Ultrafast biexciton spectroscopy in semiconductor quantum dots: evidence for early emergence of multiple-exciton generation

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Understanding multiple-exciton generation (MEG) in quantum dots (QDs) requires in-depth measurements of transient exciton dynamics. Because MEG typically faces competing ultrafast energy-loss intra-band relaxation, it is of central importance to investigate the emerging time-scale of the MEG kinetics. Here, we present ultrafast spectroscopic measurements of the MEG in PbS QDs via probing the ground-state biexciton transients. Specifically, we directly compare the biexciton spectra with the single-exciton ones before and after the intra-band relaxation. Early emergence of MEG is evidenced by observing transient Stark shift and quasi-instantaneous linewidth broadening, both of which take place before the intra-band relaxation. Photon-density-dependent study shows that the broadened biexciton linewidth strongly depends on the MEG-induced extra-exciton generation. Long after the intra-band relaxation, the biexciton broadening is small and the single-exciton state filling is dominant.

The limiting factor for improving solar-cell efficiency lies in the simple physics that single-photon absorption generates one electron-hole pair. The possibility of generating multiple charge carriers per photon, known as carrier multiplication (CM) or multiple exciton generation (MEG), is of crucial importance for developing efficient solar-cell devices. Semiconductor quantum dots (QDs) represent well-defined structures to explore the quantum limit of harnessing solar-conversion efficiency. By engineering the sizes of QD composites, it has been demonstrated that not only the optical properties, but also the MEG efficiency in QDs can be modified. MEG in a photo-excited QD system is a prominent route for enhancing the conversion efficiency because carriers confined in spatial dimensions that are smaller than the bulk exciton Bohr radius lead to the formation of discrete excitonic states such that efficient MEG is possible either by suppressing the ultrafast electron-phonon relaxation or by enhancing the Coulomb interactions via reduced dielectric screening at the QD surface.

Numerous investigations have shown that the kinetic origin of MEG dynamics in QDs is intrinsically complex because the photo-generated single exciton initially suffers from extremely fast intra-band relaxation, whose interaction time-scale is typically in the range of a few ps. To enhance the MEG efficiency, it is desirable to circumvent the ultrafast energy-loss intra-band process via virtual single excitonic or biexcitonic optical transition or coherent superposition among multi-exciton states. Other investigation suggests that the intra-band relaxation rate competes with the MEG formation rate.

The above mentioned photo-physical complexity of MEG is largely due to the nature of intrinsic multi-particle (or multi-exciton) interaction. When more than two excitons are created under high-energy excitation condition, the lowest lying energy state is not the single exciton; the mutual interaction between two excitons results in the formation of a Coulomb-correlated two excitonic state, called biexciton. The biexciton is energetically more stable than the single exciton such that it exists below the single-exciton state. Recent studies have reported that the final biexciton density strongly influences the solar-conversion efficiency. Although it is important to study the impact of the MEG on the transient biexciton spectra, no experimental investigations have been provided to compare the MEG-induced biexciton dynamics with the intra-band relaxation dynamics.
The key experimental observation in this study is that the optically-induced MEG is an extremely fast process, arising before the intra-band relaxation. By exploring the lowest observable biexciton dynamics, we directly measure that the biexciton bleaching comes from early emergence of the photo-induced MEG, in which the effect of extra-exciton generation is manifested by the increased broadening of the biexciton linewidth via multi-exciton interaction. Note that, in contrast to the conventional single-exciton MEG spectroscopy\textsuperscript{11,36–39}, our ultrafast time-resolved experiments were performed in a regime where Auger recombination dominates the biexciton dynamics, we directly measure that the biexciton bleaching comes from early emergence of the photo-induced MEG, in which the effect of extra-exciton generation is manifested by the increased broadening of the biexciton linewidth via multi-exciton interaction. Note that, in contrast to the conventional single-exciton MEG spectroscopy\textsuperscript{11,36–39}, our ultrafast time-resolved experiments were performed both in the MEG and in the non-MEG regimes via photon-energy and density-controlled measurements on the single- and biexciton spectra.

Results

Single-exciton MEG dynamics. Figure 1a shows data for the broad-band optical absorption of the colloidal semiconductor PbS QDs and Fig. 1b shows a schematic for the ultrafast pump-probe measurements (See method for the detailed description of sample preparation and ultrafast spectroscopy). The lowest single-exciton bandgap energy $E_x$ is identified as 0.93 ± 0.01 eV, and the ground-state biexciton energy $E_{xx}$ is estimated to be 0.87 ± 0.03 eV\textsuperscript{30–33}.

![Figure 1](image_url)

Figure 1 | QD absorption spectra and experimental setup. (a) Linear absorption spectra of the colloidal PbS QDs used in the study. Inset: schematic energy levels for the single-exciton $E_x$ and the ground-state biexciton $E_{xx}$, respectively. (b) Schematic for the ultrafast pump-probe measurements. For the spectrally-resolved measurements, the probe pulse is scanned through a monochromator (Newport 74125 Oriel Cornerstone 260 1/4 m) at each $\Delta t$. The measured FWHM of the pump and probe beam are 150 $\mu$m and 100 $\mu$m, respectively. All measurements are performed at room temperature.

Before the discussion on the biexciton dynamics, it is instructive to present detailed measurements on the intra-band relaxation dynamics because the linewidth broadening of single excitons and biexcitons is necessary related to the competing relaxation rate between the MEG and the intra-band dynamics, in which the time scale of the intra-band relaxation is typically a few ps\textsuperscript{30,40,41}, comparable with the MEG time scale. In the experiment, the colloidal semiconductor PbS QD sample was pumped by two different pump-photon energy $E_{pump}$ of 1.55 eV and 3.10 eV, and the average number of initially photo-generated excitons per QD ($N_0$), or initial exciton occupancy, was controlled from 0.1 to 2.2 to investigate the photon density-dependent $E_x$ dynamics.

In order to determine the intra-band relaxation rate, we measured the $E_x$ dynamics in a short $\Delta t$ range between −1 ps and 7 ps as shown in Figs. 2a and b. By examining the rising edge of the $E_x$ peak, we show that the relaxation process is completed at pump-probe delay $\Delta t = 1$ ps for 1.66$E_x$ excitation (non-MEG regime) and $\Delta t = 2$ ps for 3.3$E_x$ excitation (MEG regime). This 2 ps time constant is consistent with prior experimental studies of hot-carrier MEG dynamics in PbS quantum dots, where the reported value of intra-band relaxation is in the range of 2–2.5 ps\textsuperscript{30,40,41}.

Figure 2c shows the $E_x$ transients excited by low $E_{pump}$ (= 1.66$E_x$). The observed step-like signals with a small $A/B$ ratio (amplitude ratio of the early to late pump-probe delay $\Delta t$) are not attributed to the MEG transients, because the MEG typically requires $E_{pump}$ greater than a few $E_x$. When the QDs are excited by high $E_{pump}$ (= 3.3$E_x$), we observed fast (90 ps) and slow decay (~100 ns) components with a large $A/B$ ratio, as depicted in Fig. 2d. The experimentally determined $A/B$ ratio of the QD occupancy was modelled via Poisson statistics (Fig. 2e). Since multiple excitons generated by the MEG decay via Auger recombination, the amplitude at long $\Delta t$ (denoted by $B$ in Fig. 2c and d) provides a scaling factor for calculating the exciton multiplicity $\langle N_0 \rangle = A/B$, where $A$ is the amplitude of single-exciton population immediately after pump excitation (denoted by $A$ in Fig. 2c and d). By comparing the measured $A/B$ ratios in the limit of $\langle N_0 \rangle \rightarrow 0$, a strong indication of the MEG for the 3.3$E_x$ pump was identified\textsuperscript{43}. As reported previously\textsuperscript{16,36,38,40,44}, these observations confirm that the typical MEG dynamics are observable via probing the $E_x$ dynamics.

Transient Stark shift and biexciton linewidth broadening. The central issue to address in this paper is to investigate how the biexciton dynamics is influenced by the early formation of MEG. Figures 3a and b display the biexciton transients for the 1.66$E_x$ pump and 3.3$E_x$ pump as a function of $\Delta t$ with controlled excitations from $\langle N_0 \rangle = 0.22$ to $\langle N_0 \rangle = 2.2$. Immediately after pump excitation, the photo-induced absorption (PA) exhibits rapid bleaching at $E_{xx}$ within the first $\Delta t = 400$ fs with a much larger PA peak for the 3.3$E_x$ pump than the 1.66$E_x$ pump. While both signals decay non-exponentially, the signals pumped by 1.66$E_x$ decay to zero after a few ps, and the transients pumped by 3.3$E_x$ change their signs from positive to negative near $\Delta t = 2$ ps.

In a strong quantum-confinement regime, the pump-created local electric field induces a large transient shift of absorption, a phenomenon known as transient Stark shift\textsuperscript{42,46}. This effect is more considerable with increasing photo-generated carriers, which in turn produces a stronger local field and complicates the ultrafast PA spectra as schematically shown in Fig. 3c. Note that the increased carrier density is reflected both by the carrier-induced Stark shift and by the absorption linewidth $\Gamma$ that leads to a broader feature\textsuperscript{46–47}. As discussed later, this broadened $\Gamma$ directly determines the effect of MEG on the biexciton dynamics through extra-exciton generation.

It is expected that high $E_{pump}$ excitation, larger than $E_x$, enhances the $\Gamma$ broadening due to the extra-exciton generation. Immediately after the pump ($\Delta t = 400$ fs), we clearly observe that the biexciton $\Gamma$ is broader for the 3.3$E_x$ excitation case than for the 1.66$E_x$ one, as shown in Figs. 3d and e with two different excitations of $\langle N_0 \rangle$ for each $E_{pump}$ excitation. Thus, the observed transient PA dynamics can be understood by combined effects of both the carrier-induced transient...
Figure 2 | Single-exciton MEG dynamics. Single-exciton dynamics in a short pump-probe range between -1 and 7 ps for 1.66\(E_x\) (a) and 3.3\(E_x\) excitations (b). The differential transmission signals probed at \(E_x\) with the 1.66\(E_x\) pump (c) and the 3.3\(E_x\) pump (d) are displayed with \(\langle N_0 \rangle\) ranging from 0.11 to 2.2. Here, \(\langle N_0 \rangle\) is estimated via \(\langle N_0 \rangle = \frac{j_p s_a}{\sigma}\), where \(j_p\) is the pump fluence in unit of photons per cm\(^2\) and \(\sigma\) is the absorption cross-section in unit of cm\(^2\). (c) The experimentally measured A/B ratio is shown for the 1.66\(E_x\) pump (filled circle) and for the 3.3\(E_x\) pump (filled square). The calculated A/B ratio is obtained via Poisson distribution of the QD occupancies for the 1.66\(E_x\) pump (solid line) and for the 3.3\(E_x\) pump (dashed line).

Figure 3 | Ultrafast MEG-induced biexciton transients before the intra-band relaxation. Transient \(E_{xx}\) dynamics are shown as a function of \(\Delta t\) for the 1.66\(E_x\) pump (a) and for the 3.3\(E_x\) pump (b) with various \(\langle N_0 \rangle\). (c) Schematic illustration of the PA caused by the transient Stark shift of the single-exciton absorption (black line) and the corresponding photo-induced biexciton broadening (red line). The gray line indicates the single-exciton absorption without the pump. The differential PA spectra exhibit an energy-shifted broader feature (blue line) due to the MEG-induced exciton scattering compared to the case of no MEG (green line). The spectrally-resolved PA spectra with the probe range from 0.78 to 1.08 eV measured at \(\Delta t = 400\) fs are shown for the 1.66\(E_x\) pump (d) and for the 3.3\(E_x\) pump (e) with two different \(\langle N_0 \rangle\). Solid lines represent numerical fits using equation (1). The obtained biexciton \(\Gamma\) for the 1.66\(E_x\) pump with \(\langle N_0 \rangle = 1.1\) and 2.2 are 106 meV and 107 meV, respectively, and those for the 3.3\(E_x\) pump with \(\langle N_0 \rangle = 1.1\) and 1.2 are 118 meV and 123 meV, respectively. (f) Spectrally integrated areas of the broadened biexciton absorption. (g) The biexciton \(\Gamma\) broadening linearly increases with increasing the total number of excitons. The experimentally determined \(\Gamma\) (black filled squares) from the Figs. 3d and e are compared to the equation (2).
Stark shift and the MEG-induced biexciton $\Gamma$ broadening. We additionally notice that the spectrally-integrated areas of the broadened biexciton absorption remain the same regardless of $\langle N_x \rangle$ as shown Fig. 3f. This constraint indicates that the broadening is determined by the number of excitons, and it ensures that the biexciton PA peak is reduced by the exciton-exciton collision-induced broadening rather than the phase-space filling argument.$^{46}$

Quantitative analysis of the MEG-induced biexciton broadening and the early emergence of MEG. The entire pump-induced changes of the absorption spectra can be faithfully fit via the following third-order susceptibility function$^{1,3,5}$,

$$
\Delta \alpha \propto \Im(\chi^{(3)}(\omega)) = \Im \left( |E_z|^2 \left( - \frac{\mu_X^2}{\hbar \omega - E_X + i \Gamma} + \frac{\mu_{XX}^2}{\hbar \omega - E_{XX} + \Delta_{XX} + i \Gamma} \right) \right),
$$

where $E_z$ is the electric field of the pump, $\Delta_{XX}$ is the biexciton binding energy, and $\mu_X$ and $\mu_{XX}$ are the transition dipole moments from the ground state to $E_X$ and to $E_{XX}$, respectively. The first term represents the bleaching at $E_X$ and the second term represents the PA at ground-state $E_{XX}$. For the PA dynamics measured at $\Delta t = 400$ fs (Figs. 3d and e), because the intra-band relaxation time (2 ps) is longer than $\Delta t$ of 400 fs, the absorption change measured at $E_x$ was not induced by the single-exciton state filling. In addition, Auger recombination and impact ionization (Auger processes) can be neglected because the time-scale of Auger processes is much slower ($100 \sim 200$ ps) than the intra-band relaxation. On the other hand, the difference in $\Gamma$, obtained from a fit of equation (1) to the measured PA spectra, shows that the broadening is associated with the MEG-induced biexciton broadening.

For quantitative analysis, the biexciton $\Gamma$ is plotted as a function of the average number of total excitons per QD $\langle N_x \rangle$, and the results are displayed in Fig. 3g. Here, we note that the definition of $\langle N_x \rangle$ (obtained from the measured A/B ratios in Fig. 2c) differs from that of $\langle N_x \rangle$ in a sense that $\langle N_x \rangle$ includes both the average number of initially photo-generated excitons and the MEG-induced excitons per QD; $\langle N_{xx} \rangle$ is the average number of photo-generated exciton per QD$^{15}$. In other words, the biexciton broadening is directly related to the measured PA spectra, shows that the broadening is associated with the MEG-induced biexciton broadening.

Figure 4 | Biexciton broadening at longer delays than 400 fs. The single- and biexciton absorption change spectra at $\Delta t$ of 1 ps (a,b), 2 ps (c,d), 10 ps (e,f) and 500 ps (g,h) with two $E_{\text{pump}}$. (i) Schematic illustration of the PA bleaching dynamics at longer $\Delta t > 2$ ps for the $1.66E_x$ pump (blue line) and for the $3.3E_x$ pump (orange line). (j) Transient $\Gamma$ broadening is shown as function of $\Delta t$. 

to the total number of excitons \( \langle N_x \rangle \), not by the initial exciton occupancy \( \langle N_0 \rangle \). By plotting the \( \Gamma \) as a function of \( \langle N_x \rangle \), we obtain a linear relationship of

\[
\Gamma(N_x) = \Gamma(0) + \gamma N_x,
\]

where \( \gamma = 6.8 \text{ meV per exciton} \) is the \( \Gamma \) broadening parameter per exciton. Because \( \Gamma(0) \) represents the linewidth broadening in the absence of photo-generated excitons, the value should correspond to the \( E_x \) broadening in Fig. 1a. A simple Gaussian fit shows that the \( E_x \) broadening in Fig. 1a is 100 ± 5 meV, well corroborated with the fitted \( \Gamma(0) = 98 \text{ meV} \) of the biexciton broadening. The characteristic broadening of \( \Gamma \) with increasing \( \langle N_x \rangle \) entails the effect of MEG, i.e. as more excitons are injected, more broaden feature of biexciton \( \Gamma \) is expected.

Discussion

The early emergence of the MEG is substantiated by measuring the single- and biexciton spectra before/after the intra-band relaxation of 2 ps. It is expected that \( \Gamma \) should be large if \( \Delta t \) is shorter than the intra-band relaxation time, i.e. if the MEG-induced exciton-exciton scattering occurs earlier than the intra-band relaxation, \( \Gamma \) before the intra-band relaxation is larger than \( \Gamma \) after intra-band relaxation. Figures 4 (a) and (b) show the PA signals at \( \Delta t = 1 \text{ ps} \). As expected, the \( \Gamma \) broadening at \( \Delta t = 1 \text{ ps} \) is smaller than at \( \Delta t = 400 \text{ fs} \), but larger than at \( \Delta t = 2 \text{ ps} \). Figures 4c and d show the spectra at \( \Delta t = 2 \text{ ps} \) for the 1.66\( E_x \) pump and for the 3.3\( E_x \) pump, respectively. The \( \Gamma \) at 2 ps for 3.3\( E_x \) with \( \langle N_0 \rangle = 2.2 \) is 110 meV while the \( \Gamma \) at \( \Delta t = 400 \text{ fs} \) with same condition is 123 meV. Indeed, we clearly see that \( \Gamma \) at \( \Delta t = 2 \text{ ps} \) is smaller than that of before intra-band relaxation both for the \( \langle N_0 \rangle \) excitations (see Fig. 3e and Figs. 4b and d).

Long after the intra-band relaxation finishes, the carrier-induced Stark shift becomes weak, and the single-exciton state filling is dominant (Figs. 4e–h). As schematically shown in Fig. 4i, the weak Stark shift is rendered as the absence of PA signals at 0.85 eV, but the effect is not completely vanished; negative PA peaks appear at 0.97 eV instead of the single-exciton energy of 0.93 eV in Fig. 1a. Because the PA peak is proportional to the generated exciton numbers, the magnitude of bleaching is larger for the case of 3.3\( E_x \) pump than the 1.66\( E_x \) pump case. We note that the chosen two \( E_{\text{pump}} \) (1.66\( E_x \) and 3.3\( E_x \)) set the below and upper limit on the occurrence of MEG such that the observed two dynamics (before and after the intra-band relaxation) are distinguishable in comparing the MEG-induced biexciton lineshape and the single-exciton-dominated one. There is a possibility that significant re-shaping of single-exciton spectra can be observed at longer \( \Delta t \), which may occur when as many as 50% of QDs are occupied by multiple electron-hole pairs (i.e. \( \langle N_0 \rangle < 1 \)). This scenario can be excluded in our investigation because the PA peaks at \( \Delta t = 2 \text{ ps} \) show negligible energy shifts even when \( \langle N_0 \rangle > 1 \).

To investigate the effect of Auger and single-exciton recombinations on \( \Gamma \), we compare the PA spectra at \( \Delta t \) of 10 ps and 500 ps. We noted that the single-exciton decay dynamics consists of two relaxation components (see Figs. 2c and d); one is "fast" Auger recombination (known as biexcitonic relaxation component\(^{30}\)) and another is "slow" single-exciton recombination (referred to as excitonic background\(^{30}\)). Figures 4e and f display the PA spectra at \( \Delta t = 10 \text{ ps} \). Because the Auger recombination is not completed, \( \Gamma \) at \( \Delta t = 10 \text{ ps} \) is smaller than \( \Gamma \) at \( \Delta t = 2 \text{ ps} \). After the Auger recombination is finished, \( \langle N_0 \rangle \) at \( \Delta t = 500 \text{ ps} \) approaches one both for the 1.66\( E_x \) and 3.3\( E_x \) pump cases. Because nearly one exciton is left at \( \Delta t = 500 \text{ ps} \), \( \Gamma \) for both \( E_{\text{pump}} \) (Figs. 4g and h) is identical with \( \Gamma \) of 100 meV, representing negligible effect of single-exciton recombination on \( \Gamma \).

The measured data are summarized in Fig. 4j. Two main aspects are addressed. First, \( \Gamma \) at \( \Delta t = 400 \text{ fs} \) is the largest compared to the \( \Gamma \) at \( \Delta t > 400 \text{ fs} \), providing an evidence for the large biexciton \( \Gamma \) broadening in early \( \Delta t \). Second, by observing the fact that the decreasing
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