SUPPORTING INFORMATION
for

Trapped-Hole Diffusion in Photoexcited CdSe Nanorods

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I. Band-edge absorption and emission of non-uniform CdSe nanorods

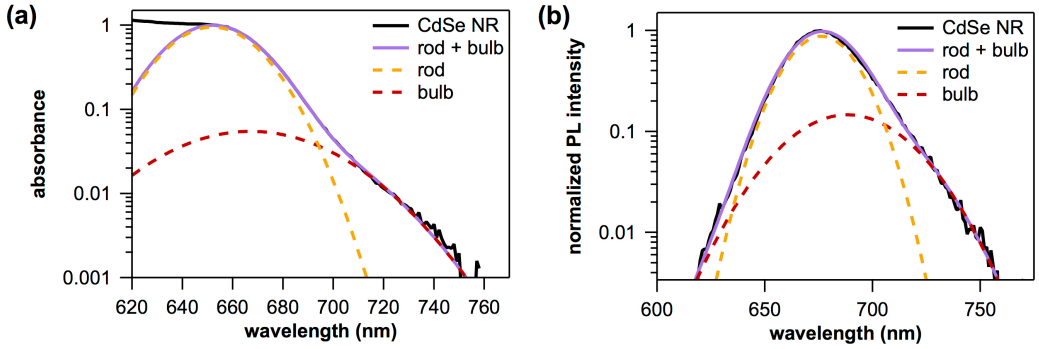

Figure S1. Contributions of the rod and bulb transitions to the band-gap absorption and photoluminescence (PL) of non-uniform CdSe nanorods. (a) Absorption spectrum and (b) PL spectrum from Figure 1 on semi-log axes, fit to the sum of two Gaussian peaks for the lowest-energy rod and bulb transitions. In the absorption spectrum, the rod and bulb peaks are centered at 652 nm and 675 nm, respectively, with a full-width half maximum (FWHM) of 39 nm and 71 nm respectively. In the PL spectra, the rod and bulb peaks are centered at 667 nm and 691 nm, respectively, with a FWHM of 32 nm and 52 nm, respectively.

II. TA spectra of CdSe nanorods over time

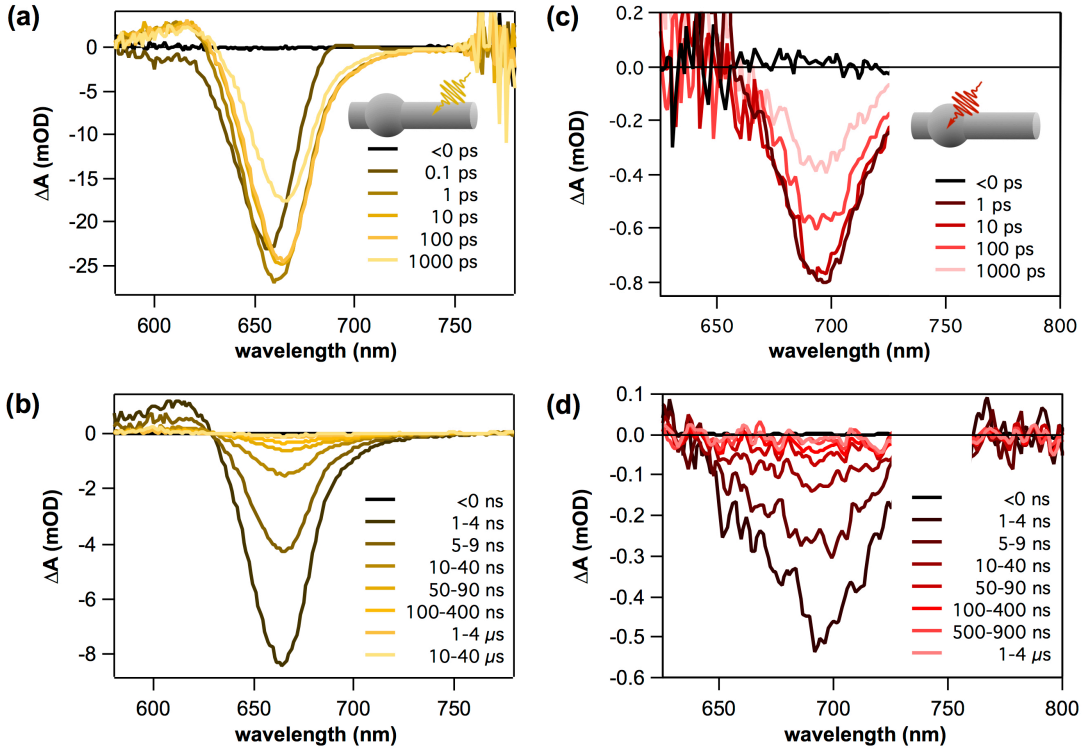

Figure S2. TA spectra of CdSe nanorods over 0.1 ps to 40 μs after excitation at 600 nm (a,b) and 745 nm (c,d). Insets show which morphological feature is being excited at each wavelength. The TA spectra after 600 nm excitation undergo an apparent redshift over time, which originates from the relative amplitude changes of the overlapping rod and bulb bleach peaks. In the first few hundred picoseconds, the rod bleach decays while the bulb bleach has a corresponding rise (a). For times around 10 ps and longer (b) both bleach peaks decay but the bulb signal decays more slowly than the rod. In contrast, the spectral shape of CdSe nanorods excited by 745 nm light (c,d) does not change over time because only a single electronic state, the bulb, is populated at all times.

III. Diffusion model with radiation boundary condition

The derivation of eq 1 was described previously.[1] In that model, the conditional probability density of the trapped hole—the probability of finding it at a distance z from the bulb at time t given that it started at z_0—satisfies the one-dimensional diffusion equation:

$$\frac{\partial}{\partial t}p(z,t|z_0) = D\frac{\partial^2}{\partial z^2}p(z,t|z_0). \tag{S1}$$

The TA spectroscopy experiment measures the survival probability of the electron in a given state. The conditional survival probability—the probability that the trapped hole has lived for a time t given that it started at position z_0 such that $p(z,0|z_0) = \delta(z - z_0)$—is obtained by integrating the probability density over space: $S(t|z_0) = \int dz\, p(z,t|z_0)$. We assume that the electron does not decay by any pathway other than recombination and thus the survival probabilities of the electron and the trapped hole are identical. The survival probability used to fit the bulb electron signal (eq 1 of the manuscript) was found by solving the diffusion equation on a semi-infinite half line $[0,\infty)$ with a perfectly absorbing boundary condition at the origin ($p(0,t|z_0) = 0$), then finding the conditional survival probability, and then averaging over the initial distribution of trapped holes, $p(z_0)$, which was approximated to be uniform on $0 \le z \le \ell$.[1]

With the perfectly absorbing boundary, the electron leaves the system via recombination whenever the trapped hole reaches it. If, instead, a finite number of holes re-engage in the random walk after encountering the bulb at the origin, the boundary is partially absorbing, which is known as the radiation boundary condition of the diffusion–annihilation equation, $\partial p(z,t|z_0)/\partial z|_{z=0} = \kappa p(0,t|z_0)$.[2,3] This boundary condition introduces a new adjustable parameter, κ, with units of inverse length. The left-hand side of this equation is the diffusive flux of the trapped holes out of the bulbs while the right-hand side is the current of recombination with the electron. This is a steady-state condition that accounts for a finite recombination rate by matching these two currents, with κ defining their ratio.[2,3] When $\kappa \to \infty$, one recovers the absorbing boundary.

The conditional survival probability for the partially absorbing boundary is[3]

$$S(t|z_0) = S_0\left[\mathrm{erf}\left(\sqrt{{z_0}^2/4Dt}\right) + e^{\kappa z_0}e^{D\kappa^2 t}\,\mathrm{erfc}\left(\sqrt{{z_0}^2/4Dt} + \sqrt{D\kappa^2 t}\right)\right]. \tag{S2}$$

Equation S2 can be reduced to a two-parameter model by substituting $\tau_0 = {z_0}^2/4D$ (not to be confused with $\tau = \ell^2/4D$ from eq 1) and $\tau_\mathrm{r} = 1/D\kappa^2$:

$$S(t|z_0) = S_0\left[\mathrm{erf}\left(\sqrt{\tau_0/t}\right) + e^{\sqrt{4\tau_0/\tau_\mathrm{r}}}e^{t/\tau_\mathrm{r}}\,\mathrm{erfc}\left(\sqrt{\tau_0/t} + \sqrt{t/\tau_\mathrm{r}}\right)\right]. \tag{S3}$$

Note that while it is tempting to think of τ_r as the electron–hole recombination time constant, it includes the spatial aspect of recombination and there is no direct relationship between this and the "well mixed" recombination time constant one would compute or measure from a spatially uniform distribution of electron and hole populations. Incorporating the partially absorbing boundary into the model affects the pre-asymptotic decay but not the long-time behavior: eq S3 exhibits a $t^{-1/2}$ power-law tail at long times just like eq 1. When applying eq S3 to bulb decay after charge separation in Figure 3, the value of the Pearson correlation coefficient between τ_0 and τ_r is large at $\rho = 0.9$ and the reduced chi-squared value is not significantly improved. This

indicates that including a finite κ, even if ignoring the initial distribution of hole positions, leads to a model that overfits the data. Including a distribution in the initial positions of trapped holes in addition to the radiation boundary, as in the model of eq 1,[1] does not quantitatively change this situation, again giving a two-parameter model with a high correlation between fit parameters. Thus the experimental data are not sensitive to a finite electron–hole recombination rate at room temperature, but are sensitive to the width of the initial distribution function for hole positions, $p(z_0)$.

IV. References

(1) Utterback, J. K.; Grennell, A. N.; Wilker, M. B.; Pearce, O.; Eaves, J. D.; Dukovic, G., Observation of trapped-hole diffusion on the surfaces of CdS nanorods. *Nat. Chem.,* **2016,** *8*, 1061-1066.

(2) Redner, S., *A guide to first-passage processes*. Cambridge University Press: Cambridge, **2001**.

(3) Carslaw, H. S.; Jaeger, J. C., *Conduction of Heat in Solids*. 2nd ed.; Oxford University Press: Amen House, London, E.C.4, **1959**.