Electronic Supplementary Information

Hot excitons are responsible for increasing photoluminescence blinking activity in single lead sulfide/cadmium sulfide nanocrystals

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1. Single nanocrystal PL measurements

Single nanocrystal PL experiments were performed on a home built scanning confocal photoluminescence microscope based on a Olympus IX71 inverted optical microscope equipped with a 1.4 NA, 100x oil objective lens for excitation and photoluminescence collection, two continuous wave lasers of 488nm (Melles Griot Ar-ion) and 633nm (He Ne Thorlabs) coupled via a single mode fiber for sample excitation, a 805nm long pass dichroic mirror (Semrock) and a 935/134nm band pass (Semrock) for rejecting the laser from the collected photoluminescence. The collected photoluminescence was further filtered by a 100 μm pinhole positioned in the image plane and detected by a near infrared enhanced single photon counting avalanche photodiode (SPCM-NIR, Excelitas Technologies). Signals from the photodiode were read by a time analyzer (PicoHarp 300, Picoquant) synchronized with a pulse generator in order to be able to perform time-tagged time-resolved measurements. Data acquisition and data analysis was performed with a commercial imaging and probing software (Symphotime 64.)

2. Power dependent experiments

Power dependent experiments were performed on PbS/CdS nanocrystals in solution (toluene) at a concentration of 100nM by using the same confocal PL microscope described in the main text and previous section. Power dependent experiments for the two wavelengths are shown in Figure S1 and they both present slopes near unity, confirming the lack of biexciton formation for power ranges extending over the powers used in single nanocrystal experiments. Assuming confocal detection for which the estimated lateral and axial resolutions are $d_{xy}=0.61\lambda_{exc}/NA$ $d_z=2n\lambda_{exc}/(NA)^2$ with n-refractive index of oil and the estimated confocal volume is $V_{conf}=\pi^{3/2}k(w)3$ with $k= d_z/d_{xy}$ and w-the e^{-2} laser beam radius we can estimate the nanocrystal occupancy per confocal volume in the assumption of $w\cong d_{xy}$. We obtain for 488nm laser a confocal volume $V_{conf.}(488nm)=0.1fL$ and for 633nm laser a confocal volume of $V_{conf.}(633nm)=0.3fL$. For a whole

size of 9 nm for the PbS/CdS nanocrystal which includes a 3nm core, a 2x0.7nm shell and a 2.3 nm ligand, the volume displaced by a nanocrystal is $3.05x10^{-6}$fL, leading to occupancies of $3*10^5$ (633nm) and 10^5 (488nm) per confocal volume. In reality, given the used nanocrystal concentration (100nM), the occupancy is 18.6 nanocrystals at 633nm and 6.2 nanocrystals at 488nm. Therefore, each nanocrystal in solution and subjected to power dependent measurements experiences similar conditions as in the case of immobilized single particle experiment.

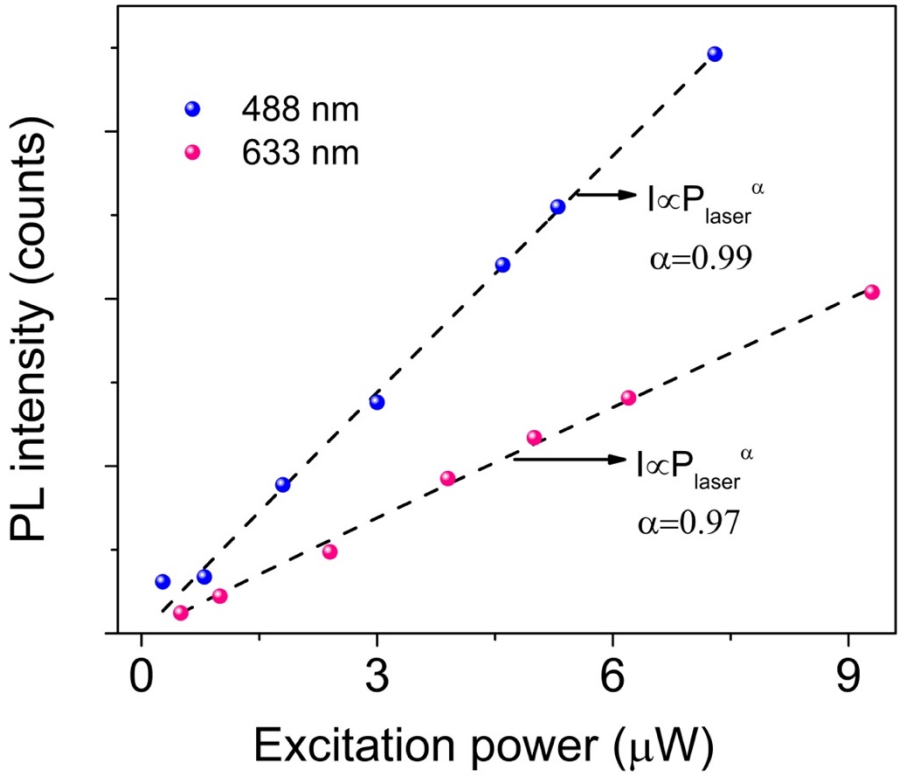

Figure S1. Excitation power dependent PL intensity of PbS/CdS QDs.