Supporting Information

Deciphering Ultrafast Carrier Dynamics of Eco-Friendly ZnSeTe-based Quantum Dots: toward High-Quality Blue-Green Emitters

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**Figure S1.** Absorption and normalized PL spectra of a series of ZnSeTe core/shell CQDs synthesized with various Te/Se feed molar ratios.

**Figure S2.** X-ray diffraction (XRD) patterns of ZnSeTe-based CQDs synthesized with different Te/Se molar ratios.

**Figure S3.** The transmission electron microscopy (TEM) images of (a) thin-shell, (b) thick-shell of 500nm-emission. The scale bars are 10 nm.
Figure S4. The time-resolved PL decaying profiles of a series of ZnSeTe core/shell CQDs synthesized with various Te/Se feed molar ratios.

Table S1. Biexponential fitting parameters of PL decay curves of all CQDs.

<table>
<thead>
<tr>
<th>Samples</th>
<th>A_1 (%)</th>
<th>(\tau_1) (ps)</th>
<th>A_2 (%)</th>
<th>(\tau_2) (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>470 nm</td>
<td>66.1%</td>
<td>3.2 ± 0.2</td>
<td>33.9%</td>
<td>36.7 ± 3.2</td>
</tr>
<tr>
<td>500 nm (Thick-shell)</td>
<td>65.8%</td>
<td>3.0 ± 0.2</td>
<td>34.2%</td>
<td>33.0 ± 2.7</td>
</tr>
<tr>
<td>525 nm</td>
<td>73.3%</td>
<td>2.1 ± 0.1</td>
<td>26.9%</td>
<td>30.9 ± 2.4</td>
</tr>
<tr>
<td>Thin-shell</td>
<td>78.3%</td>
<td>2.7 ± 0.2</td>
<td>21.7%</td>
<td>16.7 ± 1.9</td>
</tr>
</tbody>
</table>

The average lifetime \(\tau\) can be calculated as follow:

\[
<\tau> = \frac{A_1\tau_1 + A_2\tau_2}{A_1 + A_2}
\]  

(1)
Figure S5. Normalized transient photoinduced bleach (PB) signals $\Delta S(t_0)$ (purple ball) and $\Delta S(t_L)$ (blue ball) in the samples with (a) thin-shell, (b) thick-shelled 500 nm-emission, (c) 470 nm-emission and (d) 525 nm-emission as a function of excitation density. The red solid lines are fits according to the model described in Equation S3 and S4.
Figure S6. (a) Pseudocolor transient absorption (TA) spectroscopies of thick-shell, at $<N> \sim 0.6$. (b) The corresponding spectral distribution at different delay time.

Figure S7. Pseudocolor TA spectroscopies and the corresponding spectral distribution at different delay time of the (a, b) 470 nm and (c, d) 525 nm samples at a low pump fluence $<N> \sim 0.6$. 

S5
**Figure S8.** Normalized broadband TA spectra of 470 nm sample (a) and 525 nm sample (b) fitted by Gauss curve.

**Figure S9.** Auger recombination lifetime of thin-shell sample subtracted from low pump fluence, and the solid lines represent single-exponential decay functions.
Figure S10. Auger recombination kinetics for (a) 470nm and (b) 525nm samples subtracted from low pump fluence, and the solid lines represent single-exponential decay functions.

Figure S11. TEM images of (a) 470 nm and (b) 525 nm samples. The scale bars are 10 nm.

Figure S12. The model analysis of two-body interaction by using $N_0/N(t) - 1$ as a function of delay time fitted by Equation S6. This non-linear line makes it clear that the Auger process is not two-body.
**Figure S13.** The model analysis of three-body interaction in (a, b) 470nm and (c, d) 525nm CQDs that the \(N_0^2/N^2(t)\) as a function of delay time in different \(<N>\) and the \(\alpha N_0^2\) as a function of pump fluence. This nice linear behavior indicates the Auger process in other two CQDs also is three-body.

**Figure S14.** The comparison of the rising time in samples of different ZnSeTe core components fitted by global fitting, where \(<N>\) is about 3.3.
Supporting Note 1: Experimental section

Synthesis of ZnSeTe core/shell CQDs: To generate triple-shelled ZnSeTe core/shell CQDs, a sequence of ZnSe, ZnSeS, and ZnS as the respective inner, intermediate, and outer shells were consecutively formed onto the ZnSeTe core. In a synthesis of ZnSeTe core for a blue-emitting, 2 mmol of Zn acetate and 2 mL of oleic acid (OA) mixed with 15 mL of 1-octadecene (ODE) were degassed in a three-neck flask and heated to 120°C for 1 h and further heated to 200°C while the flask was being purged with N₂. Then, 0.5 mL of Se-DPP (2 mmol of Se dissolved in 1 mL of DPP) solution and 0.3 mL of Te-TOP (1.176 mmol of Te dissolved in 5 mL of TOP) solution were co-injected into the reactor. The shell growth was enabled by injection shell precursors step by step. An equivalent amount of Zn (OA)₂ solution along with 1 mL of S-TOP were introduced into the mixture described above. All the shelling formation reaction maintained at 270 °C for 60 min. The resulting multishelled ZnSeTe CQDs were repeatedly purified with mixed solvents of hexane and excess acetone with centrifugation. In the synthesis of 500 nm or 525 nm samples, 1.2 mL or 1.5 mL Te-TOP solution was co-injected, and all the other experimental procedures were kept the same as that for 470 nm described above.

Ultrafast absorption system: Transient absorption (TA) spectroscopy measurements were performed using a femtosecond amplified Ti: Sapphire laser source (Solstice Ace), whose pulse duration is ~ 100 fs and the central wavelength is 800 nm. The laser output is divided into two parts and the major part is used to generate pump beam through the double-frequency method. The white light can be focused onto sample by an off-axis parabolic mirror. The time delay between pump and probe beam is controlled by a motorized stage, whose resolution can reach 10 fs. All experimental data are corrected for the chirp induced by the nonlinear process in whit light generation and performed at room temperature.

Supporting Note 2: Carrier density calculation
In quantum dots, the initial average number of excitons per QD $<N>$ is usually employed to represent the carrier density through the following equation:

$$<N> = \sigma j = \sigma \frac{F}{h \nu},$$

where $\sigma$ is the absorption cross-section and $j$ is the photon fluence per pulse. $F$ and $h \nu$ represent the pump fluence and the photon energy, respectively.  

To determine the constant $\sigma$, it is assumed that the probability ($P_n$) of a quantum dot absorbing $n$ photons obeys the Poisson distribution:

$$P_n = \frac{<N>^n}{n!} e^{-<N>}$$

First of all, at the early time $t_0$ prior to the many-body effect of excitons, the intraband relaxation has just been completed and the density of excitons at the edge of the band reaches its maximum, so the normalized transient bleach signal follows:

$$\Delta S(t_0) = 2 - (2 + <N>) e^{-<N>}$$

At long delay time $t_L$ when there only single exciton states remain and per particle is independent of the initial excitons, the TA amplitude can be described as:

$$\Delta S(t_L) = 1 - f(0) = 1 - e^{-<N>}$$

We plotted the variation of the bleach amplitude measured at different $t_0$ and $t_L=1000$ ps versus a function of excitation densities in all QDs according to Equation (3) and (4). All the experimental data can be well fitted with the Poisson statistics model and the values of the only fitting parameter $\sigma$ were calculated apart as shown in Figure S5.

**Supporting Note 3: The model of two-body Auger**

At high excitation densities occurring multiple exciton interactions, one exciton recombines and transfers its energy to the other exciton as a whole, namely two-body Auger recombination or Exciton-Exciton Annihilation. The recovery kinetic of two-body can be modelled by the simple rate equation:

$$\frac{dN}{dt} = -\gamma N^2$$
with solution:

\[
\frac{N_0}{N(t)} - 1 = \gamma N_0 t
\]  

(6)

where \(N_0\) is the initial exciton density, positive correlation with pump fluence, and \(\gamma\) is the two-body Auger recombination rate constant. If Auger process is two-body, \(N_0/N(t)-1\) should be linear dependence with the delay time in different injected densities. However, our result is the opposite of the conjecture in Figure S12.

While if the process indeed is three-body, the relationship between the initial exciton density \(N_0\) and photocarrier density \(N(t)\) should satisfy the form:

\[
\frac{N_0}{N(t)} - 1 = \frac{\alpha N_0^2 t + 1}{1 - 1}
\]  

(7)

In other words, when we utilize the second order model to analyze a three-body process, \(N_0/N(t)-1\) should present exponential relationship dependence on the time, which exactly matches what we have observed and points out the three-body Auger recombination mechanisms in ZnSeTe core/shell QDs.
Reference:


