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SUPPLEMENTAL MATERIAL

Influence of surface charges on the emission polarization properties of single CdSe/CdS dot-in-rods

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Contents

1 Histograms of the PL intensities

The PL intensity traces of single DRs on glass and in ITO were measured under same excitation condition ($\langle N \rangle$ = 0.1). The histograms of the PL intensities (on level) for ~100 single DRs on glass and in ITO are presented in Figs. S1(a) and S1(b). The histograms are fitted by Gauss functions with mean values and standard deviations to be 394 ± 134 (on glass) and 253 ± 111 Counts/10ms (in ITO), respectively. Therefore, single QDs in ITO have a lower PL intensity than that on glass due to the extra non-radiative recombination processes (electron or energy transfer) introduced by ITO [1-3].

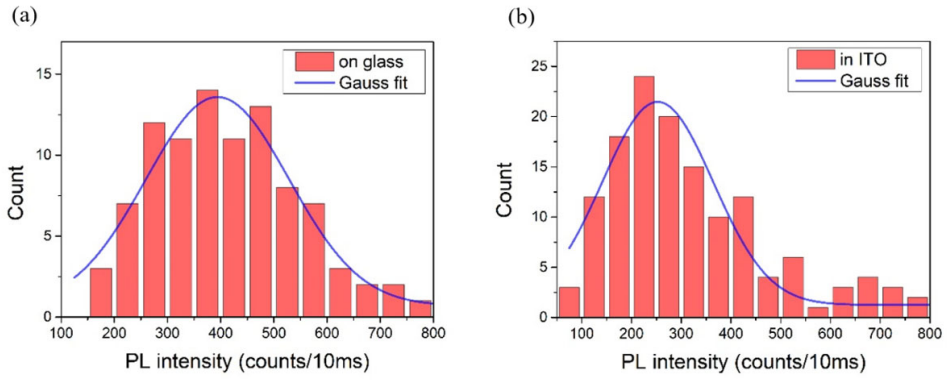

Fig. S1 The histograms of the PL intensities (on level) for ~100 single DRs on glass **(a)** and in ITO **(b)** under same excitation condition.

2 The fluorescence lifetime-intensity distribution (FLID)

The fluorescence lifetime-intensity distribution (FLID) can be obtained by averaging the arrival times of PL photons for each time bin of 100 ms for the PL trajectories. Figures S2(a) and S2(b) present the typical FLID maps for single DRs on glass and in ITO. The color changing from blue to red corresponds to increasing probability of occurrence of a given state in intensity-lifetime space. The FLID maps show a linear correlation between the PL lifetimes and intensities, indicating the PL blinking originating from the activation and deactivation of surface trap states of single DR [4-7]. Single DRs in ITO have a smaller probability of occurrence in the area with smaller PL lifetimes and lower intensities than that on glass, indicating that single DRs in ITO have less PL blinking.

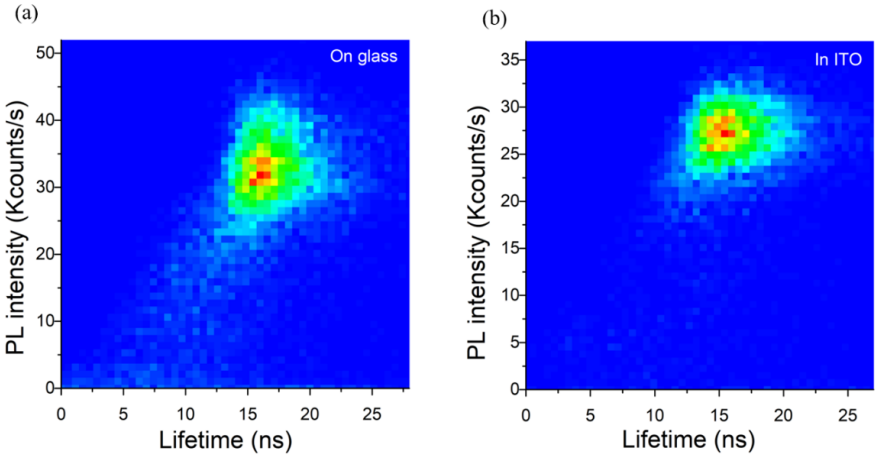

Fig. S2 The typical fluorescence lifetime-intensity distribution (FLID) for single DRs on glass **(a)** and in ITO **(b)**. The linear correlation between the PL lifetimes and intensities indicates that the PL blinking originates from the activation and deactivation of surface trap states.

3 Probability densities of on- and off-state

In order to compare the blinking dynamics of single DRs in ITO and on glass, we calculate their on- and off-state probability densities $P_{\text{on}}(t)$ and $P_{\text{off}}(t)$ with the equation, $P_i(t) = \frac{N_i(t)}{N_{i,total}} \times \frac{1}{\Delta t_{i,av}}$, ($i$ = on or off) [8], where $N_{i,total}$ is the total number of on- or off- state events, $N_i(t)$ is the number of on- or off-state events in duration time of t, and $\Delta t_{i,av}$ is the average of the time intervals. The average power law exponents ($\langle \alpha_i \rangle$, i = on or off) were obtained by analyzing $P_{\text{on}}(t)$ and $P_{\text{off}}(t)$ of ~100 single DRs on glass and in ITO, respectively. Single DRs on glass: $\langle \alpha_{\text{on}} \rangle$ = 1.15 ± 0.13 and $\langle \alpha_{\text{off}} \rangle$ = 1.45 ± 0.15; single DRs in ITO: $\langle \alpha_{\text{on}} \rangle$ = 1.01 ± 0.15 and $\langle \alpha_{\text{off}} \rangle$ = 1.49 ± 0.21. Compared with that on glass, single DRs in ITO have a smaller $\langle \alpha_{\text{on}} \rangle$ but a larger $\langle \alpha_{\text{off}} \rangle$, indicating increased probability densities of long on-state events and reduced probability densities of long off-state events. Therefore, the PL blinking of single DRs in ITO is suppressed due to the interfacial electron transfer from ITO to single DRs removing the surface trap states and the valence band holes of single DRs [1, 2].

4 Estimation of the parameters η and Δ

The electron-hole exchange interaction η can be written as [9]

$$\eta = \left(\frac{a_{ex}}{a} \hbar \omega_{ST} \chi(\beta) \right), \quad (1)$$

where $a_{ex} = 56\text{Å}$ is bulk exciton Bohr radius, a is the radius of CdSe core, $\hbar\omega_{ST}$ is the energy split of the triplet and singlet states of the ground state, and the dimensionless function $\chi(\beta)$ can be written in the electron and hole radial wave functions [10],

$$\chi(\beta) = \left(\frac{1}{6}\right) a^2 \int_0^a dr \sin^2\left(\frac{\pi r}{a}\right)\left[R_0^2(r) + 0.2R_2^2(r)\right] \tag{2}$$

with $|\psi_e\rangle \propto \sin(\pi r / a)/r$, is the radial wave function of the electron, and

$$\langle\psi_{h,3/2}|\psi_{h,3/2}\rangle \propto \int dr r^2\left[R_0^2(r) + 0.2R_2^2(r)\right], \tag{3}$$

where $R_0(r)$ and $R_2(r)$ are associated with the radial wave function of the holes, which are described by Eq. (2) in Ref. [9].

Recently study demonstrates the exchange interaction is proportional to the squared electron-hole wave function overlap [11], that means we can write the exchange interaction η as

$$\eta \propto \left|\langle\psi_e(r)|\psi_{h,3/2}(r)\rangle\right|^2. \tag{4}$$

For the net-splitting Δ, the positive charges and negative charges on the surface of the DRs could strongly affect the potential of the electron and hole in the DRs. Generally, the charges could affect the depth and width of the potential. The depth of the potential shifts the energy states causing the red or blue shift, and the energy states of the light- and heavy-holes could shift almost the same values. So, we just consider the width's effect.

In the effective mass approximation approach, the wave functions of the electron and hole in the DR can be simply written as [10]

$$|\psi_{e,h}(r)\rangle \propto \sqrt{1/a}\sin(\pi x / a) \tag{5}$$

and the energy states $E_n \propto 1/a^2$, with a the effective potential width.

The external charges change the width of the potential, then

$$\Delta E \propto -2E\frac{\Delta a}{a}. \tag{6}$$

The influence on the wave function can be simply expressed as

$$\Delta|\psi_{e,h}\rangle \propto -\frac{\Delta a}{a}|\psi_{e,h}\rangle. \tag{7}$$

Finally, one could obtain

$$\frac{\left|\langle\psi_e(r)|\psi_h(r)\rangle\right|^2_{charge}}{\left|\langle\psi_e(r)|\psi_h(r)\rangle\right|^2_{no}} = 1 - 4\frac{\Delta a}{a} \tag{8}$$

and

$$\frac{E_{charge}}{E_{no}} = 1 - 2\frac{\Delta a}{a}. \tag{9}$$

Here, we consider the negative charges decreasing the potential width of the hole. Finally, one could obtain the squared electron-hole wave function overlap decreasing from 1 to 0.5, the exchange interaction η also decreasing from η to 0.5η, and the net-splitting Δ increasing from Δ to 1.25Δ.

5 Calculated band-edge exciton fine structure

Another band-edge exciton fine structures of single DRs were deduced by taking into account the sample parameters, and the emission polarization. Figure S3 presents the band-edge exciton fine structure levels for two typical polarization degrees of 0.25 and 0.35. The calculated exciton fine structures were derived without considering the influence of surface electrons. Note that the swapping of the energy levels happens when polarization degrees change from 0.25 to 0.35. For example, the $|0^{U}\rangle$ and $|\pm1^{U}\rangle$ levels, and the $|\pm2\rangle$ and $|0^{L}\rangle$ levels.

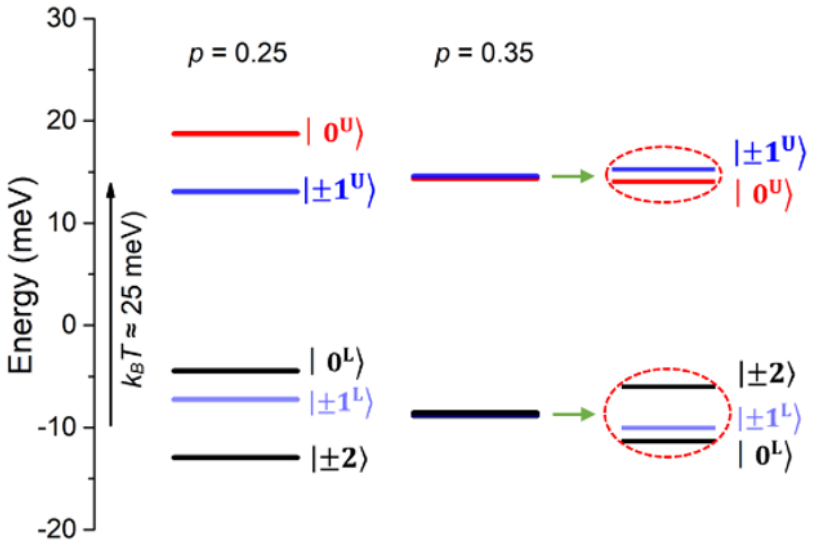

Fig. S3 The band-edge exciton fine structures calculated for p = 0.25 and 0.35, which were deduced by considering the sample parameters and the emission polarization (without considering the influence of surface electrons). The swapping of the energy levels happens when polarization degrees change from 0.25 to 0.35.

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