SUPPORTING INFORMATION

Mechanism of the Electrophoretic Deposition of CdSe Nanocrystal Films: The Influence of the Nanocrystal Surface and Charge

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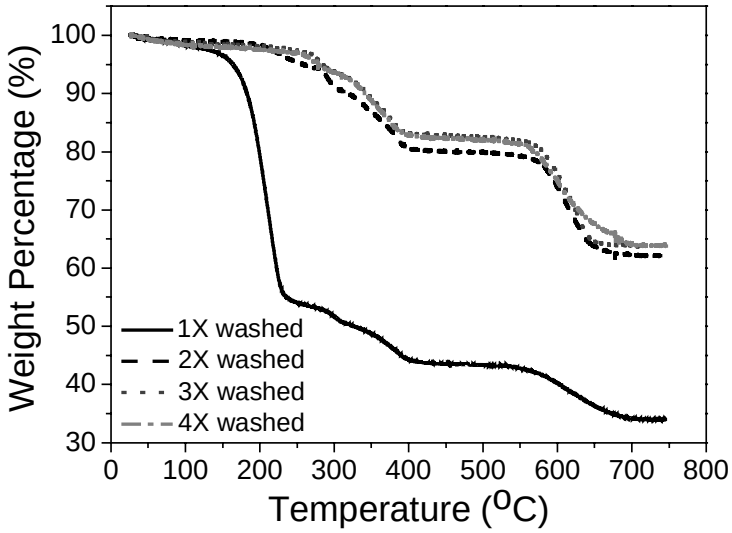

Figure S1. The TGA weight percentage vs. temperature curve, of 3.2 nm CdSe nanocrystals washed different numbers of times, taken under an oxygen atmosphere,. The ramp rate is 10 ^{o}C/min. (See Table S2.)

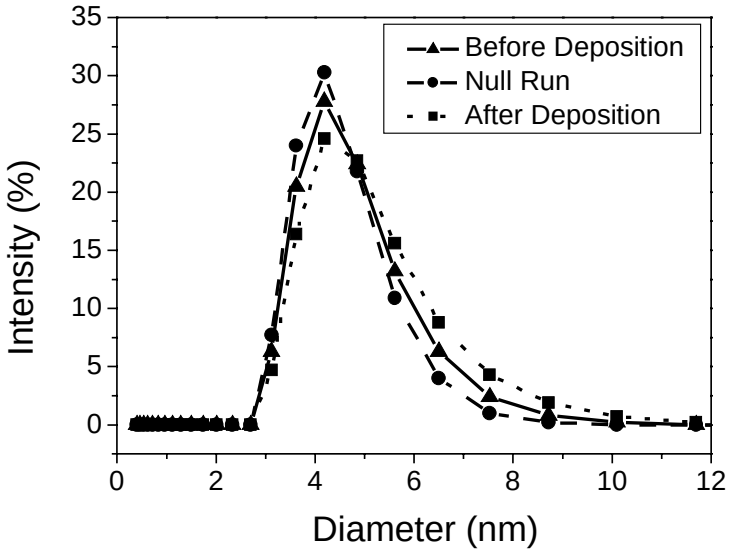

Figure S2. Size distribution (by number) of 2× 3.2 nm CdSe nanocrystals before and after deposition, and after a "null" run, taken by laser light scattering. Each distribution peaks near 4.2 nm, which indicates that the nanocrystals are not significantly aggregated.

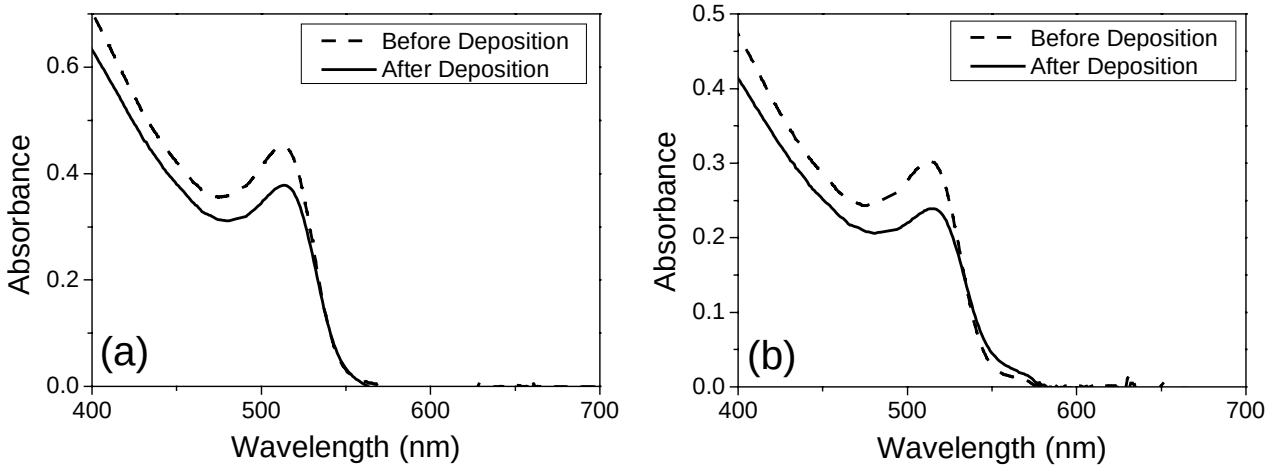

Figure S3. Transmission spectra of (a) 4× 2.3 nm and (b) 5× 2.3 nm CdSe nanocrystal solutions before and after deposition (Method 2) (plotted in terms of the absorbance, assuming no scattering loss). (See Figs. 2c and 2d; Table S5.)

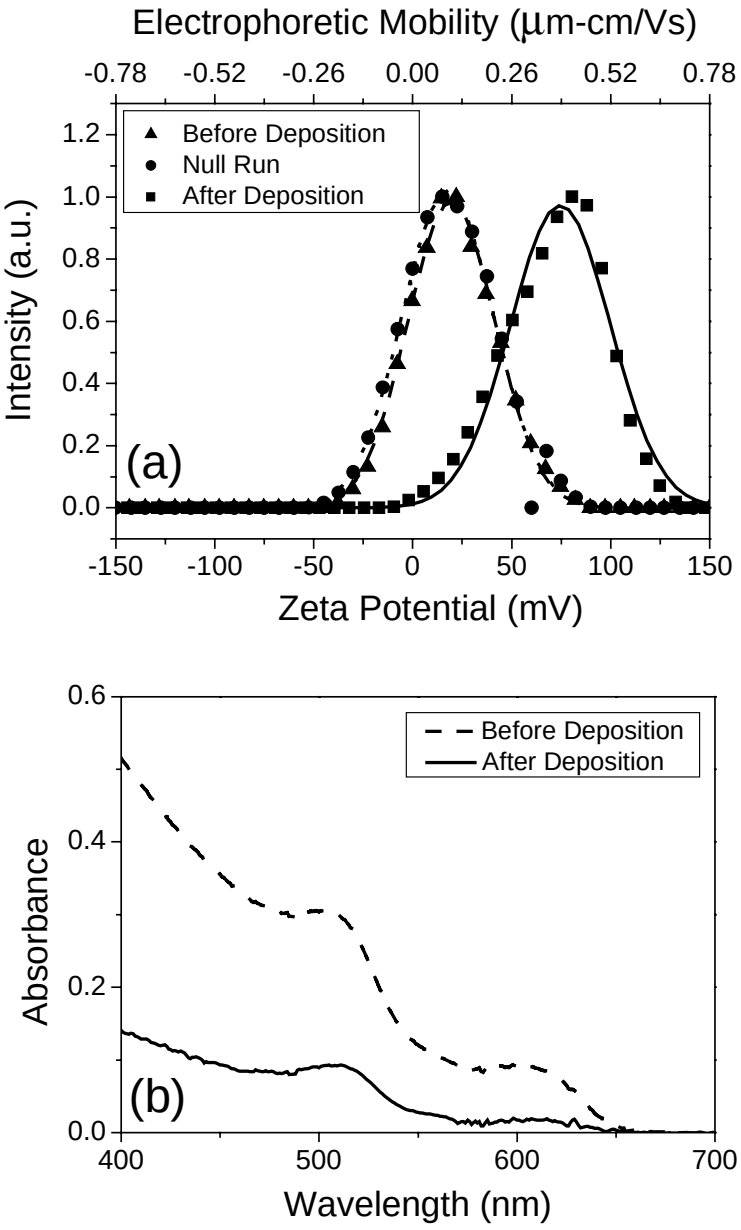

Figure S4. (a) Zeta potential and mobility distributions of a mixture of 4× 2.3 nm and 2× 5.0 nm CdSe nanocrystal solutions before and after deposition, and after a "null" run (Method 2) and (b) transmission spectra of the nanocrystal mixture solution before and after deposition (plotted in terms of the absorbance, assuming no scattering loss). (See Table S7.)

Nanocrystal Type	Cd atoms	Se atoms	Core atoms	Ligand sites (expected)	Ligand sites (max, shell)	P atoms
1× 2.3 nm	252	181	433	233	198	191
4× 2.3 nm	250	183	433	234	198	106
5× 2.3 nm	251	182	433	234	198	96
1× 3.2 nm	653	523	1176	488	295	866
2× 3.2 nm	651	526	1177	489	295	392
3× 3.2 nm	649	529	1178	489	295	365
1× 5.0 nm	2359	2180	4539	1283	551	1605
2× 5.0 nm	2425	2087	4512	1275	551	918
4× 5.0 nm	2428	2082	4510	1275	551	531

Table S1. Numbers of atoms (from ICP-AES) and ligand sites [calculated from the number of atoms within 0.262 nm of the surface (expected) and assuming a shell of TOPO molecules (max, shell)] of CdSe nanocrystals with different core diameters subjected to different numbers of reprecipitation cycles, using a cubic nanocrystal assumption.

Nanocrystal Type	Ligand sites (expected)	Free TOPO	Loosely bound ligands	Strongly bound ligands	Ligands
1× 3.2 nm	256	185	51	46	282
2× 3.2 nm	256	5	39	41	85
3× 3.2 nm	256	1	35	46	82
4× 3.2 nm	256	2	33	44	79

Table S2. The number of ligands in 3.2 nm CdSe nanocrystals washed different numbers of times, as determined by TGA under an oxygen atmosphere. The ramp rate is 10 ^{o}C/min. (See Fig. S1.) The expected number of ligand sites comes from Table 1. The mass lost from ~100^{o}C to 230^{o}C is identified as free TOPO, that lost from ~230^{o}C to 400^{o}C is identified as from loosely-bound ligands, and that lost from ~400^{o}C to 700^{o}C is identified as from strongly-bound ligands. At ~700^{o}C it is assumed here that only the core remains.

CdSe Nanocrystal	Zeta Potential (mV)	Peak Width (mV)	Fraction with Negative Zeta Potential (%)
1× 2.3 nm	19.2±2.0	43.7±2.6	18.1±1.3
2× 2.3 nm	20.1±0.5	18.3±1.0	1.9±1.3
3× 2.3 nm	40.2±2.1	21.8±1.6	0.3±0.2
1× 3.2 nm	16.5±0.7	48.2±0.9	19.5±3.2
2× 3.2 nm	27.4±1.1	37.8±1.0	7.7±3.6
3× 3.2 nm	18.1±0.9	30.3±1.8	11.5±4.6

Table S3. Zeta potential peak position and peak width, and fraction of distribution with negative zeta potential for 2.3 nm and 3.2 nm CdSe nanocrystal solutions washed different numbers of times. (Transferred using Method 3.) (See Fig. 1.)

CdSe Nanocrystal	Run*	Zeta Potential (mV)	Peak Width (mV)	Fraction with Negative Zeta Potential (%)	Fraction of Nanocrystals Deposited (from electrophoretic mobility)** (%)	Fraction of Nanocrystals Deposited (from absorbance) (%)
Run 1 (1100 nm thick films, Fig. 2a)	Before After After (two days later)	20.6±2.0 35.2±0.4 20.8±1.9	44.9±1.9 24.3±0.4 28.3±1.6	18.0±7.1 0.4±0.9 8.8±1.5	35.5	N/A
Run 2 (2300 nm thick films)	Before After	8.6±3.9 32.7±2.5 75.3±3.7	50.3±4.9 33.5±3.0 42.2±4.1	36.3±5.8 1.3±0.6	71.9	79.0
Run 3 (1800 nm thick films)	Before After	21.3±1.4 21.9±2.2	52.3±9.5 24.7±3.0	21.5±1.3 4.3±0.7	37.6	51.4
Run 4 (750 nm thick films, Fig. 2b)	Before Null Run After	18.6±2.5 21.0±2.6 64.5±8.0	23.2±2.0 36.8±5.6 41.8±2.3	5.8±2.0 13.0±4.7 1.9±0.5	8.1	40.9

* Solution before or after EPD, or after a "null" run.

** This is equal to $2(f_{nb}-f_{na})/(1-2f_{na})$. f_{nb} and f_{na} are the fractions of nanocrystals with negative zeta potential before and after electrophoretic deposition.

Table S4. Zeta potential peak position and peak width, and fraction of distribution with negative zeta potential for 2× 3.2 nm CdSe nanocrystal solutions before and after deposition, and two days after deposition for Run 1 and after the "null" run for Run 4,

along with EPD film thickness, and the fraction of nanocrystals deposited as determined from zeta potential or transmission data. The absorbance at the 546 nm first exciton peak decreases from 0.62, 0.37, and 0.22 before deposition to 0.13, 0.18, and 0.13 after deposition for Runs 2, 3, and 4, respectively. (Transferred using Method 1 for Runs 1-3 and Method 2 for Run 4.) (See Figs. 2a and 3 (Run 1), and 2b (Run 4).)

CdSe Nanocrystal	Run*	Zeta Potential (mV)	Peak Width (mV)	Fraction with Negative Zeta Potential (%)	Fraction of Nanocrystals Deposited (from electrophoretic mobility)** (%)	Fraction of Nanocrystals Deposited (from absorbance) (%)
4× 2.3 nm (350 nm thick films, Fig. 2c)	Null Run After	0.4±0.4 12.0±0.9	29.6±4.6 26.6±2.1	48.8±1.0 18.7±3.4	96.2	15.6
5× 2.3 nm (300 nm thick films, Fig. 2d)	Null Run After After (two days later)	15.1±0.6 21.2±0.8 31.8±2.1	27.4±0.5 24.1±1.5 53.9±3.3	13.7±1.2 4.7±1.1 11.6±1.7	19.9	20.0

* Solution after a "null" run or EPD.

** As in Table S4.

Table S5. Zeta potential peak position and peak width, and fraction of distribution with negative zeta potential for 4× and 5× 2.3 nm nanocrystal solutions after a "null" run and after deposition, along with EPD film thickness, and the fraction of nanocrystals deposited as determined from zeta potential or transmission data. The absorbance at the 510 nm first exciton peak decreases from 0.45 and 0.30 before deposition to 0.38 and 0.24 after deposition for the 4× and 5× nanocrystals, respectively. (Transferred using Method 2.) (See Figs. 2c, 2d, and S3.)

CdSe Nanocrystal	Run*	Zeta Potential (mV)	Peak Width (mV)	Fraction with Negative Zeta Potential (%)
2× 2.3 nm	Before Deposition	20.1±0.5	18.3±1.0	1.9±1.3
	After Addition of 10 mg TOPO	-28.1±2.4	28.9±1.5	97.4±1.3
2× 3.2 nm	Before Deposition	20.6±2.0	44.9±1.9	18.0±7.1
	After Addition of 5 mg TOPO	-10.4±1.5	23.8±1.7	86.8±2.2
2× 5.0 nm	Before Deposition	3.8±0.8	23.4±1.0	38.6±3.0
	After Addition of 10 mg TOPO	-8.3±1.4	18.9±0.4	81.0±4.1

* Solution before EPD, either before or after addition of TOPO.

Table S6. Zeta potential peak position and peak width, and fraction of distribution with negative zeta potential for 2× 2.3 nm, 2× 3.2 nm, and 2× 5.0 nm CdSe nanocrystal solutions before and after the addition of TOPO. (Transferred using Method 3.) (See Fig. 4.)

Run	Zeta Potential (mV)	Peak Width (mV)	Fraction with Negative Zeta Potential (%)	Fraction of Nanocrystals Deposited (from electrophoretic mobility)* (%)	Fraction of Nanocrystals Deposited (from absorbance)
Before Deposition	18.6±1.4	44.0±0.2	19.9±1.8	39.6	70% 2.3 nm 86% 5.0 nm
Null Run	17.6±0.1	45.0±1.6	22.1±0.1		
After Deposition	29.3±5.5	51.7±1.9	0.2±0.2		

* As in Table S4.

Table S7. Zeta potential peak position and peak width, and fraction of distribution with negative zeta potential for a mixture of 4× 2.3 nm and 2× 5.0 nm CdSe nanocrystal solutions before and after deposition, and after a "null" run. The absorbances at the 510 nm first exciton peak of the 2.3 nm nanocrystals before and after deposition are 0.30 and 0.09, whereas for the 5.0 nm nanocrystals the absorbances at the 609 nm first exciton peak before and after deposition are 0.091 and 0.013. (See Fig. S4.)