

Defect-Mediated CdS Nanobelt Photoluminescence Up-Conversion

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AFM data of individual CdS NBs

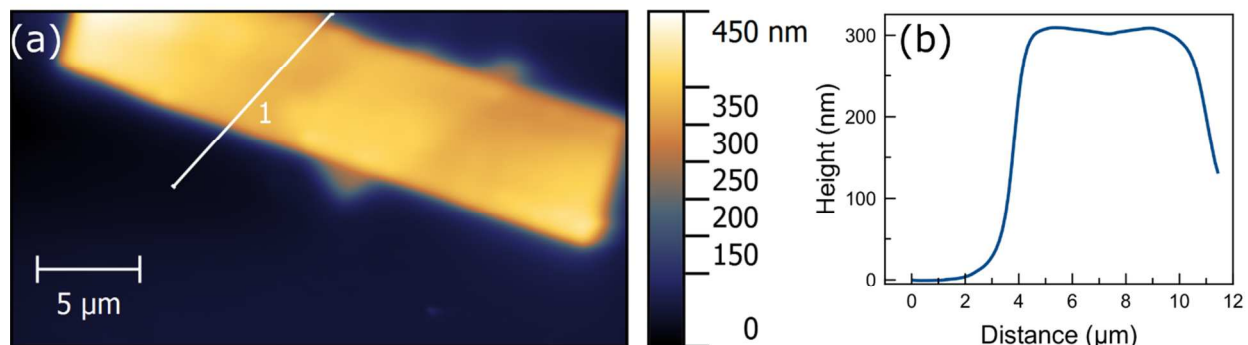


Figure S1. (a) AFM image of a CdS NB along with (b) a corresponding height profile, showing a thickness of 305 nm.

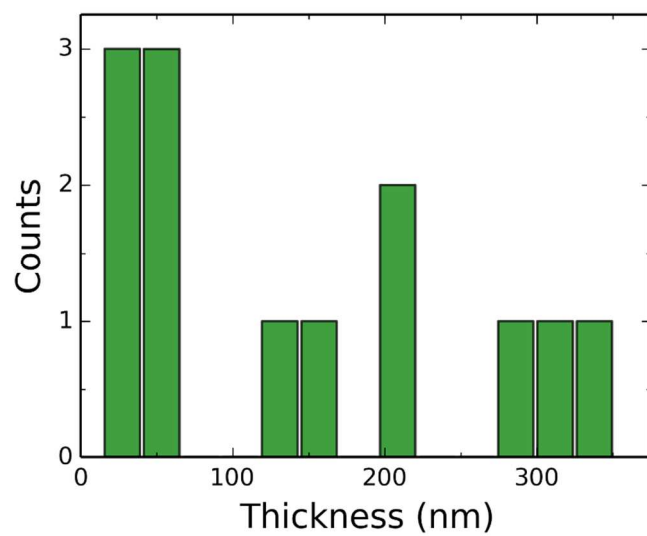


Figure S2. AFM thickness histogram of CdS NBs. An average thickness is 142 ± 110 nm. Sample size=13 NBs.

Additional TEM images of CdS NBs

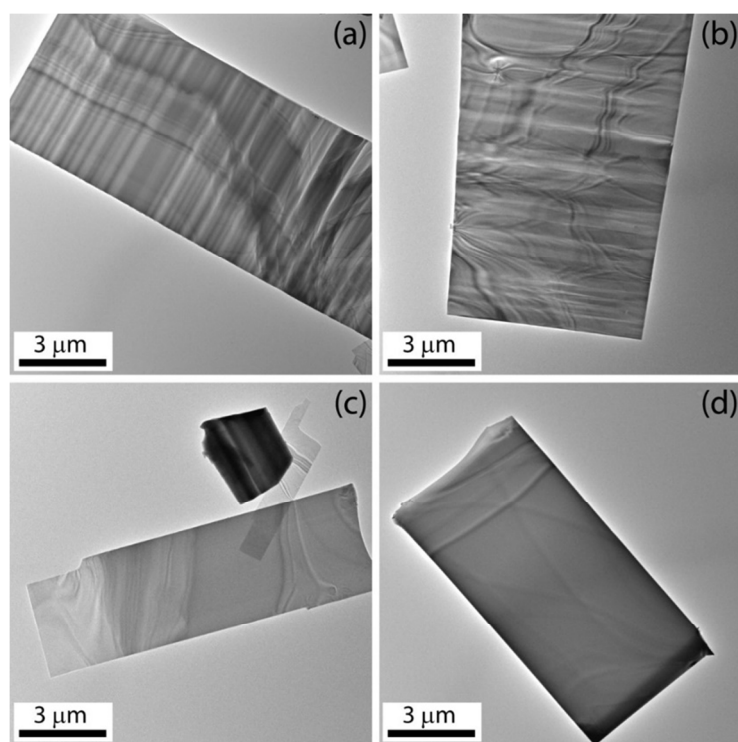


Figure S3. Low-magnification TEM images of individual CdS NBs.

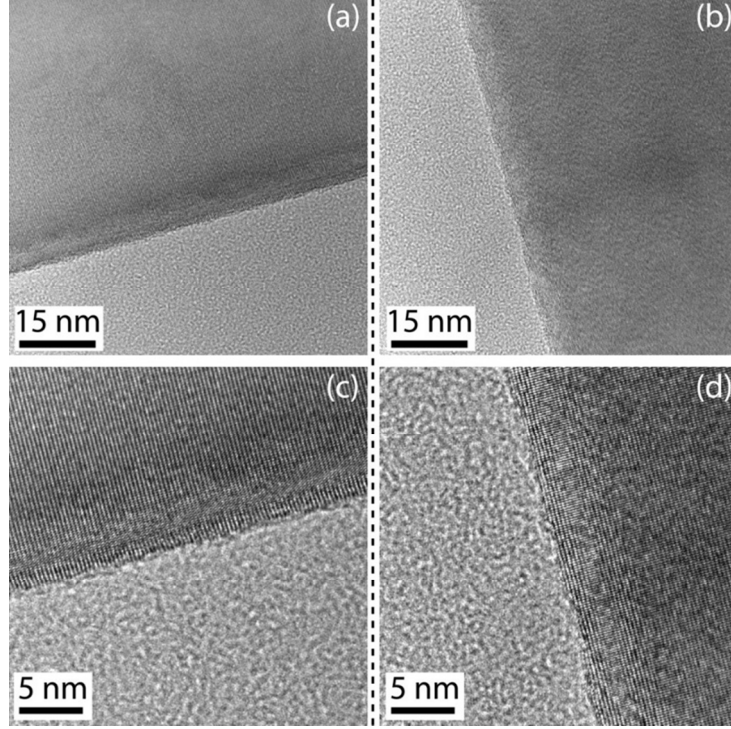


Figure S4. High-magnification TEM images of CdS NBs.

Comparison of the up-conversion probability involving multiple phonons to $G(\Delta E, T)$

To compare the up-conversion probability involving multiple phonons ($P_{multiple}$) to the overall Bose Einstein distribution $G(\Delta E, T)$ used in the main text, we first write the probability, $P_{single}(\hbar\omega_{LO}, T)$, for a carrier in a DAP state to interact with a single phonon of energy $\hbar\omega_{LO} = 37$ meV. This is $P_{single}(\hbar\omega_{LO}, T) \propto G(\hbar\omega_{LO}, T) \propto \left[e^{\frac{\hbar\omega_{LO}}{kT}} - 1 \right]^{-1}$. The associated joint probability, $P_{multiple}$, of a DAP state interacting with n ($n > 1$) phonons is then

$$P_{multiple}(\hbar\omega_{LO}, T) \propto \left[e^{\frac{\hbar\omega_{LO}}{kT}} - 1 \right]^{-n}.$$

We now compare $P_{multiple}$ to $G(\Delta E, T)$ by plotting both between 380 K and 80 K (**Figure S5**). The graph shows that both functions vary at most by a factor of 3.92. Discreteness in $P_{multiple}$ stems from the fact that n takes integer values. Consequently, $P_{multiple} \approx G(\Delta E, T)$.

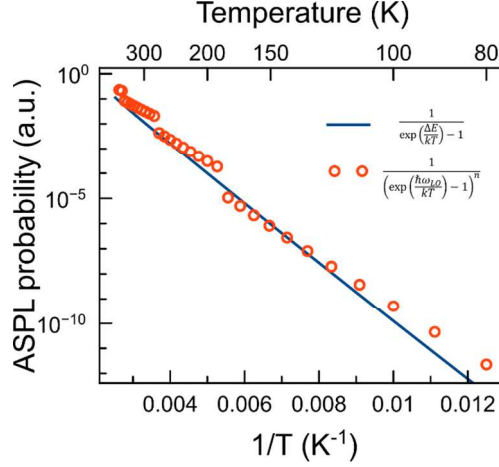


Figure S5. Comparison of $G(\Delta E, T)$ (solid blue line) to the up-conversion probability involving multiple phonons (open red circles).

I_{ASPL} temperature- and energy-dependencies and Bose-Einstein statistics

To quantitatively compare the temperature-dependent I_{ASPL} with predictions of Bose-Einstein statistics, the CdS NB band gap variation with temperature was accounted for using the Varshni equation

$$E_g(T) = E_0 - \frac{\alpha T^2}{T + \beta}. \quad (S1)$$

In **Equation S1**, $E_g(T)$ is the temperature-dependent band gap of the CdS NB, E_0 is its band gap at 0 K, and α (β) are Varshni coefficients obtained from Reference 1 [$E_0 = 2.5511$ eV, $\alpha = 0.00043$ eV/K, and $\beta = 78.2$ K].

Consequently, in **Figure 3a** of the main text we fit the experimental data with $G(\Delta E, T) = A \left[e^{\frac{\Delta E}{kT}} - 1 \right]^{-1}$ where $\Delta E = E_g(T) - E_{exc}$ with $E_{exc} = 2.33$ eV and where the temperature-dependent band gap of CdS, $E_g(T)$, has been explicitly accounted for using the Varshni Equation. The only fitting parameter is A .

The solid green line in **Figure 3c** is likewise a fit to the experimental data using the same function. In this case, the temperature is fixed to $T=298$ K with A the only fitting parameter.

Low temperature ASPL power dependence

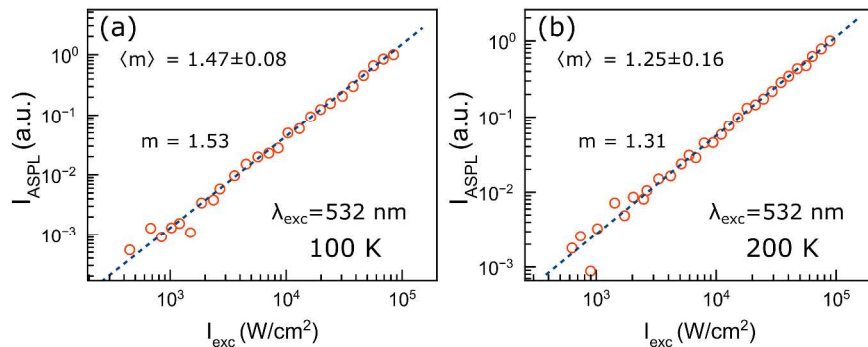


Figure S6. Single NB I_{exc} dependence of I_{ASPL} (open red circles) and corresponding fit (dashed blue line) at (a) 100 K and (b) 200 K. In both cases, $\lambda_{exc}=532$ nm. An average $T=100$ K m -value is $\langle m \rangle = 1.47 \pm 0.08$ (sample size 11 NBs). An average $T=200$ K m -value is $\langle m \rangle = 1.25 \pm 0.16$ (sample size 21 NBs).

Additional ASPL detuning spectra of CdS NBs

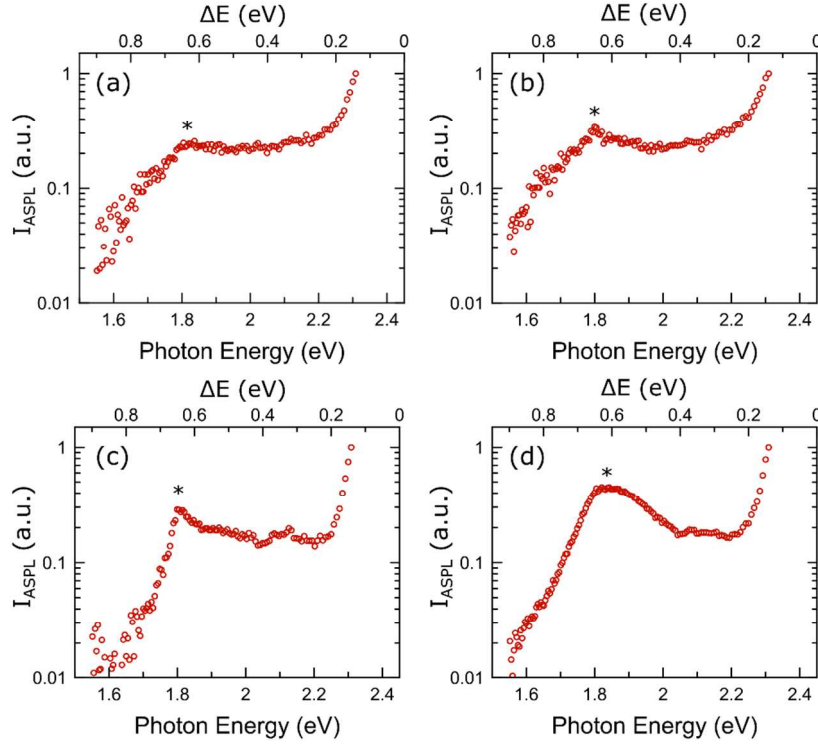


Figure S7. (a-d) ASPL detuning spectra of different individual CdS NBs. All measurements were performed at $T = 298$ K. Asterisks denote energies where the ASPL detuning spectrum peaks deep within the gap.

Additional large detuning I_{ASPL} versus I_{exc} traces and relationship to NB EQEs

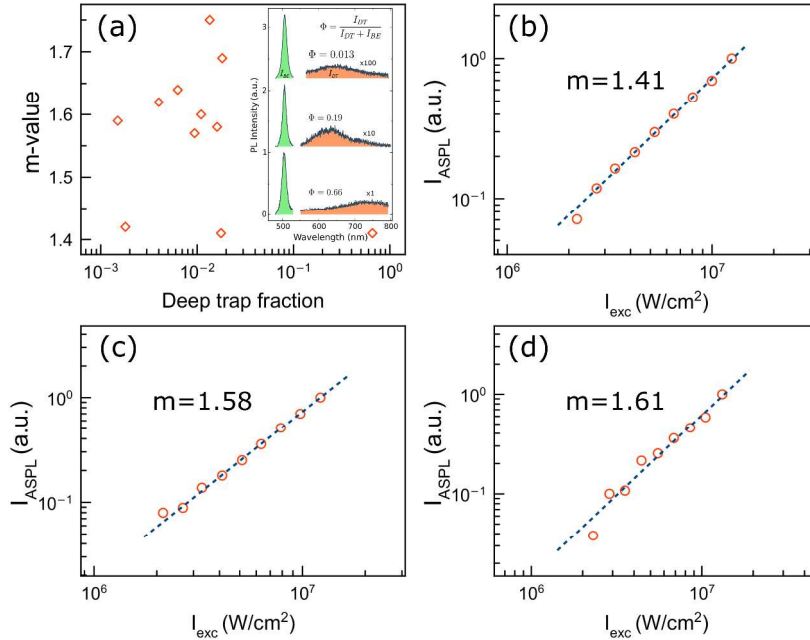


Figure S8. (a) Correlation between large detuning ($\Delta E = 632$ meV, $\lambda_{exc} = 680$ nm, $T = 298$ K) m -value and fraction (Φ) of deep trap PL for different NBs. The inset shows full PL spectra of 3 different NBs showing different deep trap fractions. (b-d) I_{exc} dependence of I_{ASPL} (open red circles) and corresponding fit (dashed blue line) under large detuning conditions ($\Delta E = 632$ meV, $\lambda_{exc} = 680$ nm, $T = 298$ K) for different CdS NBs. Extracted m -values shown.

In addition, the eleven NBs studied possess different EQEs as evidenced by the different fractions of deep trap emission in their PL spectra (**Figure S8a**). To better correlate experimental m -values with EQE we define a deep trap fraction Φ as $\Phi = \frac{I_{DT}}{I_{DT}+I_{BE}}$, where I_{DT} is the deep trap PL intensity integrated over the spectral range 550 – 800 nm and I_{BE} is the band edge PL intensity integrated over the spectral range 480 – 540 nm. Extracted m -values are then plotted versus Φ to establish whether there are any correlations, which indicate a possible change in ASPL mechanism. **Figure S8a** reveals that there is no apparent correlation between m -value and Φ . We conclude that there is no variation of the large detuning ASPL mechanism for samples possessing different EQEs.

Temperature-dependent single NB absorptance measurements

Temperature-dependent absorptance spectra were taken in the same manner as described in the Methods section of the main text. Spectra were acquired at different temperatures from 80 K to 400 K and are shown in **Figure S9a** for an individual CdS NB. At each temperature, the absorptance at 532 nm (A_{532}) has been extracted. **Figure S9b** shows the corresponding temperature dependence of A_{532} . The plot shows that A_{532} is near temperature independent above 150 K and decreases at temperatures below this.

Absorptance changes below 150 K likely occur due to the temperature-dependent density of available states. Namely, in the main text, we have attributed DAP states as responsible for one photon/phonon up-conversion. Consequently, increasing the temperature leads to an increased number of singly ionized DAP states available for light absorption. At lower temperatures, less thermal energy is available to ionize these DAP states. Consequently, this reduces their absorption at low temperatures.

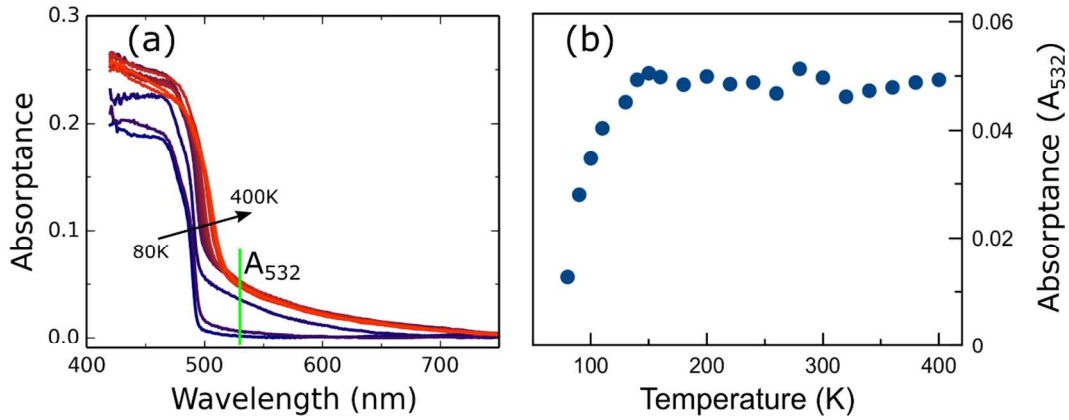


Figure S9. Temperature-dependent absorptance of an individual CdS NB at 532 nm. (a) Absorptance spectra acquired between 80 – 400 K. (b) Extracted A_{532} values at different temperatures.

Temperature-dependent band edge emission and ASPL for another CdS NB

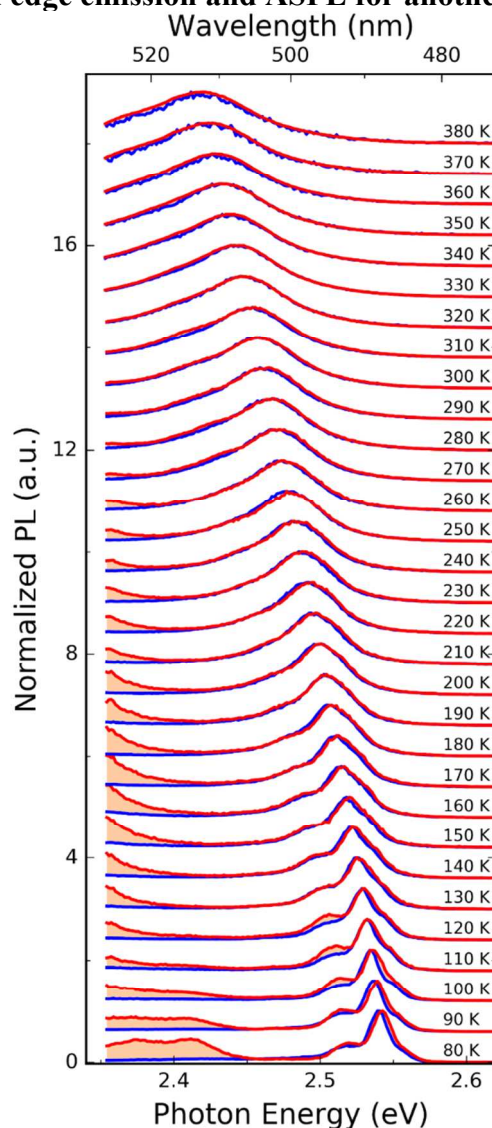


Figure S10. Comparison of band edge emission (blue lines) and ASPL spectra (red lines) at different temperatures from 80 K to 380 K.

Kinetic modeling of experimental I_{em}/I_{exc} traces to obtain I_{exc} -dependent EQE values

Experimental I_{em}/I_{exc} data are fit to a model-generated expression for the concentration-dependent EQE of a CdS NB, $EQE(n_o)$. Under pulsed excitation conditions, we numerically solve **Equations 1-3** for $t > 0$ (i.e. $G=0$) to obtain relevant, time-dependent, electron/hole concentrations (n and p). Initial electron and hole concentrations (n_o and p_o) are estimated from the incident excitation intensity and NB absorption coefficient ($\lambda_{exc}=470$ nm, $\alpha_{470\text{ nm}} = 8 \times 10^5 \text{ cm}^{-1}$) through

$$n_o = p_o = \frac{I_{exc} \tau_{pulse} \alpha}{h\nu} \quad (\text{S2})$$

where $\tau_{pulse} = 12$ ps is the laser pulse width. We additionally assume that electron traps are initially unoccupied, i.e. $n_t=0$. Rate constants and N_t in **Equations 1-3** are initially set to:

- $\eta_e k_b = 10^{-11} \text{ cm}^3/\text{s}$ [reference 2, also the product of η_e and k_b is used as an effective rate constant]
- $k_t = 2.0 \times 10^{-10} \text{ cm}^3/\text{s}$ [references 3,4,5,6]
- $k_h = 8.0 \times 10^{-12} \text{ cm}^3/\text{s}$ [references 3,4,7]
- $k_{Auger} = 10^{-30} \text{ cm}^6/\text{s}$ [reference 8]
- $N_t = 10^{16} \text{ cm}^{-3}$ [reference 9]

and are floating parameters in subsequent fits to the experimental data. The corresponding time-dependent emission intensity then follows from

$$I_{em}(t) = \eta_e k_b \times n(t) \times p(t)$$

whereupon the associated concentration-dependent EQE is the fraction of initially created carriers undergoing radiative recombination

$$EQE(n_0) = \frac{\int_0^\infty I_{em}(t) dt}{n_0}. \quad (\text{S3})$$

Experimentally-obtained I_{em}/I_{exc} traces are fit using **Equation S3** to obtain absolute EQE values at each excitation intensity.

For the NB shown in **Figure 6** of the main text, the following best fit rate constants and other parameters are obtained

- $\eta_e k_b = 9.55 \cdot 10^{-12} \text{ cm}^3/\text{s}$
- $k_t = 6.31 \cdot 10^{-11} \text{ cm}^3/\text{s}$
- $k_h = 1.0 \cdot 10^{-11} \text{ cm}^3/\text{s}$
- $k_{Auger} = 1.0 \cdot 10^{-30} \text{ cm}^6/\text{s}$
- $N_t = 3.24 \cdot 10^{17} \text{ cm}^{-3}$

and agree well with the initial literature estimates employed. **Figure S11** reproduces the model plot shown in **Figure 6** of the main text.

A. Analytical low power limit

For the case of low power excitation where electron trapping is much faster than radiative recombination we can analytically model the I_{em} versus I_{exc} growth behavior. To do this we assume that traps are far from saturation so $n_t \approx 0$. Under this condition:

$$\begin{aligned} \frac{dn}{dt} &\approx -k_t N_t n \\ \frac{dp}{dt} &\approx 0. \end{aligned}$$

Solving for $n(t)$ above yields $n(t) = n_0 \cdot \exp(-k_h N_t t)$ and $p=p_0=n_0$. The time-dependent emission intensity is therefore

$$I_{em}(t) \propto \eta_e k_b n(t)p(t) = \eta_e k_b n_0^2 \exp(-k_h N_t t)$$

whereupon the time-integrated emission intensity observed in the experiment becomes

$$\langle I_{em} \rangle \propto F \int_0^\infty I_{em}(t) dt = F \eta_e k_b n_0^2 \int_0^\infty \exp(-k_h N_t t) dt = \frac{F \eta_e k_b n_0^2}{k_h N_t}. \quad (S4)$$

In **Equation S4**, F is the laser repetition rate. Since $n_0 \propto I_{exc}$, $\langle I_{em} \rangle \propto I_{exc}^2$ (i.e. $b=2.0$) at low excitation intensities. For more details see Reference 6.

B. Analytical higher power limit

At higher excitation intensities, where electron traps are effectively saturated due to their finite number, radiative recombination ($\eta_e k_b np$) dominates both trapping $k_t(N_t - n_t)n$ as well as Auger recombination ($k_{Auger} \cdot n^2 \cdot p$). We can therefore rewrite **Equations 1-3** as:

$$\frac{dn}{dt} = -\eta_e k_b np$$

$$\frac{dp}{dt} = -\eta_e k_b np.$$

Under these conditions, $n(t)=p(t)$ so that

$$\frac{dn}{dt} = -\eta_e k_b n^2.$$

Integrating the above equation we obtain $n(t) = \frac{n_0}{1+n_0 \eta_e k_b t}$. Consequently,

$$I_{em}(t) \propto \eta_e k_b \times n(t) \times p(t) = \eta_e k_b \times \frac{n_0^2}{(1+n_0 \eta_e k_b t)^2}.$$

The corresponding time integrated emission is

$$\langle I_{em} \rangle \propto F \int_0^\infty I_{em}(t) dt = F \eta_e k_b n_0^2 \int_0^\infty \frac{1}{(1+n_0 \eta_e k_b t)^2} dt = \frac{F \eta_e k_b n_0^2}{n_0 \eta_e k_b} \int_0^\infty \frac{1}{(1+x)^2} dx = F n_0. \quad (S5)$$

Since $n_0 \propto I_{exc}$, $\langle I_{em} \rangle \propto I_{exc}$ and the expected growth exponent becomes $b=1.0$.

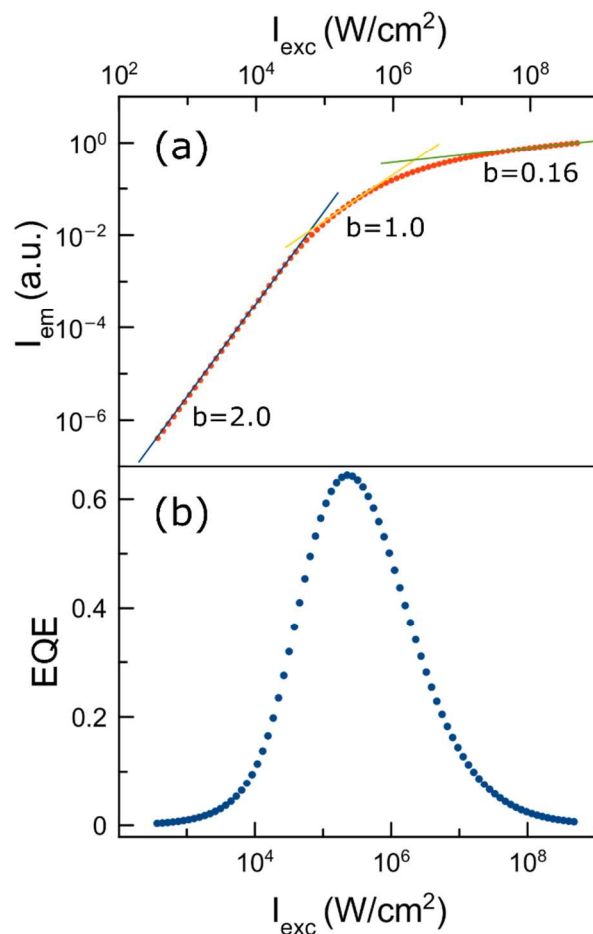


Figure S11. Results of the EQE modeling over a wide range of I_{exc} -values. (a) I_{exc} -dependence of I_{em} (red circles). The blue line indicates quadratic I_{em} growth ($b=2.0$). The yellow line shows linear ($b=1.0$) growth around an optimal I_{exc} . The green line shows a region of sublinear growth beyond a critical I_{exc} , where the corresponding power law coefficient becomes $b=0.16$. (b) Corresponding EQE plot.

EQE fits for other individual CdS NBs

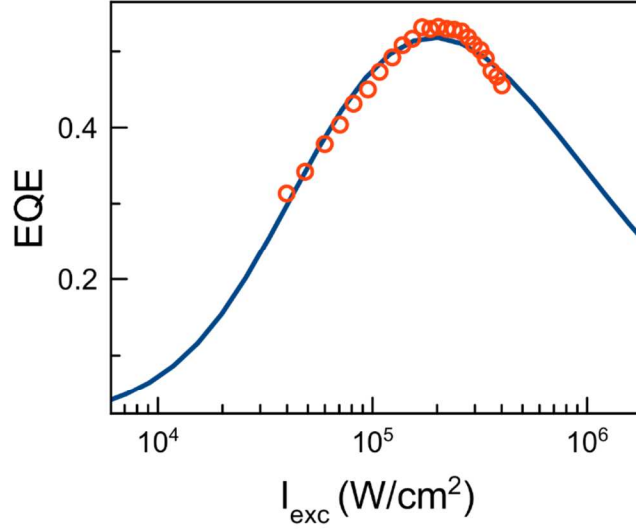


Figure S12. Single NB EQE values (open red circles) and corresponding model fit (blue line) yielding $\eta_{opt} = 0.52$.

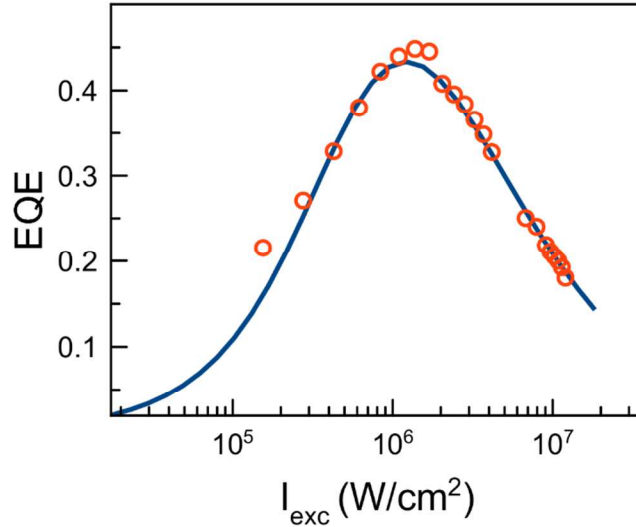


Figure S13. Single NB EQE values (open red circles) and corresponding model fit (blue line) yielding $\eta_{opt} = 0.44$.

Derivation of Equation 4 in the main text

To derive the EQE required for laser cooling, we assume the absorption of N photons to an intermediate sub-gap state. The fraction of excitations which advance to the CdS band edge is $N\eta_{ASPL}$. In parallel, a fraction $(1 - \eta_{ASPL})f$ recombines nonradiatively and contributes to heating while another fraction $(1 - \eta_{ASPL})(1 - f)$ recombines radiatively.

A. Heating contribution:

$$Q_{heating} = N\eta_{ASPL}(1 - EQE)E_g + N(1 - \eta_{ASPL})f(E_g - \Delta E).$$

Assuming that $\Delta E \ll E_g$

$$Q_{heating} = N\eta_{ASPL}(1 - EQE)E_g + N(1 - \eta_{ASPL})fE_g.$$

B. Cooling contribution:

$$Q_{cooling} = N\eta_{ASPL}EQE(\Delta E).$$

The threshold for establishing cooling occurs when

$$Q_{cooling} = Q_{heating}.$$

Consequently, EQEs required to achieve cooling are

$$EQE > \left(\frac{E_g}{E_g + \Delta E} \right) \left[\frac{f - f\eta_{ASPL} + \eta_{ASPL}}{\eta_{ASPL}} \right]. \quad (S6)$$

An expression relating complementary η_{ASPL} and f pairs which lead to physical solutions can be found from

$$\eta_{ASPL} = \frac{f}{A + f - 1}$$

where

$$A = EQE \frac{E_g + \Delta E}{E_g}.$$

A plot of self-consistent η_{ASPL} and f values is

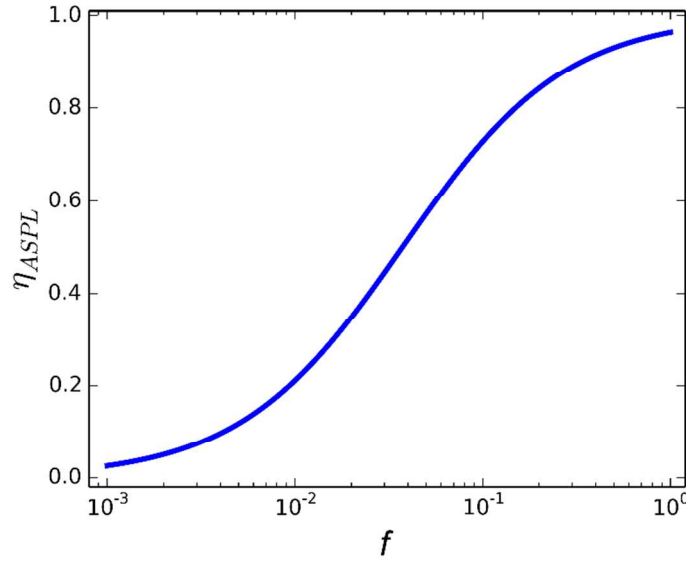


Figure S14. Plot of self-consistent η_{ASPL} and f pairs.

Derivation of Equation 5 of the main text

To estimate the ASPL up-conversion efficiency, we find the intensities of the Stokes excitation at $\lambda_{exc} = 470$ nm ($I_{exc,470\text{ nm}}$) and the anti-Stokes excitation at $\lambda_{exc} = 532$ nm ($I_{exc,532\text{ nm}}$) which yield the same emission intensity at 505 nm (i.e. $I_{em} = I_{ASPL}$). Corresponding expressions for I_{em} and I_{ASPL} are

$$I_{em} = I_{exc,470\text{ nm}} A_{470\text{ nm}} EQE \quad (S7)$$

$$I_{ASPL} = I_{exc,532\text{ nm}} A_{532\text{ nm}} EQE \eta_{ASPL} \quad (S8)$$

where $A_{470\text{ nm}}$ and $A_{532\text{ nm}}$ are NB absorptances at the given wavelength. In practice, experimental $A_{470\text{ nm}}$ and $A_{532\text{ nm}}$ values are found from **Figure 1a** of the main text.

By equating **Equations S7** and **S8** we then find

$$\eta_{ASPL} \approx \left(\frac{I_{exc,470\text{ nm}}}{I_{exc,532\text{ nm}}} \right) \left(\frac{A_{470\text{ nm}}}{A_{532\text{ nm}}} \right) \quad (S9)$$

which is **Equation 5** of the main text.

The following values, obtained from experiment, were used to estimate the up-conversion efficiency:

- $A_{470\text{ nm}} = 0.16$
- $A_{532\text{ nm}} = 0.00456$
- $I_{exc,470\text{ nm}} = 2 \times 10^4 \text{ W/cm}^2$
- $I_{exc,532\text{ nm}} = 6.1 \times 10^6 \text{ W/cm}^2$

Ensemble and single NB time-resolved PL decays

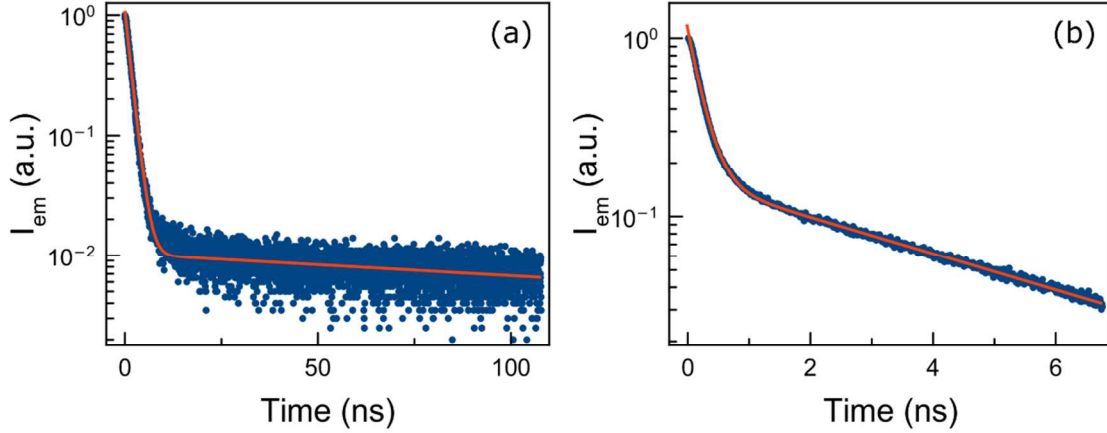


Figure S15. (a) Time-resolved $T=298$ K PL decay of a CdS NB ensemble monitored at 520 nm ($\lambda_{exc}=371$ nm) and corresponding biexponential fit with 1.43 ns and 239 ns time constants. (b) Time-resolved $T=298$ K PL decay ($\lambda_{exc}=470$ nm) of a single CdS NB whose 490-530 nm integrated intensity was monitored. Also shown, corresponding biexponential fit with 0.218 ns and 4.28 ns time constants.

Derivation of a critical DAP concentration

The NB EQE can be expressed using effective first order radiative (k_r) and non-radiative (k_{nr}) recombination rate constants. In the limit where recombination through donor-acceptor states dominates all other non-radiative recombination channels:

$$EQE = \frac{k_r}{k_r + k_{DAP} + \sum k_{nr}} \approx \frac{k_r}{k_r + k_{DAP}}. \quad (S10)$$

Consequently, to maintain (or enhance) a near unity EQE, k_{DAP} must satisfy:

$$k_{DAP} \leq k_r \left(\frac{1-EQE}{EQE} \right). \quad (S11)$$

An approximate expression for k_{DAP} can be found using the following literature expression for the distance-dependent recombination lifetime of DAP centers^{9,10}

$$\tau_{DAP} = \tau_0 \exp(2r/a_D) \sim \frac{1}{k_{DAP}} \quad (S12)$$

where $\tau_0 \sim 2$ ns^{9,10}, $a_D=2.5$ nm¹⁰ is the CdS donor Bohr radius, and r is the nominal donor-electron/acceptor-hole separation. An alternate version of **Equation S11** in terms of time constants is

$$\frac{1}{\tau_{DAP}} \leq \frac{1}{\tau_r} \left(\frac{1-EQE}{EQE} \right). \quad (S13)$$

On substituting **Equation S12** into **S13** and solving for r we obtain

$$r \geq \frac{a_D}{2} \ln \left[\frac{\tau_r}{\tau_0} \left(\frac{EQE}{1-EQE} \right) \right]. \quad (S14)$$

Then assuming a uniform distribution of donors and acceptors, an estimate for the critical donor-acceptor pair concentration, N_{DAP} , below which a near unity EQE can be maintained (or enhanced) is $N_{DAP} = \frac{1}{r^3}$. When written out, the requirement is

$$N_{DAP} \geq \frac{1}{a_D^3} \frac{8}{\left[\ln\left(\frac{\tau_r}{\tau_0} \frac{EQE}{1-EQE}\right) \right]^3}. \quad (S15)$$

Example of NB heating under above gap excitation.

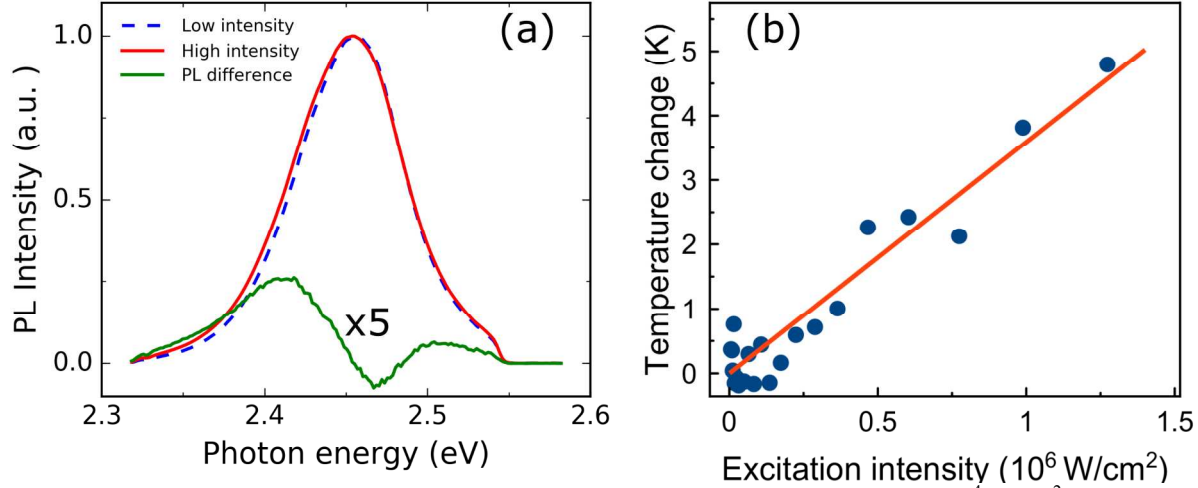


Figure S16. (a) Single CdS NB PL spectrum ($\lambda_{exc}=480 \text{ nm}$) acquired at low ($I_{exc}=4.3 \times 10^4 \text{ W/cm}^2$, dashed blue line) and high ($I_{exc}=1.2 \times 10^6 \text{ W/cm}^2$, solid red line) excitation intensities. A difference spectrum is shown in green. (b) I_{exc} -dependent temperature change of the same NB for $\lambda_{exc}=480 \text{ nm}$. A linear fit is shown by the solid red line.

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