<u>Supporting Information</u>

Charge-Transfer Processes in Single CdSe/ZnS Quantum Dots with p-type NiO Nanoparticles

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S1. Experimental Section

Mercaptoundecanoic acid-functionalized CdSe/ZnS core/shell QD with a CdSe core of ~1.5 nm radius and overcoated with ~4 monolayers of ZnS was obtained from NN-Labs (Batch number: 101309-JS). Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, 98%) and sodium hydroxide (NaOH, 99.998%) were obtained from Alfa Aesar and Sigma-Aldrich, respectively.

Nickel hydroxide sol was prepared using a method described elsewhere.[S1,S2] 5 ml of 1.0 M NaOH solution was added slowly to 10 ml of 0.2 M $Ni(NO_3)_2$ solution under vigorous stirring. The solution was allowed to settle overnight, and the $Ni(OH)_2$ deposit was dialyzed against deionized water for 24 h. Nanostructured NiO film was prepared by spin coating $Ni(OH)_2$ sol onto cleaned coverslips and the $Ni(OH)_2$ sol was annealed at 350 $^{\circ}C$ for 3 h. Single-molecule samples were prepared by spin casting a dilute solution (~ 0.1 - 1 nM) of CdSe/ZnS onto either glass coverslips or NiO nanoparticle films.

Single-molecule fluorescence spectroscopy measurements were performed using a time-resolved confocal microscope (MicroTime 200, PicoQuant). Basically, an inverted microscope (IX71, Olympus) equipped with a scanning stage (P-733.2CL, Physik Instruments) was used to detect single molecules. The excitation source used is a 470 nm pulsed laser diode (LDH-P-C-470B, PicoQuant) with a repetition rate of 10 MHz. The excitation light passed through an excitation filter (Z470/10, Chroma) and reflected by a dichroic mirror (Z467rpc, Chroma) before being focused through an oil immersion objective lens (100×, N.A. 1.4, Olympus) which was also used to collect the fluorescence. The fluorescence then passed through the dichroic mirror and an emission filter (HQ 490 LP, Chroma) before being detected by a single-photon avalanche diode (SPAD, SPCM-AQR-15, Perkin-Elmer). Time-correlated fluorescence decay profiles were recorded using the time-correlated single-photon counting technique with the TimeHarp 200 PCI-board (PicoQuant). All measurements were performed by using an excitation intensity of $I = 280$ W/cm^2 at ambient conditions and the data were analyzed using the SymPhoTime software (PicoQuant).

The time-dependent fluorescence spectra and fluorescence intensity time traces of single QDs were simultaneously recorded using a 50%/50% beam splitter which divided the fluorescence signal into a SPAD and a CCD camera (Pixis 100, Princeton Instruments) coupled to a monochromator (SP2150i, Acton Research) for intensity trajectory and fluorescence spectrum measurements, respectively. The excitation intensity used was 280 W/cm^2 for QDs on a glass substrate while a higher intensity of 560 W/cm^2 was employed for QDs on a NiO film in order to record good S/N data. The integration times per frame for QD on glass and NiO are 1 s and 3 s, respectively.

The steady-state absorption and emission spectra were recorded using a Cary 100 UV-vis spectrometer (Varian) and a Cary Eclipse fluorescence spectrometer (Varian).

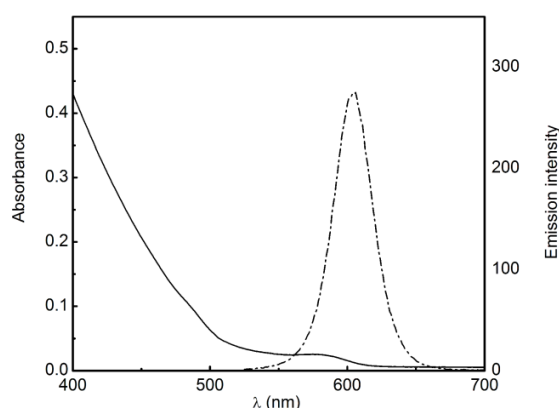## S2. Steady-state absorption and emission spectra of QD

Figure S1. The first exciton (solid line) and emission (dash line) peaks of CdSe/ZnS QD in water. The excitation wavelength used in the fluorescence measurement is 470 nm.

The first exciton and emission peaks of the CdSe/ZnS QD are located at 575 and 606 nm, respectively (Figure S1). The absence of NiO nanoparticle absorption band in the range of 400 to 700 nm suggests that electronic energy transfer does not occur between QD and NiO.

S3. Calculating the redox potentials for the QD conduction band and valence band

The redox potentials of the conduction band (CB) and valence band (VB) of the CdSe/ZnS QD used in this study are estimated to be E_{CB}(CdSe) = -0.57 eV and E_{VB}(CdSe) = +1.59 eV *vs* NHE, respectively, when the band gap and CB redox potential of bulk CdSe are taken to be 1.7 eV and -0.2 eV, respectively.[S3] The reported energy of the VB edge of NiO (E_{VB}(NiO) = +0.54 V *vs* NHE) is located between E_{CB}(CdSe) and E_{VB}(CdSe), while the potential of the CB of NiO (E_{CB}(NiO) = -3.06 V *vs* NHE) is above E_{CB}(CdSe).[S4]
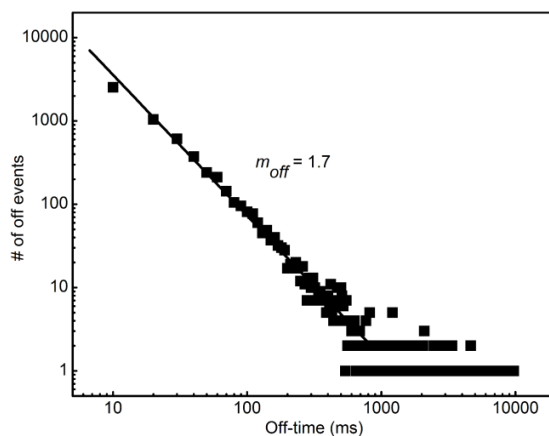
S4. Off-time distribution

Figure S2. Off-time distribution for 125 blinking dots on a glass substrate.

Figure S2 shows the off-time duration histogram for a collection of 125 blinking dots on a glass substrate. The linear log-log plot is described using a power-law distribution

$$P\left(\tau_{off}\right) = P_o\, \tau_{off}^{-m_{off}}$$

where m_{off} (= 1.7) is the power-law exponent.
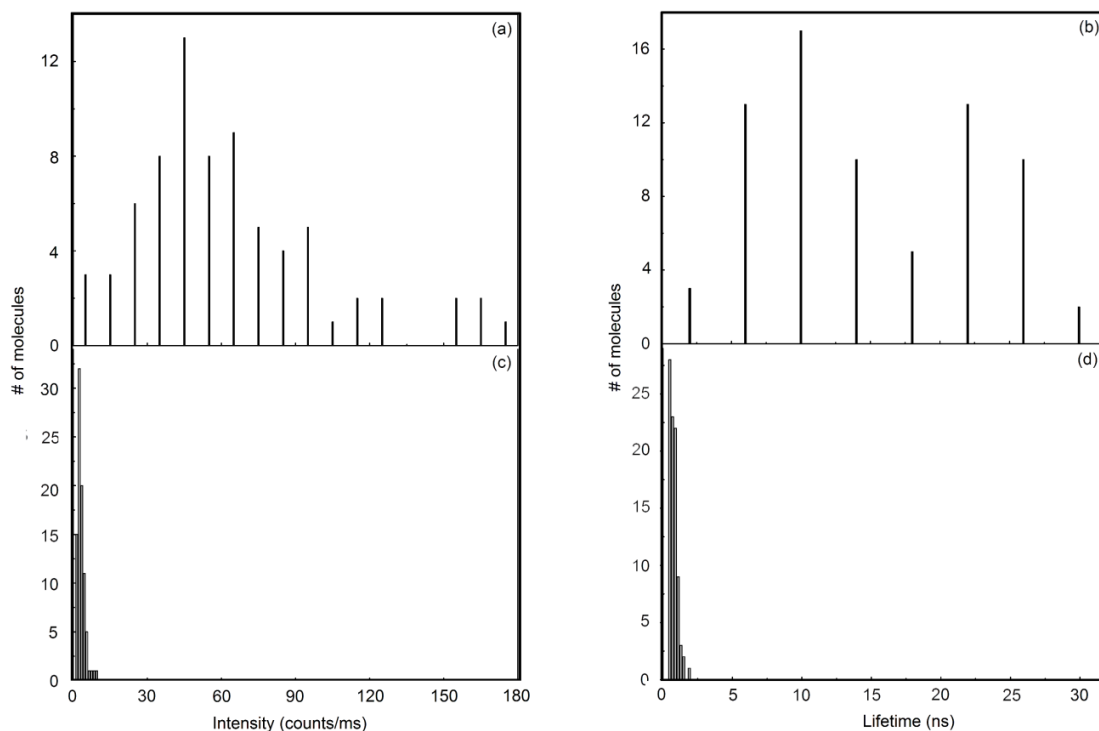
S5. Fluorescence lifetime distribution

Figure S3. Distributions of the maximum emission intensities (a) and fluorescence lifetimes (b) of single QDs on a glass substrate obtained by fitting the fluorescence decay profiles, constructed from the maximum intensity range, to a single exponential decay function. Distributions of the emisson intensities and long lifetime component of the double exponential fit of the fluorescence decay curves of QDs on NiO are also presented in (c) and (d), respectively.

The fluorescence lifetime decay curves of 73 single QDs on a glass substrate, constructed from photons in the maximum intensity range, were fitted to a single exponential decay function and the distribution of the lifetimes is given in Figure S3(a). On the other hand, the fluorescence lifetime decay profiles of 87 QDs on NiO were fitted to a double exponential decay function with a short lifetime component that is shorter than the resolution of the instrument (~150 ps) and a long lifetime component whose distribution is presented in Figure S3(b). The averaged lifetime and maximum emission intensity of single QDs on glass are 15.0 ns and 63.6 counts/ms, respectively, and on NiO are 0.8 ns and 3.3 counts/ms, respectively. The exact nature of the short lifetime component is not clear at the present

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moment. Clearly, the fluorescence lifetimes of QDs on NiO are quenched as compared to those of QDs on a glass substrate.

S6. Blue shift rate

The emission spectra for the QDs on NiO (Figure 4 of main text) were measured using a higher intensity of I = 560 W/cm^2 in order to obtain good signal-to-noise data for both the emission spectra and intensity trajectories collected simultaneously. The intensity of I = 560 W/cm^2 was not used for QDs on glass substrate since the dots photobleached too quickly at this intensity to allow an accurate determination of the blue shift rate. This is possibly due to a greater number of excitation cycles and faster trapping of ejected charges by deep traps. At the higher intensity (560 W/cm^2), the QDs on NiO still showed long survival times and slower blue shift rates as compared to QDs on glass substrate (excited with I = 280 W/cm^2) demonstrating the fast transfer of charge carriers from dots to NiO and a low probability of charges ejected to the QD surface.

The blue shift rate of a single QD was calculated using the expression (*wavelength-shift*/*time*), where *wavelength-shift* is the difference in the peak wavelength of the spectrum in the final frame before the dot photo-bleaches and the spectrum in the initial frame, and *time* is the time between the final and initial frames.[S6] Only QDs that yielded more than 3 frames of spectra were considered in the analysis. The average blue-shift rates for QDs on a glass substrate and a NiO film are calculated to be 1.5 nm/s (based on 66 dots) and 0.4 nm/s (based on 77 dots), respectively. Clearly, the spectral shift rate is slower for QD on NiO as compared to that for QD on a glass substrate.

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