Direct Probe of Spectral Inhomogeneity Reveals Synthetic Tunability of Single-Nanocrystal Spectral Linewidths

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1 Explanation of Notation

In S-PCFS, the intensities at both outputs of the interferometer are measured and the intensity cross-correlation function \( g^{\times}(\delta, \tau) \) is calculated at different interferometer path-length differences \( \delta \) for temporal spacings between photons \( \tau \). Reference [1] introduces the governing equation of S-PCFS, which relates \( g^{\times}(\delta, \tau) \) to the single-emitter and ensemble spectral correlation functions.

\[
g^{\times}(\delta, \tau) = g^{(2)}(\tau) - \frac{1}{2} FT \left\{ p^{\text{ens}}(\zeta) + \left( g^{(2)}(\tau) - 1 \right) p^{\text{single}}(\zeta, \tau) \right\}_{\zeta \to \delta} \tag{1}
\]

This is equivalent to the governing equation in [2] where \( g^{(2)}(\tau) = g^{\text{FCS}}(\tau) \) represents the autocorrelation function of the total intensity before entering the interferometer. This correlation function describes fluctuations in the total signal and accounts for the diffusion of the particles as in fluorescence correlation spectroscopy (FCS) [3] as well as fluctuations in the single-emitter signal (e.g. “blinking”).

Here, we introduce the notation \( \tilde{g}(\delta, \tau) \) as the Fourier transform of the spectrally-relevant component of the cross-correlation function. This is equivalent to the “\( \delta \)-dependent component” of \( g^{\times}(\delta, \tau) \) because \( g^{(2)}(\tau) \) arises from the sum of the detector intensities and should show no dependence on the interferometer path-length difference.

\[
\tilde{g}(\delta, \tau) = FT \left\{ p^{\text{ens}}(\zeta) + \left( g^{(2)}(\tau) - 1 \right) p^{\text{single}}(\zeta, \tau) \right\}_{\zeta \to \delta} \tag{2}
\]

\( \tilde{g}(\delta, \tau) \) is the “PCFS interferogram” that is equivalent to the Fourier transform of the “diffusion weighted spectral correlation” described in [2].

We have further split \( \tilde{g}(\delta, \tau) \) into its single-emitter and ensemble components. This gives us \( \tilde{g}^{\text{single}}(\delta, \tau) = FT \left\{ p^{\text{single}}(\zeta, \tau) \right\}_{\zeta \to \delta} \) and \( \tilde{g}^{\text{ens}}(\delta) = FT \left\{ p^{\text{ens}}(\zeta) \right\}_{\zeta \to \delta} \). The ensemble component does not have a \( \tau \) dependence because it is determined by the statistics of different particles entering and exiting the focal volume, which is governed by Poisson statistics.

2 Fitting

In the absence of spectral dynamics, \( p(\zeta, \tau) \) is the spectral autocorrelation. For both the single-NC and ensemble components, we have assumed here that the true spectral lineshape \( s(\omega) \) is well-approximated by an effective spectral lineshape composed of the summation of an arbitrarily large number of Gaussian functions. In practice, we find that for all samples measured here, both \( \tilde{g}^{\text{single}}(\delta) \) and \( \tilde{g}^{\text{ens}}(\delta) \) are well-fit by a spectrum composed of the sum of two Gaussian functions with amplitudes \( A, B \) and widths \( c, d \), but centered at the same frequency \( \omega_0 \) as follows. The inclusion of additional Gaussian functions into the model does not improve the fit.

\[
s(\omega) = Ae^{-\frac{(\omega-\omega_0)^2}{2\omega^2}} + Be^{-\frac{(\omega-\omega_0)^2}{2d^2}} \tag{3}
\]
The model gives a spectral correlation $p(\zeta)$ that is a sum of three Gaussians: one term from the first Gaussian, the second term from the second Gaussian and a cross-term. Fourier transform to $\tilde{g}(\delta)$ gives another sum of three Gaussians resulting in the fitting equation below. The absence of the center frequency $\omega_0$ in the fitting equation indicates that absolute frequencies are indeed lost but information regarding spectral breadth is conserved.

$$\tilde{g}^{\text{single/ens}}(\delta) = 2\pi \left( A^2 e^{-4\pi^2 c^2 \delta^2} + B^2 e^{-4\pi^2 d^2 \delta^2} + 2ABcd e^{-2\pi^2 (c^2+d^2)\delta^2} \right)$$

(4)

In Figure 2c, the ratio of the areas of the two Gaussians is approximately 2:1, indicating that both Gaussians contribute significantly to the fitting.

3 Ensemble Spectrum: S-PCFS vs. Fluorometer

![Figure S1: Comparison of Fluorescence Data from S-PCFS and Fluorometer](image)

a) Spectral correlations for the ensemble spectrum of CdSe/CdS core/shell particles with 4.0 monolayers of CdS taken by both S-PCFS and the fluorometer agree well with each other. b) Though the effective spectral lineshape for the ensemble calculated from fitting to the PCFS interferogram cannot capture the slight asymmetry of the spectrum, the linewidths are nearly identical.

To illustrate the accuracy of S-PCFS and our fitting, we compare the ensemble component obtained through S-PCFS to the ensemble spectrum obtained through a conventional fluorometer for the same batch of particles. As also shown in [2], $p^{\text{ens}}(\zeta)$ obtained from S-PCFS is remarkably consistent with the energy autocorrelation of the spectrum obtained through traditional spectroscopy (Supplementary Figure S1a). In Supplementary Figure S1b, we plot the effective spectral lineshape (ESL) calculated from our fit to the S-PCFS data to the actual spectrum from the spectrometer. Because our model is based on overlapping Gaussians, it cannot account for the slight asymmetry in the spectrum. However, the linewidths are nearly identical, giving credence to our method.
4 Transmission Electron Microscopy

Figure S2. Transmission Electron Micrographs a) Qdot® 545, b) Qdot® 605, c) Qdot® 655, d) InP core/shell particle, e) CdSe with 4.0 monolayers CdS shell, f) CdSe with 10.0 monolayers CdS shell

5 InAs/ZnS Synthesis

A 0.05 M indium myristate (InMy$_3$) stock solution was made by adding 5 mmoles indium(III) acetate (99.99%, Alfa Aesar) and 15 mmoles myristic acid (98%, Spectrum Chemicals) to 100 mL of 1-octadecene (90%, technical grade from Sigma Aldrich).

The synthesis of the InAs/ZnS core/shell particles was adapted from [4]. 3 mL of 0.05 M InMy$_3$ stock solution (0.15 mmole) was added to a 15 mL four-neck round bottom flask attached to a Schlenk line. The solution was heated to 100°C and the flask was evacuated to a pressure of 100 mtorr.

The injection syringe was prepared by mixing 0.115 mmoles tris(trimethylsilyl)arsine (TMS$_3$As) prepared as described previously [5] with 0.75 mL tri-n-octylphosphine (98%, Strem) in a nitrogen glovebox. Overcoating syringes were prepared by adding 1.1 mmoles diethylzinc (99%, Strem) with 5 mL tri-n-octylphosphine (98%, Strem) and 1 mmole bis(trimethylsilyl)sulfide (99%, Strem) with 5 mL tri-n-octylphosphine (98%, Strem).

The TMS$_3$As solution was rapidly injected into the vigorously stirred InMy$_3$ solution at 150 °C and promptly heated to 250°C for 40 min. The solution was cooled to 175°C for overcoating. The overcoating solutions were injected dropwise at 1.5 mL/hr.
6 CdSe/CdS Synthesis

A detailed description of the CdSe/CdS synthesis can be found in [6]. CdSe cores were synthesized by a modification of the method described in [7]. For the shell growth reaction, a hexane solution containing 100 nmol of CdSe nanocrystals were loaded in a mixture of 3 mL 1-octadecene (ODE, 90%, Alfa Aesar) and 3 mL oleylamine (OAm, 70%, Aldrich). The reaction solution was degassed under vacuum at room temperature for 1 hr and then at 120 °C for 20 min to totally remove the hexane, water and oxygen inside the reaction solution. After that, the reaction solution was heated up to the growth temperature under nitrogen flow and magnetic stirring. Once the reaction solution was heated to 240 °C, a desired amount of Cd-oleate (dilute in 6 mL ODE) and one equivalent amount of octanethiol (dilute in 6 mL ODE) were infused into the growth solution with a rate of 3 mL/hr using a syringe pump. Shortly after starting addition, the reaction temperature was further elevated to 310 °C and maintained for the rest of the reaction. Precursor addition was stopped for ~5 min at a time to take aliquots. The resulting CdSe/CdS core/shell QDs were precipitated with acetone addition and the redispersed in hexane. The particles were further purified by precipitation-redispersion for two more rounds and finally suspended in ~5 mL hexanes.

References


