Energy Transfer of Biexcitons in a Single Semiconductor Nanocrystal

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ABSTRACT: Photoluminescence (PL) decay dynamics of multiexcitons in semiconductor nanocrystals (NCs) are dominated by the nonradiative Auger effect, making it difficult to explore their basic optical processes such as radiative recombination and energy transfer (ET). Here we constructed a single-particle ET system by attaching several acceptor dyes to the surface of a donor NC to study the ET of biexcitons at a single-NC level. By comparing the single-exciton and biexciton PL lifetimes of the same donor NC before and after the acceptor dyes were bleached, their respective ET lifetimes could be reliably extracted without the Auger influence. From statistical measurements on a large number of single ET particles, the average ET rate ratio between biexcitons and single excitons was estimated to be larger than four, and the same scaling rule could be naturally extended to their radiative rates.

KEYWORDS: Nanocrystal, biexciton, energy transfer, time-resolved

When two or more electron–hole pairs exist simultaneously inside the excitation volume of a single semiconductor nanocrystal (NC), a multiexciton state is formed from their mutual interactions to yield a rich spectrum of fundamental physics. Multiexcitons are unavoidably encountered in various device applications of semiconductor NCs ranging from lasers, photodetectors, and solar cells to light-emitting diodes where high electrical currents are normally applied to dense NC films. Because of enhanced carrier–carrier interactions within the quantum confinement regime, higher-order excitons (such as a biexciton) of a multiexciton state are dissipated mainly through a nonradiative Auger process at a subnanosecond time scale, which is much shorter than the radiative lifetime of tens of nanoseconds for a single exciton. Consequently, due to the difficulty of resolving the biexciton radiative lifetime it was normally proposed or indirectly determined to be \( \sim 2 \)–5 times faster than that of single excitons in previous time-resolved measurements of ensemble NCs. The same scaling rules could be applied to the energy transfer (ET) lifetimes of biexcitons and single excitons because two electron–hole pairs are also involved in the dipole-related ET process of the donor NC. In contrast to the intensive research efforts devoted to single-exciton ET of semiconductor NCs, the biexciton ET process has been rarely studied in the literature with the associated lifetimes being either the same as or four times faster than that of single excitons from the assumptions of two previous reports. Given the emerging importance of biexciton generation and collection in NC-based photovoltaic devices, it is imperative to quantify and control the biexciton ET lifetime so that it can compete with the Auger one for the biexcitons to be efficiently extracted by acceptor materials and eventually converted to enhanced photocurrents.

Here we attached several acceptor dyes to the surface of a donor NC to construct a single-particle ET system where the ET process could be turned off by simply bleaching the acceptor dyes. With the presence of both single excitons and biexcitons in the ET process, the donor NC possessed a biexponential photoluminescence (PL) decay with the fast and slow lifetimes arising from the Auger, ET, and radiative decays of biexcitons and the ET and radiative decays of single excitons, respectively. After subsequent bleaching of acceptor dyes, PL decay of the same single NC was still biexponential but with the biexciton and single-exciton ET components being removed from the fast and slow lifetimes, respectively. By comparing the above two PL decay dynamics, the ET lifetimes of both single excitons and biexcitons could be reliably obtained, the average ratio of which was larger than four from statistical measurements on a large number of single ET particles. Our current work has not only provided the first experimental characterization of the multiexciton ET process in single semiconductor NCs but also paved the way toward judicious collection of multiexcitons through the ET process in photovoltaic devices.

As reported previously, we covalently linked to the surface of a single CdSe/ZnS NC (Qdot605, from Life Technologies) \( \sim 2 \)–8 dye molecules (ATTO647N, from ATTO-TEC) to synthesize a single donor–multiple acceptors ET system (see ref 27 for the absorption and emission spectra of solution NCs and dyes). Successful attachment of dye molecules to the NC...
surface was confirmed from the ensemble PL decay (intensity) measurement showing an ET-induced shortening (quenching) of the NC PL lifetime (intensity) (Figure S1, Supporting Information). One drop of the as-prepared sample solution was spin-coated onto a fused silica substrate to form a low-density solid film for the optical characterizations of single ET particles at room temperature. The 490 nm output of a 7.8 MHz, picosecond supercontinuum fiber laser (EXR-1S, from NKT Photonics) was used as the excitation source for donor NCs to avoid direct fluorescence from acceptor dyes. The laser beam was focused by a 100x immersion-oil objective onto the sample substrate loaded at a home-built confocal scanning optical microscope. PL signal of a single ET particle was collected by the same objective and sent through a beam splitter to two avalanche photodiodes (APDs) in a time-correlated single-photon counting (TCSPC) system with a time resolution of ~250 ps. A band-pass filter was placed before each of these two APDs to detect the NC (600 ± 20 nm) and the dye (700 ± 20 nm) photons separately. The TCSPC system was operated under the time-tagged time-resolved (TTTR) mode so that the arrival times of each photon relative to the laboratory time and the laser pulse time could be both obtained to yield the PL intensity time trajectory and the transient PL curve, respectively. As a reference, we also performed the TTTR measurements on single CdSe/ZnS NCs without surface dyes using similar optical setups to those described above.

With \( \langle N \rangle \) representing the average number of photons absorbed per NC per pulse, we first set the pump fluences of the excitation laser at \( \langle N \rangle = \sim 0.1 \) and \( \sim 1.0 \) to measure the TTTR properties of single CdSe/ZnS NCs without surface dyes. The exciton number \( \langle N \rangle \) was calculated from \( \langle N \rangle = \sigma f \), where the pump fluence \( J \) is a controllable parameter in our experiment and the absorption cross section \( \sigma \) is calculated to be \( 4.21 \times 10^{-15} \text{ cm}^2 \) at the excitation wavelength of 490 nm using an extinction coefficient of 1 100 000 cm\(^{-1}\) M\(^{-1}\) provided by Life Technologies. As plotted in Figure 1A for the PL time trajectory of a representative NC, mainly single excitons were created at \( \langle N \rangle = \sim 0.1 \) and the PL blinking “on” periods demonstrated a dominant appearance over the “off” ones. When \( \langle N \rangle \) was increased to \( \sim 1.0 \) to generate both single excitons and biexcitons in the same single NC, more frequent PL blinking behavior was observed in the PL time trajectory shown in Figure 1B due to the biexciton ionization effect.\(^{28-30}\)

In Figure 1C, the “on”-period PL decay curve of the single NC excited at \( \langle N \rangle = \sim 0.1 \) was fitted by a single-exponential function with a radiative lifetime of \( \sim 14.36 \pm 0.04 \text{ ns} \) for single excitons. Also plotted in Figure 1C, the “on”-period PL decay curve of this single NC excited at \( \langle N \rangle = \sim 1.0 \) could be fitted well only by a biexponential function of \( A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \) with \( A_1 \) (\( A_2 \)) and \( \tau_1 \) (\( \tau_2 \)) being the amplitude and the value of the slow (fast) lifetime component, respectively. Almost the same radiative lifetime \( \tau_1 \) of \( \sim 14.45 \pm 0.04 \text{ ns} \) was obtained for single excitons and the appearance of an additional fast lifetime \( \tau_2 \) of \( \sim 0.80 \pm 0.01 \text{ ns} \) was caused mainly by the biexciton Auger recombination process. From similar TTTR measurements of \( \sim 50 \) single CdSe/ZnS NCs, the average radiative lifetime of single excitons and PL lifetime of biexcitons were calculated to be \( \sim 14.77 \pm 3.02 \) and \( \sim 0.76 \pm 0.20 \text{ ns} \) (Figure S2, Supporting Information), respectively, which were the two main optical parameters of a single NC to be focused in the following ET studies.

Next in our experiment, we excited single ET particles at \( \langle N \rangle = \sim 0.1 \) to elucidate fundamental interactions between the donor NC and the acceptor dyes in a single-exciton ET process. The PL time trajectories of a representative CdSe/ZnS NC and its surface dyes are plotted in Figure 2A,B, respectively, where their PL blinking patterns were strongly correlated to each other for the first \( \sim 12 \) s of the laser excitation. Then the acceptor dyes were completely bleached to turn off the ET process, boosting the “on”-period PL intensity of the donor NC to its normal level. The increase of the donor PL intensity with the ET studies of ensemble fluorescent molecules.\(^{31}\) The photobleaching effect of a dye molecule during the ET process could be attributed to occasional fillings of the triplet states that are reactive in the photolysis process to destruct its internal structures.\(^{32}\) As shown in Figure 2C, the “on”-period PL decay curve of the single NC without ET was fitted by a single-exponential function to yield the single-exciton radiative lifetime \( \tau_1 \) of \( \sim 18.90 \pm 0.06 \text{ ns} \). Meanwhile, the “on”-period PL decay of the same NC with ET was also single-exponential with a lifetime \( \tau_1 \) of \( \sim 3.90 \pm 0.01 \text{ ns} \). This lifetime shortening of “on”-period photons is caused by ET instead of charge transfer,\(^{33}\) because the NC would be charged in the latter case to start the blinking “off” period. From the single-exciton PL decay rate \( k_1 = 1/\tau_1 = 1/\tau_1^{\text{rad}} + 1/\tau_1^{\text{ET}} \) for the
donor NC, the ET lifetime $\tau_{1}^{\text{ET}}$ and the ET efficiency $\eta_{1} = 1 - \tau_{1}^{\text{ET}}/\tau_{1}^{\text{rad}}$ for this specific ET particle could be both derived to be $\sim 4.9$ ns and $\sim 79\%$, respectively. By adjusting the number of acceptor dyes on the surface of a single donor NC, the ET efficiency could be effectively tuned even to $\sim 100\%$ and here we focused only on those particles with ET efficiencies smaller than $\sim 80\%$ so that both the single-exciton and the biexciton PL lifetimes could be long enough to be resolved by our TCSPC system.

After understanding the biexciton Auger and single-exciton ET processes, we moved to the final step to resolve the biexciton ET lifetimes of single ET particles excited at $\langle N \rangle = \sim 1.0$. When two excitons are present simultaneously in the single NC, the first exciton (biexciton) can go through the radiative decay, the nonradiative Auger recombination or the ET process, after which a single exciton is left to go through the radiative decay or the ET process. The correlated PL time trajectories of a representative CdSe/ZnS NC and its surface dyes are plotted in Figure 3A,B, respectively, where the acceptor dyes were bleached after $\sim 10$ ns of the laser excitation. In Figure 3C, the "on"-period PL decay curve of the donor NC without ET was fitted by a biexponential function with a single-exciton radiative lifetime and a biexciton PL lifetime of $\tau_{1}^{\text{rad}} = 17.31 \pm 0.05$ ns and $\tau_{2} = 1.21 \pm 0.01$ ns, respectively. Here the biexciton PL lifetime $\tau_{2}$ is related to the biexciton radiative ($\tau_{1}^{\text{rad}}$) and Auger ($\tau_{1}^{\text{Auger}}$) lifetimes from the expression of $1/\tau_{1} = 1/\tau_{1}^{\text{rad}} + 1/\tau_{1}^{\text{Auger}}$. Also in Figure 3C, the "on"-period PL decay curve of the donor NC with ET was fitted by a biexponential function with the single-exciton and biexciton PL lifetimes of $\tau_{1} = 6.28 \pm 0.02$ ns and $\tau_{2} = 0.80 \pm 0.01$ ns, respectively. From $1/\tau_{1} = 1/\tau_{1}^{\text{rad}} + 1/\tau_{1}^{\text{ET}}$ and $1/\tau_{2} = 1/\tau_{2}^{\text{rad}} + 1/\tau_{2}^{\text{Auger}} + 1/\tau_{2}^{\text{ET}} = 1/\tau_{2}^{\text{ET}} + 1/\tau_{2}^{\text{Auger}}$, the single-exciton and biexciton ET lifetimes of $\tau_{1}^{\text{ET}}$ and $\tau_{2}^{\text{ET}}$ could be both obtained to be $\sim 9.9$ and $\sim 2.4$ ns, respectively. Then the ET rate ratio $r_{1}^{\text{ET}}/r_{2}^{\text{ET}}$ between biexcitons and single excitons was calculated to be $\sim 4.13$ for this specific ET particle. For each of the $\sim 50$ single ET particles studied in our experiment, we could obtain the single-exciton and biexciton lifetimes with and without ET (Figure S2, Supporting Information) from which a statistical histogram of the ET rate ratios between biexcitons and single excitons was constructed. As shown in Figure 4A, the ET rate ratio of $r_{1}^{\text{ET}}/r_{2}^{\text{ET}}$ between biexcitons and single excitons peaks at four but has an asymmetric distribution toward larger values, implying that it is averagely larger than what is expected by simply counting the number of available electron–hole dipoles for ET in the donor NC.

Whereas the exact origin for these larger ET rate ratios shown in Figure 4A is worth further investigations, here below we will provide several tentative explanations. First, the biexciton lifetime measured in the ET process might be shorter than the real one because it is close to the system time resolution of $\sim 250$ ps for some of the ET particles studied in our experiment. To resolve this time resolution issue it might be helpful in future work to replace the Qdot605 CdSe/ZnS donor NCs by other heterostructures with longer biexciton Auger lifetimes such as type-II CdS/ZnSe NCs and giant CdSe/CdS NCs. Second, although we intended to place mainly single excitons and biexcitons in the donor NC by setting $\langle N \rangle = \sim 1.0$, there is still a Poisson probability of $\sim 8\%$ to create higher-order multie excitons with shorter Auger lifetimes and larger ET rates than those of biexcitons. As shown in Figure S4 of the Supporting Information, there does exist a weak tendency for the shorter biexciton lifetimes to be correlated with the larger ET rate ratios, implying that the biexciton PL dynamics might have contributions from higher-order multie excitons. Third, when two electrons and two holes are excited in a donor NC, the attractive/repulsive interactions would set them at different spatial locations, leading to different values of the four available dipole moments (Figure 4B). Meanwhile, there are several acceptor dyes on the NC surface whose distances and/or alignment angles to the NC axis are slightly different. The first ET event (biexciton ET) could occur from the electron–hole pair with the largest dipole moment to

Figure 3. PL time trajectories of (A) a donor CdSe/ZnS NC excited at $\langle N \rangle = \sim 1.0$ and (B) its surface acceptor dyes, respectively. The dashed lines in (A) mark the intensity level above which the fluorescent photons are categorized into the blinking “on” periods. (C) “On”-period PL decay curves of the CdSe/ZnS NC before and after the acceptor dyes were bleached, each of which was fitted with a biexponential function. The IRF (instrument response function) of the TCSPC system is also displayed with a time resolution of $\sim 250$ ps. The same PL decay curves are plotted in Figure S3 of the Supporting Information at a shorter time window between 0 and 5 ns.

Figure 4. (A) Statistical histogram for the distribution of ET rate ratios between biexcitons and single excitons from $\sim 50$ single ET particles. (B) Schematic diagram showing the PL and ET processes of single excitons and biexcitons in the donor NC.
the dye molecule with the shortest distance and/or the smallest alignment angle. The second ET event (single-exciton ET) would proceed at a smaller rate because the remaining electron–hole pair now has a smaller dipole moment. Moreover, if the dye molecule involved in the first ET process is still occupied by an ET-excited electron with a radiative lifetime of \( \sim 5 \) ns, \(^{27}\) a different dye molecule might serve as the acceptor in the second ET process to further reduce the ET rate.

For the single ET particle whose PL properties are presented in Figure 3, the single-exciton ET efficiency was calculated to be \( \eta = 1 - \frac{\tau_f}{\tau_{1\text{rad}}} = \sim 64\% \), which is relatively larger than that of \( \eta = 1 - \frac{\tau_f}{\tau_{1\text{rad}}} = \sim 34\% \) for biexcitons because their ET process has to compete with the nonradiative Auger decay in addition to radiative recombination. For each of the \( \sim 50 \) single ET particles studied in our experiment, we could obtain the biexciton ET efficiency, the single-exciton ET efficiency, and their ratio, whose statistical distributions are plotted in Figure S5 of the Supporting Information. As discussed earlier in the text, we intentionally selected the ET particles with single-exciton ET efficiencies smaller than \( \sim 80\% \) for reliable estimations of the single-exciton and biexciton PL lifetimes. In practice, the single-exciton ET lifetime could be easily reduced to the subnanosecond time scale for single ET particles studied here\(^{2}\) or ensemble CdSe/ZnS NCs embedded inside a dense matrix of acceptor dyes.\(^{25}\) Meanwhile, single-exciton ET lifetimes of hundreds of picoseconds have been realized in previous reports\(^{21,36}\) using smaller- and larger-sized ensemble CdSe NCs as the donors and acceptors, respectively. So there is still enough room for the ET process of biexcitons to be greatly accelerated to favor their efficient extractions into various acceptor materials for subsequent manipulations in photo voltaic devices.

To summarize, we have synthesized single ET particles in which each consisted of a donor CdSe/ZnS NC and several acceptor dyes on its surface, which allowed us to realize the first optical characterization of the biexciton ET process with a single-NC precision. For most of the single ET particles studied in our experiment, the ET rates of biexcitons were measured to be approximately four times larger than that of single excitons, which can be qualitatively understood by simply counting the number of available electron–hole dipoles for ET in the donor NC (Figure 4B). For the other single ET particles, the ET rate ratios between biexcitons and single excitons deviated from four toward larger values, which was tentatively attributed by us to the inadequate system time resolution, the involvement of higher-order multie excitons, or most likely, the slight difference in the single-exciton and biexciton dipole moments. The same scaling rule discovered here in the ET rate ratio between biexcitons and single excitons could be naturally extended to their radiative rate ratio because there are also four dipole moments involved in the biexciton radiative decay process (Figure 4B). Then a deeper understanding of the biexciton ET process in semiconductor NCs might be alternatively obtained by theoretical modelings of the single-exciton and biexciton radiative transitions taking into account the size- and shape-dependent electronic structures, as well as their possible influences on the fine carrier relaxation processes.\(^{37,38}\) Experimentally, more detailed optical characterizations of the biexciton ET process at the single-NC level are still needed to probe its dependences on the donor–acceptor spectral overlap and separation distance. Moreover, the replacement of the CdSe NCs studied here by the PbSe or PbS NCs as ET donors would also be interesting because these two types of metal–chalcogenide NCs possess dramatically different exciton degeneracies at the lowest quantized states\(^{9,40}\) involved in the biexciton ET process. Overall, we hope that the current work could stimulate intensive theoretical calculations and experimental measurements of the multie exciton ET and radiative processes to guide their efficient applications in a variety of optoelectronic devices.

**REFERENCES**