# Selected Article

## Nanoparticle Research with the NanoLog™

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Increased interest in research and applications of nanoparticles requires rapid qualitative and quantitative analysis of nanoparticle samples. The development of the NanoLog™ spectrofluorometer and associated Nanosizer™ software takes advantage of nanoparticles' fluorescence in the near-IR, and allows researchers to rapidly and accurately assess the composition and properties of samples of single-wall carbon nanotubes and quantum dots.

## Introduction

HORIBA Jobin Yvon's NanoLog™ spectrofluorometer, specially optimized for recording near-IR fluorescence from nanoparticles, includes a double-grating excitation monochromator, imaging emission spectrograph with a selectable-grating turret, and a variety of detectors. It has optimal excitation optics[*1] for single-wall carbon nanotube (SWNT) research or *any* solid sample in right-angle or front-face mirror configurations. The NanoLog can be customized to provide steady-state and lifetime information about quantum dots as well, for quantum-dot photoluminescence is becoming an important tool in the fields of materials science, biology, medicine, and energy.

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

## EEMs with the NanoLog

Corrected emission spectra[*2] of carbon nanoparticles can provide excitation-emission matrices (EEMs) for a range of excitation wavelengths. Acquisitions take only minutes ($\lambda_{exc}$ = 500–800 nm at 1-nm intervals, $\lambda_{em}$ = 830–1350 nm at ~1 nm per pixel). EEMs are compiled by HORIBA Jobin Yvon's Nanosizer™ software. A double-convolution algorithm (U.S. pat. pending) in the software simultaneously computes excitation and emission wavelength coordinate lineshapes for each species within minutes; contributions from all spectral bands in a region of interest are found.

EEM data (Figure 1) and simulations (contour maps) of two SWNT suspensions from two different manufacturing processes are distinguished by their different size and helical distributions: high-pressure carbon-monoxide method (Figure 1(a)(b))[*3]. HiPCO forms a broad size distribution of SWNTs (0.6–1.3 nm diam) with many helical angles and >50 species. CoMoCAT has a narrower average size (~0.8 nm diam) and smaller helical-angle distribution; just two species–(6,5) and (7,5)–comprise ~58% of the intensity. Figure 1(a) identifies five main HiPCO species, while Figure 1(b) identifies four main CoMoCAT species in the specified regions of interest. Figure 1(c) shows a comparative helical map of species found in Figure 1(a) and Figure 1(b), and plots the helical angle versus SWNT diameter (in nanometers) against intensity of emission (symbol size/color). HiPCO tubes have a larger average diameter than CoMoCAT.

*2 : Detector dark-signal and spectral response, and lamp output.

*3 : D.E. Resasco, *et al., J. Nanoparticle Res.* ***4****, 2002*; 131-136; S.M. Bachilo, *et al., J. Am. Chem. Soc.,* ***125****, 2003*; 11186-11187.

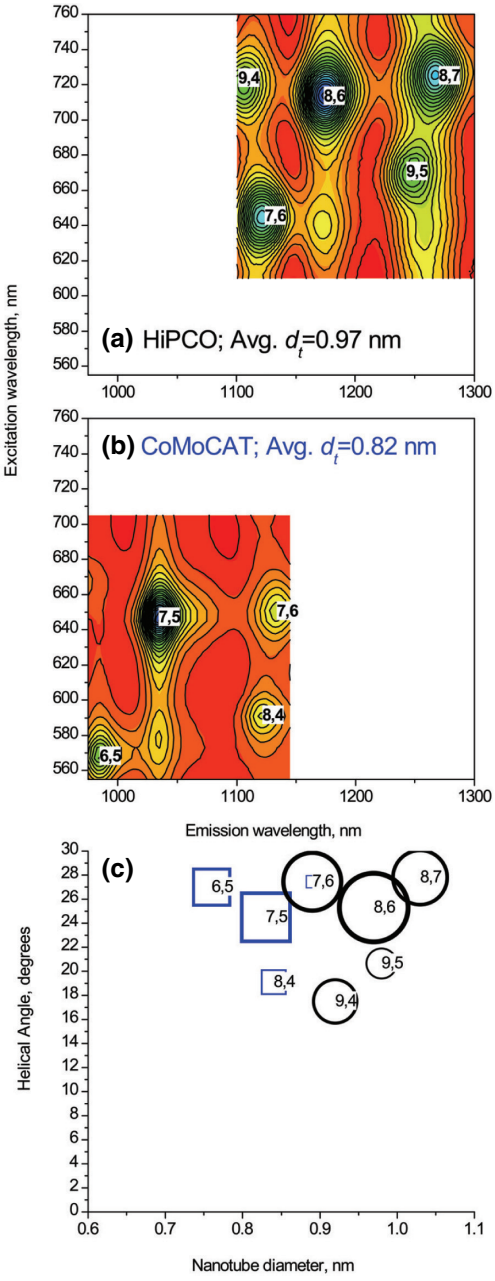


Figure 1 EEMs ((a), (b)) and Helical Maps (c) of HiPCO and CoMoCAT SWNT Suspensions
Solid lines ((a), (b)) are data; colors are simulations.
Symbol sizes (c) show relative amplitudes for HiPCO (circles) and CoMoCAT (squares), normalized to 1.
Simulation $R^2$ values = 0.997 (HiPCO) and 0.999 (CoMoCAT).

## The NanoLog's Signal-to-noise Ratio

High signal-to-noise ratio (*S/N*) is crucial to unambiguous, rapid quantitative determination of the multiple species present in SWNT samples. While the NanoLog's *S/N* varies with its configuration, to show the high *S/N* of the NanoLog, we studied a sample of SWNTs prepared by the HiPCO method. The nanotubes were dispersed in SDBS. The NanoLog consisted of a Fluorolog™-3 with a double-grating excitation monochromator and the iHR320 emission spectrograph coupled to a 512-pixel InGaAs array. Excitation = 725 nm, bandpasses = 25 nm, integration time = 1 s. Figure 2 shows an emission spectrum (a) from 835–1359 nm with known peaks, and a second excitation spectrum (b) from 600–800 nm to record noise at 850 nm. Dark noise was subtracted from both scans. Both dark-corrected spectra were then corrected by dividing by a reference signal to remove source inhomogeneities.

We define the *S/N* in Formula 1:

$$\frac{S}{N} = \frac{S_{\text{peak}} - S_{\text{background}}}{\sqrt{S_{\text{background}}}} \quad \cdots\cdots (1)$$

The peak signal, $S_{\text{peak}}$, is measured at the highest peak in Figure 2(a), 1171 nm–the (8,6) species–and the noise, $S_{\text{background}}$, in a region with no signal [Figure 2(b), 600–800 nm]. An "ideal" system has $S_{\text{background}} = 0$ at 600–800 nm. Thus Formula 1 becomes

$$\frac{S}{N} = \frac{S_{1171\text{ nm}} - S_{600\text{-}800\text{ nm}}}{\sqrt{S_{600\text{-}800\text{ nm}}}} \quad \cdots\cdots (2)$$

For Figure 2(b), the average noise was 5.443, and the maximum signal was 7357.41 at 1171 nm, giving a *S/N* = 3151. This is a very high *S/N*, not achievable using other spectrofluorometers.

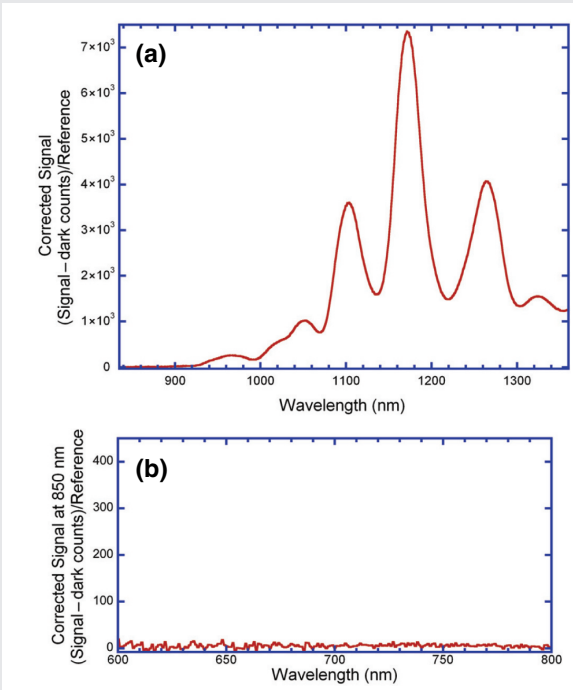


Figure 2 Emission [Plot (a), $\lambda_{exc}$ = 725 nm] and Excitation Spectra [Plot (b), $\lambda_{em}$ = 850 nm] of HiPCO Nanotubes
Spectra are corrected for excitation inhomogeneities and dark counts. Plot (b) was used to calculate noise

## Photoluminescence Lifetimes

The NanoLog can be fitted with a time-correlated single-photon counting (TCSPC) multichannel-scaling (MCS) accessory (Figure 3). A variety of quantum-dot samples, supplied by Evident Technologies[*4], were examined with this scheme. In Figure 4, the sample was a dispersion of quantum dots (PbS + polycarbonate) in $CHCl_3$. A pulsed laser-diode (50 kHz, $\lambda$ = 980 nm, pulse-width ≈ 450 ps) excited the sample. Emission was recorded at 1465 nm with a bandpass of 64 nm using MCS on a Hamamatsu 10330–75 near–IR photomultiplier tube[*5]. (With our TCSPC and MCS cards, the 10330-75 can resolve lifetimes from 60 ps to DC.) Time per channel was 100 ns. Measurements were continued until the peak channel reached 100 000 counts. Reconvolution was unnecessary when fitting the decay, for the laser pulse occupied only one channel.

*4 : Evident Technologies, 216 River Street, Suite 200, Troy, NY 12180.

*5 : Sensitivity = 950–1700 nm, time-transit spread = 300 ps.

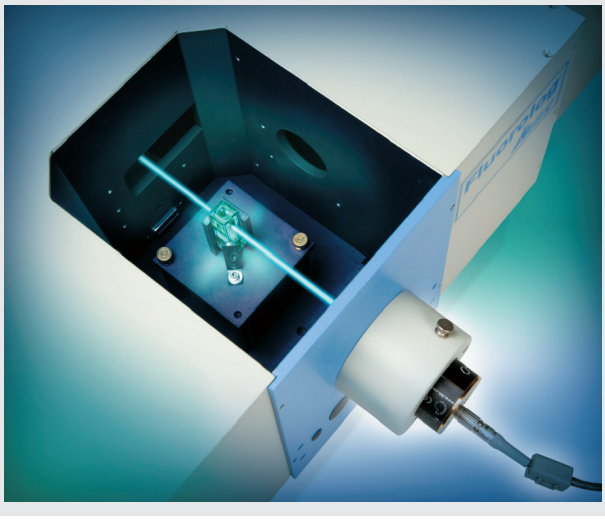

Figure 3 TCSPC/MCS Accessory Attached to the Sample Compartment of a NanoLog™

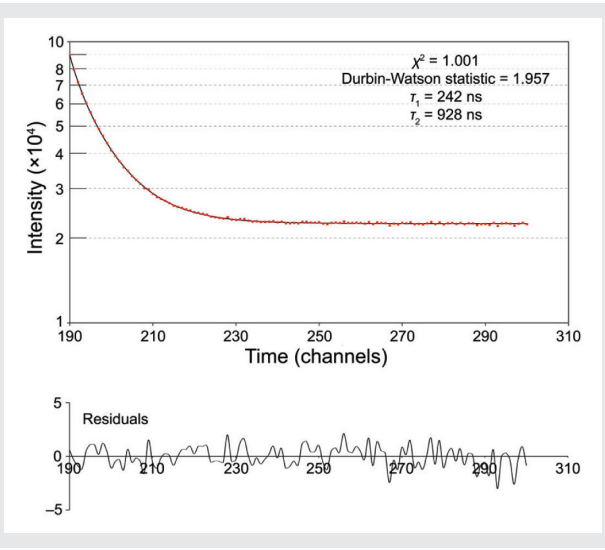


Figure 4 Fluorescence Decay (upper plot) of PbS-polycarbonate Quantum Dots in $CHCl_3$ (Evident Technologies) and Residuals to the Fit (lower plot)
Low residuals plus excellent $\chi^2$ and Durbin-Watson statistics show that the data fit well to the model.

Using a bi-exponential model, the $\chi^2$ = 1.001 and a Durbin-Watson statistic = 1.957 were found, indicating an excellent fit to the data in Figure 2. The two recovered lifetimes for the quantum dots were $\tau_1$ = 242 ns and $\tau_2$ = 928 ns. Table 1 shows lifetimes found for a variety of PbS quantum-dot dispersions.

Table 1 Near-IR Lifetimes and $\chi^2$s for a Variety of Quantum-dot Mixtures Using a Bi-exponential Model and the NanoLog™.

| Dispersant | $\tau_1$ (µs) | $\tau_2$ (µs) | $\chi^2$ |
|---|---|---|---|
| $\lambda_{abs}$ = 1040 nm; $\lambda_{exc}$ = 980 nm | | | |
| Polystyrene | 1.82 | 0.69 | 0.91 |
| PMMA | 2.52 | 1.37 | 0.97 |
| Polycarbonate | 2.22 | 0.79 | 1.10 |
| Flexographic ink | 0.57 | 0.17 | 1.10 |
| $\lambda_{abs}$ = 1400 nm | | | |
| Polystyrene ($\lambda_{exc}$ = 980 nm) | 1.00 | 0.61 | 1.14 |
| Polystyrene ($\lambda_{exc}$ = 635 nm) | 0.93 | 0.57 | 1.19 |
| PMMA ($\lambda_{exc}$ = 980 nm) | 1.12 | 0.62 | 1.03 |
| PMMA ($\lambda_{exc}$ = 635 nm) | 1.11 | 0.62 | 1.20 |
| Polycarbonate ($\lambda_{exc}$ = 980 nm) | 0.93 | 0.24 | 1.00 |
| Polycarbonate ($\lambda_{exc}$ = 635 nm) | 0.96 | 0.40 | 1.13 |
| Flexographic ink ($\lambda_{exc}$ = 980 nm) | 0.30 | 0.14 | 0.95 |

## Conclusion

The NanoLog is an indispensable tool for studying fluorescence lifetimes of samples whose luminescence is primarily in the near-IR, such as quantum dots and single-wall carbon nanotubes. With the Nanosizer software, the composition of mixtures of SWNTs can be determined. Using the TCSPC/MCS accessory, luminescence lifetimes of quantum dots can be measureed. Other uses for the NanoLog include solid-state research, biosensing, and cancer detection. The NanoLog is also available with TCSPC multichannel-scaling options of 500 ns/channel and 2 ns/channel, as well as a broad-band 5509 photomultiplier tube, sensitive from 300–1700 nm, with a time-transit spread of 1.5 ns.

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