotube suspensions,[4] identified as PL emission from deep excitonic (DE) states. These features are redshifted by ~ 40 and 130 meV relative to the main eh_{11} PL emission peaks. These DE satellites can be observed in isolated nanotube suspensions if they are not

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[4] O. Kiowski, *et al.*, “Direct Observation of Deep Excitonic States in the Photoluminescence Spectra of Single-Walled Carbon Nanotubes”, *Phys. Rev. Lett.* **99**(2007), 237402.

shadowed by the intense exciton-exciton resonances of other nanotube species. EET is a major relaxation channel for exciton decay in nanotube bundles, explaining the low luminescence yield of large-gap tubes and strong enhancement of luminescence yield of small-gap tubes. DE emission satellites are expected to be weaker in bundles than in isolated nanotubes.

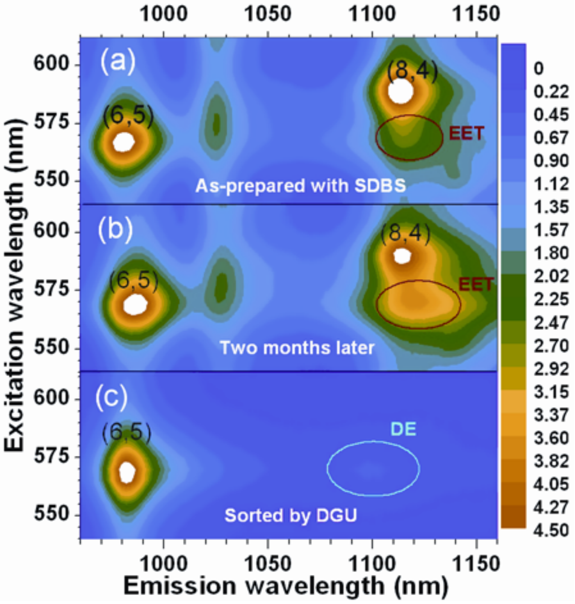

Fig. 4. *PLE maps for (a) as-prepared suspensions in SDBS; (b) suspensions after two months; and (c) as-prepared suspensions in sodium cholate by density-gradient ultracentrifugation. All PLE maps were normalized to the intensity of the (6,5)* (eh_{22},eh_{11}) *resonances. Red ellipses show the EET-induced features; the pink ellipse indicates the DE emission satellites of (6,5) tubes.*

- Fig. 4 compares PLE maps of nanotube suspensions enriched in bundles [Figs. 4(a) and (b)] and isolated tubes [Fig. 4(c)]. DE satellites are much weaker than EET features. The intensity and peak position of DE satellites for a given nanotube species are only determined by its main eh_{11} PL emission peak. The peak position of EET features is dependent on both donors and acceptors. Donors determine the excitation position and acceptors the emission position of EET features. Their intensity is dominated by the bundle donor and acceptor composition. Hence the EET features can be comparable to—or even much stronger than—the PL emission from the associated donors or acceptors. Therefore the EET features can be distinguished from DE emission satellites in the PLE maps. Because the range of exciton energy transfer is limited to a few nm,[5] EET is not efficient between individual nantubes in suspensions. Thus, the EET-induced PLE features are a direct, simple, and independent way to identify the presence of bundles.

Conclusions

Photoluminescence between SWNTs is explained by invoking transfer of excitons via FRET between SWNTs within bundles. The HORIBA Jobin Yvon NanoLog® modular near-IR spectrofluorometer proved indispensable in analyzing such single-wall carbon nanotube samples.

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[5] H.H. Qian, *et al.*, "Exciton Energy Transfer in Pairs of Single-Walled Carbon Nanotubes", *Nano Lett.* **8**(5), 2008, 1363–1367.

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