Supporting Information

Hyperfine-Induced Electron-Spin Dephasing in Negatively Charged Colloidal Quantum Dots: A Survey of Size Dependence

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1. Sample information

A series of octadecylamine-stabilized CdSe colloidal quantum dots (QDs) and octadecenoic-stabilized CdS colloidal QDs with different QD sizes in toluene solution are purchased from Hangzhou Najing Technology Co., Ltd. The initial concentrations of all samples are 5 mg/mL. Figure S1 (Figure S2) shows the transmission electron microscopy (TEM) image and particle size distribution of CdSe (CdS) QDs with different sizes. The left panel of Figures S1 and S2 denote the average diameter size of each sample. The hole acceptor $Li[Et_3BH]$ purchased from Sigma Aldrich, captures photoexcited holes and provides negatively photocharged QDs.[1] In a nitrogen-filled glove box, $Li[Et_3BH]$ is diluted to a certain concentration with toluene solution, and then mixed evenly with the as-grown QDs in an airtight cuvette. The molar ratio of $Li[Et_3BH]$ to QDs ranges from tens to hundreds, depending on the sample. The molar ratio of $Li[Et_3BH]$ to QDs is selected so as to get stable photocharging in each dependence measurement as described the main text, typically under the illumination of ambient room light and pump/probe laser pulses themselves. The final QD concentrations of all samples used in the spin dynamics measurements are kept the same at 2.5 mg/mL.

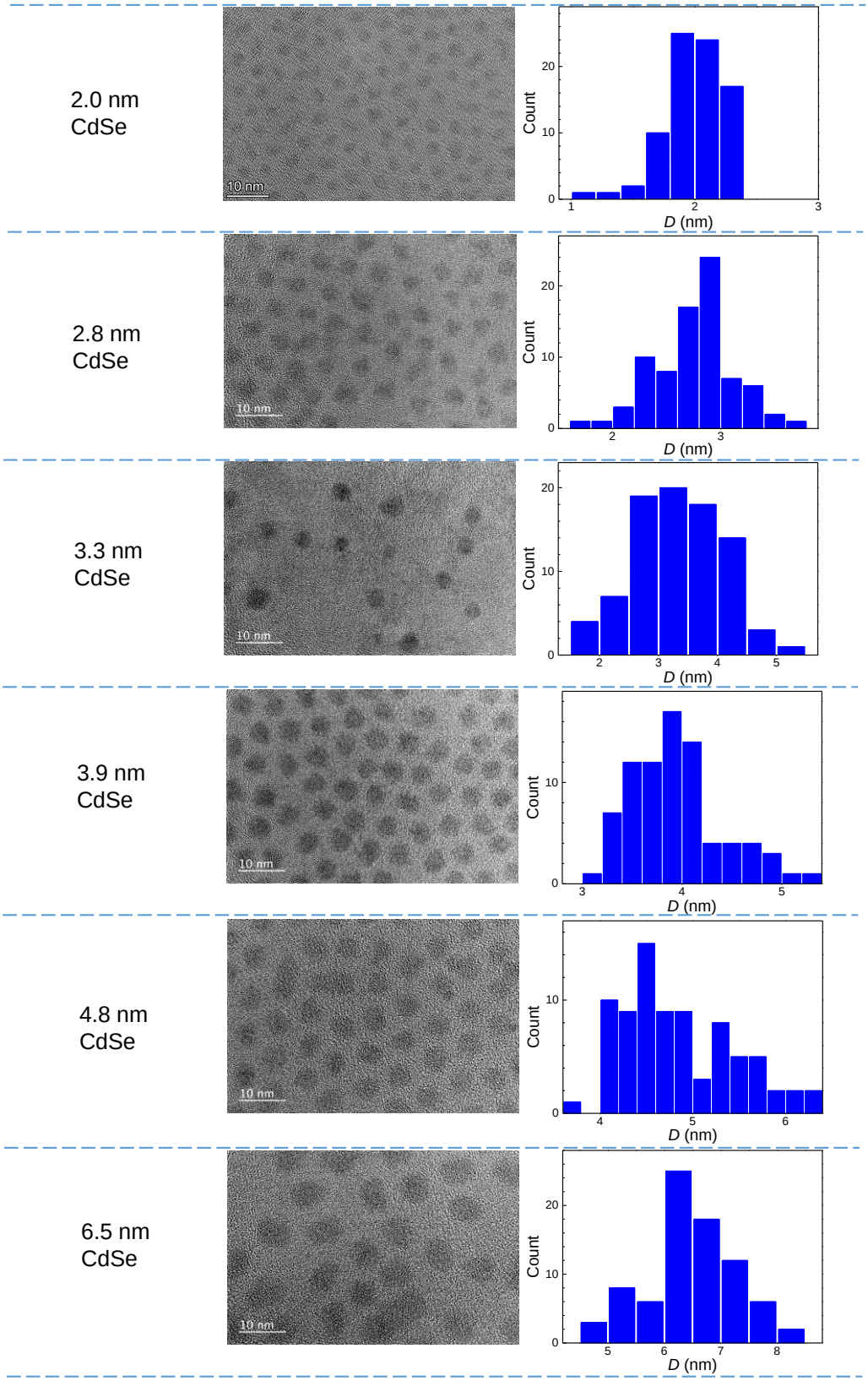

Figure S1. TEM image and particle size distribution of CdSe QDs with different sizes.

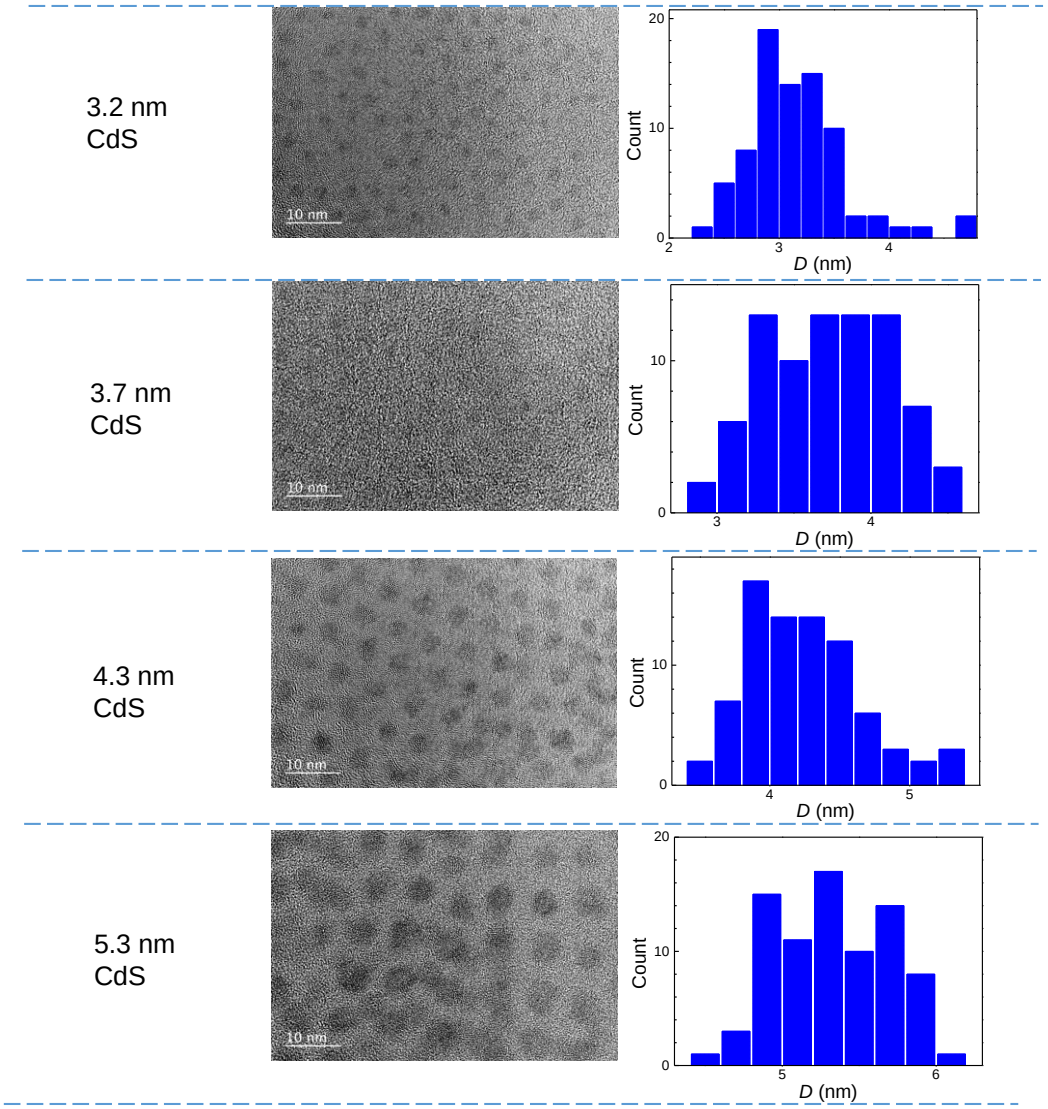

Figure S2. TEM image and particle size distribution of CdS QDs with different sizes.

2. Time-resolved ellipticity measurements

The laser system is based on a 1030 nm Yb-KGW femtosecond laser amplifier combined with an optical parametric amplifier (OPA). The wavelength-degenerate pump and probe laser pulses are emitted from OPA with a pulse duration of ~190 fs, a line width of ~109 cm^{-1} and a laser repetition rate of 50 kHz. The circularly polarized pump pulse generate spin polarization in the sample. The linearly polarize probe pulses becomes partially elliptically polarized after transmitting through the spin-polarized QDs, due to the absorption difference of left- and right-circularly polarized light. As shown in Figure S3, the transmitted probe light goes into a quarter waveplate, a Wollaston prism and a balanced photodetector for lock-in detection. The ellipticity is proportional to the intensity difference of left- and right-circularly polarized light components in the transmitted probe pulses,[2] which is converted to the signals of the balanced photodetector after transmitting through the optical polarization bridge combined by the quarter waveplate and the Wollaston prism. The spin dynamics is monitored by the ellipticity change of the linearly polarized probe pulse as a function of pump−probe time delay which is adjusted by a mechanical delay line. The pump/probe wavelengths are set at the point where there are strongest ellipticity signals for each sample, corresponding electron-to-trion resonant excitation (typically at the wavelength a bit redshift to the first exciton absorption peak). Transverse magnetic fields $B_{\perp}$ up to 700 mT and longitudinal magnetic fields $B_{\parallel}$ up to 50 mT are provided by an electromagnet with and without iron poles, respectively. All measurements are performed at room temperature.

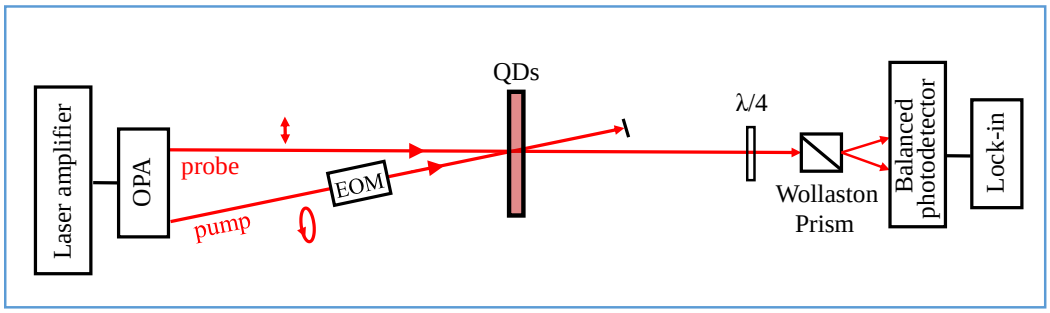

Figure S3. Schematic for time-resolved ellipticity measurements.

3. Spin excitation scheme for negatively charged QDs

Figure S4 shows the scheme of spin excitation in negatively charged QDs. Without the pump pulses for spin excitation, the photodoped electron has equal possibilities for spin-up ($+1/2$) and spin-down ($-1/2$) states. Under σ^+ circularly polarized light excitation, $+1/2$ electron will be excited to $+3/2$ trion whose spin is defined by the hole spin and relaxes fast, generating a net spin-down polarization in the photodoped electron. Likewise, σ^- excitation will generate a net spin-up polarization in the photodoped electron.

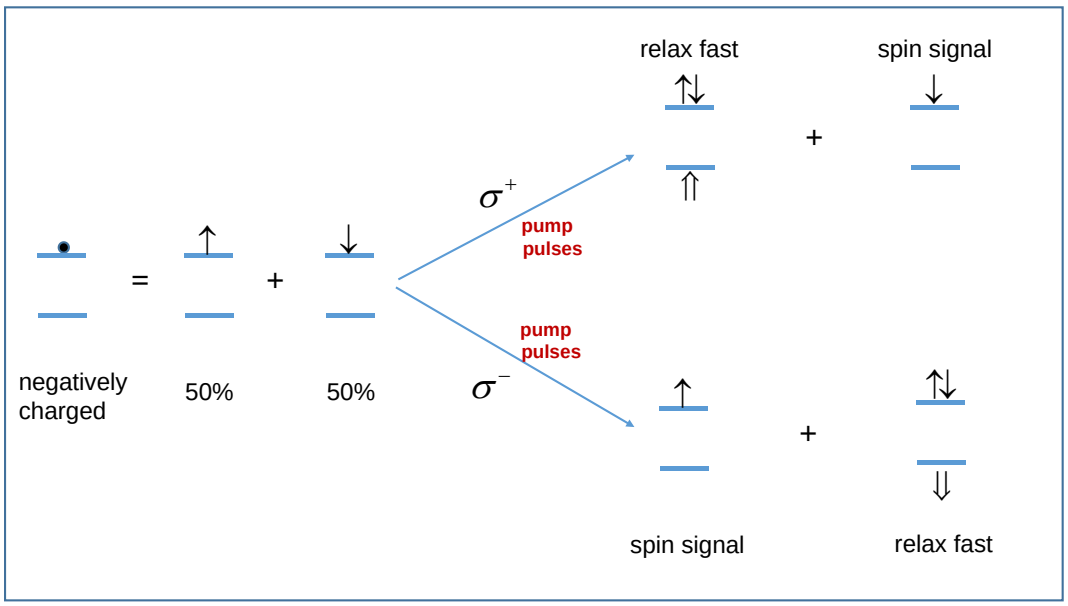

Figure S4. Scheme of spin excitation in negatively charged QDs. $\uparrow$ and $\downarrow$ are $+1/2$ and $-1/2$ electron spin, respectively. $\Uparrow$ and $\Downarrow$ are $+3/2$ and $-3/2$ hole spin, respectively.

4. Transverse magnetic field dependence of spin dephasing rate

The transverse magnetic field dependence of spin dephasing time of all samples can be described by[3]

$$\frac{1}{T_2^*(B_\perp)} = \frac{1}{T_2^*(0)} + \frac{\Delta g \mu_B B_\perp}{\hbar} \qquad \text{(S1)}$$

Where Δg is the spread of the g factor for the optically excited spin ensembles. The spin dephasing rates are linearly dependent on the transverse magnetic field as shown in Figure S5. The Δg value can be evaluated from the slope in the linear fit.

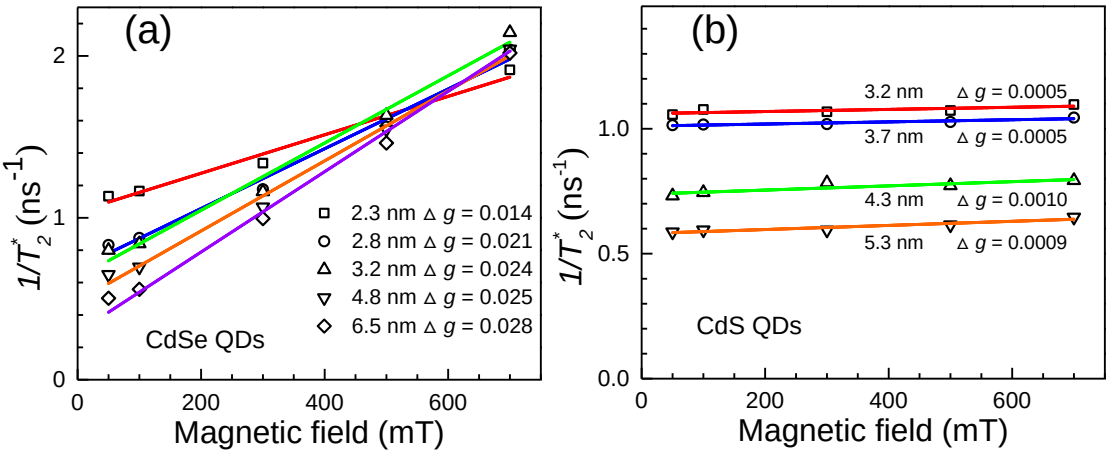

Figure S5. (a) The transverse magnetic field dependence of electron spin dephasing rates in (a) CdSe and (b) CdS QDs with the hole acceptor $Li[Et_3BH]$. The black geometry is the experimental data, and the lines of other colors are liner fits.

5. Calculation of hyperfine-induced electron spin dephasing time

In the absence of external magnetic field, the electron spin dephasing time induced by the hyperfine interactions can be described by[3]

$$T_2^*(0) = \hbar \sqrt{\frac{3N_L}{2\sum_j I_j(I_j+1)A_j^2 y_j}} \qquad \text{(S2)}$$

Here the sum of all types of nuclear isotopes in the QDs, N_L is the number of nuclei in the QD volume, and I_j is the nuclear spin. A_j is the hyperfine constant, and y_j is the probability to find

the particular type of nuclear isotope, i.e. the isotope abundance. The number of nuclei can be given by

$$N_L = \frac{nV_L}{v_0} \qquad \text{(S3)}$$

Where n is the number of nuclei of the unit cell, $V_L = \frac{\pi D^3}{6}$ is the QD volume, and v_0 is the unit cell volume. CdSe QDs have a wurtzite crystal structure where each hexagonal cell contains six Cd-Se molecules, i.e., twelve atoms. Then the volume of the cell is $v_0 = \frac{3\sqrt{3}}{2}a^2c$, where the lattice constant $a = 0.4300$ nm and $c = 0.7011$ nm .[4] Thus, $T_2^*(0) = 0.188D^{3/2}$ ns can be estimated for CdSe QDs by eq S2. CdS QDs have a zinc blende crystal structure where each cubic cell contains four Cd-S molecules, i.e., eight atoms. The unit cell volume $v_0 = a^3$ and the lattice constant $a = 0.5825$ nm .[4] Thus $T_2^*(0) = 0.223D^{3/2}$ ns can be obtained for CdS QDs using eq S2. In the calculation for CdS QDs, we neglected the influence of S atoms due to the very low natural abundance with nonzero nuclear spins (only 0.76% for ^{33}S isotopes).

Table S1. Parameters of Nuclear Isotopes with Nonzero Spin Isotopes Used for the Calculation of Electron Spin Dephasing Times

species	I_j	Abundance (%)	A_j (μeV)
^{111}Cd	1/2	12.8	37.4[a]
^{113}Cd	1/2	12.3	39.1[a]
^{77}Se	1/2	7.58	33.6[a]
^{33}S	3/2	0.76	NA

[a]From ref 3.

6. Comparison of electron spin dynamics between QDs with different hole acceptors

A test has been made in 5.3 nm CdS QDs by replacing $Li[Et_3BH]$ with another hole acceptor 1-octanethiol. The addition of 1-octanethiol may also generates long-lived negative photocharging in N_2 atmosphere. Different hole acceptors $Li[Et_3BH]$ and 1-octanethiol show almost the same dynamic behavior (Figure S6), indicating that surface conditions have no strong influence on the spin dynamics of the electron confined in the middle of the QD. The surface conditions include dangling bond spins and the nuclei in the surface ligands or the surrounding media. However, the surface conditions might affect the spin dynamics of the electron in the vicinity of the surface,[5] which goes beyond the scope of the present paper.

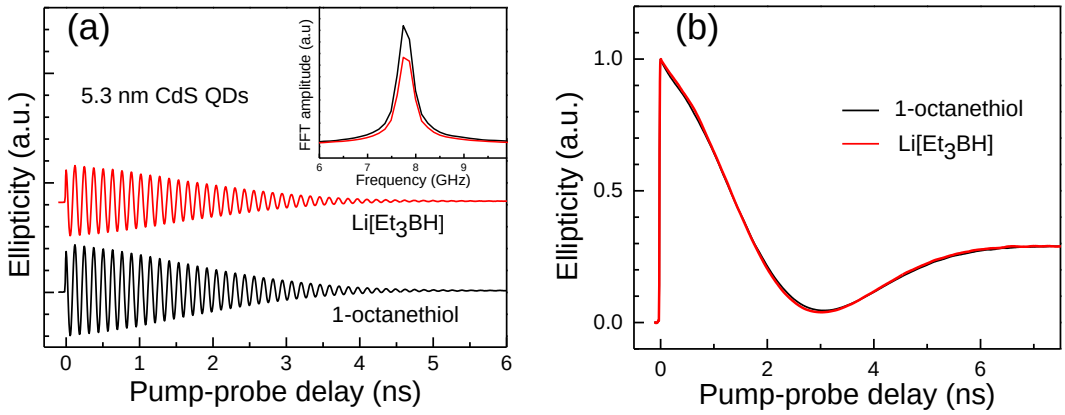

Figure S6. Comparison of electron spin dynamics between QDs with different hole acceptors $Li[Et_3BH]$ and 1-octanethiol. The molar ratios of $Li[Et_3BH]$ and 1-octanethiol to QDs is 10 and 100, respectively. (a) B = 300 mT, showing the same Larmor precession frequency. (b) B = 0 mT where the normalized ellipticity signals are almost identical, indicating that the hyperfine-induced electron spin dephasing is not affected by the surface conditions.

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