Absorption cross-section spectrum of single CdSe/ZnS nanocrystals revealed through photoluminescence excitation spectroscopy

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The absorption spectrum represents an important aspect of single semiconductor nanocrystals (NCs), revealing the morphology and orientation of the NCs. By conducting quantitative photoluminescence excitation spectroscopy based on a single-photon counting method, we succeed in clarifying the absorption cross-section spectrum of neutral excitons in single CdSe/ZnS NCs. With the values of the absorption cross section, we reveal that the intensity saturation of the neutral-exciton emission can be explained by considering the Poisson statistics for incident photons and by the small quantum yield of the biexciton emission. We also evaluated quantitatively the biexciton emission contribution and the ionization rate of NCs that appear at increased incident photon fluxes.

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I. INTRODUCTION

Semiconductor nanocrystals (NCs) have been studied intensively for two decades, which has clarified our understanding of the fundamental physics associated with the quantum confinement effect [1]. Since they exhibit high emissivity, they can be used for applications of various photonic devices, such as light-emitting diodes and single-photon emitters [2,3]. The neutral excitons, formed with an electron in the conduction band and a hole in the valence band, are the most fundamental excited states in NCs. The optical transitions of neutral excitons—photoabsorption and photoemission—are characterized by several parameters, such as the absorption cross section (σ), the photoluminescence (PL) lifetime (τ), and the quantum yield (QY) [4–11]. The value of σ determines the ratio between the incident photon flux and the average exciton density [4–6], whereas the QY is defined as the ratio between τ and the radiative recombination lifetime [7–14]. Both σ and QY are crucial parameters for characterizing the NCs; thus, it is an important task to establish experimental methods for evaluating them. Concerning σ, however, there have been no experiments, to our knowledge, on single NCs that achieved its evaluation in a unit of absorption cross section for a wide spectral range. This is because NCs have σ values that are typically on the order of $10^{-14}$–$10^{-15}$ cm$^2$ [4–6], which is too small to be evaluated by measuring the optical transmittance [15–23].

The measurement of neutral-exciton emission QY on single NCs is also experimentally challenging [7,8]. Because of the difficulties associated with evaluating σ and QY, the unique properties of individual NCs—such as the nonlinear effect that appears at high incident photon fluxes—have been difficult to elucidate quantitatively. New aspects of single-NC photoemission have been studied using various methods based on single-photon counting methods, such as the measurements of second-order photon correlation and time-dependent fluctuations of PL spectrum and lifetime [6,10,14,28]. These studies have enabled us to estimate the QY of the biexcitons and the neutral excitons. This means that, by conducting quantitative PLE spectroscopy based on the single-photon counting method, one can measure the absorption spectrum of single CdSe/ZnS NCs. In this way, an experimental basis for measuring the absorption spectrum of single semiconductor NCs can be established.

In this paper, we quantitatively investigate the absorption cross-section spectrum and emission QY of neutral excitons in single CdSe/ZnS NCs using an experimental technique that combines PLE spectroscopy and single-photon counting method. We determine the QY of neutral-exciton emission from the relationship between the fluctuating PL intensity and incident photon flux. The quantitative values of QY and σ enable us to reveal that the PL of neutral excitons show an intensity saturation induced by Poisson statistics for the incident photons and by the small biexciton quantum yield. The biexciton emission contribution and the ionization rate of NCs at increased incident photon fluxes are also studied quantitatively.

II. EXPERIMENT

For the conversion from PL intensity to σ, the following equation is used:

$$\sigma(h\nu) = I / (F \cdot \xi \cdot \eta_X \cdot j_{\text{exc}}).$$  \hspace{1cm} (1)

where $h\nu$ is photon energy, $I$ is the detected photon count rate $(\text{s}^{-1})$, $F$ is the repetition rate of the excitation pulse $(\text{s}^{-1})$, $\xi$ is the detection efficiency, $\eta_X$ is the QY of the neutral exciton emission, and $j_{\text{exc}}$ is the excitation photon flux $(\text{photons/cm}^2)$. This equation is obtained from the following two equations related to the average exciton density $\langle N \rangle$:

$$\langle N \rangle = \sigma(h\nu) \cdot j_{\text{exc}}(h\nu),$$  \hspace{1cm} (2)

$$I = F \cdot \xi \cdot \eta_X \cdot \langle N \rangle.$$  \hspace{1cm} (3)
values of intensity of a single CdSe/ZnS NC (red dots) measured at various counting (TCSPC) board. (b) A TEM image of the sample. (c) PL excitation setup for the quantitative PL excitation spectroscopy. The total sizes of the CdSe/ZnS NCs are 14 × 7 × 7 nm³. Because the Qdot655 have nonspherical morphologies, the value of σ depends on the orientation of the particles. The PL from the NCs was collected by a 100× oil-immersion objective lens with numerical aperture (N.A.) of 1.3 (N100×-PFO; Nikon). The experiments were performed at room temperature.

The PL from a single NC was selectively extracted by a pinhole with a diameter of 0.4 mm, which corresponds to a detection area of 12.6 μm². The PL from a single NC was filtered by long-pass filters (LPFs), and then detected by a set of avalanche photodiodes (APDs) placed under Hanbury Brown-Twiss geometry. These APDs were used to measure the PL lifetime and second-order photon correlation simultaneously. We measured the excitation power at the position between the pinhole and the LPFs, and evaluated the PL excitation power densities were kept at almost the same value for various excitation wavelength by using variable neutral density (ND) filters. We measured the optical transmittance from the position after the objective lens to the position before the APDs for 655 nm, and determined it to be 0.26. We estimated the coupling efficiency between the polarized PL and the objective (with an N.A. of 1.3) to be 0.3 ± 0.1 [7]. The APD has a detection efficiency of 0.35 at 655 nm. From these values, we determined ξ to be 0.03 ± 0.01.

III. RESULTS AND DISCUSSION

Figure 1(c) shows the PL intensities measured at various values of杰克逊从2.4 × 10¹² to 1.4 × 10¹⁴ photons/cm². The wavelength of the excitation light (λexc) was set at 520 nm. For each value of λexc, which is shown by the solid black line, the PL was integrated for 4 s with 0.5 s intervals. The PL intensities, shown as red dots, are plotted with units of counts (cts) per binning time (bin), where we set the bin time at 50 ms. In Fig. 1(d), we plot the PL intensity as a function of λexc. For λexc = 2.4 × 10¹³ photons/cm², the PL is dominated by a signal with an intensity of 150 cts/bin. This contribution shows a linear increase with λexc and dominates the PL signal for the weak excitation regime below 2 × 10¹³ photons/cm² (i.e., <85 s). These signals, showing the highest PL intensities, are attributed to emissions from neutral excitons [11–13]. For values of λexc above 2 × 10¹³ photons/cm², the appearance of additional contributions with smaller intensities increases. These signals are attributed to the emission of so-called intermediate states, such as charged excitons, doubly charged excitons, and dark states associated with surface trap states [11–13]. To reveal the characteristics of neutral exciton emissions, the incident photon flux should be adjusted to minimize the appearance of these intermediate states.

In order to experimentally evaluate these parameters, we developed the measurement system shown in Fig. 1(a). Monochromatic light obtained from a supercontinuum light source (SC-400PP, Fianium) operating at a repetition rate of 5 MHz was used as an excitation source. The bandwidth of the excitation light was set at 8 nm by using a tunable bandpass filter (Super Chromat; Fianium). The samples of single CdSe/ZnS NCs (Qdot655; Life Technologies), which were prepared by spin coating on cover glass with a film of polymethylmethacrylate, were illuminated by the excitation light through an achromatic lens with a focal length of 2.5 cm. Figure 1(b) shows a transmission electron microscope (TEM) image of the sample. The total sizes of the CdSe/ZnS NCs are 14 × 7 × 7 nm³. Because the Qdot655 have nonspherical morphologies, the value of σ depends on the orientation of the particles. The PL from the NCs was collected by a 100× oil-immersion objective lens with numerical aperture (N.A.) of 1.3 (N100×-PFO; Nikon). The experiments were performed at room temperature.

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Next, we show PL data of the same NC, integrated for 200 s at λexc = 1.3 × 10¹³ photons/cm². Figure 2(a) shows time-dependent PL intensities plotted for 120–160 s. The right panel shows a histogram of occurrences integrated for 200 s. Figure 2(b) shows the corresponding PL lifetimes obtained by applying a single exponential fitting to the PL decay curves for each bin time, as we have reported in a previous paper [28]. Figure 2(c) shows the relationship between PL lifetime and intensity, which is known as the fluorescence
at a fixed value of \( \lambda_{\text{exc}} \) ranged from 590 to 434 nm with a step size of 4 nm. The excitation photon energies (2.1–2.86 eV) are much smaller than the bandgap energy of the ZnS shell (3.7 eV). This means that the optical excitation usually results in creations of carriers inside the CdSe core. The excited carriers relax to the ground states in the core and emit photons with QY of near unity. This means that the effects of nonradiative recombination processes associated with trap states inside and outside the NCs are negligible, and thus, it enables us to consider that the relaxation process of excited carriers does not depend on the excitation photon energy. For each value of \( \lambda_{\text{exc}} \), the data were integrated for 4 s with 0.5 s intervals. We selectively plot the neutral-exciton contribution with red dots, assuming that the signals with lifetimes from 15 to 30 ns correspond to neutral exciton contributions. Other contributions of intermediate states are plotted with black dots. On the right side of the \( y \) axis, the value of \( \langle N \rangle \) is also presented, which was determined using Eq. (3). The results confirm that the PL was measured for \( \langle N \rangle < 0.16 \), which means that the \( \langle N \rangle \ll 1 \) condition was satisfied for this measurement. Since \( \xi \cdot \eta_{\text{exc}} \cdot \langle N \rangle < 0.005 \), the detection count rate is less than 0.5% of trigger frequency. This enables us to consider that the effect of counting loss is negligible.

Figure 3(b) shows the result of the absorption cross-section spectrum of neutral excitons, obtained by averaging the neutral exciton contributions shown in Fig. 3(a). The values of \( \sigma \) were evaluated from PL intensities by converting them via Eq. (1). For the purpose of reproducibility, we conducted the measurements three times, as plotted by circles, squares, and triangles. The values of \( \sigma \) ranged from \( 5 \times 10^{-15} \) to 2.1 eV to \( 3 \times 10^{-14} \text{ cm}^2 \) at 2.7 eV. The data show a gradual increase of \( \sigma \) for higher energies, including an onset structure at around 2.3–2.5 eV. These characteristics of the absorption spectrum were also observed by using transmission spectroscopy. The absence of sharp structures in the excited states for the CdSe/ZnS NCs with large sizes of \( 14 \times 7 \times 7 \) nm\(^3\) is consistent with the experimental data with the following equation:

\[
\eta \sim k_{\text{NR}} = 1 - (k_{\text{NR}} \cdot \tau) \]

The contributions with long lifetimes (i.e., >30 ns) are attributed to neutral excitons modified by quantum-confined Stark effect (QCSE), whose radiative recombination lifetimes increase because of the decrease in the overlap between electrons and holes [28]. As indicated by the blue dotted line, the QCSE-modified neutral excitons show a slight decrease in PL intensity for longer lifetimes. Since the QCSE changes the radiative recombination lifetime, while it does not result in a significant change of nonradiative recombination rate \( k_{\text{NR}} \), the value of \( k_{\text{NR}} \) can be determined by comparing the experimental data with the following equation:

\[
\eta_{\text{X}} = 1 - (k_{\text{NR}} \cdot \tau) \]

From the slope of the blue line, we determine that \( k_{\text{NR}} = 5 \mu \text{s}^{-1} \). Thus, for the main contribution of neutral excitons at 20 ns, \( \eta_{\text{X}} \) can be estimated as 0.9.

Figure 3(a) shows the PL intensity measured as a function of \( \lambda_{\text{exc}} \), where \( \lambda_{\text{exc}} \) ranges from 590 to 434 nm with a step size of 4 nm. The excitation photon energies (2.1–2.86 eV) are much larger than the bandgap energy of the ZnS shell (3.7 eV). This means that the optical excitation usually results in creations of carriers inside the CdSe core. The excited carriers relax to the ground states in the core and emit photons with QY of near unity. This means that the effects of nonradiative recombination processes associated with trap states inside and outside the NCs are negligible, and thus, it enables us to consider that the relaxation process of excited carriers does not depend on the excitation photon energy. For each value of \( \lambda_{\text{exc}} \), the data were integrated for 4 s with 0.5 s intervals. We selectively plot the neutral-exciton contribution with red dots, assuming that the signals with lifetimes from 15 to 30 ns correspond to neutral exciton contributions. Other contributions of intermediate states are plotted with black dots. On the right side of the \( y \) axis, the value of \( \langle N \rangle \) is also presented, which was determined using Eq. (3). The results confirm that the PL was measured for \( \langle N \rangle < 0.16 \), which means that the \( \langle N \rangle \ll 1 \) condition was satisfied for this measurement. Since \( \xi \cdot \eta_{\text{exc}} \cdot \langle N \rangle < 0.005 \), the detection count rate is less than 0.5% of trigger frequency. This enables us to consider that the effect of counting loss is negligible.

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NCs can be written by the Poisson distribution. By using this, the function of neutral exciton emission and biexciton emission, whereas the blue line corresponds to the sum of intermediate states. The green line corresponds to the contribution of neutral exciton emission and biexciton emission. In addition, we discuss the nonlinearity of the PL intensity by showing a comparison between the experimental results and calculated results. Because we have determined the values of $\xi$, $\eta$, and $j_{\text{exc}}$, we can plot $I/F \cdot \xi \cdot \eta \cdot j_{\text{exc}}$, which corresponds to $\sigma$ for the weak excitation limit. Figure 4 shows the $j_{\text{exc}}$ dependence of $I/F \cdot \xi \cdot \eta \cdot j_{\text{exc}}$ for neutral exciton emission (red dots) and for other contributions of intermediate states (black dots). The blue line corresponds to the result of calculations for $I_X + I_{XX}$, where $I_X$ is the neutral exciton contribution and $I_{XX}$ is the biexciton emission contribution. We consider that the effect of the peak shift due to Coulomb interactions in biexciton excited states is negligible, since the absorption structure is broader than the order of Coulomb shift. According to previous works [6,10,14], the excitation probability of single NCs can be written by the Poisson distribution. By using this, the contributions of neutral excitons and biexcitons can be written as the following equations:

$$I_X = F \cdot \xi \cdot \eta_X \cdot (\langle N \rangle + \langle N \rangle^2/2 + \langle N \rangle^3/6) \cdot \exp(-\langle N \rangle),$$

where $\eta_X$ is the QY of biexciton emission. From the ratio between the center peak and side peaks of the second-order photon correlation shown in Fig. 2(d), we determine that $\eta_{XX} = 0.23$ [6,10,14]. The green line corresponds to $I_{XX}$. The calculated result of $I_X + I_{XX}$, which shows a saturation curve for large values of $j_{\text{exc}}$, agrees with the experimental results. This agreement means that the PL of neutral excitons shows an intensity saturation governed by Poisson distribution.

In addition, the particle-dependent nonlinearity—i.e., the appearance of charged excitons ($X^-$) and doubly charged excitons—could also be revealed by using our method. The appearance of $X^-$ at high excitation power indicates that the occurrence of PL blinking strongly depends on the incident photon flux. This feature can be explained by a model considering the Auger-assisted ionization process, as discussed in earlier works [13,30]. By using the determined value of $\sigma$, we estimate that the transition from the neutral-exciton-dominated regime to the charged-exciton-dominated regime occurs at $\langle N_X \rangle \sim 10^{-15}$ to $10^{-14}$ cm$^2$. The appearances of the range of values are consistent with our expectations; because the current samples of Qdot655 have nonspherical morphologies [29], the values of $\sigma$ depend on the orientation of the particles. This ability to obtain QY and $\sigma$ for individual NCs is an important advantage of single-particle absorption spectroscopy, which enables us to reveal morphology-dependent optical absorption properties.

In summary, we showed that the emission QY and the absorption cross-section spectrum of neutral excitons in single CdSe/ZnS NCs can be revealed by measurements of fluctuating PL intensity and lifetime, second-order photon correlation, and the quantitatively determined values of detection efficiency and excitation photon flux. We showed that the obtained QY and $\sigma$ values of neutral excitons are consistent with the incident-photon-flux-dependent PL intensities, showing a saturation curve governed by Poisson distributions. The current technique of quantitative PLE spectroscopy can be applied to smaller molecules with values of $\sigma$ that are less than $10^{-14}$ cm$^2$, which are difficult to measure with conventional methods based on optical transmittance measurements. Thus, this paper establishes an experimental basis for a deep understanding of the crucial roles of the morphologies, charging, QCSE, and orientation on the optical properties of nano-objects. This can be extended to various nanostructures such as NCs with unique morphologies (e.g., CdSe/CdS core-shell particles), quantum heterostructures, and carbon nanotubes.

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