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Photoluminescence of SWNTs

FL-01

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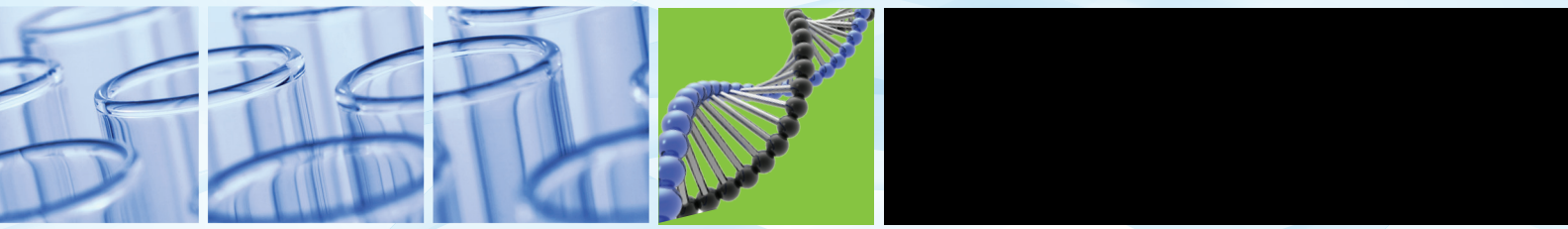

Introduction

Most research into single-walled carbon nanotubes (SWNTs) has been focused on individual tubes, rather than bundles. Dr. 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, and individual nanotubes have a low quantum yield in PL, so it seemed reasonable to examine excitons in bundles of SWNTs. Using PL maps of SWNT bundles might lead to better characterization of samples of SWNTs.

Fig. 1. NanoLog® modular spectrofluorometer.

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 Scientific 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.

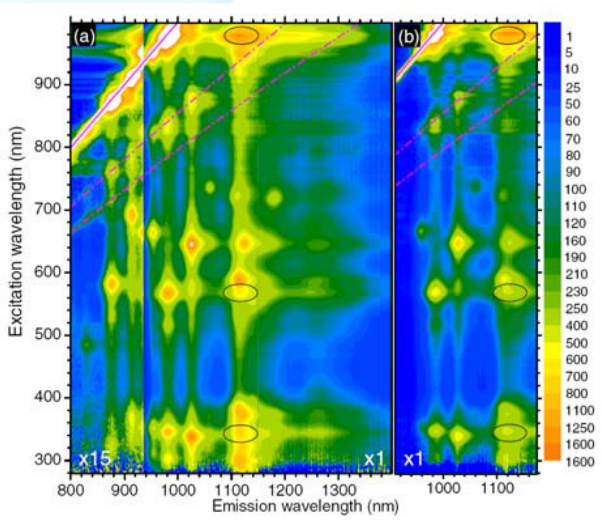

Fig. 2. PL map for (a) as-prepared suspensions and (b) after two months. Solid lines at upper left corners are resonances with identical excitation and recombination energies. Broken lines are the range of phonon sidebands. Emission from (8,4), (7,6), and (9,4) SWNTs is circled, with excitation matching eh11, eh22, eh33 of (6,5).

Ferrari and his coworkers found sixteen different SWTN species in the CoMoCAT sample, their chirality marked with

[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.

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the standard notation (m,n) in Fig. 3.[3] Certain intense peaks (black ovals on Fig. 2) indicated excitons (symbolized as eh_{ii}, where i is the i^{th} electronic interband transition E_{ii} = 1, 2, 3, 4,...). The ehii wavelengths of most SWNTs here were redshifted 3–10 nm longer than expected, meaning that the SWTNs are bundled. 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.

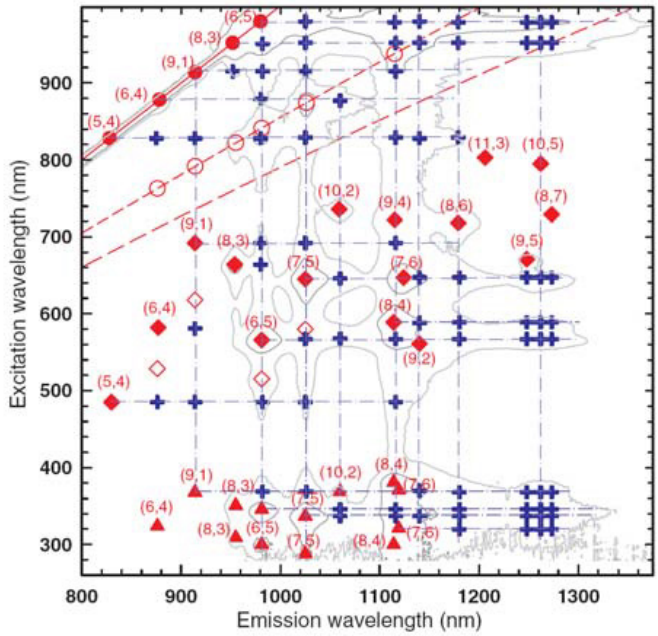

Fig. 3. Assigned peaks of as-prepared SWNTs (Fig. 1[a]). Solid circles, diamonds, and triangles are eh11 emission of SWNTs with excitation matching their eh_{11}, eh_{22}, eh_{33}, eh_{44} transitions. Each peak is labeled with its SWNT chiral index. Open circles and diamonds are EET between s-SWNTs. Gray contours include both exciton related resonances and EET spectral features.

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) bacame 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. Ferrari and colleagues assigned these peaks to energy-transfer between bundles of SWNTs, rather than between individual nanotubes.

The efficiency of exciton-exciton transfer IA/ID (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 T_{nrD}, T_{rD}, T_{nrA}, and T_{rA} are the radiative (r) and nonradiative (nr) lifetimes. For nanotube diameters 0.75–0.95 nm, the eh_{11} radiative lifetime is around 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 IA/ID. Under eh_{11} excitation of the (5,4) SWNTs, the ratio of photoluminescence intensity of all acceptor 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 SWTNs, the most efficient mechanisms of energytransfer are (1) exciton tunneling, (2) photon-exchange, and (3) Förster resonance energy-transfer (FRET). Ferrari, *et al*., attribute EET in SWNT bundles to FRET, by ruling out the other mechanisms as follows:

- Exciton-tunneling requires that the exciton wavefunctions are coupled together, with the tunneling rate sensitive to the eh11 difference in energy. For the sixteen different nanotube species present in the CoMoCAT sample, diameters vary from 0.65–1.05 nm, eh11 varies from 0.06–0.5 eV, and chiral angle variation is 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 eh11 of (5,4) is quite similar to the absorption profile beyond 850 nm, with no preference for a particular (n,m). Hence exciton tunneling is not the major method, and shape or size is not important. Rather, concentration is the crucial factor.
- Photon-exchange is a specific form of exciton-photon coupling, lacking and acceptor. This energy-transfer method has a smaller dependence on the distance between the donor and acceptor (RDA) 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, suggest that it is not dominant between adjacent tubes in a given bundle.
- FRET is quite efficient EET mechanism using 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 RDA, and by 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 distance from one wall to the next distance.

Conclusions

Examination of the photoluminescence between SWNTs is explained by invoking transfer of excitons via FRET between SWNTs within bundles. The HORIBA Scientific NanoLog® modular near-IR spectrofluorometer proves to be indispensable in analyzing samples such as single-wall carbon nanotubes.

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