Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Detecting Electronic Structure Evolution of Semiconductor Nanocrystals by Magnetic Circular Dichroism

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Part I. Experiment and characterization

Chemicals. All reactants and solvents were used without further purification. Trioctylphosphine oxide (TOPO, 90%), trioctylphosphine (TOP, 90%), tributylphosphine (TBP, 90%), hexadecylamine, octadecylamine, stearic acid (TA, 98%), CdO (98%), and Se powder (>99.5%) were purchased from Aldrich Company. Tetradecylphosphonic acid (TDPA, >99%), octadecylphosphonic acid (ODPA, >99%), hexylphosphonic acid (HPA, >99%), tetramethylammonium hydroxide (TMAH, 25% w/waq. soln.), L-cysteine hydrochloride monohydrate (99%) and D-cysteine hydrochloride monohydrate (99%) were bought from TCI Company. Methanol, toluene, hexane, dodecylamine, chloroform and acetone were obtained from VWR Company.

1.1 Synthesis and characterization of CdSe NCs.

CdSe QDs:[1] 0.0254 g (0.2 mmol) CdO and 0.2280 g (0.8 mmol) TA were loaded into a 50 mL three-neck flask and heated to 150°C under Ar flow. After CdO was completely dissolved, the mixture was allowed to cool to room temperature. TOPO and hexadecylamine, 3.88 g of each, were added to the flask, and the mixture was heated to 320°C under Ar flow to form an optically clear solution. At this temperature, the solution of 0.158 g (2 mmol) Se dissolved in 0.476 g (2.36 mmol) TBP and 3.362 g dioctylamine was quickly injected into the reaction flask. After injection, the temperature was set at 250°C for growth of QDs.

Optical active L- or D-cysteine stabilized CdSe QRs:

Synthesis of CdSe QRs with different aspect ratio (AR):[2, 3]

AR 1.7: 0.0514 g CdO (0.4 mmol), 0.09 g TDPA (0.32 mmol), and 3 g TOPO were loaded into a 25 mL flask. The mixture was heated to 360°C under Ar flow, and CdO was then dissolved in TDPA and TOPO. Se solution (0.0411 g Se powder dissolved in 1.5 g TOP, operated in glovebox) was injected when the temperature of the solution was cooled to 350°C. After injection, QRs grew at 280°C to reach the desired size.

AR 1.9: 0.0257 g CdO (0.2 mmol), 0.1340 g ODPA (0.4 mmol) and 2.8403 g TOPO were loaded into a 25 mL flask. The mixture was heated to 340°C under Ar flow. Then, CdO was dissolved in ODPA and TOPO (about 1.5 h). Se solution (0.079 g Se powder dissolved in 1 g TOP, operated in glovebox) was injected when the temperature of the solution was cooled to 320°C. After injection, QRs grew at 250°C to reach the desired size.

AR 2.7: 0.0514 g CdO (0.4 mmol), 0.2679 g ODPA (0.8 mmol) and 2.681 g TOPO were loaded into a 25 mL flask. The mixture was heated to 340°C under Ar flow. Then, CdO was dissolved in ODPA and TOPO. Se solution (0.0503 g Se powder dissolved in 2 g TOP) was injected when the temperature of the solution was cooled to 320°C. After injection, QRs grew at 260°C to reach the desired size.

AR 4.2: 0.0514 g CdO (0.4 mmol), 0.2232 g TDPA (0.8 mmol) and 2.7768 g TOPO were loaded into a 25 mL flask. The mixture was heated to 340°C under Ar flow. Then, CdO was dissolved in TDPA and TOPO. Se stock solution (0.0411 g Se powder dissolved in 1.5 g TOP) was injected after the temperature of the solution was cooled to 320^{o}C. After injection, QRs grew at 250^{o}C to reach the desired size.

AR 7.3: 0.0514 g CdO (0.4 mmol), 0.1674 g TDPA (0.6 mmol), 0.0332 g HPA (0.2 mmol) and 2.748 g TOPO were loaded into a 25 mL flask. The mixture was heated to 340^{o}C under Ar flow. Then, and CdO was dissolved in TDPA and TOPO. Se solution (0.0504 g Se powder dissolved in 1.5 g TOP) was injected when the temperature of the solution was cooled to 320^{o}C. After injection, QRs grew at 260^{o}C to reach the desired size.

1.2 Instrument and characterization

Transmission electron microscopy (TEM) images were carried out using Tecnai G2 20 S-TWIN at 200 kV. MCD spectra were recorded by a Jasco J-1500 spectropolarimeter in aqueous solution under the magnetic field with different intensity of 0.4T, 0.7T, 1.0T, 1.3T and 1.6T. A 1.5 mL portion of each sample was infused into a 0.5 cm quartz cell and measured at the scan speed of 300 nm/min with a bandwidth of 4 nm. UV-Vis absorption measurements were carried out using a Hitachi U-3010 UV-Vis spectrometer.

Part II: Supporting figures and tables

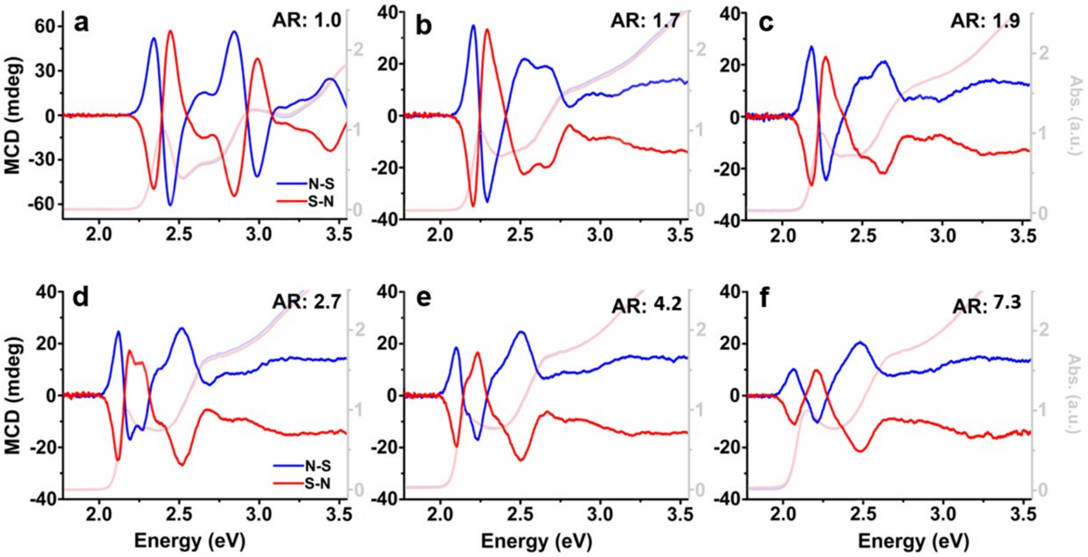

Figure S1. MCD and absorption spectra of CdSe NCs with different AR of 1.0 (a), 1.7 (b), 1.9 (c), 2.7 (d), 4.2 (e) and 7.3 (f). Blue curves are measured by applying the magnetic field along the light propagation from north to south (N-S), whereas the red curves are recorded by applying the magnetic field along the light transmission from south to north (S-N).

Table S1. Peak intensity in MCD spectra of CdSe NCs appeared in Figure 1 with magnetic strength of 1.6T.*

	AR 1.0	AR 1.7	AR 1.9	AR 2.7	AR 4.2	AR 7.3
Peak *a*	52.04	34.75	27.10	24.69	18.07	10.26
Peak *b*	-60.70	-33.34	-24.39	-17.07	-7.33	----**
Peak *c*	----	----	----	-13.32	-17.12	-10.46
Peak *d*	15.40	21.97	15.08	10.34	----	----
Peak *e*	56.50	18.77	21.28	25.96	24.39	13.86
Peak *f*	-41.29	3.36	6.01	4.00	6.71	----
b:a	-1.17	-0.96	-0.90	-0.69	-0.41	----
c:a	----	----	----	-0.54	-0.95	-1.02
d:a	0.30	0.63	0.56	0.42	----	----
e:a	1.09	0.54	0.79	1.05	1.35	1.35
f:a	-0.79	0.10	0.22	0.16	0.37	----

*: The MCD spectra of all CdSe NCs are detected when the peak intensity of the first excitonic transitions in UV-Vis spectra is controlled to 1.0.

**: inconspicuous peak.

Table S2. Peak intensity of the fitted MCD spectra appeared in Figure 2.

	AR 1.0	AR 1.7	AR 1.9	AR 2.7	AR 4.2	AR 7.3
Peak α	-6.85	3.87	3.43	6.18	9.14	4.19
Peak β	0	-3.53	-3.16	-7.42	-14.73	-6.32
Peak I_a	139.63	67.23	60.43	37.85	31.43	8.46
Peak I_b	-137.22	-69.93	-65.08	-40.08	-32.99	-6.54
Peak II_a	-11.95	-18.78	-10.82	-7.31	-5.74	-3.64
Peak II_b	15.25	20.68	10.64	6.46	5.46	3.74
Peak III_a	56.91	17.82	20.82	25.38	24.22	20.39
Peak III_b	-45.40	3.36	6.01	4.00	6.71	----
α:I_a	-0.049	0.057	0.057	0.16	0.29	0.50
β:I_a	0	-0.052	-0.052	-0.20	-0.47	-0.75

Table S3. Zeeman splitting of the first exciton of CdSe NCs obtained from MCD spectra and Equation 1-2.

	σ (eV)	θ (mdeg)	ΔE_{Zeeman}
AR: 1.0	0.14	52	0.44
AR: 1.7	0.11	35	0.23
AR: 1.9	0.12	27	0.20
AR: 2.7	0.10	24	0.15
AR: 4.2	0.10	19	0.12
AR: 7.3	0.15	10	0.09

Part III: Introduction of the theory of MCD spectrum

The theory to the analysis of MCD spectrum is based on the standard semiclassical radiation theory. Hence, the atom is treated quantum-mechanically in its interaction with a classical electromagnetic field. The basic problem would be the light induced electronic transition under magnetic field. The subjects concerned would be the transition of an A state to a J state under the first order perturbation of a state of K. Due to the complicated equation of MCD, the equation is always simplified by the sum of the segment of three terms (the famous $A, B\ and\ C$ terms, Figure S2). Every term reflects different information of electron transition states. The basic equations are as follows:[4]

$$\Delta A = \gamma\mu_B B\left[A_1\left(-\frac{df(E)}{dE}\right) + \left(B_0 + \frac{C_0}{k_B T}\right)f(E)\right] \qquad (S1)$$

And,

$$A = \gamma D_0 f(E) \qquad (S2)$$

where, ΔA is the different absorption of LCP and RCP. A is the absorption. A_1, $B_0\ and\ C_0$ parameters define the MCD $A, B\ and\ C$ terms, respectively. D_0 is the dipole strength parameter, and γ is a constent, the value dependent on the units chosen. In Gaussian units and the electric dipole matrix elements are expressed in Debye units, γ equals approximately to 326.6cl (c is the concentration of solution; l is the path the light past the samples). μ_B is the Bohr magneton, B is the magnetic field, k_B is the Boltzmann constant, T is the temperature, E is the energy. $f(E)$ is the lineshape function, and its definition is as follows:

$$f(E) = \left(\frac{1}{N_G}\right)\sum_g N_g \sum_j |\langle g\,|\,j\rangle|^2 \rho_{gj}(E) \qquad (S3)$$

Where, $|g\rangle$ and $|j\rangle$ are the vibrational functions, and $N_G = \sum_g N_{A\alpha g} = \sum_g N_g$:

$$A_1 = \left(\frac{1}{|A|}\right)\sum_{\alpha\lambda}(\langle J\lambda\,|\,L_z + 2S_z\,|\,J\lambda\rangle - \langle A\alpha\,|\,L_z + 2S_z\,|\,A\alpha\rangle) \times (|\langle A\alpha\,|\,m_{-1}\,|\,J\lambda\rangle|^2 - |\langle$$

$$B_0 = \left(\frac{1}{|A|}\right)Re\sum_{\alpha\lambda}[\sum_{K \neq J\kappa} 1/(W_K - W_J)(\langle J\lambda\,|\,L_z + 2S_z\,|\,K\kappa\rangle \times (\langle A\alpha\,|\,m_{-1}\,|\,J\lambda\rangle\langle K\kappa\,|\,m$$
$$\langle K\kappa\,|\,m_{-1}\,|\,A\alpha\rangle) + \sum_{K \neq A,\kappa} 1/(W_K - W_A)(\langle K\kappa\,|\,L_z + 2S_z\,|\,A\alpha\rangle$$
$$\times (\langle A\alpha\,|\,m_{-1}\,|\,J\lambda\rangle\langle J\lambda\,|\,m_{+1}\,|\,K\kappa\rangle - \langle A\alpha\,|\,m_{+1}\,|\,J\lambda\rangle\langle J\lambda\,|\,m_{-1}\,|\,K\kappa\rangle)] \qquad (S5$$

$$C_0 = -\left(\frac{1}{|A|}\right)\sum_{\alpha\lambda}\langle A\alpha\,|\,L_z + 2S_z\,|\,A\alpha\rangle \times (|\langle A\alpha\,|\,m_{-1}\,|\,J\lambda\rangle|^2 - |\langle A\alpha\,|\,m_{+1}\,|\,J\lambda\rangle|^2) \qquad (S6)$$

$$D_0 = \left(\frac{1}{(2|A|)}\right)\sum_{\alpha\lambda}(|\langle A\alpha\,|\,m_{-1}\,|\,J\lambda\rangle|^2 + |\langle A\alpha\,|\,m_{+1}\,|\,J\lambda\rangle|^2) \qquad (S7)$$

where, $|A|$ is the electronic degeneracy of the ground state A. The subscript α, λ and κ are the components of the states A, J and K, respectively. $A\alpha$, $J\lambda$ and $K\kappa$ serve as group-theoretic irreducible representation labels; the first and second symbols respectively designate the irreducible representation and component thereof. Thus states belonging to a given degenerate set (for example, the $|A\alpha\rangle$ set) have the same irreducible presentation label (*A*), but differ in component label (α). W is the energy of the state.

For the component transition $A\alpha \rightarrow J\lambda$ to contribute to A_1 it must absorb left circular polarized (LCP) light and right circular polarized (rcp) light in different extent, and the two states must Zeeman-shift by different amounts. A_1 is obtained by summing over all possible transitions between Zeeman components of the two electronic states. Note that A_1 must be zero for a transition between two nondegenerate states. This is because $\langle K \,|\, \mu_z \,|\, K \rangle = 0$ if *K* is nondegenerate.

C_0 is dependent on both field-induced population shifts among Zeeman components of the ground state and differentical absorption of lcp and rcp light. C_0 is zero if the ground state is nondegenerate, since $\langle A \,|\, \mu_z \,|\, A \rangle = 0$, as discussed with respect to A_1 above. If the excited state is nondegenerate, $C_0 = A_1$.

The B_0 term arises because the magnetic field mixes the (zero-field) wave-functions of the system. In general B_0 calculations are feasible only if very few mixing states need to be considered. This is typically the case that a state is close in energy to either A or J and therefore be assumed to dominate the mixing process because of the small energy denominator involved.

All the theoretic representation retains the formation from the classic book from Suan B. Piepho and Paul N. Schatz[4].

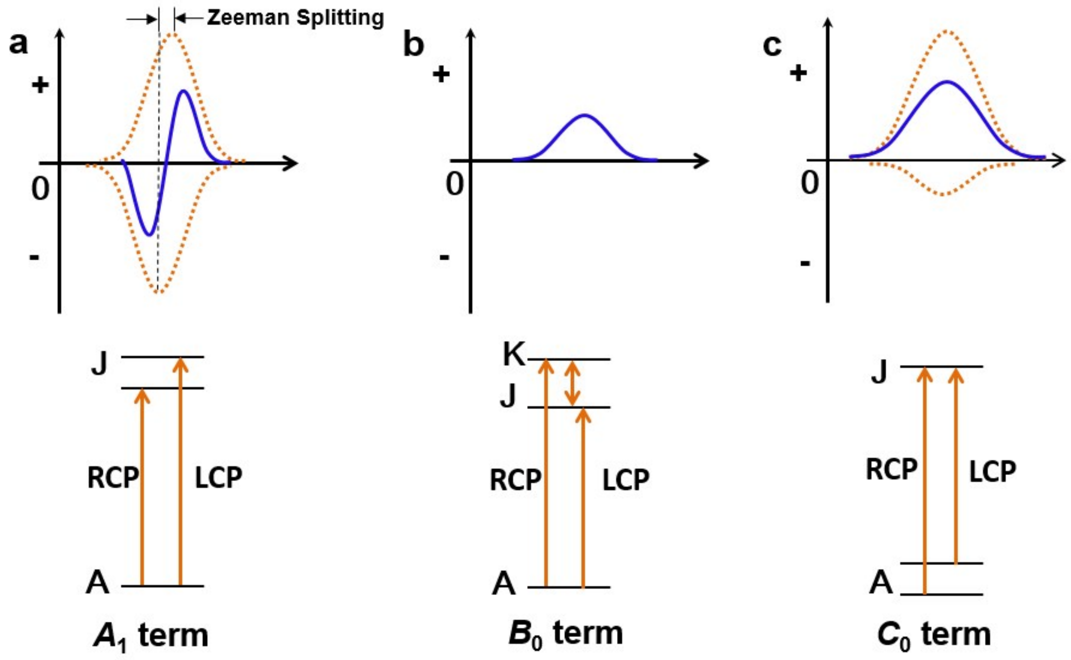

Figure S2. Simplified diagram of *A* (a), *B* (b) and *C* (c) terms in MCD.

Part IV: k•p method for *ellipsoid*–shape quantum rods

For quantum ellipsoidal rods, we write the k•p Hamiltonian as follows:

$$H_{e0} = \frac{p^2}{2m_a} - \frac{1}{2m_b}\sqrt{\frac{2}{3}}P_0, \qquad (S8)$$

$$H_{h0} = \frac{1}{2m_0}\begin{pmatrix} P_1 & S & T \\ S^* & P_3 & S \\ T^* & S^* & P_1 \end{pmatrix} \qquad (S9)$$

where the P_0, P_1, P_3, S, T terms are combinations of p^2 and p's second tensor, m_a and m_b are effective mass parameters. The Bloch state of equation S8 is mainly the Cd-*s* state while the Bloch state of equation S9 is mainly the Se-p states. The spin-orbit coupling effect is included in the calculation by adding the following term:

$$H_{so} = \begin{vmatrix} -\lambda & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{2}\lambda & 0 & 0 \\ 0 & 0 & \lambda & 0 & -\sqrt{2}\lambda & 0 \\ 0 & \sqrt{2}\lambda & 0 & \lambda & 0 & 0 \\ 0 & 0 & -\sqrt{2}\lambda & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\lambda \end{vmatrix} \qquad (S10)$$

where λ = -139.3 meV for CdSe. In the presence of magnetic field, the momentum operator changes into:

$$p \rightarrow p + eA \qquad (S11)$$

and for magnetic field along z direction with magnitude B_z, in the symmetric gauge,

$$A = \left(-\frac{1}{2}B_z y, \frac{1}{2}B_z x, 0 \right) \qquad (S12)$$

For quantum spheres, the wave function basis set can be given in Bessel function and spherical harmonics. For quantum ellipsoidal rods, we apply a coordination transformation to the form of Hamiltonian as well as basis set, *i.e.* $z' = \frac{z}{e}$ (e is the aspect ratio).

The calculated electronic structure of CdSe quantum ellipsoidal rods with diameter of 3.0 nm for B_z = 0 T is shown in Figure S3. Due to the errors from the assumption of infinitely high potential barrier surrounding the QRs, the k•p method could not accurately predict the relative positions of the energy levels. Therefore, we will focus on the effect of the magnetic field (less affected by the infinitely high potential barrier) on the first valence state and the first conduction state that form the $1S_{3/2}1S_e$ exciton.

The relative polarization of the electronic structures at B_z = 1.6 T in Figure 6a is calculated as follows:

$$P = \frac{(p_+^{h1} - p_-^{h1})/(p_+^{h1} + p_-^{h1}) - (p_-^{h2} - p_+^{h2})/(p_-^{h2} + p_+^{h2})}{(p_+^{h1} - p_-^{h1})/(p_+^{h1} + p_-^{h1}) + (p_-^{h2} - p_+^{h2})/(p_-^{h2} + p_+^{h2})}, \qquad (S13)$$

with p_+^{hi} (p_-^{hi}) being the composition of p_+ (p_-) state in the *hi* hole state (*i* = 1 or 2) split under magnetic field.

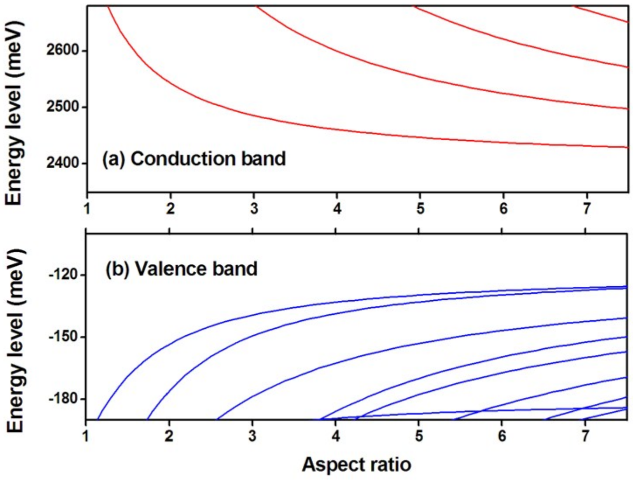

Figure S3. Electronic structure of CdSe quantum rods with diameter of 3.0 nm in absence of magnetic field.

References

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