

## 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.<sup>1</sup> 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.

### Experimental method

Cobalt-molybdenum (CoMoCAT) catalytic method SWNTs were suspended in D<sub>2</sub>O with a surfactant of sodium dodecylbenzene sulfonate (SDBS).<sup>2</sup> 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.

Ferrari and his coworkers found sixteen different SWNT species in the CoMoCAT sample, their chirality marked with the standard notation (m,n) in Fig. 3.<sup>3</sup> Certain intense peaks (black ovals on Fig. 2) indicated excitons (symbolized as  $eh_{ij}$ , where  $i$  is the  $i^{\text{th}}$  electronic interband transition  $E_{ij} = 1$ ,

2, 3, 4,...). The  $eh_{ii}$  wavelengths of most SWNTs here were redshifted 3–10 nm longer than expected, meaning that the SWNTs are bundled. Other unusual features compared with previous studies were:

- Exciton resonances' shapes were elongated horizontally and vertically;
- New peaks appeared, including ( $\lambda_{\text{exc}} = 645 \text{ nm}$ ,  $\lambda_{\text{em}} = 1265 \text{ nm}$ ) 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 ( $eh_{ij}$ ,  $eh_{11}$ ) ( $i = 2, 3, 4$ ) 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

where  $nrD$ ,  $rD$ ,  $nrA$ , and  $rA$  are the radiative ( $r$ ) and nonradiative ( $nr$ ) lifetimes. For nanotube diameters 0.75–

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

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

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

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 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  $\geq 75$ . 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 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  $eh_{11}$  difference in energy. For the sixteen different nanotube species present in the CoMoCAT sample, diameters vary from 0.65–1.05 nm,  $eh_{11}$  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  $eh_{11}$  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 an 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  $RDA^{-6}$ . 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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