Supplementary Material for

Layer-dependent optical and dielectric properties of CdSe semiconductor colloidal quantum wells characterized by spectroscopic ellipsometry

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1. Preparation of CdSe CQWs

1.1 Reagents.

Cadmium nitrate tetrahydrate (Macklin, 99%), sodium myristate (Macklin, > 98%), selenium powder (Aldrich, 99.5%), $NaBH_4$ (Sigma, > 98%), Tributyl phosphine (TBP) (TCI, > 95%), Tri-n-octylphosphine (Sigma-Aldrich, 97%), cadmium acetate dihydrate $(Cd(Ac)_2 \cdot 2H_2O)$ (Aladdin, 99.99%), Oleylamine (OLA) (Aladdin, 80−90%), 1-octadecene (Macklin, > 90%) (ODE), oleic acid (Macklin, 90%), N-Methylformamide (NMF) (TCI, > 99%), Acetonitrile (Aladdin, > 99.8%). Toluene (99.9%), ethanol (99.5%), n-hexane (> 99%), and acetone (> 99%)
All chemicals were used without further purification.

1.2 Synthesis of precursor

Synthesis of Cadmium Myristate $(Cd(myr)_2)$: 3.13 g of sodium myristate and 1.23 g of cadmium nitrate were dissolved in 250 mL and 40 mL of methanol, respectively. Stir the solution separately on a test bench overnight at room temperature. Then, the cadmium nitrate solution was gradually added to the sodium myristate solution and stirred continuously until the thick state. The cadmium myristate was then filtered and washed with methanol several times. Finally, the solvent was drained in the glove box and the cadmium myristate was bottled.
A 1M solution of Selenium in TOP (TOP-Se) was utilized as the source of Selenium. This solution was prepared by dissolving 2 mmol of elemental Selenium in 1 liter of TOP with a concentration of 1 M.

A 0.3 mM solution of Selenium in ODE (ODE-Se) was employed as the source of Selenium. To prepare this solution, 12 g of selenium powder and 10 mL of ODE were dissolved in a 25 mL three-necked flask under high temperature conditions. Initially, the temperature was gradually raised to 100 °C, and a vacuum was applied for 1 hour. Subsequently, the temperature was gradually increased to 240 °C. When the selenium powder had completely dissolved, the solution was cooled to room temperature and then transferred into a bottle for storage.

The sodium selenide ($SeNa_2$) reducing agent was prepared as follows: 40 mg of $NaBH_4$ was dissolved in 0.5 mL of NMF and 0.5 mL of ethanol in an empty container. Subsequently, 24 mg of selenium powder was added to the mixture and stirred vigorously. After 10 minutes, the mixture should become a colorless solution with no remaining bubbles. The resulting $SeNa_2$ solution can be used for atomic layer deposition in colloids and should be handled and stored in a vacuum tank.

1.3 Synthesis of 2 ML CdSe CQWs

A mixture of 860 mg of cadmium acetate, 1 mL of oleic acid, and 60 mL of ODE was degassed at 80 °C for 1 hour. Subsequently, the mixture was heated to 120 °C under an argon atmosphere, and 2 mL of TOP-Se (1 M) was rapidly added. The reaction was maintained at 120 °C for 10 minutes. At this temperature, 2 mL of TOP-Se (0.1 M) was injected at a rate of 1 mL/h. Finally, the reaction was allowed to cool to room temperature, signifying its completion.

1.4 Synthesis of 3 ML CdSe CQWs

A mixture of 240 mg of cadmium acetate and 15 mL of ODE 25 mL was degassed at 100 °C for 60 minutes until no bubbles are generated during agitation. Next, raise the temperature to 190 °C under an argon atmosphere. At this temperature, inject a mixture of 200 μL of OA, 400 μL of TOP-Se (1 M), and 3.5 mL of ODE at a rate of 5 mL/h to initiate growth. Finally, the reaction was allowed to cool to room temperature, signifying its completion.

1.5 Synthesis of 4 ML CdSe CQWs

A mixture of 340 mg of $Cd(myr)_2$, 48 mg of Se, and 30 mL of ODE was degassed at 100 °C for 30 minutes until no bubbles are generated during agitation. Next, raise the temperature to 240 °C under an argon atmosphere. When the mixture reached 205 °C, 120 mg of $Cd(Ac)_2·2H_2O$ was quickly added. After 5 minutes, the reaction was stopped. 1 mL of OA was added at approximately 180 °C. Finally, the reaction was allowed to cool to room temperature, signifying its completion.

1.6 Synthesis of 5 ML CdSe CQWs

A mixture of 170 mg of $Cd(myr)_2$ and 14 mL of ODE was degassed at 100 °C for 1

hour until no bubbles are generated during agitation. Next, raise the temperature to 250 °C under an argon atmosphere. Quickly inject 1 mL of ODE-Se (0.3 mM) into the mixture. After 1 minute, add 120 mg (0.45 mM) of $Cd(OAc)_2·2H_2O$. After 10 minutes, the reaction was stopped. Finally, inject 1 mL of OA into the solution at 180 °C, and cool the reaction mixture to room temperature.

1.7 Synthesis of 6 ML and 7 ML CdSe CQWs

2 mL of NMF, 40 μL of TBP, 20 μL of ethanol, and 500 μL of $SeNa_2$ were added to a 4 ML (5 ML) CdSe CQWs to prepare 6 ML (7 ML) CdSe CQWs. A color change from yellow to orange (orange-red) was observed when the solution was vigorously shaken to transfer it completely from n-hexane to NMF. The solution was then removed from the glove box, and the upper n-hexane layer was decanted. The CdSe CQWs in NMF were initially washed with a mixture of 3 mL of n-hexane, 20 μL of TBP, and 20 μL of ethanol, followed by a wash with a mixture of 3 mL of n-hexane and 20 μL of ethanol. Afterward, 2 mL of acetonitrile and 8 mL of toluene were added, and the mixture was centrifuged at 6500 rpm for 3 minutes. The resulting solid was then dissolved in 1.5 mL of NMF, and 600 μL of $Cd(OAc)_2·2H_2O$ solution was added. The solution was vigorously shaken until it turned red (dark red). Subsequently, the CQWs were transferred back to n-hexane using 100 μL of OLA and 50 μL of OA. Finally, 4 ML (5 ML) of CdSe CQWs were precipitated and dispersed in 0.5 mL of n-hexane. To improve the crystallinity of the CQWs, a mixture of 15 mL of ODE, 150 mg of $Cd(Ac)_2·2H_2O$, 140 μL of OA, 100 μL of TBP, and 0.5 mL of the 4 ML (5 ML) CdSe CQWs solution was prepared in a 25 mL three-necked flask and vacuumed at room temperature for 30 minutes. The upper n-hexane layer was then removed. The mixture was heated at 230 °C for 25 minutes under an argon flow until the optical properties were restored. Finally, 6 ML (7 ML) of CdSe CQWs were precipitated with ethanol and dispersed in 10 mL of n-hexane.

1.8 Purification of synthesized samples

The heating jacket is removed and the reaction is quenched. When the solution reached room temperature, a mixture of n-hexane/ethanol = 3:1 was added to separate CdSe CQWs from the CdSe cube and spherical nanoparticles. Then, the mixed solution was centrifuged at 6500 rpm for 5 minutes, most of the supernatant solution was discarded, and the precipitated CdSe CQWs was dispersed in 5mL n-hexane for preservation.

1.9 Preparation of the CdSe CQWs film

First, the quartz substrate is cleaned: the 1 cm×1 cm square substrate is placed in a beaker, ultrasonic for 5 minutes in acetone and ethanol respectively, and then plasma cleaning is carried out. After the CdSe CQWs solution is diluted that displays an O.D.

of 0.1 at the first exciton peak. Spin 200 μL CdSe CQWs onto the substrate (1500 rpm, 30 s).

2. Characterization method

2.1 Atomic force microscopy

The surface morphology, roughness, and thickness of the CdSe films were evaluated using atomic force microscopy (AFM, HORIBA France SAS) in non-contact (AC) mode. Scans were typically performed at a scan rate of 0.3 Hz within an imaging range of 20 μm × 20 μm.
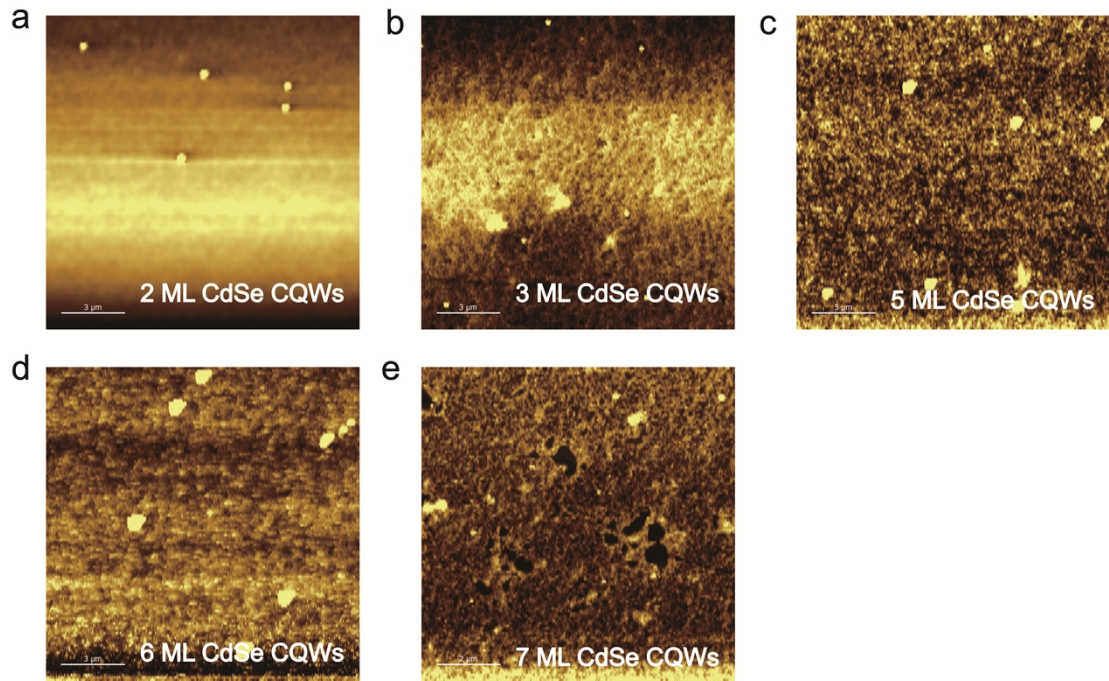

Fig. S1. (Color online) The AFM images of (a) 2 ML CdSe CQW films, (b) 3 ML CdSe CQW films, (c) 5 ML CdSe CQW films, (d) 6 ML CdSe CQW films and (e) 7 ML CdSe films CdSe CQW films. Scale bar: 3 μm.

2.2 X-ray diffraction

The lattice structure of CdSe CQWs films was determined using X-ray diffraction (XRD) analysis performed on a Rigaku Ultima IV instrument. The XRD measurements were conducted using a Cu Kα radiation source with a wavelength of 1.5418 Å. The X-ray source operated at an energy of 40 kV and a current of 40 mA.

The crystallite size can aslo be obtained by utilizing Scherrer formula, which involves substituting the full-width-half-maximum (FWHM) and position of the diffraction peaks obtained from X-ray diffraction (XRD) analysis. The formula is presented below:

$$D = \frac{K\gamma}{B cos\theta}, \tag{1}$$

D, *K*, *B*, *θ* are the crystallite size, Scherrer constant (0.89), FWHM and Bragg angle of the measured sample. γ is the X-ray wavelength, which is taken as 1.5418 Å in this work.

Table S1. Peak positions, calculated lattice constants and crystallite size for CdSe CQWs films gained from XRD.

Sample	2θ in (111) plane (°)	Lattice constant (Å)	FWHM (degree)	Crystallite size (nm)
2 ML CdSe CQW	23.86	6.125	2.5119	0.5586
3 ML CdSe CQW	24.64	6.116	2.5084	0.5599
4 ML CdSe CQW	24.88	6.108	2.5002	0.5621
5 ML CdSe CQW	25.14	6.095	2.4981	0.5628
6 ML CdSe CQW	25.22	6.079	2.4944	0.5637
7 ML CdSe CQW	25.34	6.072	2.4878	0.5654

2.3 Absorption spectra and photoluminescence (PL) spectra

The purified CdSe CQWs were dispersed in 3 mL of n-hexane and placed in a cuvette for testing. The absorption spectra of CdSe CQWs were measured using a UV-3600 double beam spectrophotometer produced by Shimazu Company. The test range was 300 nm to 700 nm (corresponding to energy levels of 1.8 eV to 4 eV). The PL spectra were measured using a fluorescence spectrophotometer (Shimazu, RF-6000). For 2 ML CdSe CQWs, the measurement range was set from 330 nm to 500 nm, with incident light excitation at 300 nm. For 3 ML and 4 ML CdSe CQWs, the incident light excitation was set at 350 nm, and the measurement range was from 400 nm to 600 nm. For 5 ML, 6 ML, and 7 ML CdSe CQWs, the incident light excitation was set at 450 nm, and the measurement range was from 500 nm to 700 nm.
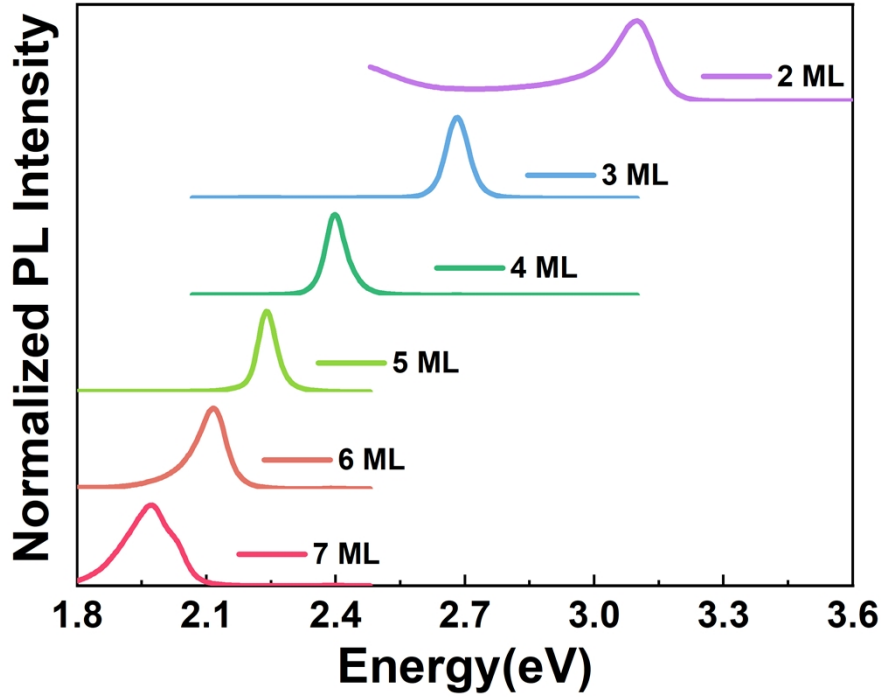
Fig. S2. (Color online) Photoluminescence spectra of 2 to 7 ML CdSe CQWs.

2.4 First-principles density functional theory (DFT)

We carried out our calculations using the Cambridge Sequential Total Energy Package (CASTEP) module package of Materials Studio software. We employed the gradient approximation method (GGA) to calculate the exchange-correlation energy, and set an 8*8*1 k-points mesh. To prevent interlayer interactions from affecting the band structure of the 4MLs CdSe CQWs, a vacuum layer of 20 Å in our model is set.

2.5 Spectroscopic ellipsometry (SE)

The SE-VM ellipsoid spectrometer based on Jones matrix (Wuhan Yitang Technology Co., LTD.) was utilized to measure and analyze the optical constants of CdSe CQWs films. The spectral range was set from 300 nm to 700 nm (equivalent to energy levels of 1.77 eV to 4.13 eV), with a spectral resolution of 0.6 nm. The incidence angle was fixed at 65°, and the measurements were conducted at room temperature. We employed the Eometrics software to fit the ellipsometric parameter *Psi* and *Delta*.

The model expression is as follows[1]:

$$\varepsilon_1 = \varepsilon_\infty + \frac{2}{\pi} P \int_{E_g}^{\infty} \frac{\xi \varepsilon_2(\xi)}{\xi^2 - E^2} d\xi, \tag{2}$$

$$\varepsilon_2 = \begin{cases} \frac{A E_{n0} C (E_n - E_g)^2}{\left(E_n^2 - E_{n0}^2\right)^2} \cdot \frac{1}{E_n} & E_n > E_g \\ 0 & E_n \leq E_g \end{cases}, \tag{3}$$

It can be observed that the Tauc-Lorentz model can be described by five parameters, namely ε_∞, A, C, E_{n0}, and E_g, to characterize the dielectric constants of all the samples.

These parameters represent the high-energy value, amplitude parameter, broadening parameter, peak transition energy, and bandgap energy, respectively.
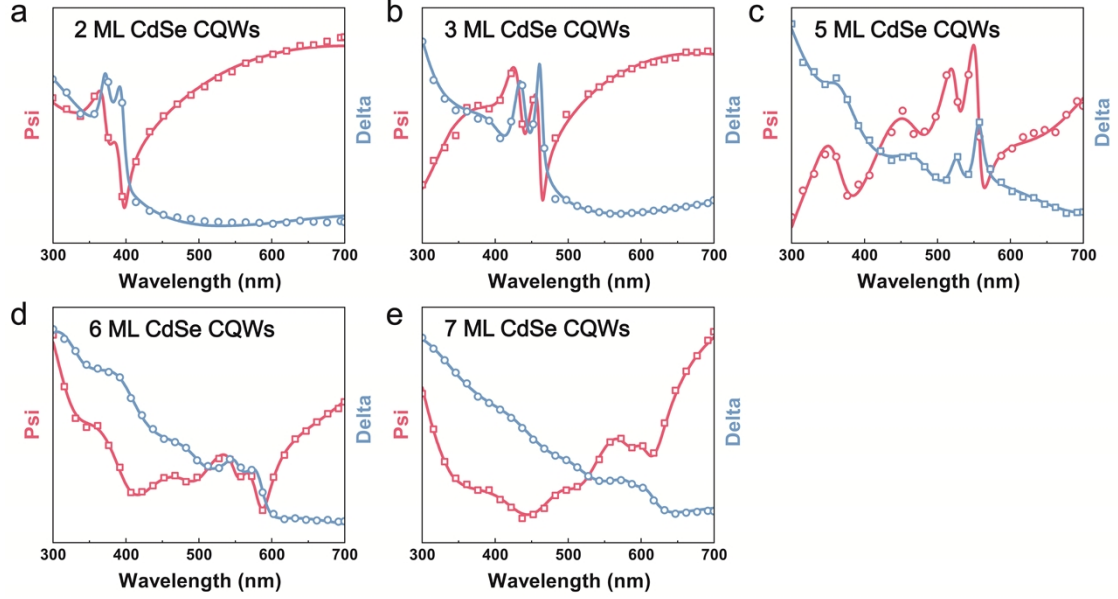

Fig. S3. (Color online) Experimental spectroscopic ellipsometry spectra (solid lines) and best-fit curves (dots) for (a) 2 ML CdSe CQWs, (b) 3 ML CdSe CQWs, (c) 5 ML CdSe CQWs, (d) 6 ML CdSe CQWs and (ae) 7 ML CdSe CQWs at a 65° incidence angle.

Table S2. Comparison of the thickness and roughness of CdSe CQWs measured using AFM and SE, mean square error (MSE) between the measured value and the fit value from SE.

Sample	Thickness by SE (nm)	Thickness by AFM (nm)	Roughness by SE (nm)	Roughness by AFM (nm)	MSE
2 ML	130	134	3.525	4.121	1.853
3 ML	125	132	3.874	4.762	1.745
4 ML	128	130	3.887	4.843	1.024
5 ML	127	125	4.351	5.048	1.952
6 ML	124	129	4.257	5.447	1.232
7 ML	125	127	5.435	5.861	1.021

The MSE quantifies the error between the best-fitting data and the experimental data using the following equation[2]:

$$MSE = \sqrt{\frac{1}{2n-m}\sum_{i=1}^{n}\left[\left(\frac{\psi_i^{mod}-\psi_i^{exp}}{\sigma_{\psi,f}^{exp}}\right)^2 + \left(\frac{\Delta_i^{mod}-\Delta_i^{exp}}{\sigma_{\psi,i}^{exp}}\right)^2\right]}, \quad (4)$$

Where m represents the number of wavelength points involved in the fitting process, n denotes the number of parameters involved in the fitting. The subscripts exp and mod respectively indicate the fitted data and the measured data.

Table S3. The optimum fitting-parameters in the Tauc-Lorentz of 2 to 7 ML CdSe CQW films.

Sample		A (eV)	C (eV)	E_{no} (eV)	E_g (eV)	$\varepsilon_1\,(\infty)$
	Peak1	0.8859	2.784	3.023	2.910	
	Peak2	0.1497	0.1721	3.138	2.914	2.139
	Peak3	0.0913	0.1651	3.332	2.911	
	Peak4	0.1869	0.6727	4.026	2.903	
3 ML CdSe CQW	Peak1	1.686	0.0724	2.673	2.504	
	Peak2	1.309	0.0868	2.829	2.471	1.7679
	Peak3	11.68	0.6131	4.415	2.441	
	Peak4	13.67	23.55	11.78	2.314	
4 ML CdSe CQW	Peak1	5.575	0.0418	2.417	2.377	
	Peak2	1.59	0.1022	2.564	2.236	1.6352
	Peak3	4.4313	0.5908	2.909	2.331	
	Peak4	2.309	1.244	2.452	2.264	
5 ML CdSe CQW	Peak1	1.74	0.1102	2.385	2.085	
	Peak2	3.019	0.4365	2.689	1.975	1.9794
	Peak3	1.531	0.4285	2.247	1.921	
	Peak4	3.779	1.922	3.432	2.048	
6 ML CdSe CQW	Peak1	2.367	0.0736	2.122	1.756	
	Peak2	1.008	0.1265	2.512	1.812	1.9372
	Peak3	0.539	0.3976	3.22	1.803	
	Peak4	0.416	0.8508	4.779	1.784	
7 ML CdSe CQW	Peak1	0.9255	0.1026	2.05	1.63	
	Peak2	0.7094	0.7423	2.915	1.702	2.4465
	Peak3	2.309	1.276	4.216	1.746	
	Peak4	0.4417	0.2511	2.165	1.787	

3. Deconvolution of the Linear Absorption Spectrum

We fit the absorbance spectrum of the CdSe CQWs used in this study by means of an approach that takes exciton localization into account by means of asymmetric broadening[3−5]. Here, absorbance is seen as a superposition of exciton lines (p) and free carrier transitions (C):

$$A(E) = p_X(E) + C(E), \tag{5}$$

To describe $p_X(E)$, which should yield the line shape of the exciton absorbance, we use an analytical expression that takes into account the asymmetrical broadening of this transition to higher energies (erf: error function):

$$p_x(E) = \frac{A}{2\eta}\left[erf\left(\frac{E - E_X}{\gamma} - \frac{\gamma}{2\eta}\right) + 1\right]exp\left(\frac{\gamma^2}{4\eta^2} - \frac{E - E_X}{\eta}\right), \tag{6}$$

The free carrier absorbance $C(E)$, which reflects the broadened absorption of the free carrier transition, we describe by:

$$C((E)) = \frac{A_C}{2}[erf]\left(\frac{(E - E_X) - \Delta_X}{\gamma_C}\right) + 1, \tag{7}$$

Here, we refer to E_X and Δ_X as exciton energy and exciton binding energy, respectively. Total absorbance A is the sum of exciton and free carrier absorption associated with light (LH) and heavy hole (HH) transitions:

$$A(E) = p_{X,HH}(E) + C_{HH}(E) + p_{X,LH}(E) + C_{LH}(E), \tag{8}$$

All materials were fitted according to the parameters listed in Table S3.

Table S3. Parameters used to fit the absorbance spectrum of the large CQWs using a sum of exciton and free carrier absorbance for the HH and LH transitions. The column labeled HH and LH list the parameters used for the HH and the LH contribution, respectively.

|	HH_2	LH_2	HH_3	LH_3	HH_4	LH_4
E_b (meV)	210	360.9	200	290.9	185.4	255.8
Ex (meV)	3125	3293	2660	2830	2398.4	2555.5
γ (meV)	51.9	82.9	29	70	14.6	64.4
A_C (meV)	0.2	0.3	0.4	0.2	0.4	0.7
γ_C (meV)	45	65	55	25	55.7	15.3
η (meV)	34.5	31	43	10	49.9	9.6
A	111	121	84	73	72.7	62.2
	HH_5	LH_5	HH_6	LH_6	HH_7	LH_7
E_b (meV)	165.4	250.9	155.6	308.2	120.6	355
Ex (meV)	2231	2360	2116	2232.4	2024.1	2110.1
γ (meV)	12.5	56.1	33.6	60.1	42.7	55.7
A_C (meV)	0.5	0.4	0.6	0.1	0.8	0.1
γ_C (meV)	50.2	8.5	50.6	50.9	50.9	15
η (meV)	42.9	11.9	50.1	20.1	17	10.9
A	62.5	57.1	97.3	78.9	77.1	70.3
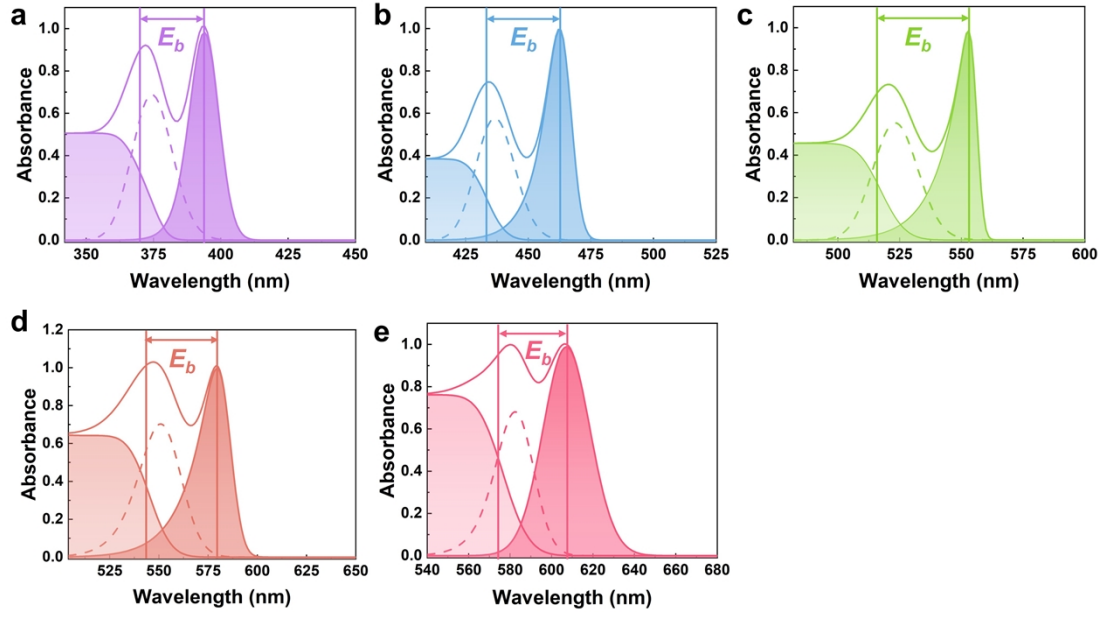
Fig. S4. (Color online) Deconvolution of the absorption spectra for (a) 2 ML CdSe CQWs, (b) 3 ML CdSe CQWs, (c) 5 ML CdSe CQWs, (d) 6 ML CdSe CQWs and (e) 7 ML CdSe CQWs, showing contributions from light-hole (LH) and heavy-hole (HH) excitons as well as free carriers.

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