Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Ultrafast Dynamics and Single Particle Spectroscopy of Au-CdSe Nanorods

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Transient Absorption (TA) spectra of Au-CdSe NRs

Figure S1 gives TA spectra of solutions of bare CdSe NRs and Au-CdSe NRs corresponding to several delays between the pump pulse and the probe pulse. In this example, the pump intensity is 2.5 μW, which corresponds to an initial average number of excitons per QD of about ~0.1. As shown in the figure, all the TA spectra have features dominated by the contribution of CdSe NRs, and are not impacted in the presence of Au NPs.

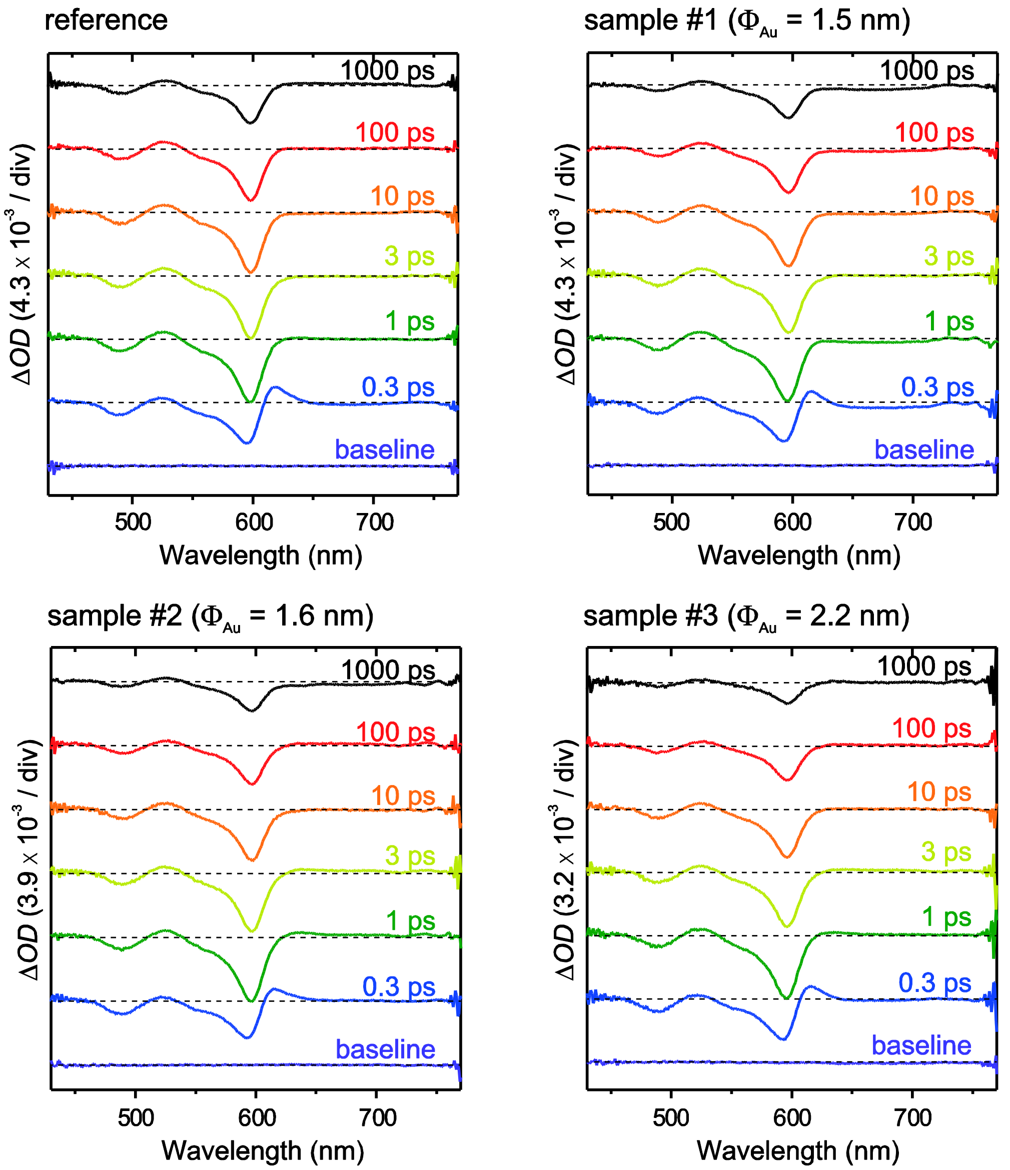

Figure S1. Transient absorption spectra of solutions of CdSe NRs and Au-CdSe NRs.

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Single particle spectroscopy - Experimental setup

The fluorescence properties of individual NRs were measured using a Hanbury-Brown and Twiss type photon correlation set-up in combination with a picosecond-pulsed laser diode (405 nm, 10 MHz, 100 ps FWHM) and a home-built sample-scanning confocal microscope. The instrumental set-up is schematically illustrated in Figure S2. The excitation light source was circularly polarized by a Gran-Thomson polarizer and a $\lambda/4$ waveplate. To introduce the excitation laser beam into an inverted microscope (IX71, Olympus), the beam was reflected by a dichroic mirror (Semrock), and then focused onto the sample by an oil-immersion objective lens (100×, N.A.: 1.4 Olympus). A fluorescence image of the sample on the piezo stage was recorded by raster scanning the sample over the focused incident laser spot. Then, the focused spot was moved to an isolated fluorescence spot, which corresponds to a single NR in the fluorescence image, and the emission properties of the individual NR were measured. The emitted photons from the NRs were collected by the same objective lens and were passed through a 100 µm optical pinhole, and a long-pass filter (LP02-488RU, Semrock). A half of the emitted photons was detected by a spectrometer (SpectraPro2358, Acton Research Corporation) with a cooled CCD camera (PIXIS400B, Princeton Instruments). The remaining half of the photons were divided equally by a 50/50 nonpolarizing beam splitter cube into two beam paths and then detected by two avalanche single-photon counting modules (APD: SPCM-AQR-14, PerkinElmer). The signals from both APDs were connected to a router of a time-correlated single-photon counting (TCSPC) PC board (SPC630, Becker & Hickl). The signal from one of the two APDs was delayed using a delay generator (DG535, Stanford Research) to compensate for the dead time of the TCSPC board. A synchronization signal, which detected a part of the excitation laser, was used as a synchronization signal for the lifetime measurement. Time-resolved data were acquired using first-in-first-out mode in which the arrival time after the beginning of the acquisition, the time delay between the start and stop pulse, and the detection channel were registered for every detected fluorescence photon. The data were analyzed using a homemade LabVIEW routine that allowed the time traces of fluorescence intensity and lifetime and the photon correlation histogram of single NRs to be measured simultaneously.

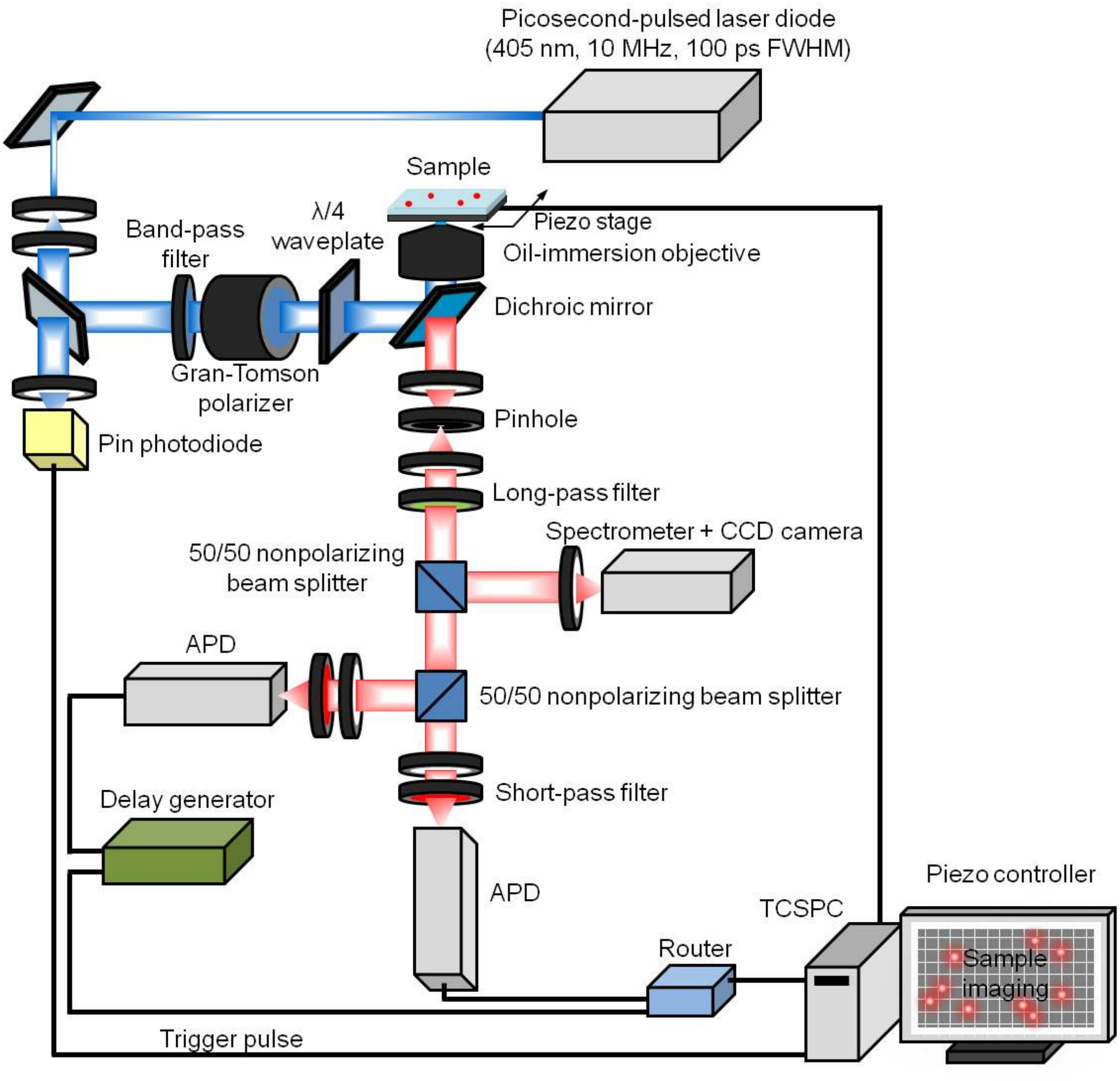

Figure S2. Diagram of single-particle spectroscopy set-up.

Single particle PL decay - Analysis of ON and OFF states by deconvolution

The PL decay of single NRs can be decomposed into 2 components corresponding to the PL decay of neutral NRs (bright ON states) and ionized NRs (dark OFF states). Even if fast non-radiative pathways dominate the excited state dynamics in ionized NRs, fluorescence still remains detectable in such states and the PL decay corresponding to OFF states can be plotted with reasonable SNR ratio by using long (few seconds) time-integration windows. Figure S3 gives a zoom of the time trace intensity corresponding to long OFF-state which shows slightly higher signal that the background level (blue dashed line).

All the ON and OFF states analyzed here are labeled in Figure S3, S4 and the corresponding deconvolution analyses are given in Table S1, S2

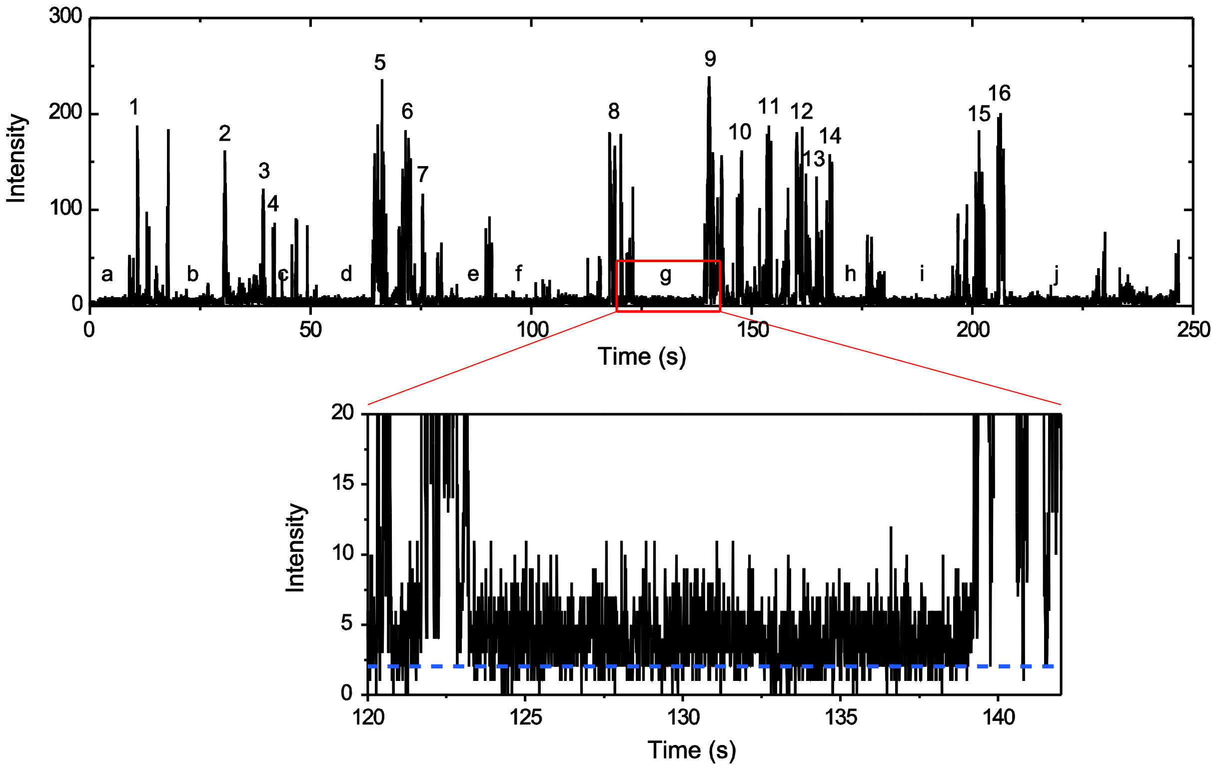

Figure S3. Time trace of fluorescence intensity of single CdSe NRs for a binning time of 10 ms.

Table S1. Fitting of PL decay of single CdSe NRs (reference sample) corresponding to photon collection restricted to bright ON states or dark OFF states. All the PL decay curves are fitted by single or bi-exponential functions.

Reference sample - ON States			Reference sample - OFF States		
N° state	**τ_1 /ns (A_1)**	**τ_2 /ns (A_2)**	**N° state**	**τ_1 /ns (A_1)**	**τ_2 /ns (A_2)**
#1	1.18 (0.53)	17.87 (0.47)	**#a**	0.37 (0.89)	21.10 (0.11)
#2	-	8.92 (1)	**#b**	0.40 (0.95)	21.70 (0.05)
#3	1.70 (0.54)	14.23 (0.46)	**#c**	0.09 (0.98)	9.09 (0.02)
#4	-	16.40 (1)	**#d**	0.69 (0.86)	22.39 (0.14)
#5	1.39 (0.49)	11.78 (0.51)	**#e**	0.35 (0.94)	13.98 (0.06)
#6	-	10.79 (1)	**#f**	0.33 (0.98)	15.64 (0.02)
#7	1.16 (0.40)	11.99 (0.60)	**#g**	0.09 (0.98)	10.17 (0.02)
#8	2.10 (0.57)	11.02 (0.43)	**#h**	0.15 (0.96)	13.47 (0.04)
#9	0.96 (0.41)	20.51 (0.59)	**#i**	0.55 (0.73)	14.52 (0.27)
#10	1.47 (0.42)	17.48 (0.58)	**#j**	0.35 (0.96)	11.23 (0.04)
#11	1.00 (0.70)	17.86 (0.30)			
#12	1.00 (0.40)	21.98 (0.60)			
#13	2.94 (0.50)	22.14 (0.50)			
#14	2.94 (0.42)	19.61 (0.58)			
#15	4.11 (0.58)	17.41 (0.42)			
#16	1.03 (0.43)	16.77 (0.57)			

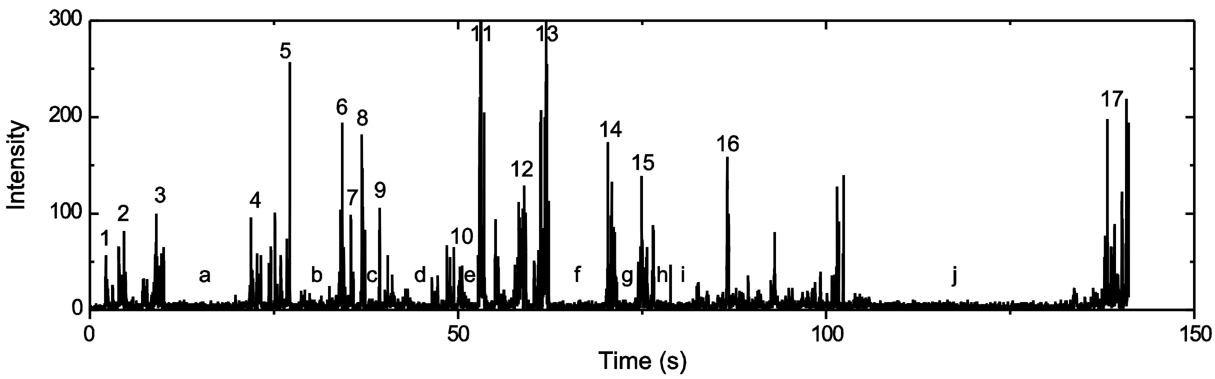

Figure S4. Time trace of fluorescence intensity of single Au-CdSe NRs (sample #3) for a binning time of 10 ms.

Table S2. Fitting of PL decay of single Au-CdSe NRs (sample #3) corresponding to photon collection restricted to bright ON states or dark OFF states. All the PL decay curves are fitted by single or bi-exponential functions.

Sample #3 - ON States			Sample #3 - OFF States		
N° state	τ_1 /ns (A_1)	τ_2 /ns (A_2)	**N° state**	τ_1 /ns (A_1)	τ_2 /ns (A_2)
#1	0.32 (0.93)	3.29 (0.07)	**#a**	0.05 (0.97)	2.46 (0.03)
#2	0.17 (0.91)	3.44 (0.09)	**#b**	0.08 (0.98)	3.30 (0.02)
#3	0.98 (0.73)	8.76 (0.27)	**#c**	0.14 (0.99)	5.89 (0.01)
#4	0.26 (0.95)	2.57 (0.05)	**#d**	0.10 (0.94)	2.77 (0.06)
#5	0.23 (0.93)	4.84 (0.07)	**#e**	0.34 (0.97)	10.50 (0.03)
#6	0.18 (0.92)	3.89 (0.08)	**#f**	0.09 (0.97)	3.78 (0.03)
#7	0.54 (0.91)	12.10 (0.09)	**#g**	0.12 (0.96)	4.77 (0.04)
#8	0.33 (0.91)	11.07 (0.09)	**#h**	0.14 (0.99)	6.31 (0.01)
#9	<0.04 (0.94)	5.71 (0.06)	**#i**	<0.04 (0.99)	4.17 (0.01)
#10	0.50 (0.93)	13.11 (0.07)	**#j**	0.05 (0.98)	3.80 (0.02)
#11	0.36 (0.86)	17.44 (0.14)			
#12	0.94 (0.77)	10.33 (0.23)			
#13	1.04 (0.72)	18.43 (0.28)			
#14	1.09 (0.79)	15.52 (0.21)			
#15	0.64 (0.81)	12.52 (0.19)			
#16	2.07 (0.55)	21.04 (0.45)			
#17	0.72 (0.89)	9.13 (0.11)			