Supporting Information

Long-Lived Negative Photocharging in Colloidal CdSe Quantum Dots Revealed by Coherent Electron Spin Precession

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1. Sample information

The colloidal CdSe quantum dots (QDs) (diameter of 2.4 nm) in toluene with octadecylamine stabilizing ligands were fabricated by Hangzhou Najing Technology Co., Ltd. The dot diameter is estimated from the wavelength of the first exciton absorption peak at 508 nm.[1] 1-Octanethiol (OT) was purchased from Sigma-Aldrich. OT is a hole acceptor, i.e., it captures photoexcited holes and therefore provides negatively photocharged QDs.[2] The OT solution in toluene with different OT concentrations is mixed with the CdSe QD toluene solution in an airtight quartz cuvette to obtain various molar ratios of OT to QD (R_{OT}) from 7 to 30000. The cuvette has a size of 1 mm×10 mm×40 mm and a total volume of ~400 μL. The concentration of CdSe QDs is kept the same in all measurements. The samples are prepared either under an air or N_2 atmosphere in a glovebox.

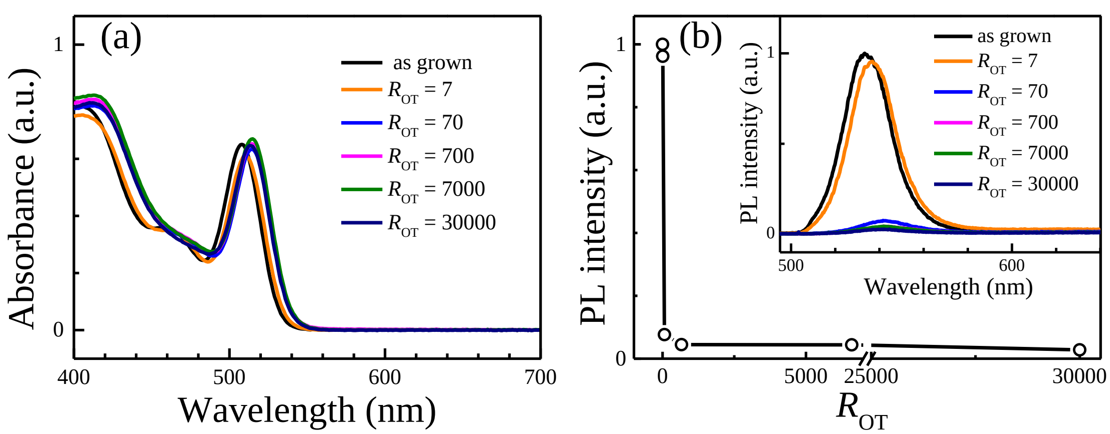

Figure S1. Absorption and photoluminescence (PL) spectra of 2.4 nm CdSe QDs with different molar ratios of OT to QD (R_{OT}). (a) Absorption spectra. (b) PL intensity as a function of R_{OT}. Inset shows the corresponding PL spectra. $T = 300$ K.

Figure S1 shows the absorption and PL spectra of 2.4 nm CdSe QDs with different R_{OT}. After adding OT, the absorption peak is red-shifted up to 5 nm for high OT concentrations (Figure

S1a). Due to the charge separation induced by hole transferring to the OT hole acceptors, the PL intensity of CdSe QDs decreases strongly with increasing R_{OT} as shown in Figure S1b.

2. Optical and spectroscopic measurements

The coherent spin dynamics of carriers is measured by three-beam or two-beam pump−probe time-resolved ellipticity spectroscopy.[3,4] The laser source is based on a Ti:sapphire laser amplifier (pulse duration of 50 fs, central wavelength of 800 nm, and pulse repetition rate of 1 kHz), which pumps an optical parametric amplifier (OPA). The OPA output is split by beam splitters into three beams (prepump, pump and probe). The prepump light is broad-band with a bandwidth of ~12 nm, whose center wavelength is 515 nm (near the first absorption peak of the QD sample). The pump and probe light are narrow-band with center wavelengths of 515 nm and are cut out of the broad-band light with bandpass filters with a bandwidth of 1 nm. The pump fluence in all measurements is ~100 μJ/cm^2, and the probe fluence is 10 times weaker.

The prepump light is linearly polarized and used to generate photocharged QDs. The pump light is circularly polarized. An electro-optical modulator (EOM) in combination with a quarter waveplate provides modulation of its helicity at a frequency of 850 Hz between left- and right-circular polarization. The pump light is used to polarize the electron spins and the subsequent spin dynamics is monitored by the change of the ellipticity of linearly polarized probe light.[3] The time delay between the pump and probe pulses is controlled by a mechanical delay line. An additional mechanical delay line is introduced to adjust the time delay between the prepump and pump pulses, which is actually fixed at 1 ns for the repeated measurements. The pump and probe laser beams are focused into the same spot with a diameter of about 200 μm on the sample. The prepump light is typically not focused, having a beam diameter of ~10 mm, or even expanded in order to reduce the QD diffusion effects.

The detection of the ellipticity change is done using a combination of a quarter waveplate, a Wollaston polarizer and a balanced photodiode detector, which is connected to a lock-in amplifier for a better signal to noise ratio. The spin precession measurements are performed in an external magnetic field of B = 0.43 T supplied by an electromagnet and applied perpendicular to the laser light wave vector, i.e., in the Voigt geometry. All measurements are carried out at room temperature.

In some photocharging measurements, the broad-band femtosecond prepump light is replaced by a 473 nm continuous-wave (CW) laser in order to increase the photocharging efficiency because of its higher power, especially in the case where the light needs to be expanded to avoid the QD diffusion effect.

The steady-state absorption is measured with a spectrophotometer (Varian Cary 100). The PL is excited by a 473 nm CW laser and detected by an Ocean Optics USB 2000+ spectrometer.

3. Spin excitation scheme for negatively charged QDs

Figure S2 shows the scheme of spin excitation in negatively charged QDs. The spin signal results from polarization-selective electron-to-negative trion excitation. The optically excited, singlet ground state of the negative trion consists of two electrons with opposite spin orientations (thin arrows) and a single hole with spin ±3/2 (thick black arrow), with the total spin defined by the hole spin. The optical selection rules only allow +1/2 (-1/2) electrons to be excited into the +3/2 (-3/2) trion states by $\sigma^+(\sigma^-)$ circularly polarized laser pulses, leaving a net part of spin-down (spin-up) polarized electrons in their ground states.

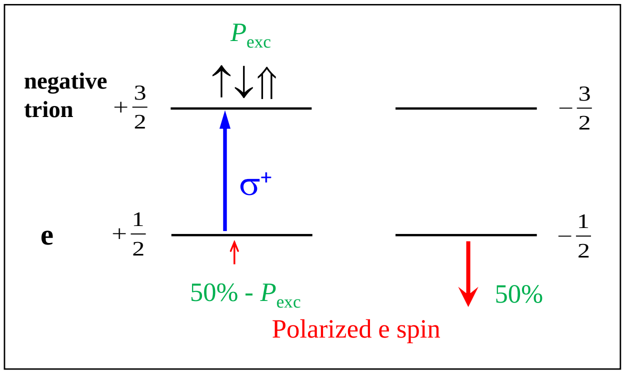

Figure S2. Scheme of spin excitation in negatively charged QDs.

4. Spin excitation scheme for positively charged QDs

Figure S3 shows the scheme of spin excitation in positive charged QDs. The spin signal comes from polarization-selective hole-to-positive trion excitation. The optically excited, singlet ground state of the positive trion consists of two holes with opposite spin orientations (thick black arrows) and a single electron with spin $\pm 1/2$ (red arrow), where the total spin is defined by the electron spin. According to the optical selection rules, $\sigma^+(\sigma^-)$ circularly polarized pulses can only excite -3/2 (+3/2) holes to -1/2 (+1/2) trion states and generate spin-down (spin-up) polarized electrons in the positive trion states.

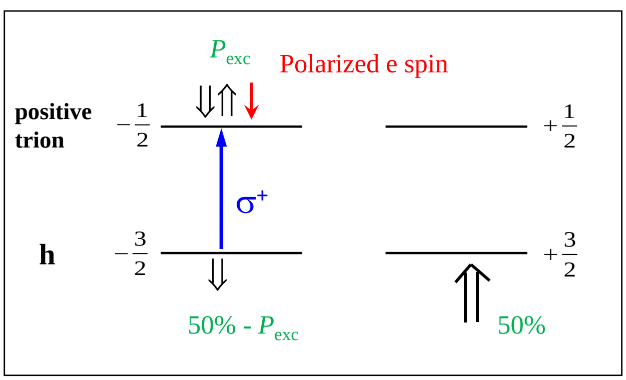

Figure S3. Scheme of spin excitation in positively charged QDs.

5. Electron spin dephasing time for the two types of negative photocharging states

Figure S4 shows the electron spin dynamics in CdSe QDs with a diameter of 2.4 nm in the presence of OT. The spin dynamic curves with ν_2 and ν_1 Larmor precession frequencies correspond to the data shown in Figure 1c in the main text for the condition of prepump on 0 and 10 min, respectively. The spin dephasing time T_2^* is equal to 730 and 250 ps for the ν_1 and ν_2 spin signals, respectively.

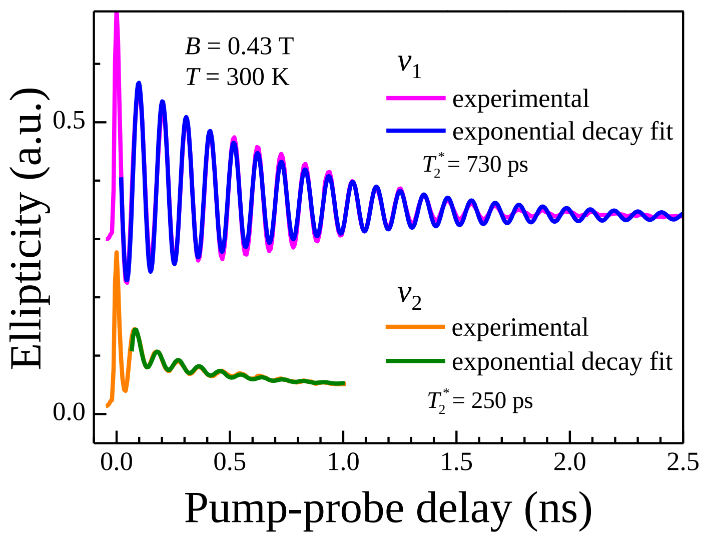

Figure S4. Comparison of the electron spin dephasing time for the two types of negative photocharging states. The orange and magenta curves correspond to the data shown in Figure 1c in the main text. The orange curve: prepump on 0 min. The magenta curve: prepump on 10 min.

6. Time-resolved ellipticity signals in as-grown colloidal CdSe QDs

Figure S5 shows the time-resolved ellipticity signals in as-grown colloidal CdSe QDs in the absence of OT. The spin signal is very weak and cannot be detected both with and without the prepump illumination.

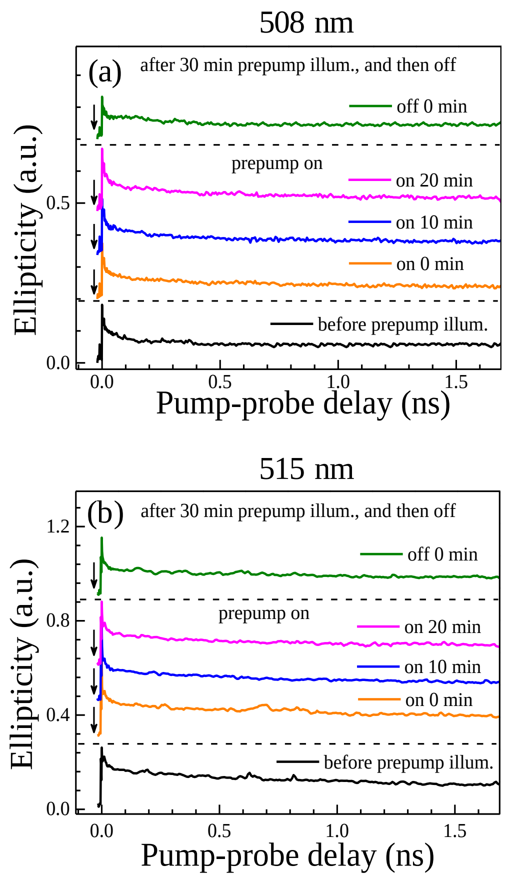

Figure S5. Time-resolved ellipticity signals in as-grown colloidal CdSe QDs for laser wavelengths near the bandgap. (a) The prepump−pump−probe central wavelength is 508 nm, set to the first exciton absorption peak. The prepump is a broad-band femtosecond laser. The pump and probe pulses are cut out at 508 nm from the broad-band light using bandpass filters with a bandwidth of 1 nm. (b) Same as before but with a central wavelength of 515 nm. The black arrows denote the start point for counting the prepump-on or prepump-off time. The sample is prepared under air atmosphere without adding OT. Magnetic field B = 0.43 T.

7. Pump−probe measurements for CdSe QDs with OT hole acceptor

Figure S6 shows the two-beam pump−probe measurement results for CdSe QDs with OT hole acceptor. Before the prepump illumination, we only observe the second type of negative photocharging, which is corresponding to the Larmor precession frequency ν_2 = 10.73 GHz. Even with a continuous irradiation of the pump and probe light up to 1 hour, the spin signal related to the first type of negative photocharging does not show up.

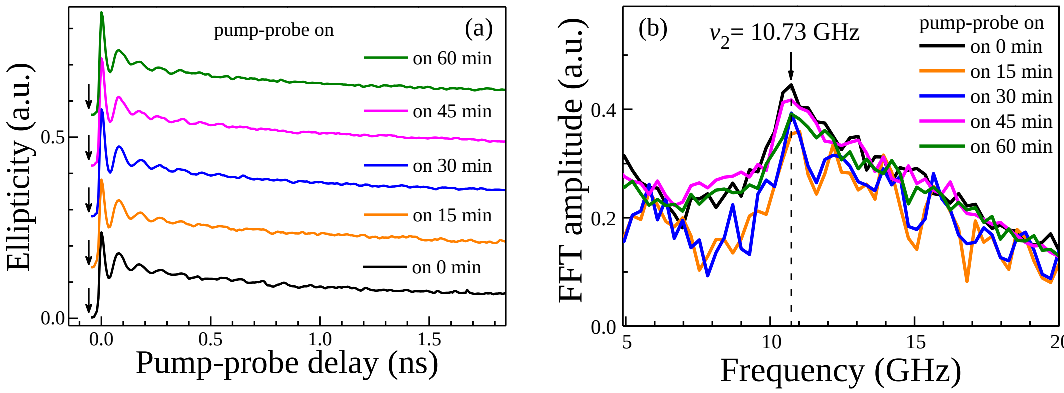

Figure S6. Pump−probe measurements for CdSe QDs with OT hole acceptor. (a) Time-resolved ellipticity signals for different continuous pump−probe illumination times. The black arrows denote the start point for counting the pump−probe illumination time. (b) Fast Fourier transform spectra of panel (a). The sample is prepared under air atmosphere. The QD size is 2.4 nm and R_{OT} is 700. B = 0.43 T.

8. QD diffusion measurements

The QD diffusion measurement results are shown in Figure S7. The prepump spot is located 4 mm below the pump/probe spin detection position as shown in the inset of Figure S7a. The main panel of Figure S7a shows the spin amplitude of the ν_1 = 9.48 GHz precession frequency signal at the spin detection position as a function of the prepump illumination time. Figure S7b shows several time-resolved ellipticity signals for the prepump illumination time from 0 to 50 min with an interval of 10 min. Due to the diffusion of the photocharged QDs generated by the prepump, the amplitude of the ν_1 spin signal increases with increasing prepump illumination time, and tends to level off after ~40 min prepump illumination.

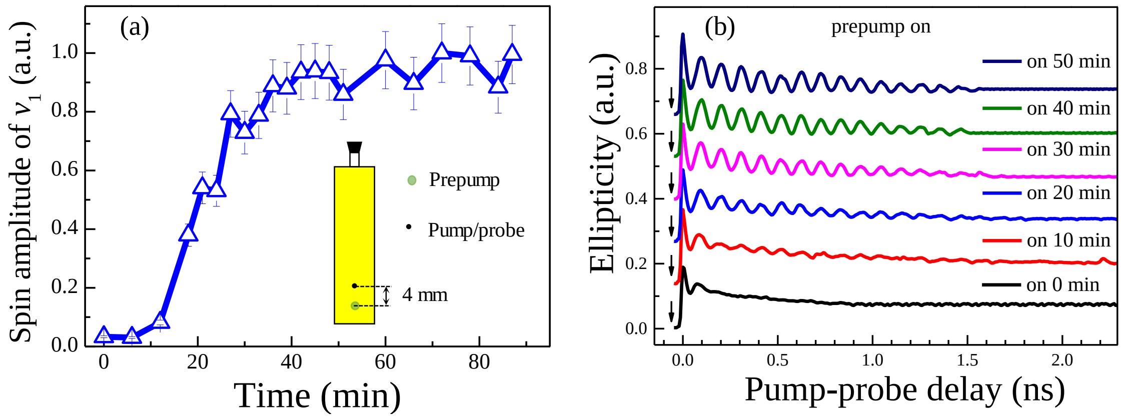

Figure S7. QD diffusion measurements. The QD size is 2.4 nm and R_{OT} = 30000. The sample is prepared under an air atmosphere. Magnetic field B = 0.43 T. The prepump is a broad-band femtosecond laser with a central wavelength of 515 nm and fluence is 500 μJ/cm^2. (a) ν_1 spin amplitude at the pump/probe spin detection position as a function of the prepump illumination time. Inset shows the laser spots and relative distance between the prepump and pump/probe beams. (b) The right panel shows typical time-resolved ellipticity signals for several prepump illumination times in the QD diffusion measurements. The black arrows denote the start point for counting the prepump-on time.

References

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