Nanophotonics with Fluorescence Instruments

Introduction

HORIBA Jobin Yvon's spectrofluorometers have many applications in nanophotonics research: single-walled carbon nanotubes (SWNTs), quantum dots (QDs), and organic light-emitting diodes (OLEDs). Quantum confinement affects nanomaterials' photoluminescence: when the semiconducting nanoparticle is smaller than the bulk material's Bohr-exciton radius, the bandgap energy is inversely proportional to the nanoparticle size. Smaller nanoparticles usually have higher energy-absorbance and emission properties than larger nanoparticles of the same material.

SWNTs and the NanoLog®

Fig. 1 illustrates semiconducting-SWNT photoluminescence. Decreasing absorption and emission energies of individual SWNT species correlate directly with diameters from Raman spectroscopic analysis of radial breathing modes. Certain (n,m) values of semiconducting SWNTs match predicted band-gaps between valence and conductance bands. (Metallic and semi-metallic SWNTs with continuous valence and conductance bands show little luminescence.)

A NanoLog® (double-grating excitation monochromator, imaging emission spectrograph with a selectable-grating turret, and multichannel liquid-N_2-cooled InGaAs-array detector) has optimal excitation optics[1] for SWNT research or *any* solid sample in right-angle or front-face mirror configurations. The emission spectrometer has selectable gratings in a turret mount for rapid, easy acquisition of spectra. One grating has single-shot coverage of > 500 nm with a detector sensitive from 800–1700 nm.[2]

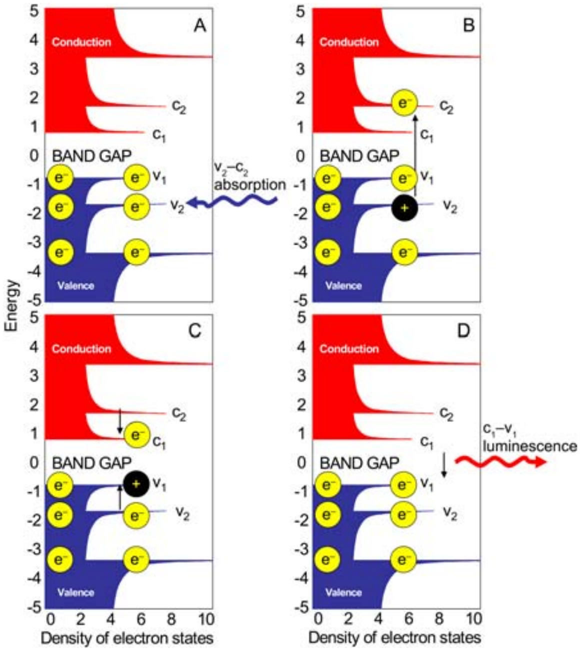

Fig. 1. *Semiconducting-SWNT photoluminescence absorption and emission. Conduction bands are red; valence bands are blue, electrons are yellow, holes are black. Black arrows are radiative or nonradiative transitions of* e^-*s or holes between band-levels.* V_x *and* c_x *are specific valence or conductance bands.*

Corrected emission spectra provide EEMs for a range of excitation wavelengths within minutes. Excitation bandpass is 0–14 nm; spectrometer slits vary from 0–16 mm with a 1200 groove/mm grating. An order-sorting filter excludes visible light from the spectrometer.

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[1] Xe lamp and reference diode: 250–1000 nm; excitation monochromator's gratings blazed at 500 nm for excitation at 333–1000 nm.

[2] Grating: 150 grooves/mm, 1200 nm blaze; detector: 512 pixels × 1″ [2.5 cm].

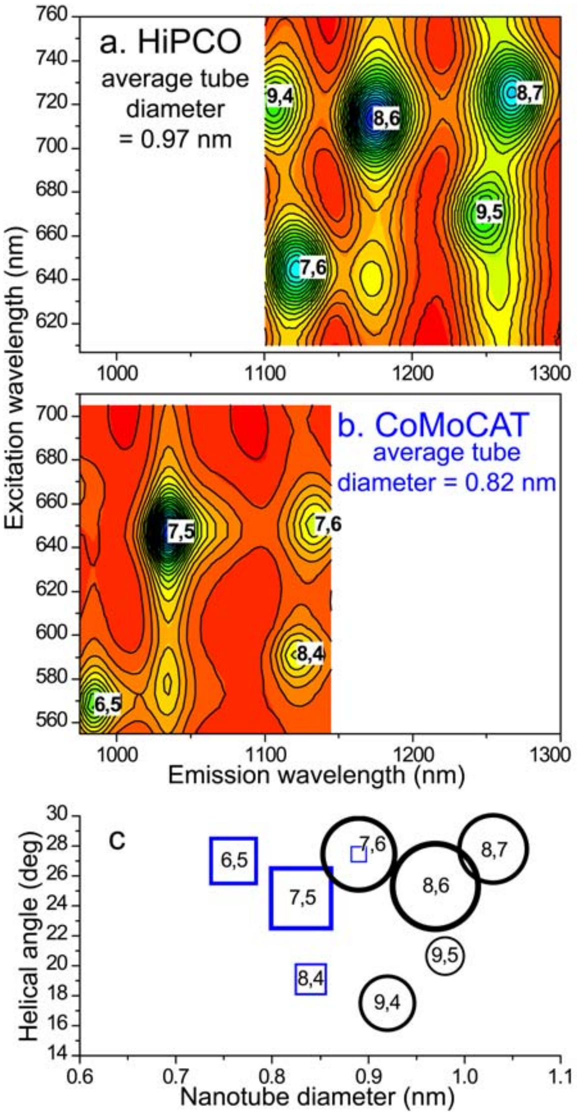

Fig. 2. *EEMs (a, b) and helical maps (c) of HiPCO and CoMoCAT SWNT suspensions, using a NanoLog®. Solid lines (a, b) are data; color contours are simulations. Symbol sizes (c) show relative amounts for HiPCO (○) and CoMOCAT (□), each normalized to 1.* R^2 *for the simulations = 0.997 (HiPCO) and 0.999 (CoMoCAT).* λ_{exc} *= 500–800 nm at 1 nm intervals;* λ_{em} *= 830–1350 nm at ~1 nm per pixel.*

Our exclusive Nanosizer® software compiles EEMs (Figs. 2a and b) to determine SWNT composition (Fig. 2c). A double-convolution algorithm (U.S. pat. pending) in the Nanosizer® simultaneously computes excitation and emission wavelength coordinate line-shapes for each species. Contributions from all spectral bands in a region of interest are found. EEM data (Fig. 2, solid lines) and simulations (contour maps) from two SWNT suspensions of different manufacturing processes distinguish different size and helical distributions: high-pressure carbon-monoxide method (HiPCO, Fig. 2a); cobalt-molybdenum catalytic method (CoMoCAT, 2b). Fig. 2a reveals five main HiPCO species; Fig. 2b indentifies four main CoMoCAT species. Fig. 2c, a chiral map of species in Figs. 2a and b, plots helical angle versus SWNT diameter against intensity of emission (symbol size). HiPCO tubes have a larger mean diameter than CoMoCAT.[3] The simulation gives precise analysis of SWNT samples in minutes.

Photoluminescence of quantum dots

QDs' absorption bands have broad spectral features and precise tunability of their emission bands. Their absorption spectra stem from many overlapping bands increasing at higher energies. Each absorption band corresponds to an energy-transition between discrete electron-hole (exciton) energy-levels; smaller QDs give a first exciton peak at shorter wavelengths. A photon is emitted when an electron crosses from conduction-band edge to valence band. Photon energy is proportional to bandgap, determined by the bulk material's Bohr-exciton radius and the QD's size (Fig. 3).

QDs' advantages compared to standard organic fluorophores are: A

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[3] HiPCO forms 0.6–1.3 nm dia. SWNTs, many helical angles, and up to 50 species. CoMoCAT has a narrower size (~0.8 nm dia.) and chiral distribution; just two species, (6,5) and (7,5), are ~58% of the intensity.

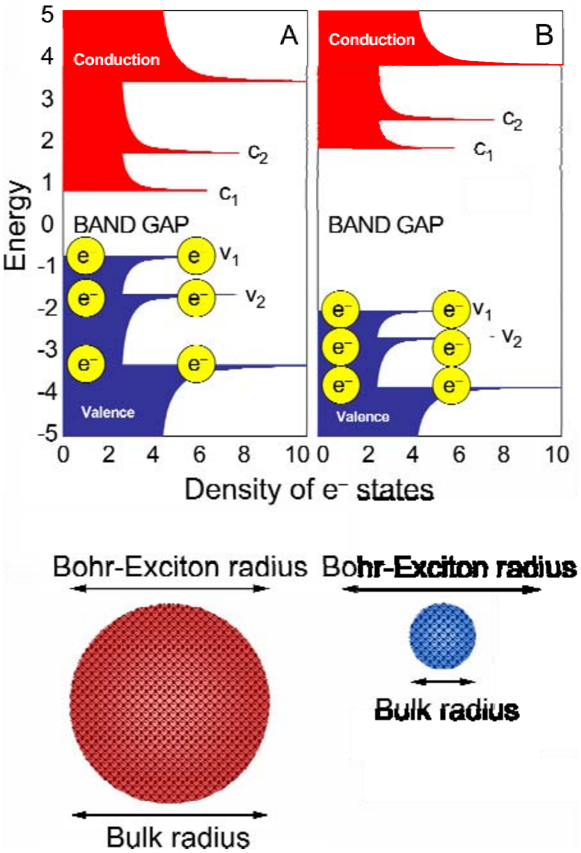

Fig. 3. *Quantum confinement for QDs. Valence (blue) and conductance bands (red) are shown. Composition of QDs A and B is identical; only the bulk radius varies relative to the fixed Bohr-exciton radius.*

single source can excite multiple QDs emitting over a broad range, giving selective exclusion of excitation light from the measured emission. QDs have high fluorescent and strong two-photon absorption yields, so they are up to 1000 times brighter for better image-resolution. Their tunable bandgaps offer applications such as white-light LEDs and other displays.

Most QDs are made of toxic elements (e.g., Pb, Cd, Se, and Te). Their photoluminescence may be sensitive to biological interactions, so QDs require a coating (usually a triblock copolymer), rendering the QDs non-toxic but also helping to conjugate the QDs to molecular probes, and protecting the QDs from biomolecular agents. Antibody-conjugate-imaging of these QDs may be useful to diagnose and treat cancer. Near-IR QDs may aid deeper tissue-imaging, for near-IR penetrates tissue deeper than visible light. QDs' excited-state lifetimes (2~10 ns) increase their worth for time-resolved fluorescence instruments. Many conjugation choices and excited-state properties of QDs make them useful for biosensors based on fluorescence resonance energy-transfer.

Photoluminescent Analysis of OLEDs

Based on thin films, OLEDs offer advantages over LCDs: no backlighting, emission of light only from active pixels (lower power), higher contrast and color-fidelity, brighter emission, wider viewing-angles, faster temporal response, better temperature-stability, and deposition on flexible or transparent substrates.

A voltage applied across an OLED circuit drives the electrons (Fig. 4A) and holes (Fig. 4B) into the organic layer where recombination occurs to emit photons (Fig. 4C). Here, photons from blue, green, and red emitters yield white light. Composition, thickness, and relation between the various layers regulate OLED luminescence. Fig. 5 shows the phosphorescent decay of a Universal Display emitter with a lifetime of > 1 μs, recorded on a TCSPC-Fluorolog®.

HORIBA Jobin Yvon instruments for QDs and OLEDs

The modular Fluorolog® spectro-fluorometer can run UV to near-IR steady-state and time-resolved meas-

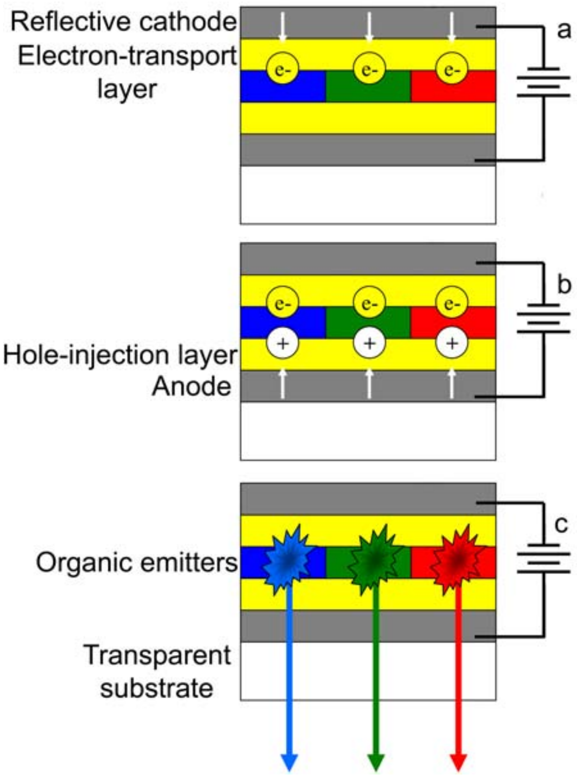

__Fig. 4.__ OLED operation in 3 steps, a to c. White arrows are flow of e^-s (yellow) and holes (white) from electrodes. Starbursts are electron-hole recombination in the organic layer followed by photon-emission.

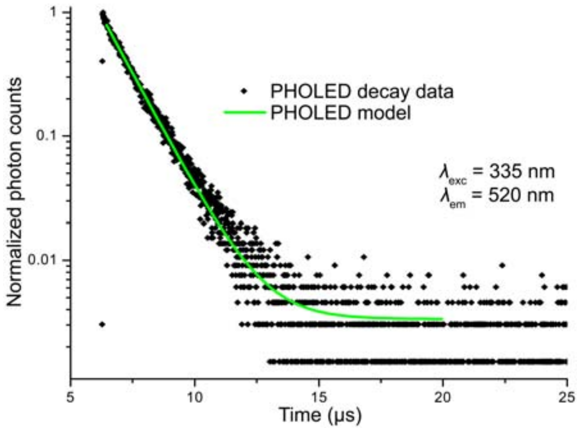

__Fig. 5.__ Phosphorescent decay of a PHOLED organic emitter, using a TCSPC-Fluorolog® in front-face mode (for solid samples), from < 100 ps to > 200 μs. NanoLED λ_{exc} = 335 nm (800 ps pulses); λ_{em} = 520 nm. Tail-fit R^2 = 0.995.

urements (from <100 ps) for photoluminescence research. The instrument can do steady-state and time-resolved anisotropy for molecular motions and shapes, with two TCSPC detectors: our TBX-05 (300–850 nm, 180 ps), and the Hamamatsu 9170-75 (900–1700 nm, 300 ps). Monochromators and gratings blazed for UV-visible or near-IR in the T-format optimize the system. A switchable adapter for Xe lamp and NanoLED converts between steady-state and time-resolved modes. NanoLEDs are pulsed TCSPC light-sources (~1 ns to ≤ 200 ps, 10 kHz–1 MHz), including deep-UV (265, 280, and 295 nm), and are interchangeable with SpectraLEDs (500 ns pulses to CW) for phosphorescence studies.

Conclusions

For researchers of SWNTs, we offer the NanoLog® and Nanosizer®. Researchers of quantum dots can use our Fluorolog®. For OLED technology, we have TCSPC instruments to resolve fluorescent lifetimes. HORIBA Jobin Yvon has the optimum spectrofluorometer for nanotechnology research in all these areas.

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