Higher-Order Photon Correlation as a Tool To Study Exciton Dynamics in Quasi-2D Nanoplatelets

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ABSTRACT: Colloidal semiconductor nanoplatelets, in which carriers are strongly confined only along one dimension, present fundamentally different excitonic properties than quantum dots, which support strong confinement in all three dimensions. In particular, multiple excitons strongly confined in just one dimension are free to rearrange in the lateral plane, reducing the probability for multibody collisions. Thus, while simultaneous multiple photon emission is typically quenched in quantum dots, in nanoplatelets its probability can be tuned according to size and shape. Here, we focus on analyzing multiexciton dynamics in individual CdSe/CdS nanoplatelets of various sizes through the measurement of second-, third-, and fourth-order photon correlations. For the first time, we can directly probe the dynamics of the two, three, and four exciton states at the single nanocrystal level. Remarkably, although higher orders of correlation vary substantially among the synthesis' products, they strongly correlate with the value of second order antibunching. The scaling of the higher-order moments with the degree of antibunching presents a small yet clear deviation from the accepted model of Auger recombination through binary collisions. Such a deviation suggests that many-body contributions are present already at the level of triexcitons. These findings highlight the benefit of high-order photon correlation spectroscopy as a technique to study multiexciton dynamics in colloidal semiconductor nanocrystals.

KEYWORDS: nanoplatelets, Auger recombination, multiexcitons, photon correlation, exciton dynamics

Nanoplatelets (NPLs), colloidal synthesized two-dimensional nanocrystals (NCs), have shown great potential for low gain threshold lasing,1,2 light emitting diodes,3,4 and photovoltaic sensitizers5 due to their unique features: tunable band gap, giant oscillator strength, narrow-band emission, and high lateral carrier mobility.6 These superb properties arise due to distinct exciton dynamics compared with their 0D and 1D counterparts. One important example is the recombination pathways of multiexcited states. When three or more charge carriers occupy a nanocrystal, an additional nonradiative recombination path opens up—the Auger process. In Auger recombination, an electron–hole pair recombines, and the excess energy is transferred to a third spectator charge. In colloidal quantum dots (QDs), the Auger rate for a biexciton (and higher multicharged states) is much higher than the radiative recombination rate, significantly reducing the quantum yield (QY) of such states.7 In contrast, due to the mean value of the lateral separation between excitons in a NPL, Auger rates are substantially lower than in QDs and the biexciton QY (BXQY) can approach that of the single exciton state.8

Previous studies concluded that since the electron–hole binding energy in NPLs is much higher than the lateral confinement energy, Auger recombination occurs through exciton–exciton collisions.9 Using ensemble experimental approaches, such as time-resolved photoluminescence (PL) and transient absorption, Li et al. concluded that the rate of Auger relaxation decreases linearly with increasing the NPL lateral area and is inversely proportional to $d^3$, where $d$ is the thickness.10 Therefore, biexcitons in large NPLs will preferably undergo radiative recombination, whereas the Auger mechanism is the probable relaxation route for biexcitons in small NPLs (see Figure 1a).10–13 While these experiments were paramount to the understanding of multiexciton dynamics in NPLs, they rely on measurements at high excitation powers, promoting the effect of charging and photobleaching, which may skew the conclusions. Moreover, as with all ensemble measurements, their interpretation is challenging due to dispersity in properties such as absorption cross-section and recombination rates. A different approach to probe multiexciton dynamics is to measure second-order photon correlations in the PL of NCs.14–16 While fluorescence correlation spectroscopy (FCS) is a common method to apply correlations in fluorescent light for biological imaging17 and molecular spectroscopy,18 typically, the observed time scales are beyond a microsecond. In contrast, photon correlations at the excited state lifetime scale are seldom applied for spectroscopy of molecules and nanostructures19–21.
and for microscopy applications. However, such a method is naturally suitable to investigate multiexcited states since it observes the statistics of photon pairs emitted within a short delay. In a photon correlation measurement, light emitted from a single nanocrystal is split into two or more detectors—a Hanbury Brown and Twiss setup (see Figure 1b). When photon pairs are binned according to the delay time between detections, a distinct dip at \( \tau = 0 \) is indicative of photon antibunching; a reduced probability for the detection of two photons simultaneously (see Figure 1c,d). As optical excitation generates a Poisson distribution of excitons in the nanocrystal, antibunching is a clear indication that BXQY is lower than the single exciton QY. This results in fewer detections of simultaneous photon pairs than expected from Poissonian statistics. In this experiment, even at excitation intensities below saturation, one can isolate the rare events in which two excitons were simultaneously present and extract the rate of Auger recombination. While generally such a modification requires some relaxation of quantum confinement, growing large area NPLs enables the production of high multiexciton QY particles without sacrificing the longitudinal confinement. Using single particle spectroscopy, Ma et al. measured BXQY as high as 0.9 of the single exciton QY for such NPLs with a large lateral area.

Here, we study the relations between photon correlation of orders two to four as a direct spectroscopic method to investigate the underlying mechanisms of multiexciton recombination in NPLs. Surprisingly, while NPLs within a single sample span almost the entire range of second-order antibunching values (0–1), we found that the values of third-
and fourth-order antibunching strongly correlate with that of the second-order antibunching value. In addition, we show that while the well-accepted binary exciton collisions model captures much of the dynamics, there are small yet significant deviations from it, indicating the effect of many-body interactions; we postulate that this modification is due to the tendency of a spectator exciton to Coulombically attract other excitons and thus promote Auger interactions.

Results and Discussion. Cores of colloidal five-monolayer CdSe NPLs were synthesized according to a previously reported procedure. By varying the reaction time, we fabricated NPL batches with three different average lateral sizes: ~5 × 12 nm, ~9 × 32 nm, and ~14 × 41 nm; in the following, these samples are referred to as small, medium, and large area NPLs, respectively. Further details about the synthesis can be found in the Materials and Methods. Figure 2a−c presents transmission electron microscope (TEM) images of the small, medium, and large CdSe samples. Figure S1 in the Supporting Information presents the lateral size distributions as analyzed from TEM images. Absorption and PL spectra for the medium NPLs sample are shown in Figure 2d. All three samples presented very similar spectra with slightly shifted peak positions, as presented in Figure 2e. The relatively narrow peaks and close peak position values are a clear indication that all three NPL samples, used in this work, have the same thickness.32

Since photon correlation measurements require a high QY and long-term photostability under relatively high excitation intensities, we passivated the surface of the NPLs cores by growing CdS shells of three monolayers.9,33,34 TEM images, absorption, and PL spectra of the core/shell NPLs are shown in Figure S2. Although the growth of the CdS shell slightly altered the lateral dimensions of the NPLs, probably due to CdS growth on the edges of the NPLs, we assume that this has a negligible effect on our results due to the inherent size dispersity of our samples and the use of single particle spectroscopy.

To understand the role of lateral size on the multiexciton interactions, we use a single-particle PL characterization setup to measure correlations in the emitted photon stream. The setup, schematically shown in Figure 1b, comprises a standard confocal microscope with a pulsed laser excitation (470 nm, ~100 ps pulses) focused onto the sample plane by an objective lens. Light emitted by the NPL is collected via the same objective lens and imaged on a multimode fiber splitter, dividing the PL equally among four single photon avalanche detectors (SPADs). The use of four SPADs enables the measurement of short-time second-, third-, and fourth-order photon correlations.55 The photons’ detection times are clocked and digitally stored by a time-correlated single-photon counting (TCSPC) module (Hydra-harp 400, PicoQuant). Additional details on the single particle spectroscopy setup are given in the Materials and Methods.

Figure 3a depicts the second-order correlation as a function of the delay time (G(2)(τ)) of a representative NPL from the medium-sized sample, presenting the number of detected photon-pairs versus the delay time between detections at the resolution of the laser pulse repetition period. In order to isolate the effect of antibunching on the correlation functions from that of classical fluctuations, we assign unity value to the plateau at nonzero, yet relatively short, delay times. Thus, we define G(2)(τ) ≡ G(2)(τ)/(G(2)(plateau)), where in our analysis G(2)(plateau) refers to the average value between one and five pulse delays. With this definition, G(2)(0) is an estimate for antibunching in the bright “on” state of the nanocrystal. For the measurement shown in Figure 3a, this value is G(2)(0) = 0.7677 ± 0.0005.

The high photon emission rate and BXQY together with the minutes-long photostability of core/shell NPLs enable us to go
beyond the standard measurements of antibunching and measure third- and fourth-order photon correlations from a single colloidal NC. Figure 3b presents the third-order correlation \(G^{(3)}(t_1, t_2)\) results, analyzed from the same data set used in Figure 3a, a measure of the number of detected photon triplets versus the delay times between the three photons. To construct \(G^{(3)}\), we randomly assign the numbers 1–3 to each detected triplet and calculate the delay time \(t_1 = t_2 - t_3\) and \(t_2 = t_1 - t_3\), where \(t_i\) is the detection time of photon \(i\) (see SI for more details on the analysis). The vertical \((0, t_j)\), horizontal \((t_i, 0)\), and diagonal \((t_i = t_j)\) lines (except for the point \((0,0)\)) signify the detection of two photons at the same time and a third delayed photon. The rest of the points describe three photons detected at different times. Most importantly, the probability to detect three photons at the same time is depicted in the point of origin, where \(t_1 = t_2 = t_3 = 0\), presenting the lowest value. From the ratio of this value to the plateau, we calculate \(G^{(3)}(0,0) = 0.46 \pm 0.004\).

As a complementary analysis for multie exciton dynamics, we observe the detections’ delay time relative to the exciting laser pulse. Each photon triplet arriving after the same excitation pulse is split into the first, second, and third arriving photons. We can then generate a separate lifetime curve for the triexciton, biexciton, and single exciton states, respectively (Section S1). Analyzing the PL of another single NPL (not the one shown in Figure 3), the individual lifetime curves were fit with a biexponential function, from which we extract the effective recombination decay rates for the different states \(\tau_{1s} = 6.7\text{ ns}, \tau_{2s} = 2.6\text{ ns}, \tau_{3s} = 1.0\text{ ns}\). Using these rates, we estimate the values of \(g^{(2)}(0)\) and \(g^{(3)}(0,0)\) to be 0.77 and 0.35, respectively, for the analyzed NPL (details are found in Section S1). The calculated values only roughly agree with the measured correlation values, \(g^{(2)}(0) = 0.81\) and \(g^{(3)}(0,0) = 0.52\), presumably since the model is limited to the case of a single exponential lifetime, while the data clearly exhibits more complex dynamics.

For the brightest of NPLs, one can go another step further and analyze the detection of four simultaneous photons. The fourth-order correlation function \(G^{(4)}(t_1, t_2, t_3)\) results for the same NPL shown in Figure 3a,b are extracted from the same measurement to produce the images presented in Figures 3c,d. Since \(G^{(4)}\) is a three-variable function of the three delay times \((t_1, t_2, t_3)\), it is more challenging to visualize. Thus, for clarity we present two constant \(t_j\) cross sections: at zero \((G^{(4)}(t_1, t_2, 0))\) and one \((G^{(4)}(t_1, t_3, 1))\) pulse delay time. The probability to detect four photons emitted simultaneously, derived from the center point in Figure 3c, is \(g^{(4)}(0,0,0) = 0.25 \pm 0.04\). As expected, \(g^{(3)}(0,0)\) and \(g^{(4)}(0,0,0)\) values are smaller than \(g^{(2)}(0)\) because the multie exciton nonradiative recombination rates increase with the number of excitons. Naively, the Auger recombination rate follows the number of exciton-pair permutations in the state, while the radiative rate grows linearly with the number of excitons. This results in a lower QY for higher orders of multie excitations. A more comprehensive explanation of the higher-order correlation analyses and examples of \(G^{(2)}\)–\(G^{(4)}\) plots of single NPL from the small-
sized and large-sized samples are shown in Section S2 and Figure S4.

To some extent, photon correlations can be affected by the average number of excitations per nanocrystal, especially when approaching the saturation intensity. In order to confirm that we work with below-saturation excitation powers, we performed a saturation experiment (described in Section S3). Figure S5, presenting the PL intensity for NPLs versus excitation power, demonstrates that saturation does not occur even at the highest pulse energy of $\sim 9 \times 10^{-14}$ J per pulse for the medium area sample. In order to ensure below-saturation excitation powers for all NPL samples, we use only $\sim 1.8 \times 10^{-14}$ J per pulse. An estimation for the average number of absorbed photons per pulse, calculated according to absorption cross-section estimated in the literature and described in full in Section S4, yields an average of 0.04, 0.2, and 0.4 excitons per pulse per NC for the small, medium, and large area samples, respectively. While the average population for the larger samples approaches saturation, the biexciton population is still substantially smaller than that of the single excitons. Therefore, it should only slightly affect the correlation function measurements. In order to allow complete relaxation of excitons between laser pulses, the repetition rate was set to 5 MHz (200 ns between subsequent pulses), much longer than the exciton lifetime ($\sim 7$ ns).

Unlike for the case of single QD spectroscopy, where emission of photon pairs is strongly suppressed and a common metric for identification of single emitters is $g^{(2)}(0) < 0.5$, the antibunching dip magnitude alone cannot be used as a signature of measuring a single NPL. We therefore use several different steps to ensure that our measurements are not contaminated with results from NPL clusters. First, we prepare sparse samples in which bright spots are separated by $\sim 5$ μm on average. Second, by observing fluorescence intermittency (“blinking”), we exclude measurements that do not present repeated periods of background-level brightness (see Figure S6). Finally, we apply a time-gating test for the $g^{(2)}$ function of each measurement. Photons that arrive at short delays relative to the excitation pulse are filtered-out and only late-arriving photons that originate preferentially from single excitons are used to construct the $g^{(2)}(\tau)$ curve. Then, by plotting the calculated $g^{(2)}(0)$ values versus increasing gating times, beyond the biexciton lifetime, we expect that single NPLs would show a significant decrease in $g^{(2)}(0)$. Measurements whose $g^{(2)}(0)$ falls below 0.5 after this filtering procedure are considered single NPLs and used for further analysis (the process is demonstrated in Figure S7). This 0.5 threshold was selected based on the formula $g^{(2)}(0) = 1 - \frac{n}{N}$, where $n$ is the number of emitters. From over 200 performed measurements of all three samples, 151 met the single particle criterion and presented a signal-to-noise ratio (SNR) of more than 10 for $g^{(3)}(0,0)$. The NPLs exhibit a broad distribution of $g^{(2)}(0)$ and $g^{(3)}(0,0)$ values, as shown in the histograms in Figure S8 and Table S1.

Figure 4a presents the dependence of the $g^{(3)}(0,0)$ values of all the measured NPLs on $g^{(2)}(0)$). Surprisingly, all the measurements follow a universal behavior, lying on a distinct monotonic line despite the very large variance of both $g^{(3)}(0)$ and $g^{(3)}(0,0)$. We attribute this observation to the fact that the QY of multie excitons is dependent on the Auger recombination rate, which is determined by the NPL’s lateral size. Therefore, while our synthesis products vary in aspect ratio and transverse size, the BXQY and triexciton QY are both essentially dependent on the NPL’s area. In accordance with this principle, the average $g^{(2)}(0)$ for small area NPLs (blue circles) is lower compared with that of the medium area NPLs. Large area NPLs present the highest $g^{(2)}(0)$ values from the three samples. This finding confirms the aforementioned trend of size-dependent antibunching in NPLs.

Note that while a qualitatively similar trend of third versus second order antibunching has been observed due to the addition of a Poissonian background to the fluorescence of a single photon emitter, the deep blinking contrast in our measurements ensures us that this is not the case here. In a typical measurement, the “on” state PL rate is more than 50 times higher than that of the “off” state and thus fluorescent background accounts for less than 2% of the detected photons (see Figure S6).

In order to examine this remarkable correspondence of second- and third-order correlations, we attempt to compare this dependence to an exciton—exciton collision model without any fit parameters (black solid line in Figure 4a). The simplified kinetic model describes exciton—exciton interactions, assuming that electron—hole pairs in quantum wells are tightly bound, and thus, Auger recombination follows second-order kinetics, i.e., it requires a collision of two excitons. A detailed description of the model is found in Section S5 and in refs 9,10. In short, the second-order correlation function at zero delay time can be expressed as

$$g^{(2)}_{\text{model}}(0) = \frac{2k_{\text{rad}}}{2k_{\text{rad}} + k_{\text{Aug}}}$$

(1)

where $k_{\text{rad}}$ is the radiative decay rate of a single exciton and $k_{\text{Aug}}$ is the Auger recombination rate of the biexciton state. Following a similar logic, the third-order correlation function can be expressed as a function of $g^{(3)}(0)$:

$$g^{(3)}_{\text{model}}(0,0) = \frac{3k_{\text{rad}}}{3k_{\text{rad}} + 3k_{\text{Aug}}} \times g^{(2)}(0) = \frac{g^{(2)}(0)^2}{2 - g^{(2)}(0)}$$

(2)

where we consider all possible exciton combinations, $\left(\frac{3}{2}\right) = 3$, for the Auger process. We note that the nonclassical nature of photon statistics can also be examined in the third-order photon correlation using the inequality $g^{(3)} < [g^{(2)}]^3$. Indeed, the expression in eq 2 fulfills the inequality for all values of $g^{(2)}$ smaller than unity, in agreement with the standard antibunching criterion.

The final expression in eq 2 suggests that $g^{(3)}(0,0)$ can be fully determined from the value of $g^{(2)}(0)$ without any further input parameters. Accordingly, Figure 4a presents a comparison of the experimental data for $g^{(3)}(0,0)$ versus $[g^{(2)}(0)]^3$ with the expression obtained through the binary collision model. A careful look at the model with respect to the experimental data in Figure 4a reveals that the experimental $g^{(3)}(0,0)$ values are consistently smaller than the model’s expectation. Figure 4b highlights the deviation of our results from the above-mentioned model (eq 2), presenting the difference between the two for each measurement point. To supply some quantitative estimate of this deviation without precise knowledge of the underlying model, we average these differences in two regions of this graph. For low $[g^{(3)}(0)]^3$ (32 measurements between 0 and 0.3), the weighted average is 2.6.
standard deviations below the model, showing a clear tendency toward values lower than predicted by the model. Even more significantly, the average difference at higher $g^{(2)}(0)$ values (96 measurements between 0.3 and 0.8) is more than 13 standard deviations below zero. This deviation shows a statistically significant disagreement between our results and the biexciton collision model and a trend of greater deviation with larger $g^{(2)}(0)$ values.

The downward deviation for moderately antibunched particles suggests that these NPLs exhibit a higher triexciton Auger recombination probability than the sum of Auger probabilities for all possible exciton pairs. We speculate that the significant triexciton interaction term is the result of an enhanced Coulomb interaction (low dielectric constant environment) between excitons in NPLs. Such enhanced interaction, manifesting in the high exciton and biexciton binding energies of NPLs, can reduce the average exciton–exciton distance in the presence of a third exciton.

In order to better understand the magnitude of the multibody effect, the results were fit to a phenomenological model that includes another contribution to the nonradiative decay rate of a triexciton, beyond random exciton–exciton collisions, $k_{3B}$ ($3B = \text{three body}$):

$$k_{3x} = 3k_{\text{rad}} + 3k_{\text{Aug}} + k_{3B}$$

(3)

The resulting corrected model for the photon correlation function is presented in full in Section S6. The dashed line in Figure 4b represents a fit of the phenomenological model to the experimental results, yielding $k_{3B} \approx (0.28 \pm 0.07)k_{\text{Aug}}$. This value can be interpreted as a ~9% enhancement of the exciton–exciton Auger recombination rate in the presence of an additional exciton in the NPL.

Figure 4c presents the dependence of the $g^{(4)}(0,0,0)$ values of all the measured NPLs against $[g^{(2)}(0)]^3$ along with the prediction of the exciton–exciton collision model. For clarity we present here only the 29 measurements for which the SNR of $g^{(4)}(0,0,0)$ is more than 4. The analysis of $g^{(4)}(0,0,0)$ results is more challenging due to the low SNR of counting the rare events in which four simultaneous photons are detected. Nevertheless, the results indicate that, in the case of triexcitons, four-exciton Auger rates are higher than predicted and marginally support the observed trend for the $g^{(3)}(0,0)$ results. Similarly to the $g^{(3)}(0,0)$ case, we applied a statistical test to quantify how much the $g^{(4)}(0,0,0)$ results deviate from the exciton–exciton collision model (the deviations are shown in Figure 4d). As a result of low SNR in the case of $g^{(4)}(0,0,0)$, only 21 measurements, whose $[g^{(2)}(0)]^3$ fall in the range between 0.3 and 0.8, were tested, yielding an average difference of 0.8 standard deviations below the model. Assuming that three-body interactions with a rate of $k_{3B}$ are present, we derive a modified expression for $g^{(4)}(0,0,0)$ (see Section S6). Figure 4d presents the deviation of this three-body interaction model from the standard binary collision model overlaid on top of the experimental data. Since this deviation is small relative to the error values of the experimental data points, one cannot determine which of the models fits the data more accurately, based on the fourth-order correlation data alone.

**Conclusions.** In summary, we demonstrate the use of higher-order photon correlation measurements for spectroscopy, investigating the interaction between excitons in single CdSe/CdS core/shell NPLs. A comprehensive experimental study of two, three, and four simultaneous photon emission from a single NPL shows that the quantum yields of the three- and four-exciton states are highly correlated with that of the biexciton state. While all correlation values differ from one nanocrystal to another, the value of the second-order correlation of a specific nanocrystal provides an excellent estimate for the third- and fourth-order correlation values at zero delay time. A careful glance at the scaling of $g^{(3)}(0,0)$ with respect to $g^{(2)}(0)$ reveals clear deviation from the well-accepted binary collision model indicating that many-body interactions play a significant role in the relaxation of multie excitonic states. Our findings may affect the implementation of NPLs in light-emitting diode lasers, where the QY of multie exciton states are critical for high performance. In addition, the method and modeling used here can be applied to the study of multie exciton states in different types of NCs that have nonzero BXQY, and in particular NPLs from different material systems.

**Materials and Methods.** **Chemicals.** Cadmium nitrate tetrahydrate ($\geq 99.0\%$, Sigma), methanol ($\geq 99.9\%$, Bio-Lab), sodium myristate ($\geq 99\%$, Sigma), 1-octadecene (ODE, 90%, Sigma), selenium (Se, $\geq 99.5\%$, Sigma), cadmium acetate dehydrate ($\geq 98.0\%$, Sigma), oleic acid (OA, 90%, Sigma), ethanol (Gadot), N-methylformamide (NMF, 99%, Sigma), aqueous ammonium sulfide (40–48 wt %, Sigma), hexane ($\geq 95\%$, Bio-Lab), acetonitrile ($\geq 99.97\%$, Bio-Lab), and oleylamine (OLA, 80–90%, Sigma).

**Preparation of Cadmium Myristate Precursor.** Cadmium nitrate (1.23 g) was dissolved in 40 mL of methanol. Sodium myristate (3.13 g) was dissolved in 250 mL of methanol using strong stirring for 1 h. After complete dissolution, the two solutions were mixed, resulting in a white precipitate. The precipitate was filtered and washed using a Buchner vacuum flask and dried under vacuum for 12 h.

**Synthesis of CdSe Core Nanoplatelets.** CdSe NPLs were synthesized according to a previous procedure from the literature with small modifications.11 Cadmium myristate (170 mg) was dissolved in 15 mL of octadecene (ODE) and degassed for 20 min. Then, temperature was raised to 240 °C under Ar flow, and a selenium precursor solution (12 mg of selenium in 1 mL of ODE) was swiftly injected into the flask. One minute later, 80 mg of cadmium acetate dehydrate were rapidly added into the flask, and after 10 min, the reaction was stopped and cooled down to room temperature. Oleic acid (OA, 1.5 mL) was added at 210 °C to stabilize the forming NCs. After the synthesis, the product was centrifuged with ethanol (1:1) at 6000 rpm for 5 min to get 5 ML-thick CdSe cores.

**Synthesis of CdSe/CdS Core/Shell Nanoplatelets.** CdS shell growth was done according to Yang et al.13 To the washed CdSe cores, 1 mL of N-methylformamide (NMF) and 50 μL of aqueous ammonium sulfide was added as a sulfur source to create phase transfer of the NPLs from hexane to NMF. After complete phase transfer, the hexane was discarded, and this step was repeated a second time. In order to avoid nucleation of CdS, excess S2− ions were removed from NMF as follows; 1.5 mL of acetonitrile and 1 mL of toluene were added to precipitate the NPLs at 3800 rpm for 3 min. The precipitate was dispersed in 1 mL of NMF, and the last step was repeated a second time with 1 mL of acetonitrile and 2 mL of toluene at 6000 rpm for 5 min. The precipitate was dispersed in 0.5 mL of NMF, and 1.5 mL of cadmium acetate dehydrate in NMF solution (0.2 M) was added as a Cd source to further grow the shell under stirring for a few minutes. Four milliliters of toluene were added to precipitate the NPLs and then dispersed in 1 mL of NMF. Afterward, 4 mL of hexane, 100 μL of oleic
acid, and 100 μL of oleylamine were added under stirring for a few minutes until complete phase separation. The formed core/shell CdS/CdSe NPLs were collected. This cycle was repeated three times to produce 3 mL of CdS shell onto the CdSe cores.

**Single Particle Spectroscopy Setup.** A 470 nm pulsed laser diode with maximal 20 MHz repetition rate (Edinburgh Instruments, EPL-470) was used for single particle excitation. The excitation laser was coupled into a microscope (Zeiss, Plan-Neofluar ×63 NA 1.4). The epi-detected signal was filtered, using a dichroic mirror (Semrock, Di02-R488–25 × 36) and a long-pass filter (Semrock, BLP01-488R-25), and coupled into a multimode fiber that equally splits the signal into four avalanche photodiode detectors (PerkinElmer, SPCM-AQ4C) that were connected to a time-correlated single-photon counting (TCSPC) system (Picoquint, Hydra-Harp 400). Single NPL saturation experiments were performed with the same setup by varying the laser excitation power in a triangular pattern (see more details in Section S3).

**Characterization Methods.** TEM images were taken on a JEOL 2100 TEM equipped with a LaB6 filament at an acceleration voltage of 200 kV on a Gatan US1000 CCD camera. UV–vis absorption spectra were measured using a UV–vis–NIR spectrometer (V-670, JASCO). The fluorescence spectrum was measured using USB4000 Ocean Optics spectrometer excited by a fiber coupled 407 nm LED in an orthogonal collection setup.

### ASSOCIATED CONTENT

#### Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.9b03442.

Further EM and light spectroscopy of the NPLs and formulation of the models used within the manuscript (PDF)

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**Funding**
Funding by the European Research Council Consolidator grant ColloQuantO and by the Crown center of Photonics is gratefully acknowledged. D.O. is the incumbent of the Harry Weinrebe professorial Chair of Laser Physics.

**Notes**
The authors declare no competing financial interest.

### ACKNOWLEDGMENTS
The authors thank Maria Chekhova for helpful discussions.

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