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Cryogenic Single Nanocrystal Spectroscopy: Reading the Spectral Fingerprint of Individual CdSe Quantum Dots

Mark J. Fernée^{1,2}, Philippe Tamarat^{1,2}, Brahim Lounis^{1,2} *

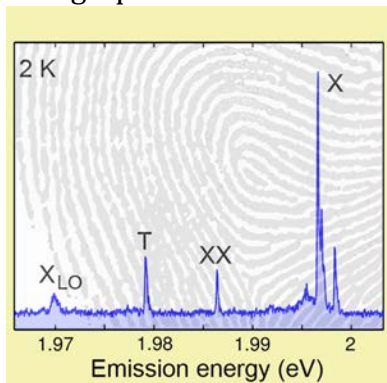
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Abstract:

Spectroscopically resolved emission from single nanocrystals at cryogenic temperatures provides unique insight into photophysical processes that occur within these materials. At low temperatures the emission spectra collapse to narrow lines revealing a rich spectroscopic landscape and unexpected properties, completely hidden at the ensemble level. Since these techniques were first used, the technology of nanocrystal synthesis has matured significantly and new materials with outstanding photophysical stability have been reported. In this perspective, we show how cryogenic spectroscopy of single nanocrystals probes the fundamental excitonic structure of the band edge, revealing spectral fingerprints that are highly sensitive to a range of photophysical properties as well as nanocrystal morphology. In particular, spectral and temporal signatures of biexciton and trion emission are revealed and their relevance to emerging technologies discussed. Overall we show how cryogenic single nanocrystal spectroscopy can be used as a vital tool for understanding fundamental photophysics and guiding the synthesis of new nanocrystal materials.

TOC graphic:



KEYWORDS: CdSe; Quantum rods; Trion; Biexciton; Nano-optics; Single nano-particle.

Semiconductor nanocrystals (NCs), also known as colloidal quantum dots, are a class of optically active material whose photophysical properties depend sensitively on the NC size, shape, structural morphology, surface properties and local environment. One of the most useful properties of these materials is that they exhibit narrow-band luminescent emission that can be tuned across a wide spectral range by simply changing the NC size, making them a useful alternative to organic dyes in many applications^{1, 2}. More challenging applications such as lasing³, photovoltaics⁴, single NC imaging⁵ and other single NC technologies place far more stringent requirements on the photophysical properties of these materials. Therefore developing a good understanding of the photophysics of NC materials is crucial for improving and designing new NC materials for future applications. A great deal of information can be gained from the investigation of ensembles of NCs, such as colloidal solutions and NCs embedded in polymers. However, ensemble techniques generally give an “average” estimate of the underlying photophysics. An excellent example of this is the phenomenon of photoluminescence blinking^{6, 7}, where ensemble measurements show reduced luminescence efficiency or quantum yield and power-law distributed noise spectra⁸, whereas the underlying single NC photoluminescence is found to be intermittent, switching between bright and dark periods. This is a clear example where single NC studies are needed to gain intimate details of the nano-scale photophysics.

Single NCs can be easily imaged in a standard epifluorescence microscope at room temperature. Such studies are extremely useful for understanding photoluminescence blinking and for imaging biological systems. In these applications the spectral information is either not required or is only obtained with low resolution. This is because the spectrum of a single NC at room temperature is broadened by interactions with acoustic phonons, which are heavily populated. By operating at cryogenic temperatures, the ambient population of acoustic phonons can be reduced to approximately zero (as evidenced by the disappearance of the anti-Stokes acoustic phonon sidebands⁹),

resulting in narrow atomic-like spectral lines¹⁰. The tradeoff is increased experimental complexity and lower optical collection efficiency. However, the benefits can outweigh the cost, because such experiments enter a regime that is not dominated by thermal effects, revealing fundamental photophysical phenomena. For example, the first cryogenic studies of single CdSe NCs found that the narrow spectral lines were not spectrally stable, but randomly shifted with increased exposure to the exciting laser; a phenomenon known as spectral diffusion¹⁰⁻¹². Subsequent studies of spectral diffusion revealed it to be photo-physical in origin as distinct dependencies on the pumping wavelength and power were reported¹². Cryogenic spectroscopy of single NCs has since yielded intimate detail of the photophysics underlying spectral diffusion¹³⁻¹⁶, which is illustrative of its importance as a tool for probing the complex photophysics of NC materials.

The technology behind colloidal NCs has progressed significantly since the first use of cryogenic single NC spectroscopy. As new NC materials are developed, it is important to give intimate feedback on the evolution of the photophysical properties. Ideally such co-operative research will give better guidance to developing new synthetic methodologies and ultimately advanced NC materials for a wider range of applications. In this perspective we show that cryogenic single NC spectroscopy is now able to directly test long-standing theoretical models with unprecedented detail, identify individual emission processes and to directly probe energy relaxation throughout the band-edge exciton manifold. For instance, the complex shape dependence of the band-edge exciton fine structure can now be studied in highly photostable NCs whose emission spectrum can reveal energy splittings and relaxation rates. Application of magnetic fields can be used to split the fine structure sub-states, revealing their Landé g-factors, or to tune the oscillator strength of a dark state by a field-induced coupling to the neighboring bright states. Magneto-optical studies of single NCs also shed light on the origin of the ground “dark” exciton radiative recombination in nearly spherical dots. Contrarily to what was anticipated in standard CdSe NCs, spectral and temporal signatures of highly efficient radiative biexcitonic recombinations have been evidenced in elongated NCs, raising the

open question of the shape dependence of the optical response of NCs in the multiexcitonic regime. We will also discuss the finding of trion (charged exciton) emission with near unity efficiency at low temperature, and its potential applications to new technologies, including quantum information processing.

CdSe NCs are the most appropriate system for studying fundamental photophysics as they represent the state-of-the-art in NC synthesis, design and engineering due to their many years of development. Furthermore, theoretical models of the exciton fine structure as well as other photo-physical properties of CdSe NCs are also well developed for this system. In particular, the band-edge fine structure of CdSe NCs is well described by a 4-band model first reported by Efros et al¹⁷. This model considers exciton states formed from a single conduction band combined with both heavy-hole and light-hole valence bands. For spherical CdSe NCs with a hexagonal “wurtzite” crystal structure, the degeneracy of the 4-band model is lifted by a combined effect of a crystal field, due to the lower symmetry of the wurtzite lattice, and the electron-hole exchange interaction. For large NCs the crystal field splitting of 20 meV dominates. Thus the entire band-edge fine structure is usually hidden in the band-edge absorbance peak as illustrated in Fig 1a. The fine structure energy splittings are dwarfed by both the thermal energy at room temperature and the ensemble size dispersion. This motivates the study of the band-edge exciton fine structure using single NCs at cryogenic temperatures. The band-edge exciton states are shown explicitly in Fig 1b sorted by their angular momentum projection. The absorption lines are shown in Fig 1a, including forbidden transitions to so called “dark states” (dotted lines): The lower $m_F=0$ state has identically zero oscillator strength, while single photon transitions involving the $|m_F|=2$ states are forbidden due to the lack of angular momentum conservation. While absorption at the band-edge directly probes the oscillator strength of the fine structure states, emission from the band-edge also involves non-radiative energy relaxation processes. In general non-radiative processes comprise relaxation via optical and acoustic phonons and relaxation via interaction with surface states¹⁸. The phonon mechanisms are mainly intrinsic to the material,

but can still be influenced by size, shape and surface properties of the NC⁹. However, non-radiative relaxation mediated by surface states is purely an extrinsic effect that can be modified by different synthetic techniques. In fact the variation of the surface state distribution and density near the band-edge amongst single NCs was recently elucidated¹⁹, suggesting that it may be possible for some NCs to be almost free from the influence of surface states in the band-edge fine structure region.

Band-edge fine structure

In well-confined NCs, spin relaxations processes have rates, γ_m , faster than the radiative rates, Γ_r , and thus redistribute the band-edge population towards the lowest energy $|m_F|=2$ states. Evidence for the lowest dark state emission stems from an observed size dependent Stokes shift of ensemble emission spectra^{20, 21}. Fluorescence line narrowing experiments on CdSe NC ensembles probing the band-edge under external magnetic fields revealed emission from the dark state²². Thus the single narrow spectral line observed at cryogenic temperatures was attributed to $|m_F|=2$ dark state emission, suggesting that the dark state is not truly dark. This stands in contrast with CdSe self-assembled quantum dots, where the dark state is truly dark and the presence of which must be inferred from other photophysical properties²³.

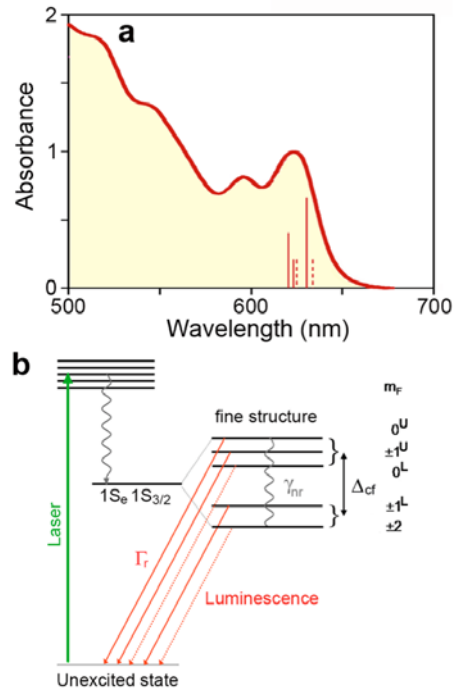


Figure 1: Band-edge exciton fine structure. (a) Ensemble absorbance for CdSe NCs at room temperature (red curve). The red vertical lines indicate the approximate distribution of fine structure states that contribute to the band-edge absorbance. The dotted lines correspond to transitions that are forbidden in the electric dipole approximation. (b) The band-edge energy structure relevant to emission processes in a spherical NC, comprising eight states whose angular momentum and their projection are labeled. Solid red arrows represent allowed optical transitions, while dotted arrows represent emission from dark states. Non-radiative energy relaxation between the states (wiggly line) competes with the radiative processes. A 20 meV crystal field splitting separates the upper manifold of states from the lower manifold.

The detection of excitonic fine structure in the emission of single NCs was first reported for CdSe nanorods using polarization resolved cryogenic spectroscopy²⁴. The acquisition of high quality photoluminescence (PL) spectra with unprecedented detail was enabled through the use of commercial CdSe NCs based on a state of the art core/shell synthesis, which display remarkable photostability at low temperatures. Biadala et al.²⁵ and Fernée et al.²⁶ reported the first conclusive detection of emission from exciton fine structure in CdSe NCs. In fig 2 we review the different properties used to identify the fine structure. NCs exhibiting two Zero Phonon Lines (ZPLs) at low temperature were found in two different NC sizes. The splittings between the two ZPLs exhibit a clear dependence on the emission energy as shown in Fig. 2a²⁶. This size dependent energy separation is a powerful characteristic of intrinsic NC properties akin to the size dependence of the band-edge exciton energy. In addition polarization

resolved measurements (see Fig. 2b) reveal that the two states usually do not share the same polarization projection, indicating that the states are indeed distinct. When the two orthogonal polarization measurements are combined, we also see that both spectral lines share the same spectral jumps. These spectral jumps are attributed to fluctuations of the electrostatic environment of the NCs²⁷. Thus the two emissive states must share the same polarizability, which is expected from the band-edge states^{24, 26}. These two properties strongly point to an assignment of the two spectral lines F and A to the lowest dark and bright fine structure states according to Fig 1b. This assignment is supported by the temperature dependence of the emission spectra displayed in Fig 2c, which show that emission from the lower energy F-state can be completely suppressed at higher temperatures due to a thermal redistribution of populations. This property is compatible with the F-state having an oscillator strength at least an order of magnitude smaller than that of the A-state^{25, 26}.

Explicit values for the relaxation rates can be obtained from the temperature dependence of the PL decay measurements (see Fig. 2d). NCs exhibiting an A-F doublet in their PL spectrum display a characteristic bi-exponential decay at low temperature, with a fast decay occurring within few nanoseconds²⁸ and a much slower one with a lifetime of a few hundred nanoseconds. At higher temperatures (>10 K), the long time component shortens and the fast component vanishes completely. This evolution is due to thermal mixing between the lowest dark and bright states via emission and absorption of acoustic phonons from a mode whose energy matches the energy splitting ΔE between those states. With a simple three-level model depicted in the inset of Fig. 2e, the long component of the PL decay can be described in terms of the two rates Γ_A and Γ_F ²⁵, the spontaneous relaxation rate, γ_0 between the A and F states, the energy separation ΔE and the phonon population N_B at the temperature T . ΔE is directly obtained from the single NC spectrum (single NC spectra are collected concurrently with the lifetime), while the rate Γ_F is determined directly from the lifetime measurement at 2 K and Γ_A is deduced from the asymptotic high temperature regime ($T > 100$ K). Thus γ_0 is determined from a fit to the temperature dependent lifetime data (shown in Fig. 2e). For the

data in Fig 2d,e, the rates obtained from the luminescence decay study²⁵ lead to the same A-F relaxation rate as that obtained using the evolution of the relative weight of the A and F lines with temperature²⁶. Comparing the results from both spectrally resolved and time-resolved measurements also leads to the conclusion that the recombination of both bright and dark exciton states are purely radiative. The spontaneous relaxation rate γ_0 was observed to fluctuate within over two orders of magnitude between different NCs^{25,26}. The heterogeneity in these findings is consistent with dot-to-dot variations of the density of phonon modes that mediate A-F relaxation^{25, 29} (although one cannot exclude the influence of nearby surface states which can facilitate relaxation within the band-edge). Importantly, relaxation between the $|m_F|=1^L$ bright state and the $|m_F|=2$ dark state requires a spin flip of one of the charge carriers, so the rate, γ_0 represents a spin flip rate in this system. Thus these results show that it is possible to significantly slow spin relaxation in this NC system, which is an important property for applications in quantum information and spintronics.

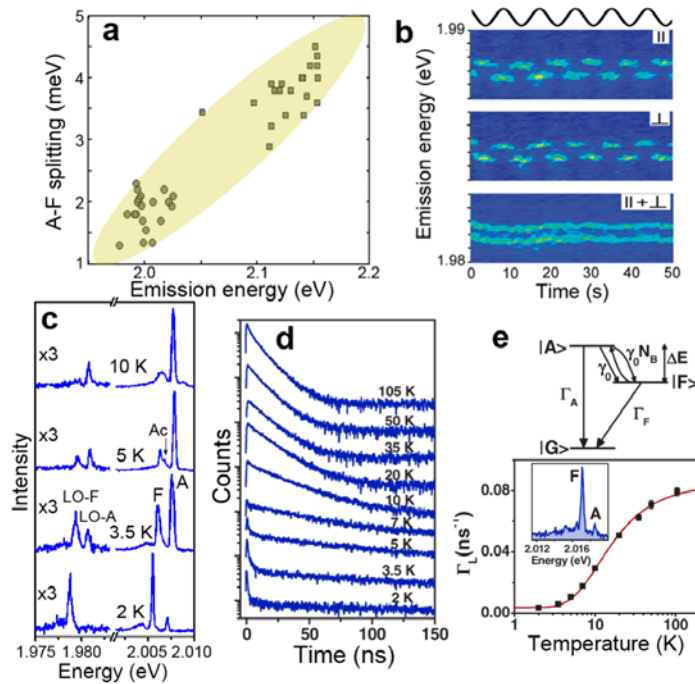


Figure 2: Band-edge fine structure emission. (a) Spectral doublet splitting as a function of emission energy for two NC samples of different sizes (ie. NCs with 655 nm and 605 nm emission at room temperature). (b) Polarization resolved spectra of a single NC as a function of time obtained with a half-wave plate rotating at $\frac{1}{4}$ the frequency indicated by the top sinusoid. Both orthogonal polarizations are

simultaneously detected and summed in the lower time series. (c) A temperature series of spectra from a single NC obtained with a 50 W/cm² pump irradiance. (d) A temperature series of photoluminescence decays obtained from a single NC pumped with an average irradiance of 20 W/cm², corresponding to less than one exciton prepared per pulse. (e) Temperature dependence of the long decay component of (d) with a fit calculated from the solutions of rate equations for the excitonic state populations, with $\Delta E = 1.4$ meV, $\Gamma_F = 0.0037$ ns⁻¹, $\Gamma_A = 0.16$ ns⁻¹ and $\gamma_0 = 0.87$ ns⁻¹. Note: (a) and (b) from ref. 26, (c) from ref. 30, (d) and (e) from ref. 25.

The assignment of the A-F states as the lower bright and dark states of the band-edge exciton fine structure is further consolidated, using polarization resolved lifetime studies as well as correlating the A and F states with different optical phonon weights³⁰. For instance, one can clearly notice in the PL spectrum of Fig. 2c at 3.5 K that the relative weights of the longitudinal optic (LO)-phonon sidebands with respect to the zero-phonon lines (ZPLs) are significantly different for the two states. This result is compatible with an increased coupling of the $|m_F|=2$ dark state to optical phonons, which was reported in early fluorescence line narrowing studies²². Nevertheless, controversy still remained over the assignment of a spectral line to the $|m_F|=2$ dark state due to the violated angular momentum selection rule³¹⁻³³. It has been suggested that the spectral line may in fact be an acoustic phonon replica³¹, corresponding to the emission of an additional acoustic phonon that carries the excess angular momentum. We test the nature of the F-state in Fig 3 using a resonant photoluminescence excitation technique¹⁶. We are able to directly excite the F-state by scanning a single-mode laser over the spectral line and detecting the frequency red-shifted LO phonon band^{16, 25}. The signal shown in Fig 3 is thus a result of directly probing the ground state of the transition, and so excludes the possibility that the spectral feature is simply an acoustic phonon replica and that the true ZPL is dark. The signal is fit with a Gaussian peak of 20 μ eV (full width at half maximum), indicating that the spectral peak is inhomogeneously broadened due to a spectral diffusion process known to occur over fast time-scales^{34, 35}.

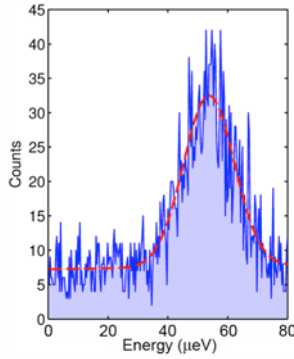


Figure 3: The sum of three consecutive resonant excitation scans of the dark state emission taken with a sample temperature at 2K and pump irradiance of 100 W/cm². The red dashed curve is a fit to a Gaussian curve with a 20 μeV fwhm.

Magneto-optical properties

Ultimately, magneto-optical spectroscopy of single NCs provides the additional information that enables an unambiguous assignment of the A-F spectral doublet³⁶. In Fig. 4 we show that both the F-state and A-state can be split in an applied magnetic field. The magnitude of the Zeeman splitting is dependent on the orientation of the NC relative to the magnetic field, which can be determined from the magnetic field dependence of the long decay component³⁶. Zeeman splitting of the F-state is easily resolved with moderate fields of 1-2 T, while splitting of the A-state is more difficult, requiring optimal alignment of NCs with resolution limited spectra and higher fields. The g-factors associated with the A and F-state were found to be, $g_A \approx 0.5$ and $g_F \approx 2.7$ respectively, in good agreement with theoretical expectations¹⁷. Notably, this direct measurement of the exciton g-factors also avoids the inferences required in previous ensemble measurements³⁷⁻³⁹. The magneto-optical spectroscopy also provides further insight into the origin of the $|m_F|=2$ dark exciton zero-phonon recombination. In Fig. 4c we see that for an applied field below 1T the lifetime of the dark state emission *increases* with the magnetic field! The red curve provides a fit to a model of an internal magnetic field component oriented such that the external field first must overcome the internal field, effectively decoupling the dark state from the neighboring bright state before the coupling then increases due to the transverse component of the field. This result is significant because it reveals that a magnetic mechanism is involved in dark state emission in NCs, which is attributed to an extrinsic influence³⁶. It has long been proposed that magnetic

defects may be implicated in the emission of the $|m_F|=2$ dark state¹⁷. Indeed, magnetic properties have been reported for CdSe NCs and attributed to a variety of sources, including dangling bonds⁴⁰, surface ligands^{41, 42}, and defects in the nanocrystals⁴³. Further magneto-optical investigations and theoretical models are needed to elucidate the physical origin of the large internal fields (several Tesla). The ability to control and tune the oscillator strength of the ground exciton state would generate potential applications in quantum information processes using all-optical spin coherent manipulations. Pioneering measurements of the dark exciton optical coherence lifetime yielded ~ 100 ps^{25, 35}, which is still orders of magnitude shorter than the radiative lifetime, due to fast dephasing fluctuations in the local nano-environment. Expanded optical coherence times require new synthetic routes to NCs with improved photo-physical properties.

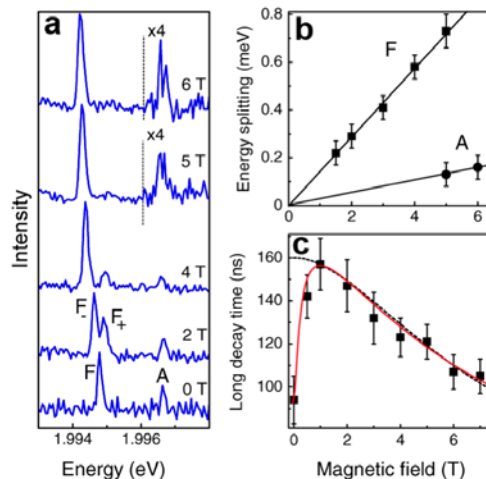


Figure 4: Magneto-optical properties of the band-edge fine structure. (a) PL spectra of a single NC at 2 K, for various intensities of the magnetic field, which is almost parallel to the NC c-axis. (b) Zeeman energy splittings of the dark (F) and bright (A) exciton sublevels. (c) Evolution of the long decay time with the magnetic field. The dashed curve is a fit to a model that considers only the external magnetic field. The solid red curve is a fit to a model that takes into account the contribution of an intrinsic magnetic field to the mixing of bright and dark exciton states. Note: (a)-(c) from ref. 36.

Spectroscopic signatures of shape

The excitonic fine structure is predicted to be sensitive to the NC aspect ratio due to the competing effects of crystal field splitting and shape anisotropy¹⁷. A TEM image (see Fig. 5a) of the larger NCs (ie. those emitting at

655 nm at room temperature) revealed a predominantly non-spherical morphology, consistent with similar reports using nominally identical NCs^{44, 45}. NC aspect ratios between 1 and 2 are clearly seen with NCs having an average width perpendicular to the c-axis of 7 nm. The morphological variations can be understood as predominantly arising from growth fluctuations along the crystal c-axis in NC cores with a wurtzite structure. The theory of Efros et al.^{17, 46} can be adapted to study the effect of varying the NC aspect ratio using an ellipsoidal perturbation. The results for a width of 5.4 nm are shown in Fig. 5b in a region compatible with the observed length dispersion of NCs in Fig 5a. The fine structure evolution is categorized into four regions: The sphere-like, rod-like and left and right crossover regions.

The sphere-like regime has already been discussed above. Using these same characterization methods, we also identify NCs in each of the regions depicted in Fig 5b. Figure 5c represents the case of a NC in the left crossover regime, for which the lowest energy ZPL is assigned to the weakly allowed $|m_F|=2$ lowest state. This line, which prevails at 2 K, is indeed dominated by optically bright states at higher temperatures, and displays a significant Zeeman splitting in a magnetic field (data not shown). A NC in the right crossover regime is shown in Fig. 5d. Its $m_F=0^L$ lowest state is truly dark and can only be revealed through mixing with the nearby $|m_F|=1^L$ state using a magnetic field. The intermediate $|m_F|=2$ state can be identified by its low oscillator strength and Zeeman splitting with an external magnetic field. Finally, the rod-like spectrum, as shown in Fig. 5e, is often observed as a single $|m_F|=1^L$ line at low temperature. At higher temperature the nearby optically active 0^U state is revealed and the lowest energy 0^L state only appears under the influence of a magnetic field. Thus the spectral fingerprint of the band-edge exciton obtained from single NCs corroborates the energy level predictions of the theory with the highest precision reported to date. In addition, we show that single NC spectroscopy at cryogenic temperature can identify the aspect ratios of individual NCs. We expect that these experiments will motivate the future development of a correlative microscopy (TEM or scanning probe combined with optical spectroscopy). Ultimately we have only begun to tap the potential of such

spectral fingerprints as they should also be sensitive to the crystal structure, charge and multiexciton states in single NCs and also for quantifying the effects of NC engineering; for example monitoring changes to the electron-hole exchange interaction⁴⁷.

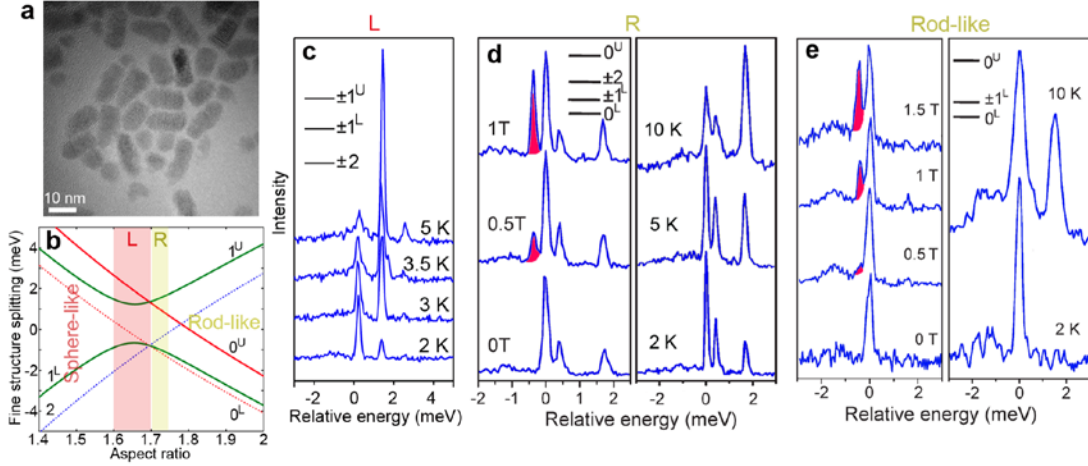


Figure 5: Spectral fine structure as a function of NC shape. (a) A high resolution TEM image of the 655 nm NCs used in this study. (b) The variation of the band-edge fine structure with aspect ratio for a NC with a 5.4 nm width. Four specific regions are indicated, including a left and right cross-over region designated L and R respectively. (c) Characteristic L spectra: Temperature series of a single NC spectra with three lines identifying the lowest $|m_F|=2$ dark state. (d) Characteristic R spectra: Both temperature and magnetic field series of spectra from a single NC identify a new lowest energy peak (shaded) only visible in the presence of an external magnetic field. A weak middle transition is also revealed in the temperature series that can exhibit Zeeman splitting when the crystal c-axis is aligned parallel to the magnetic field. (e) Characteristic rod-like spectra: Usually a single spectral line at 2 K. The lowest energy dark state is only visible in the presence of a magnetic field (shaded peak). The higher energy 0^U peak is visible at higher temperatures. Note: (d) and (e) from ref. 48.

An efficient biexciton

At the lowest temperature (~ 2 K), where thermal mixing of bright and dark states is negligible, the lifetime of the exciton can approach $1 \mu\text{s}$, which significantly increases the probability of creating a biexciton with a relatively low pump intensity. This enables the direct detection of biexcitons using a CW pump, as shown in Fig. 6. A single bi-exciton line appears in the spectrum from a single NC as the pump irradiance is increased (see Fig. 6a), exhibiting a characteristic quadratic dependence on the pump irradiance as shown in Fig. 6b. The binding energy of the biexciton is given by the ~ 12 meV red-shifted

emission relative to the exciton ZPL (See Fig. 6c). Direct detection of the biexciton under weak pump conditions indicates that the emission efficiency of the biexciton must be high. In fact a rate equation fit to the power dependence of both the exciton and biexciton emission areas led to the conclusion that a unity biexciton quantum efficiency can be obtained for some NCs⁴⁸! An independent means of directly measuring the biexciton efficiency is by directing the NC luminescence into a Hanbury-Brown-Twiss apparatus to determine the second order photon correlation function under pulsed excitation⁴⁹. The correlation histogram comprises a series of peaks due to periodic coincidences between luminescence photons emitted after different excitation pulses. The weight of the zero-delay peak reflects the probability that two photons were emitted by the NC under the same excitation pulse. For a two level quantum emitter, the central peak is missing due to photon antibunching⁵⁰. This has been the usual hallmark for the identification of single photon emitters, such as strongly confined quantum dots with efficient Auger recombination^{51, 52}. However, a quantum dot is only a good representation of a two-level quantum system in the limit of low biexciton efficiency⁵¹. If the bi-exciton emission is efficient, the temporal signature of a biexciton-exciton radiative cascade will show up in the zero delay peak. For single NCs with unity quantum yield for exciton emission⁵³ the biexciton quantum yield can be directly determined from the ratio of the central peak to the lateral one⁴⁹. In Fig. 6d we show a second order photon correlation measurement conducted at 140 K and in the weak pump regime, where the signal is directly proportional to the biexciton efficiency⁴⁹. In these conditions, the ratio of the central peak to a lateral one directly yields a biexciton quantum efficiency of $\sim 80\%$ for this NC. We point out that NCs characterized by exciton spectra from the sphere-like regime do not produce any observable biexciton emission⁴⁸, thereby associating biexciton emission efficiency with NC shape. Thus the excitonic spectral fingerprint can be used to correlate Auger efficiency with NC structural properties. However, we note that the underlying photo-physical mechanism is not completely resolved, as the effect of heavy-hole/light-hole mixing on Auger rates may also contribute to the observed correlation. Theoretical models are now needed to further understand these results and in particular to find optimal NC geometries that minimize the Auger

rates. A controlled production of NCs with high biexciton quantum yields would have direct application to the use of NCs as laser gain materials and also for application to quantum information protocols where efficient pairs of correlated photons are required.

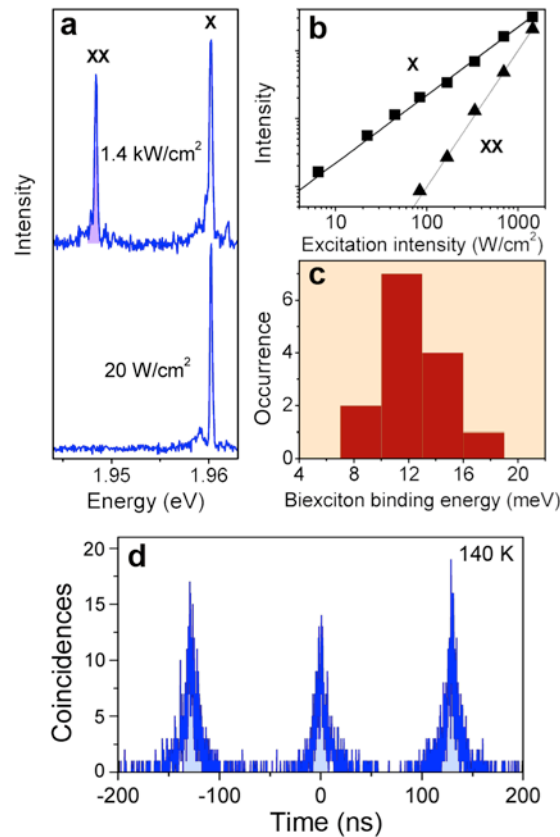


Figure 6: Biexciton emission. (a) Emission spectra of a single NC at 2 K for two cw excitation intensities. X and XX label exciton and biexciton emission lines, respectively. (b) Integrated intensities of the X (squares) and XX (triangles) structures as a function of the pump intensity. (c) Distribution of the red shift of XX with respect to X for 14 individual NCs. (d) Photon coincidence histogram of a single NC under pulsed excitation at 140 K. The mean number of exciton created per pulse is 0.2. The 7 ns characteristic decay time corresponds to the exciton lifetime. The area ratio of the central peak to a lateral peak is 0.8 and provides a direct determination of the biexciton to exciton quantum yield ratio. Note: (a)-(d) from ref. 48.

Exciton-Trion transitions

High biexciton quantum yields immediately suggest that high efficiency trion emission must be possible in these materials. This is particularly relevant to potential applications in quantum information and spintronics, as charged

quantum dots present a prototypical quantum optical system suitable for coherent manipulation of the spin degree of freedom. In Fig. 7a, we show that the emission of a single NC can switch between an exciton ZPL multiplet and a redshifted single ZPL denoted X^* that is distinct from a biexciton feature as it does not scale quadratically with pump irradiance. Such spectral jumps result from transitions between neutral and charged excitonic states^{26, 30}. The peak X^* is attributed to a trion recombination, i.e. an exciton recombination in the presence of an unpaired charge carrier in the NC core and a charge carrier trapped at the surface or in a lattice defect of the NC. In Fig. 7b we show that NCs that have switched to trion emission have a monoexponential PL decay with an average lifetime of 3 ns. The lack of a long decay component indicates that there is no lower lying dark state, which is consistent with the absence of an electron-hole exchange interaction that characterizes the trion state⁵⁴. The trion labeled X^* in Fig. 7a has a binding energy of approximately 17 meV. However, there are two possible trion charges, which are reported to have widely differing binding energies^{54, 55}. In materials with high biexciton efficiency, we expect that emission from *both* trion charges to be efficient. In Fig. 7c, we show the time evolution of a polarization-resolved single NC spectrum. This time series exhibits clear switching between a single spectral peak and a spectral doublet. The polarization-resolved measurements also reveal that the polarization state of the single peak matches that of the higher energy peak of the spectral doublet. This is attributed to the dark state emission switching on and off, indicative of switching of the electron-hole exchange interaction²⁶. However, in this case the trion state is only red-shifted by ~ 5 meV, far smaller than that of Fig 7a³⁰ and therefore is a signature of the oppositely charged trion. We note however that our previous assignments of the trion charge were tentative^{26, 30} as they relied on contradictory numerical calculations^{54, 55} and room temperature results using different materials⁵⁶. We have recently resolved this contradiction using magneto-optical spectroscopy to unambiguously show that the negative trion has a small binding energy while the positive trion has a large binding energy²⁹. It is noteworthy that trion emission from both charge types have approximately unity quantum efficiency in these materials. For example, Fig 7d shows that in the weak excitation limit, the integrated intensity for both the neutral and trion

emission was found to be approximately equivalent⁵⁷. Overall, trions with high quantum yields challenge the accepted mechanisms for photoluminescence intermittency or blinking^{58, 59}, as trions were hitherto assumed to be either weakly emitting^{60, 61} or dark⁶². Thus the characterization of trion emission is important for understanding a photo-physical property that lies at the heart of an area of active investigation. The development of NCs with stable bright trion emission will result in NCs with short radiative lifetimes that deliver most of their emission into a single ZPL. Such NCs have the potential to be superior gain materials, brighter biological probes and are also particularly attractive for the development of single photon sources and for applications in quantum information processing.

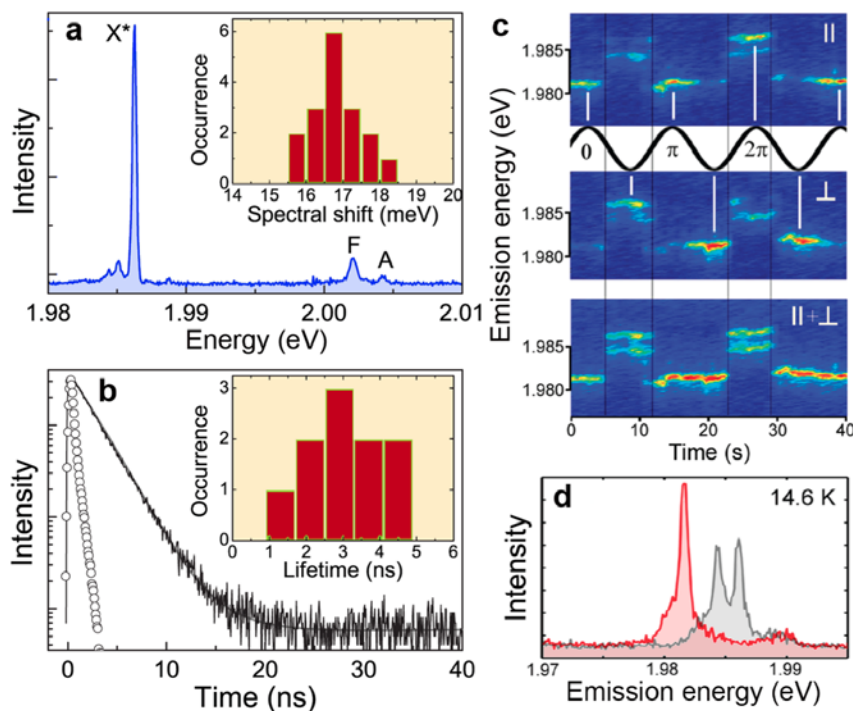


Figure 7: Trion emission. (a) Emission spectrum of a single NC at 2 K, recorded over 20 s at an excitation intensity of 50 W/cm². The peak labeled X* is attributed to the ZPL of the lowest-energy charged exciton state. Inset: histogram of the spectral shift between peaks F and X*, for 17 single NCs. (b) PL decay of a permanently charged single NC, at 2 K. (fit with a 2.4 ns monoexponential decay). The open circles correspond to the instrument response function. Inset: histogram of the trion lifetime, for ten single NCs. (c) Polarization-resolved spectra of a single NC obtained at 14.6 K with a pump irradiance of 52 W/cm² integrating for 1 s. (d) Comparison of the singlet and doublet spectra obtained in (c). The integrated peak areas indicate that the single peak trion emission has a similar quantum yield as the neutral emission. Note: (a) and (b) from ref. 30, (c) and (d) from ref. 26.

Discussion

In this perspective we have reviewed the current state-of-the-art in the spectroscopy of single NCs at cryogenic temperatures, revealing a rich band-edge fine structure. We have focused on only a single commercial NC range, as they are representative of the range of high quality materials now available, and this material is already widely studied in the literature. Work on single NCs is usually complementary to the more common ensemble techniques that require more care in drawing conclusions. For example, with the highly heterogeneous NC sample subject to this review, we can immediately see that ensemble techniques are incapable of revealing the intimate detail observed at the single NC level. In fact certain ensemble techniques, such as powerful coherent pump-probe techniques, will be completely confounded by such heterogeneous samples⁶³. However, the photo-physical properties determined in single NC studies may in fact not be representative of the ensemble, but instead only represent a high quality sub-ensemble. In fact, spectra are selected for their quality and may represent NCs with the best obtainable properties. Therefore single NC studies can serve to drive synthetic routes towards increasing the fraction of high quality NCs. For example, characterization of biexciton and trion emission can guide the engineering of NCs with improved properties suited to new applications such as lasing materials or quantum information. There are already significant efforts being made to reduce Auger effects in semiconductor NCs, which will benefit their adoption as new laser materials and entangled photon sources. Additional insights into how this may be achieved are likely using cryogenic single NC studies⁴⁸. Charged NCs are another material with a great deal of potential, especially as a quantum technological platform due to the accessible spin degree of freedom²⁹. In addition charged nanocrystals should form brighter biological probes and may even be useful as specific probes of certain biological processes such as ion channels. However, synthetic efforts to form stable charged NC are required.

A persistent problem that urgently needs addressing, if these materials are to be seriously considered for applications in quantum technologies, is spectral stability. Spectral diffusion causes rapid decoherence of individual

quantum states and currently limits the ability to use coherent control techniques with these materials. This is currently attributed to surface instabilities, most likely associated with the surface ligands^{15, 16}. A number of possible routes to achieving stable emission exist, the most direct being using thicker shells to reduce the influence of the surface. However, our observations of some remarkably stable individual NCs suggests that alternative routes towards stabilizing the surface may exist.

In recent years there have been exciting developments towards new NC materials, such as giant shells^{64, 65}, parabolic confinement potentials⁶⁶ and type II confinement potentials⁶³. The ultimate photo-physical properties arising from this cornucopia of new materials are as yet to be investigated and provide a fertile ground for the future of cryogenic single NC spectroscopy.

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QUOTES:

“As new NC materials are developed, it is important to give intimate feedback on the evolution of the photophysical properties. “

“Thus these results show that it is possible to significantly slow spin relaxation in this NC system, which is an important property for applications in quantum information and spintronics.”

“Thus the spectral fingerprint of the band-edge exciton obtained from single NCs corroborates the energy level predictions of the theory with the highest precision reported to date.”

“The development of NCs with stable bright trion emission will result in NCs with short radiative lifetimes that deliver most of their emission into a single ZPL.”

“The ultimate photo-physical properties arising from this cornucopia of new materials are as yet to be investigated and provide a fertile ground for the future of cryogenic single NC spectroscopy.”

