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

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Abstract

The spectral linewidth of an ensemble of fluorescent emitters is dictated by a combination of the single emitter linewidths and sample inhomogeneities. For semiconductor nanocrystals, efforts to tune ensemble linewidths for optical applications have focused primarily on eliminating sample inhomogeneities because conventional single-molecule methods cannot reliably build accurate ensemble-level statistics for single-particle linewidths. Photon-correlation Fourier spectroscopy in solution (S-PCFS) offers a unique approach to investigating single-nanocrystal spectra with large sample statistics, without user selection bias, with high signal-to-noise ratios, and at fast timescales. With S-PCFS, we directly and quantitatively deconstruct the ensemble linewidth into contributions from the average single-particle linewidth and from sample inhomogeneity. We demonstrate that single-particle linewidths vary significantly from batch to batch and can be synthetically controlled. These findings crystallize our understanding of the synthetic challenges facing underdeveloped nanomaterials such as InP and InAs core/shell particles and introduce new avenues for the synthetic optimization of fluorescent nanoparticles.

The past twenty years have seen great advances in the synthetic control over many critical properties of colloidal semiconductor quantum dot nanocrystals (NCs) such as size polydispersity [1], quantum yield [2], photostability [3] and photoluminescence intermittency [4]. Because of their unique and synthetically-tunable optical and electronic properties, these materials have been successfully implemented in applications such as biological imaging [5] and solid-state lighting [6] and hold promise in other applications such as solar cells [7], photodetectors [8], and lasers [9].

However, most NC-based applications are still significantly limited in performance by the broad ensemble emission linewidth of NCs at room temperature [5] [6]. While the peak spectral energy of a batch of nanocrystals is dictated by the average size of the particles [10], its spectral breadth is dictated by a combination of sample inhomogeneity and the spectral linewidths of the single particles. To date, progress in synthesizing spectrally-narrow NC batches has occurred primarily by reducing sample inhomogeneities without consideration for single-NC linewidths because we have lacked the experimental tools and theoretical

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Author contributions

J.C., L.F.M., X.B., and M.G.B. conceived of and designed the experiments. J.C. performed the S-PCFS experiments. O.C. and D.K.H. synthesized the CdSe/CdS and InAs/ZnS nanoparticles. D.D.W. and O.C. performed transmission electron microscopy. J.C. and A.P.B. analyzed the data with guidance from L.F.M., X.B., and M.G.B. The manuscript was written by J.C. and A.P.B. with contributions from all authors.

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insight necessary to definitively determine the effects of synthesis on single-nanocrystal monochromaticity [11] [12] [13].

Photon-correlation Fourier spectroscopy performed on emitters diffusion in solution (S-PCFS) offers a unique approach for investigating the spectra of single nanocrystals with large sample statistics, without user selection bias, with high signal-to-noise ratios, and at timescales fast enough to avoid the spectral diffusion commonly observed in single-NC spectroscopy [14]. In this Article, we demonstrate that S-PCFS can be used to efficiently and reliably measure the spectral profile of the average single nanocrystal within an ensemble with statistical confidence, enabling the unambiguous characterization of the links between synthetic methodologies and single-nanocrystal spectral linewidths.

Results

Theoretical Background of S-PCFS

The key to S-PCFS is measuring the energy *differences* between photons rather than measuring their absolute energies [15]. When sampling an ensemble of particles freely diffusion through a small focal volume, energy differences between photons emitted by the same particle reflect the single-NC spectral profile. In contrast, photons emitted from different particles depend on the emission energies of each particle and therefore reflect the inhomogeneously broadened ensemble spectrum. Because the detection of photons originating from the same NC is statistically enhanced at timescales shorter than the particle dwell time in the focal volume, the single-particle contribution can be disentangled from the ensemble while maintaining ensemble-level statistics [16].

S-PCFS experimentally implements this unique conceptual approach by combining the energy-resolving capabilities of interferometry with the time-resolving capabilities of Hanbury Brown and Twiss photon correlation analysis (Figure 1). The interferometer converts spectral information into intensity fluctuations, which are interpreted by photon correlation analysis as the energy difference ΔE between photons as a function of the time separation Δt between them. Analogous to Fourier transform spectroscopy, where the dependence of the output intensity on the interferometer path-length difference ΔL gives the intensity interferogram, which is the Fourier transform of the spectrum $s(\omega)$, here, the dependence of the intensity cross-correlation function on Δt gives the “PCFS interferogram” $g(\Delta t)$, which is the Fourier transform of the spectral correlation function $p(\Delta E)$ (Equation 1).

$$p(\zeta, \tau) = \langle \int s(\omega, t) s(\omega + \zeta, t + \tau) d\omega \rangle \quad (1)$$

The spectral correlation $p(\Delta E)$ can be interpreted as the distribution of energy differences ΔE for photons of temporal spacing Δt . Though the spectrum itself has been sacrificed to access spectral correlations at timescales previously inaccessible to single-molecule spectroscopy, photon-correlation provides the means of extracting single-emitter spectral information with ensemble-level statistics.

Traditional spectroscopy of particles diffusion in solution only provides the spectrum of the ensemble. However, encoded in $g(\Delta t)$ are the spectral correlation functions $p^{\text{single}}(\Delta E)$ for the average single emitter and $p^{\text{ns}}(\Delta E)$ for the ensemble [16] [17]. By analyzing $g(\Delta t)$ at timescales shorter and longer than the dwell time of the particles within the focal volume, we decompose $g(\Delta t)$ into the contributions from the average single emitter ($g^{\text{single}}(\Delta t)$) and from the ensemble ($g^{\text{ns}}(\Delta t)$), which are related by Fourier transform to their

corresponding spectral correlation functions. We refer the reader to Section 1 of the Supplementary Information and References [15] – [18] for more details regarding the theory and execution of this method.

In addition to high temporal and frequency resolution, S-PCFS overcomes many of the shortcomings of traditional single-molecule spectroscopy. Assuming a single unique emitter within the focal volume at a time, a measurement of 123 intensity correlation functions with 30 s integration times for particles with an average dwell time of 300 μs has a throughput of $\sim 10^7$ particles with no user selection bias. Furthermore, because of short exposure times, low-intensity cw excitation, and a correction for fluctuations in the total signal (see Supplementary Information Section 1), emission intermittency and bleaching are no longer experimental concerns. Finally, integration time and temporal resolution are decoupled in PCFS, which means that arbitrarily high signal-to-noise ratios can be obtained simply by increasing the integration time for each correlation function.

Extracting Single-Nanocrystal Spectral Linewidths

Though S-PCFS directly measures spectral correlation functions, additional analysis is necessary to gain insight into the underlying spectrum. Marshall *et al.* found that CdSe/CdZnS core/shell nanoparticles exhibited no appreciable spectral diffusion at submillisecond timescales approaching the lifetime of the emitters under low excitation flux and ambient conditions [17]. In the absence of spectral dynamics, the single-particle spectral correlation function $P^{\text{single}}(\Delta t)$ simply reduces to the energy autocorrelation of the spectrum. Thus, the breadth of the spectral correlation function reflects the breadth of the underlying spectrum. For both the single-particle and ensemble components, a broader spectral correlation $P(\Delta t)$ means a broader spectrum $s(\omega)$.

In order to obtain a quantitative spectral linewidth, we adopt a model to fit the data because, without assumptions, the spectrum cannot mathematically be uniquely recovered from its autocorrelation. Knowing that the single-NC spectrum at room temperature is a singly peaked, nearly symmetric function, we model the spectral lineshape using a superposition of Gaussian functions and obtain a functional form to fit $g^{\text{single}}(\Delta t)$. An effective spectral lineshape (ESL) can be calculated from the fit and its full-width at half-maximum gives the effective “single-nanocrystal linewidth”. The ensemble component is fit similarly. See Sections 2 and 3 of the Supplementary Information for more details and confirmation of the accuracy of our analysis.

Figure 2 provides an example of our data analysis. The measured $g^{\text{single}}(\Delta t)$ ($\Delta t \approx 5 \mu\text{s}$) is plotted in blue in Figure 2a for a batch of CdSe/CdS core/shell particles. We highlight the high signal-to-noise ratio at $\Delta t \approx 5 \mu\text{s}$, which is at least 3 orders of magnitude faster in temporal resolution than conventional single-molecule spectroscopy can achieve. Plotted in red is the fit to our model. Figure 2b shows that the fit is well-conserved to the spectral correlation $P^{\text{single}}(\Delta t)$ ($\Delta t \approx 5 \mu\text{s}$). The effective spectral lineshape calculated from this fit is shown in Figure 2c.

Variability and Tunability of Single-Nanocrystal Linewidths

Having demonstrated how S-PCFS can be used to measure the spectral linewidth of the average single NC, we apply our method to explore the dependence of this linewidth on several nanocrystal parameters in core/shell particles. We present three experiments that illustrate how single-NC linewidths vary in ways that challenge our current understanding of the spectra of nanomaterials.

First, we investigate the effect of the core composition on the single-NC linewidth. Given that different material compositions are associated with different effective masses, dielectric

constants, deformation-potential coupling, and other properties that affect the materials' response to optical excitations, changing the core composition was expected to have a significant effect on spectral linewidths [19]. In this experiment, we compare CdSe, InP, and InAs core/shell particles. InP was chosen because it is a Cd-free alternative to CdSe and InAs was chosen for its emission tunability into the near-infrared. These materials are of great interest for applications in displays, solid-state lighting [20], and biological imaging [21].

In Figure 3, we overlay the single-NC and ensemble spectral correlation functions for CdSe, InP, and InAs core/shell particles. The ensemble spectral correlations confirm what is often observed in InP and InAs nanocrystals – their ensemble spectra are much broader than those of CdSe particles [22] [23]. Surprisingly, however, the single-NC linewidths are nearly the same. This result shows that differences in the materials properties of the core composition do not necessarily have a dramatic effect on single-NC linewidths.

In the second experiment, however, we discover large batch-to-batch variations in the average single-NC linewidths of three sample batches of commercial CdSe core/shell particles (Qdots®) (Figure 4a). Although variation in the room-temperature spectral linewidth of single nanocrystals has been previously observed [14], this is the first report of variation in the average spectral linewidth of single nanocrystals between synthetic batches. More importantly, these large single-NC linewidth variations exist despite their same core material composition (CdSe) [24].

The first two experiments reveal that the core material composition does not solely dictate the single-NC linewidth, but instead, that other aspects of the core/shell architecture can have a predominant effect. We can begin to understand the structural origins of these linewidth variations through controlled synthesis in conjunction with S-PCFS.

In our third and final experiment, we demonstrate that the single-NC linewidth can be altered considerably by the adjustment of a synthetically-controllable structural parameter. In Figure 4b, we observe that the single-NC linewidth increases substantially for CdSe/CdS particles undergoing shell growth. In fact, Table 1 shows that the single-NC linewidth increases monotonically from 64 meV (1.8 monolayers) to an astonishing 92 meV (10 monolayers). This result does not necessarily imply that all single-NC linewidth variations, such as those observed in the second experiment, are caused by differences in shell thickness. Rather, it provides one instance in which the single-NC linewidth can be strongly influenced by structural features of core/shell particles. This experiment brings to light the feasibility of synthetic control over the single-NC linewidth.

Discussion

Our findings have far-reaching implications for our understanding of the spectra of both single nanocrystals and nanocrystal ensembles. First, and most importantly, we have shown that the room-temperature single-NC linewidth varies considerably from batch to batch in a synthetically controllable fashion (Figure 4). In fact, the broadest single-NC linewidth measured for the CdSe/CdS particles is even broader than the *ensemble* linewidth for several of the other CdSe particles (Table 1). Furthermore, single-NC linewidth synthetic tunability should be possible for nanoparticles with cores other than CdSe because the single-NC linewidth is not dictated solely by the core composition; other aspects of the core/shell architecture can greatly alter the single-NC linewidth.

The direct consequence of these results is that the effect of the single-NC linewidth on the ensemble spectral linewidth cannot be ignored. Throughout the literature, changes in the ensemble spectral linewidth have often been attributed to changes in the size distribution of

the particles [22]. However, our third experiment demonstrates that this conclusion is unwarranted. In the case of our CdSe particles undergoing CdS shell growth, the increase in the ensemble linewidth is due primarily to broadening of the single-NC linewidth (Table 1).

Conversely, it has been speculated that the broad ensemble spectral linewidths of InP and InAs core/shell particles may be dictated by broad single-NC linewidths rather than by sample inhomogeneities. Figure 3 and Table 1 reveal that the dramatically different ensemble spectral linewidths belie nearly identical single-NC spectra. The broad ensemble spectra of InP and InAs core/shell particles are limited not by the intrinsic properties of these materials, but rather by the inhomogeneities among the particles in the sample. Thus, the synthesis of InP and InAs core/shell particles with ensemble spectral linewidths as narrow as CdSe should be achievable via the reduction of sample inhomogeneities.

These insights could not have been conclusively drawn using traditional characterization tools. A comparison of Table 1 and Supplementary Figure S2 shows that both single-NC and ensemble spectral linewidths have little correlation with shell morphology in core/shell particles. Because transmission electron microscopy (TEM) cannot easily resolve the core from the shell, and because it relies on single-particle examination, it cannot provide an ideal measure of the degree of inhomogeneity within a synthetic batch. S-PCFS, on the other hand, provides a quantitative comparison of the single-NC and ensemble linewidths and is thus a direct probe of the degree of spectral inhomogeneity within a sample. This technique has allowed us to conclude that the single-NC linewidth and the sample polydispersity are independent and synthetically controllable parameters.

Finally, the single-NC linewidth variations that we observe challenge our current understanding of the physical origin of single-nanocrystals emission spectra. The breadth of the single emitter spectrum originates from broadening of the lifetime-limited natural emission spectrum by intrinsic and extrinsic interactions with the environment [25]. In the context of nanocrystals, the single-NC linewidth is believed to arise from a combination of photoinduced spectral diffusion (extrinsic) and exciton-phonon interactions (intrinsic) [26]. However, spectral diffusion has been found to be negligible in core/shell particles at the timescales investigated in the present work [17]. Thus, our results directly reflect the intrinsic single-NC spectral broadening mechanisms such as excitonic coupling to phonons within the nanoparticle, [27] [28] to vibrations in the ligands on the surface, and to the bath solvent itself [29] [30].

The single-NC linewidth broadening with shell growth observed in the CdSe/CdS particles is consistent with an increased “Frölich-like” exciton-phonon interaction due to the spatial separation between the electron and hole in these quasi-type-II heterostructures [31] [32]. Our results suggest that the batch-to-batch variations in single-NC emission linewidths measured by S-PCFS originate from a delicate interplay between various parameters that affect exciton-phonon interactions within the core/shell/ligand architecture.

conclusions

In this Article, we have demonstrated that S-PCFS enables the simultaneous characterization of ensemble and single-emitter spectral properties with unprecedented clarity. With this new class of single-molecule spectroscopy, we have discovered batch-to-batch variability and synthetic tunability in room-temperature single-nanocrystal emission linewidths. Our work highlights the fundamental importance of the single-NC spectral linewidth when characterizing and optimizing nanocrystals for applications. With the use of S-PCFS as a high-throughput characterization tool, synthetic chemists can rapidly and quantitatively assess synthetic methodologies for the rational design of future nanostructures. In fact, our

technique is already being used to help develop a new generation of nanoparticles with superior optical properties [33].

We also emphasize the broad applicability of S-PCFS. Coupled with the rich and unexplored physics now accessible by our method, we anticipate that S-PCFS may serve as a platform for new perspectives on the synthesis of nanomaterials of exceptional quality. Finally, we note that though our efforts have focused on semiconductor core/shell nanoparticles, our method can be easily extended to to characterize the inhomogeneities in and to probe the underlying physics of myriad fluorescent systems.

Methods

Experimental Details

Each sample was prepared by diluting a concentrated stock solution into a hexanes solution containing excess cadmium oleate and decylamine, which help prevent aggregation. A thin capillary tube containing a dilute solution of the nanocrystal sample was mounted onto a water-immersion objective. A cw laser at 457 nm was used in conjunction with a pellicle beamsplitter and a dielectric notch or long-pass filter in order to achieve sensitivity across the visible spectrum.

PL emission was collected through the same objective and focused through a pinhole to obtain a well-defined focal volume as in fluorescence correlation spectroscopy (FCS) [34]. The beam was recollimated and directed to a two-output Michelson interferometer. In the interferometer, the beam was split, sent to two orthogonal paths, recombined at the beam splitter and focused onto two single-photon counting modules (PerkinElmer now Excelitas Technologies). On one arm of the interferometer, a retroreflector was mounted on a linear stage that defined the path-length difference Δ . On the other arm was a retroreflector mounted with a piezoelectric actuator that translated it back and forth over short distances (“dithering”). Correlation functions were obtained through a digital correlator (ALV-7004/FAST).

Each S-PCFS experiment consisted of 123 correlation measurements over 81 path-length differences. Each step of the linear stage increased the path-length difference Δ by 1 μm , thus covering path-length differences from $-40 \mu\text{m}$ to $+40 \mu\text{m}$. The path-length differences selected for these measurements provide sufficient spectral resolution for all samples measured here. The instrument function of the interferometer is less than 15 μeV .

The center 21 positions were measured three times and the correlation function values were averaged after correcting for diffusion and the ensemble spectral correlation. The ensemble component was selected at $\Delta \sim 100 \text{ ms}$, a timescale much longer than the average particle dwell time in the focal volume. The PCFS interferogram $g^{(2)}(\Delta)$ was then averaged over $\Delta = 1 - 10 \mu\text{s}$ and reported as $\Delta \sim 5 \mu\text{s}$. The piezo actuator, receiving an input from a function generator, translated the mirror over a distance of ~ 2 emission wavelengths with a frequency of 0.04 Hz or 0.06 Hz. Afterpulse correction was performed as described in [17] except no short-time fitting was performed.

Transmission electron microscopy was performed on a JEOL 200CX General Purpose TEM operating at 120 kV and on a JEOL 2010 Advanced High Performance TEM operating at 200 kV. Ensemble fluorescence spectra were measured on a Fluoromax-3 (Horiba Jobin Yvon).

Samples

The synthesis of InAs/ZnS and CdSe/CdS core/shell particles are described in the Supplementary Information. The emission maximum of the InAs/ZnS particles was 710 nm and the emission maxima of the CdSe/CdS particles were between 600 and 620 nm.

Commercial CdSe samples Qdot® 545 (SKU No. Q21791MP, Lot No. 801737), Qdot® 605 (SKU No. Q21701MP, Lot No. 786124), and Qdot® 655 (SKU No. Q21721MP, Lot No. 691974) were purchased from Invitrogen (now Life Technologies).

The InP sample was obtained from QD Vision, Inc.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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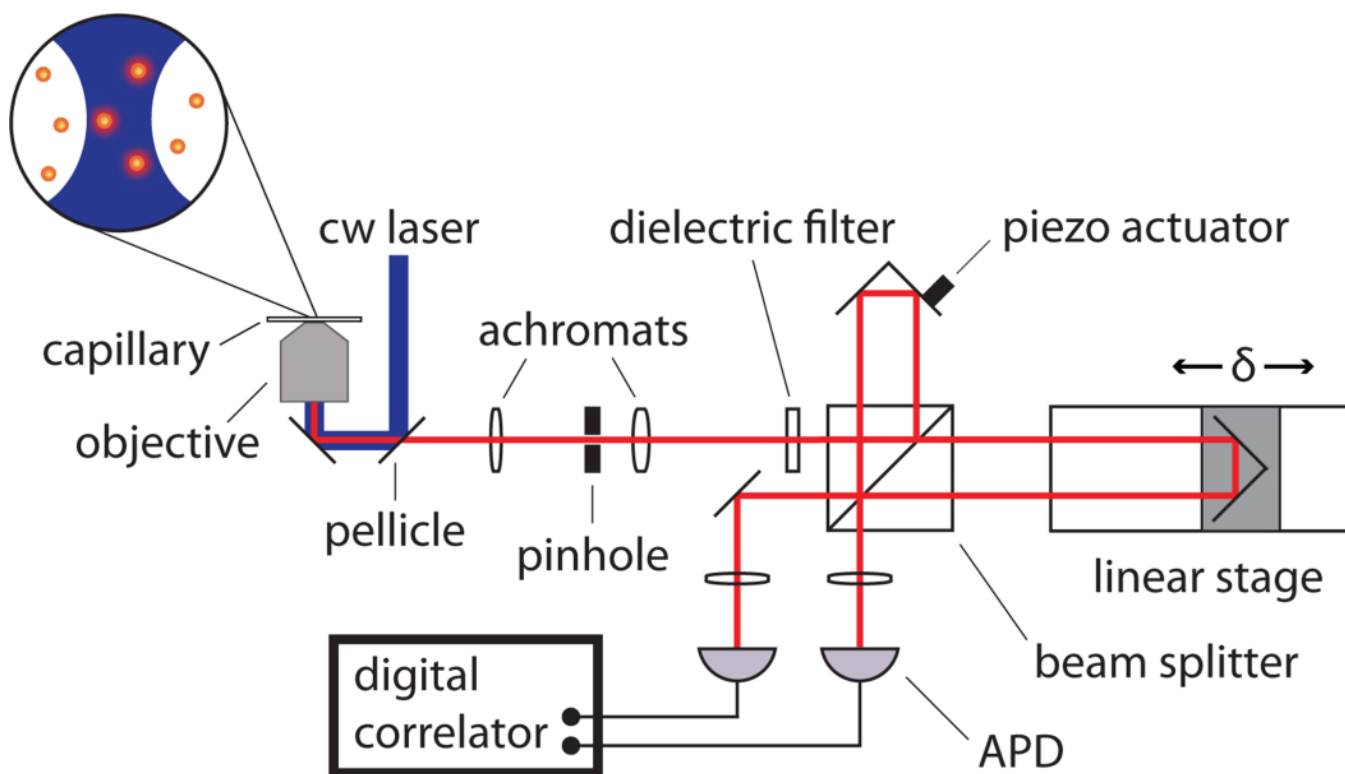


Figure 1. Experimental Setup

In S-PCFS, we pass the fluorescence from particles diffusion through a small focal volume through an interferometer. With correlation analysis of the intensities at both outputs, the spectral correlation function for the average single particle can be distinguished from the spectral correlation function for the ensemble.

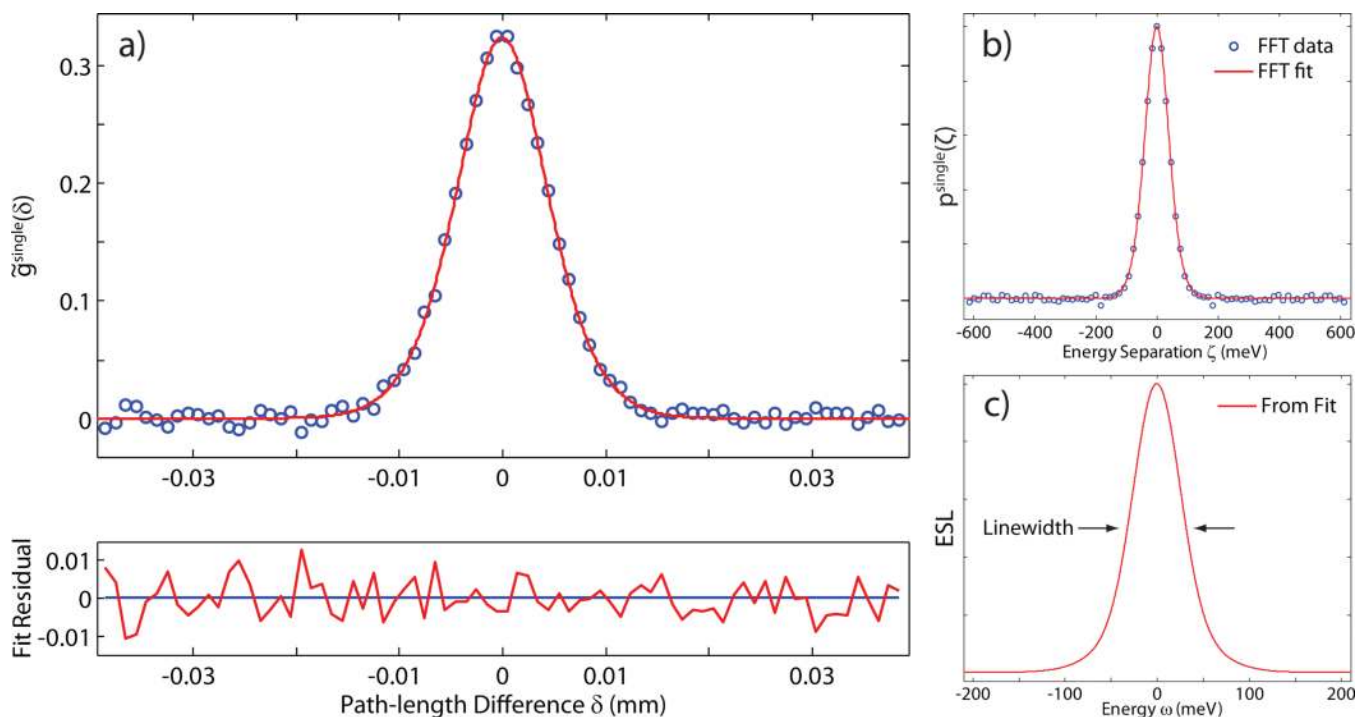


Figure 2. Demonstration of S-PCFS Data Analysis

a) Single-emitter PCFS interferogram $g^{\text{single}}(\delta)$ ($\delta \ll 5 \mu\text{s}$) along with fit and fitting residual. Note the high signal-to-noise ratio at a timescale more than 3 orders of magnitude faster than conventional methods can access. b) The Fourier transform of $g^{\text{single}}(\delta)$ ($\delta \ll 5 \mu\text{s}$) gives the spectral correlation $p^{\text{single}}(\zeta)$ ($\zeta \ll 5 \mu\text{s}$). The good fit is conserved through the transform. c) The effective spectral lineshape (ESL) is calculated from the initial fit to $g^{\text{single}}(\delta)$ ($\delta \ll 5 \mu\text{s}$) and its full-width at half-maximum is the effective “single-nanocrystal linewidth”.

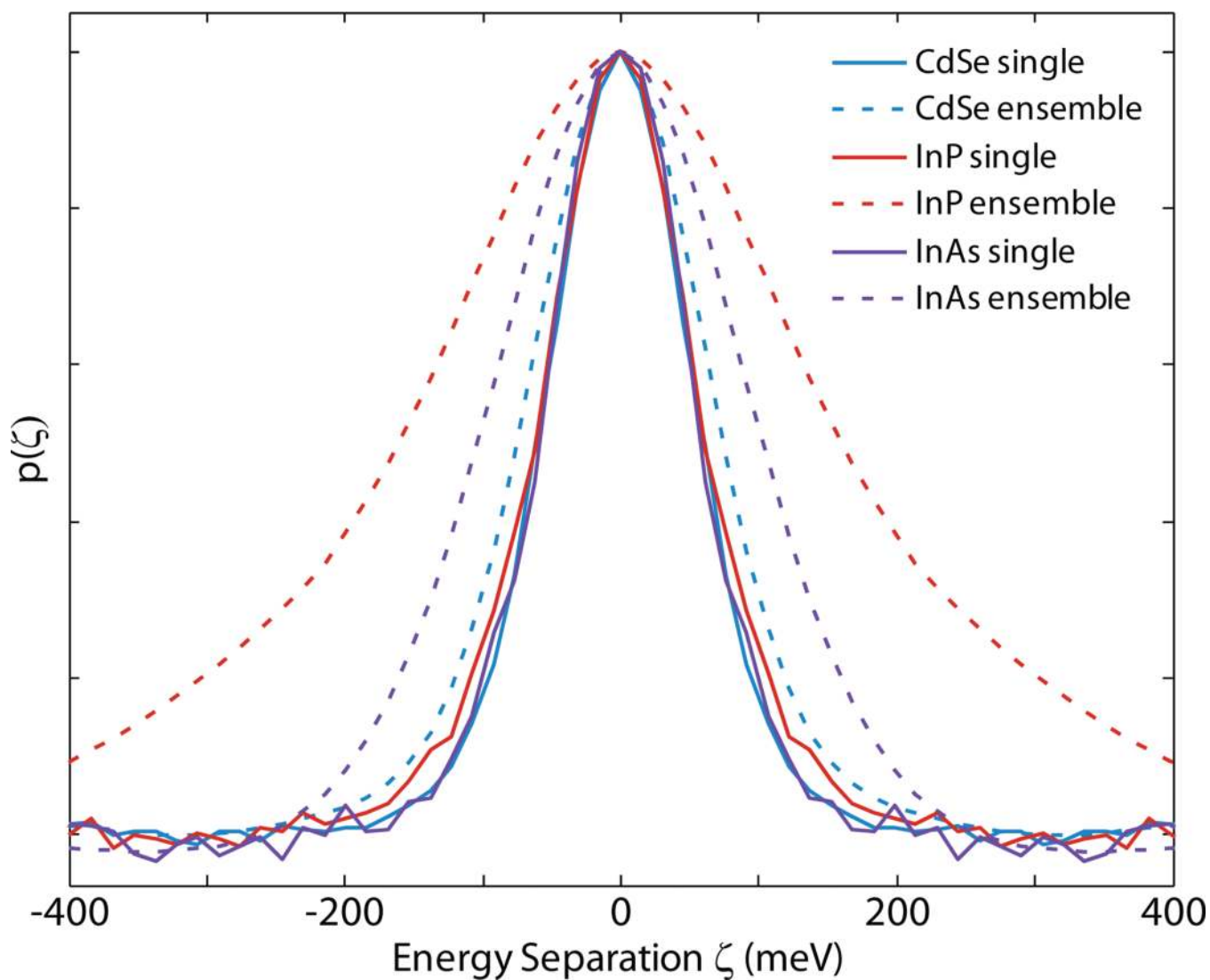


Figure 3. Comparison of Different Core Materials Composition

Single-particle (solid line) and ensemble (dotted line) spectral correlation functions $\rho(\zeta)$ (ζ is Energy Separation, μs) for core/shell particles with CdSe (blue), InP (red), and InAs (violet) cores. Despite very different material properties and ensemble spectral linewidths, the single-nanocrystal spectral linewidths are very similar.

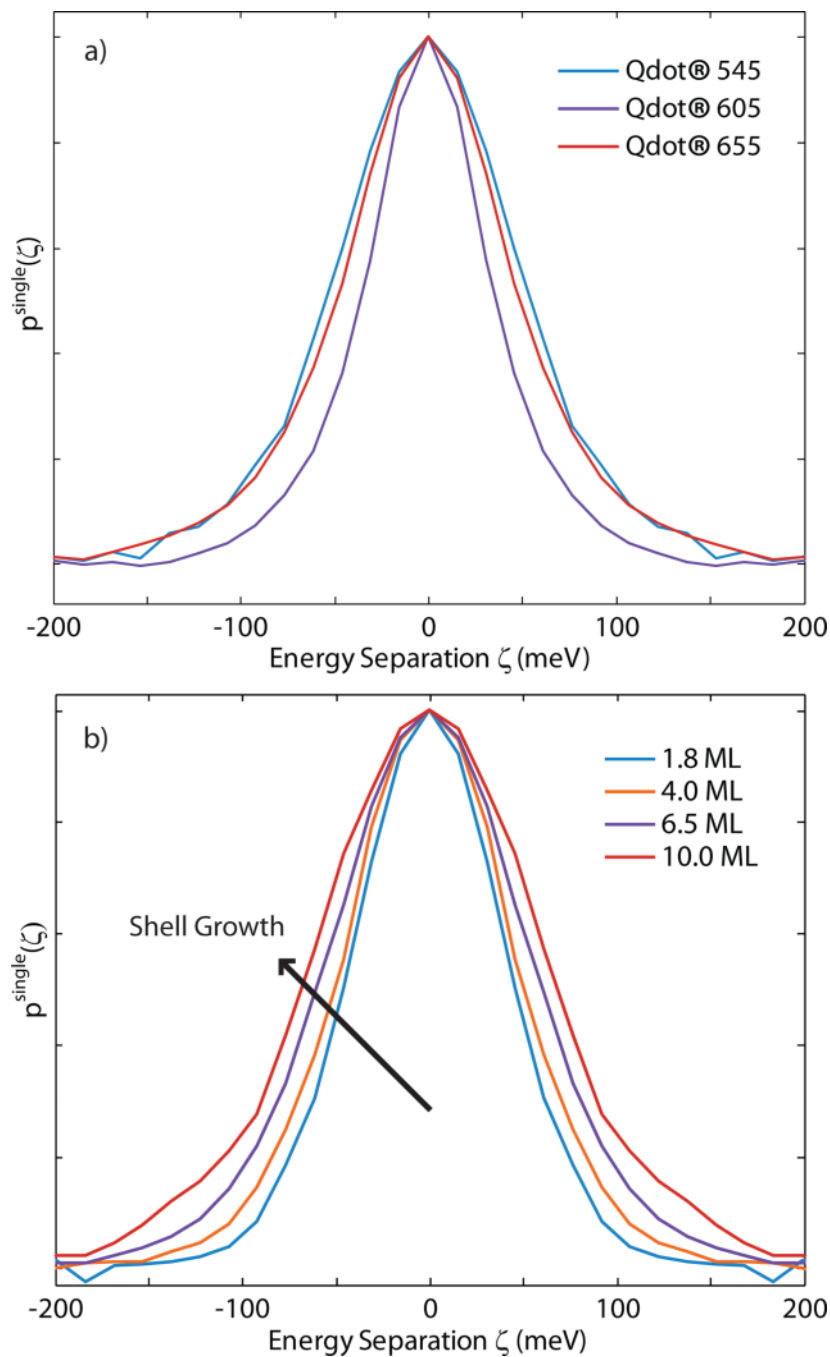


Figure 4. Comparison of Samples with CdSe Cores

a) Single-particle spectral correlation functions $p^{\text{single}}(\zeta)$ ($\tau = 5 \mu\text{s}$) for the commercial CdSe particles (Qdots®). There is great variation in the linewidths with no obvious trend according to size or shell morphology. b) Single-particle spectral correlation functions $p^{\text{single}}(\zeta)$ ($\tau = 5 \mu\text{s}$) for the CdSe/CdS core/shell particles during shell growth. The linewidth increases monotonically with shell growth.

Tables

Single-Nanocrystal and Ensemble Effective Spectral Linewidths.

Sample	Single-NC linewidth (meV)	Ensemble linewidth (meV)
Qdot@ 545	70	138
Qdot@ 605	42	75
Qdot@ 655	60	90
InP core/shell	73	178
InAs/ZnS	76	151
CdSe/CdS 1.8 ML [†]	64	87
CdSe/CdS 4.0 ML [*]	69	84
CdSe/CdS 6.5 ML	82	102
CdSe/CdS 10.0 ML	92	124

[†]This sample is included in Figure 2

^{*}This sample is included in Figure 3