Supplementary Information for

Observation of High-Density Multi-Excitons in Medium-Size CdSe/CdZnS/ZnS Colloidal Quantum Dots through Transient Spectroscopy and Their Optical Gain Property

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Supplementary Note.S1. Biexciton Auger recombination lifetime and quantum yield

The biexciton AR rates and QY was calculated according to the method published by Klimov[1] et al.:

$\tau_{XX,A}^{-1} = \tau_{XX}^{-1} - \tau_{XX,r}^{-1}$

Where the radiative lifetime is $\tau_{XX,r} = \frac{\tau_{X,r}}{4}$ and $\tau_{X,r} = \frac{\tau_X}{QY_X}$.

Biexciton QY: $QY_{XX} = 4\tau_{XX}/\tau_X$

Supplementary Note.S2. Biexciton spectrum calculation

When the pump power is low enough, the triexciton in the QD ensemble can be neglect, then only biexciton and single-exciton recombination is considered. Let f_N(t) be the exciton population inside a QDs at delay t, and the recombination of multi-exciton is step-transition[2], the rate function is:

$$\frac{df_N}{dt} = \gamma_{N+1} f_{N+1} - \gamma_N f_N$$

Considering the initial condition:

$f_N(t = 0) = P(N)$

$f_{N+1}(t = \infty) = 0$

By solving the rate equation, when <N> is small enough, the decay of a single exciton satisfies:

$$f_1 = \left(P(1) - \frac{\gamma_2}{\gamma_2 - \gamma_1} P(2)\right) e^{-\gamma_1 t} + \frac{\gamma_2}{\gamma_2 - \gamma_1} P(2) e^{-\gamma_2 t}$$

where γ_1, γ_2 are the decay rate of single-exciton and biexciton, respectively, which can be obtained from the decay curves.

Therefore, the ratio of single-exciton PL intensity at t_0 and t_1($t_1 >> \tau_{xx}$) can be calculated. The biexciton spectra can be obtained by subtracting the single-exciton PL spectra at t_0.

Supplementary Note.S3 L-L curve fit with rate function

The microcavity L-L curve was fitted by the traditional coupled rate function[3]:

$$\frac{dN}{dt} = \frac{\eta_{in} P_{in}}{\hbar\omega_{in} V} - \frac{N}{\tau_r} - G(N)P$$

$$\frac{dP}{dt} = G(N)P + \beta\frac{N}{\tau_r} - \frac{P}{\tau_c}$$

where, N is carrier density, P is photon density, η_{in} is the efficiency of pump laser, $\hbar\omega_{in}$

is the energy of pump photon, V is the volume of the gain medium, τ_r is the spontaneous emission lifetime, $G(N) = g(N - N_{tr})$ is the linear gain function, $g = \frac{\beta V}{\tau_r}$ and N_{tr} is the carrier density when transparency.

Table **S1** Comparison of Trion and Biexciton lifetime.

QDs Type	Size(nm)	τ_{x+}(ns)	τ_{x-}(ns)	τ_{xx}(ps)	Ref.
CdSe/ZnSe	6.14	0.26	-	29.6	[1]
CdSe/CdS	5.6	0.218	1.67	83	[2]
CdSeS/ZnS	6	-	0.75	140	[3]
CdSe/CdS/CdZnS	5.4	-	-	140	[4]
CdSe/CdS	5.7	0.32	0.95	150	[5]
InP/ZnSe/ZnS	7.4	-	2.2	20	[6]
$CsPbI_3$	8	-	0.235	93	[7]
CdSe/CdS	6	-	-	120	[8]
CdSe/CdZnS/ZnS	6.4	0.74	6.1	150.8	This article

References

1. G. A. Beane, K. Gong and D. F. Kelley, *Acs Nano*, 2016, **10**, 3755-3765.
2. K. Gong and D. F. Kelley, *J. Phys. Chem. C*, 2015, **119**, 9637-9645.
3. W. Qin, R. A. Shah and P. Guyot-Sionnest, *Acs Nano*, 2012, **6**, 912-918.
4. P. P. Jha and P. Guyot-Sionnest, *Acs Nano*, 2009, **3**, 1011-1015.
5. V. Pavlenko, I. Dobynde, I. Beloussov and D. Ozol, *Physica E*, 2020, **115**.
6. T. Kim, Y. H. Won, E. Jang and D. Kim, *Nano Lett*, 2021, **21**, 2111-2116.
7. N. S. Makarov, S. J. Guo, O. Isaienko, W. Y. Liu, I. Robel and V. I. Klimov, *Nano Lett*, 2016, **16**, 2349-2362.
8. C. Liao, R. L. Xu, Y. Q. Xu, C. F. Zhang, M. Xiao, L. Zhang, C. G. Lu, Y. P. Cui and J. Y. Zhang, Journal of Physical Chemistry Letters, 2016, 7, 4968-4976.

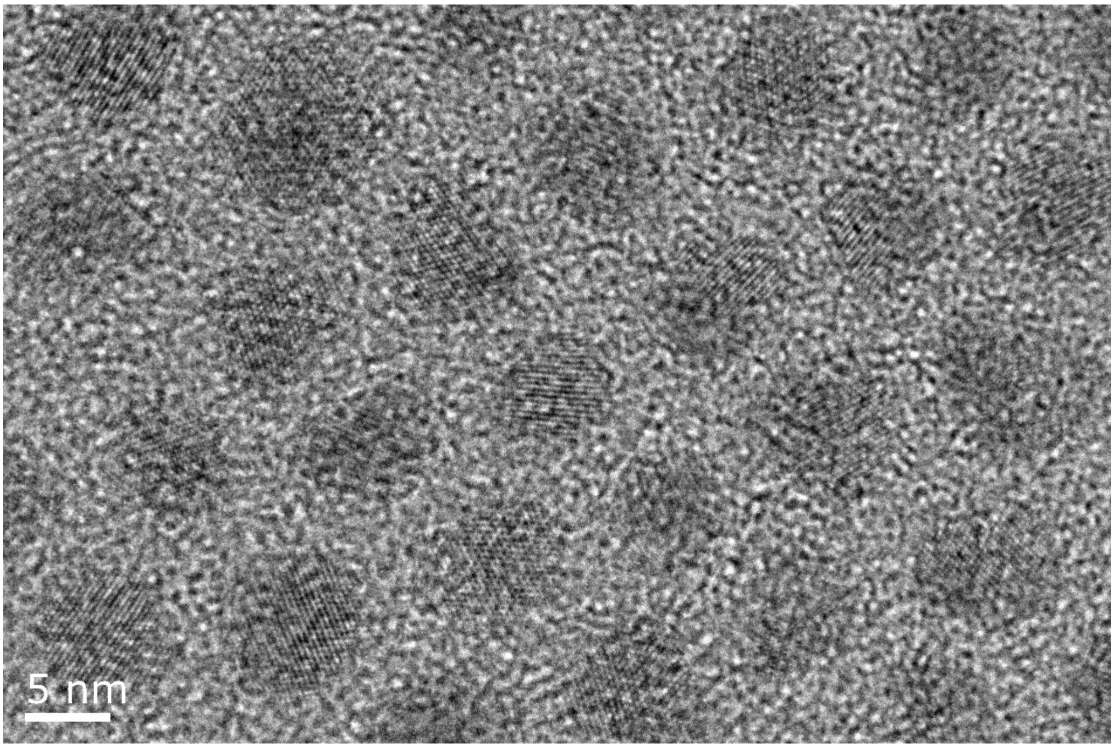

Fig.S1 HRTEM images of CdSe/CdZnS/ZnS QDs ensembles. Scale bar: 5 nm.

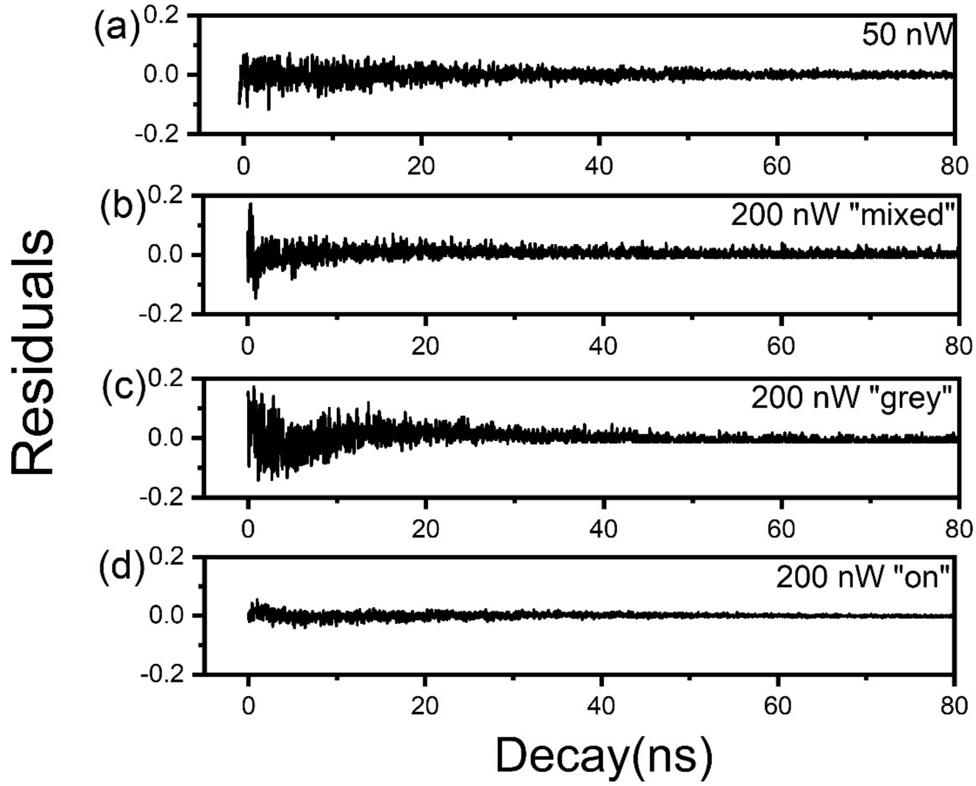

Fig. S2 (a)-(d) Residuals for the fitting results of the single-dot fluorescence decay.

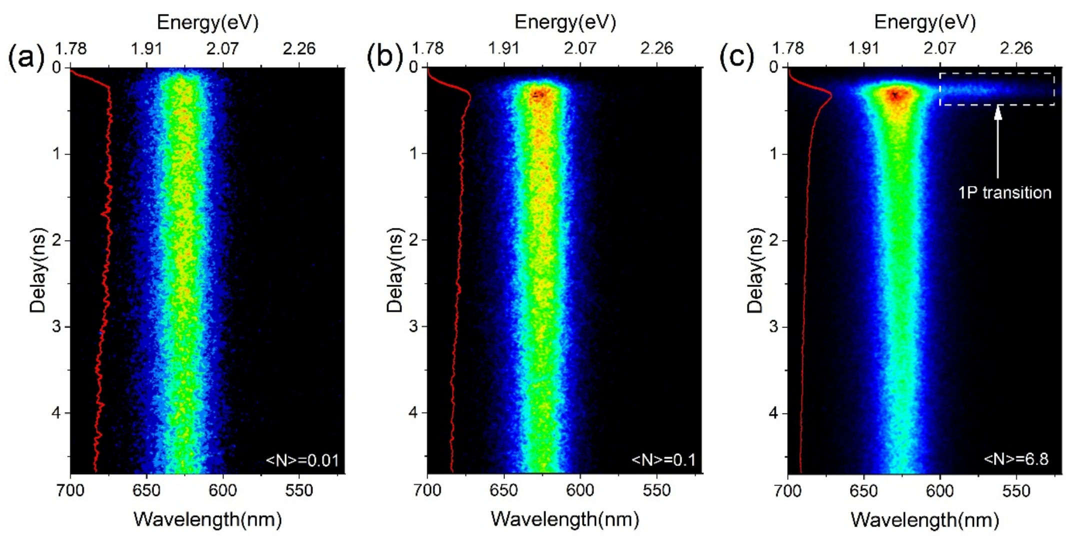

Fig.S3 (a)-(c) The streak camera image as a function of <N>. The red line corresponds to the interband decay curves.

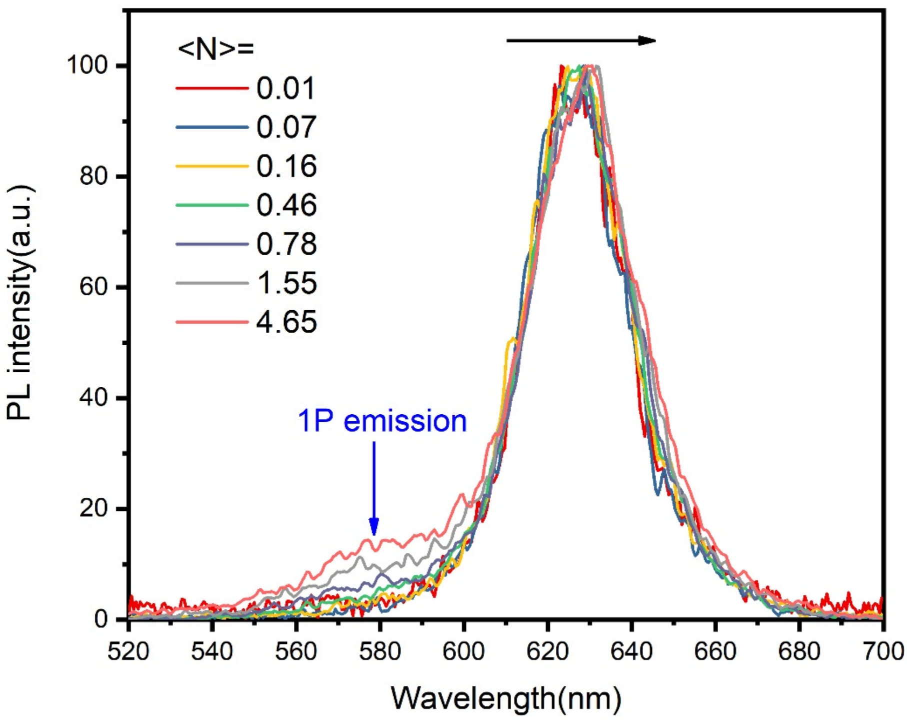

Fig.S4 The PL spectra vary with <N> obtained from the streak camera image. Integrate window:0-100 ps.

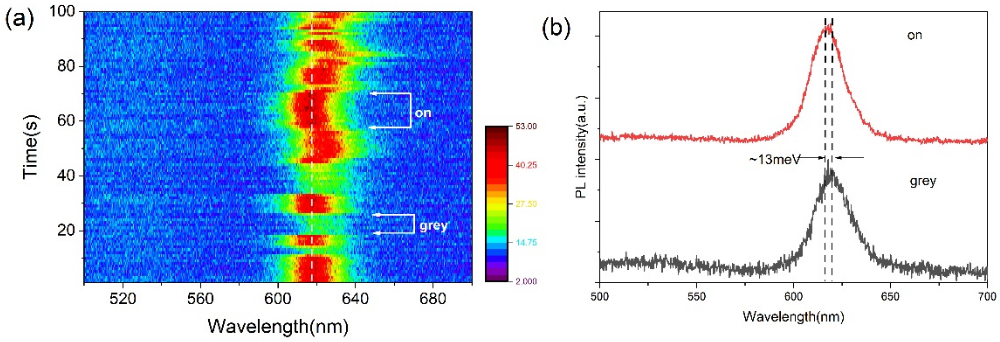

Fig.S5 (a) Single-dot spectra trace under relatively high pump intensity. The intensity distribution shows long-lived “on” states and short-lived “grey” states. Binning time:1 S. (b) The corresponding “on” and “grey” states spectra. The binning energy of 13 meV was obtained for the negative trion.

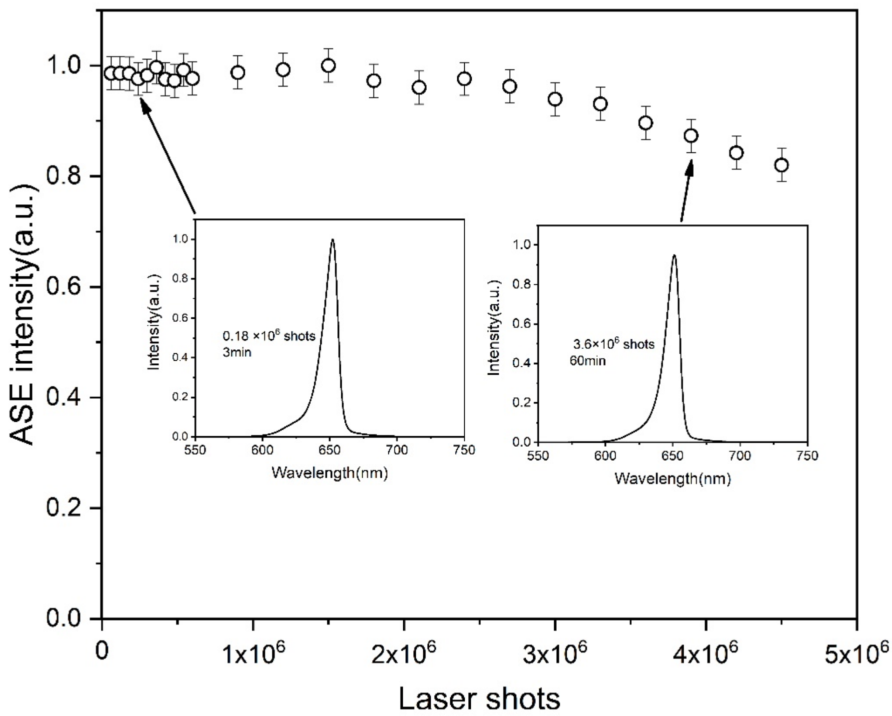

Fig.S6 Laser-shot-dependent ASE intensity under pump laser shots up to 5 × 10^{6} indicating the exceptional stability of the QDs. The inset shows the normalized ASE spectra for 0.18× 10^{6} and 3.6× 10^{6} shots. Pump intensity: 300 μJ $cm^{-2.}$

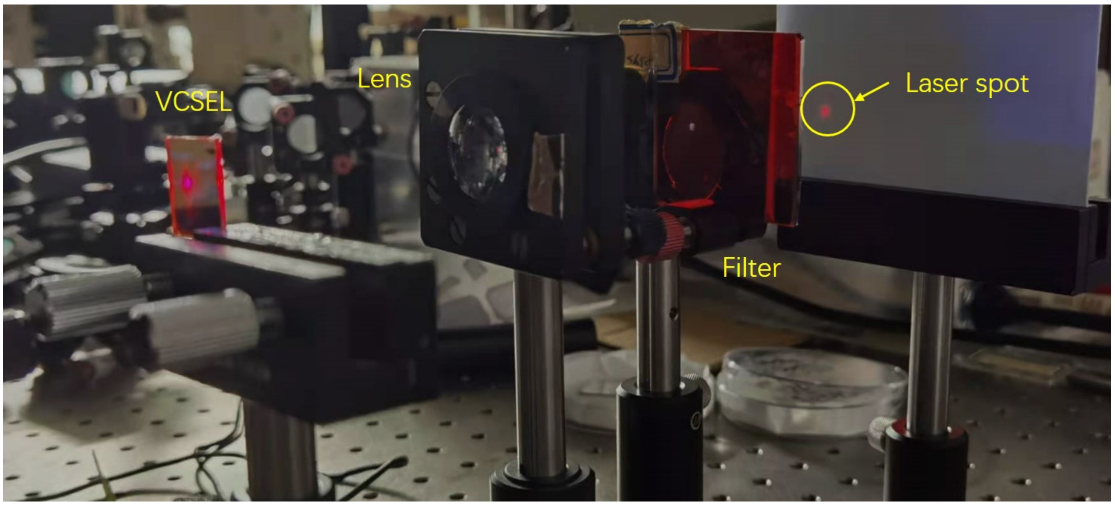

Fig.S7 Well-defined laser spot of VCSEL when exceeds threshold after the lens and long-pass filter.

References

1. W. K. Bae, L. A. Padilha, Y. S. Park, H. McDaniel, I. Robel, J. M. Pietryga and V. I. Klimov, *Acs Nano*, 2013, **7**, 3411-3419.
2. V. I. Klimov, A. A. Mikhailovsky, D. W. McBranch, C. A. Leatherdale and M. G. Bawendi, *Science*, 2000, **287**, 1011-1013.
3. G. Bjork and Y. Yamamoto, *Ieee J Quantum Elect*, 1991, **27**, 2386-2396.