Reducing Strain and Fracture of Electrophoretically Deposited CdSe Nanocrystal Films: I: Post-deposition Infusion of Capping Ligands

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Supporting Information

1. Details of Film Formation, Treatment and Analysis

Additional experiments details are presented here concerning the synthesis and properties of the films presented in the main paper. This run is labeled Run III here.

i. Film III Preparation

CdSe NC Preparation

12 g of TOPO (99%) and 0.90 g of tetradecylphophonic acid were added to a 50 ml three-neck flask. The mixture was heated to 110°C for 2 h under vacuum to remove residual water and oxygen. Temperature was then increased to ~360°C under nitrogen. Heat was removed from the reaction flask and the reaction mixture was allowed to cool. As the solution cooled through 350°C a mixture containing 4.986 g TOP, 1.555 g 1M TOP-Se, and 0.15 g dimethylcadmium was rapidly injected. Following injection the reaction temperature was allowed to reach 280°C

where it was held for 20 min before cooling to room temperature. The final diameter of the CdSe NCs was determined to be approximately 4.0 nm using UV-vis absorption spectroscopy.

When the NC solution reached 60°C approximately 10 mL of toluene was added and the combined liquid was withdrawn and divided between two 50 mL centrifuge tubes, each containing 5 mL of butanol (to prevent solidification of the now cool NC solution). 10 mL of acetone and 10 mL of methanol were added to each tube and then centrifuged. The precipitate was redissolved in hexane and once again centrifuged. The supernatant was recovered and filtered through a 0.2 μm pore size PTFE filter and stored in a nitrogen filled glove box.

Electrophoretic Deposition Procedure

2 mL of stock CdSe NC solution (1×) was combined with 3 mL of clean hexane and then precipitated/dissolved in methanol/hexane three additional times in order to create a solution of NCs that had been reprecipitated a total of four times (4×). The 5× solution (5 mL) was combined with 40 mL of clean hexane in a 60 mL beaker open to air. Two pre-scored silicon electrodes (~7.6 cm × 2.5 cm) coated with 50 nm Au and 10 nm Cr were immersed in the deposition solution and held 2 cm apart (Au surfaces facing). A DC bias of 800 V was applied to the two electrodes for 10 min.

TOPO Treatment Procedure

Immediately after deposition, both positive and negative electrodes were quickly moved from the deposition solution to separate 30 mL baths of clean hexane. While fully submerged in hexane both electrodes were cleaved along preexisting score lines. Individual pieces of each electrode (~1 cm × 1 cm) were rapidly moved from the clean hexane bath to new baths of 0 mM,

5 mM, 10 mM, 15 mM, 20 mM, and 30 mM TOPO in hexane. Each sample remained in its respective bath (covered to prevent evaporation) for 30 min. Each sample was then removed from its respective bath and allowed to air dry.

ii. Film Analysis

Elastic moduli were determined assuming a film Poisson ratio $\nu = 0.18$, but the obtained moduli were insensitive to the choice of ν (Figure S1).

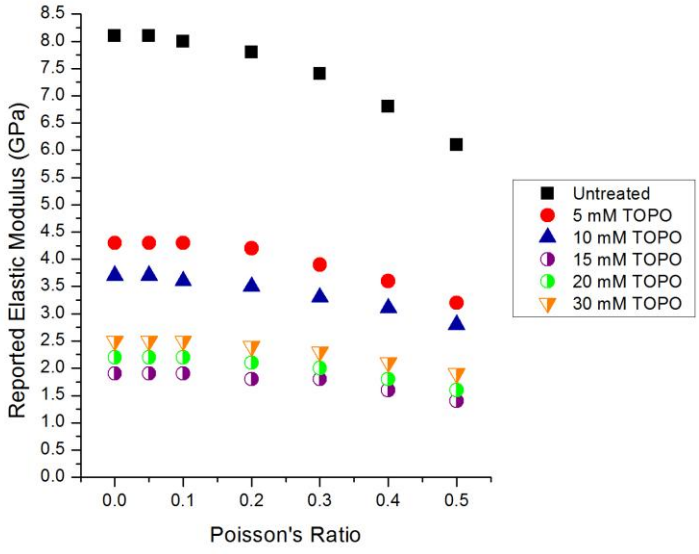

Figure S1. Elastic modulus modulus from nanoindentation, using different values of the film Poisson ratio in the analysis.

iii. Film Properties

Additional data describing properties of the film described in the main paper (from Run III) are presented here.

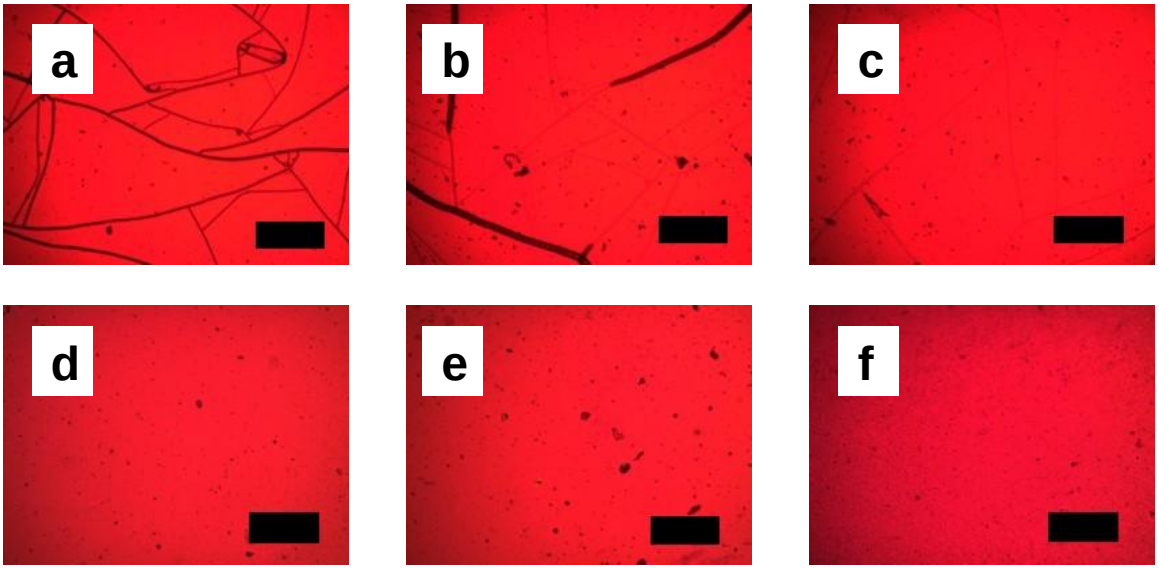

Figure S2. Optical micrographs of EPD CdSe NC films on the negative electrode in Run III treated with (a) 0 mM, (b) 5 mM, (c) 10 mM, (d) 15 mM, (e) 20 mM, (f) 30 mM TOPO. The scale bar is 500 μm wide.

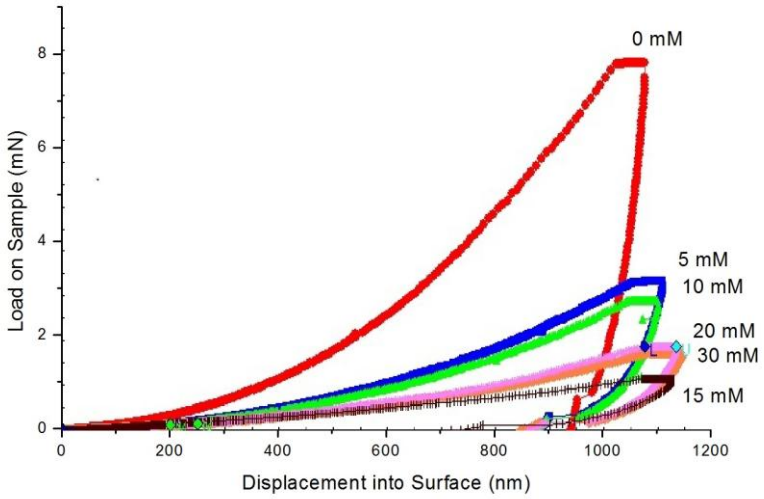

Figure S3. Nanoindenter force-displacement plots (8 nm/s) for the positive film electrode in Run III, after treatment by the TOPO solutions and drying.

2. Additional Runs of Film Formation, Treatment and Analysis

The main paper presented the complete results from a series of studies in which NCs from one synthesis run were washed[1] and then used to form a large-area EPD film, which was diced and then immersed in TOPO solutions, dried and then analyzed (Run III). The results from three other runs are presented here. The observations of fracture suppression, lower elastic modulus, and increased photoluminescence intensity with TOPO treatment for these runs and those presented in the main paper are the same. The slight increase in film thickness with TOPO treatment is less certain for the runs presented here.

A. Additional Run (I) With No Tetradecylphophonic Acid Added During the Nanocrystal Synthesis

i. Film Preparation

In the earliest runs, NCs were synthesized and washed multiple times, and used for EPD, and as in earlier studies[1], except using cadmium oxide as the Cd source instead dimethylcadmium. EPD of thick CdSe NC films was not always successful, independent of the number of washing cycles. The results of a successful run are presented here. Thick films formed on both electrodes, as in previous studies. Only the film on the positive electrode was analyzed; the film on the negative electrode was used in the companion study[2].

This difficulty in forming thick EPD films was first thought to be possibly related to differences on the surfaces of the cores of the synthesized CdSe NCs attributable to the different source of cadmium. However, analysis did not find a significant difference, and EPD was then seen to be challenging with using the dimethylcadmium precursor. Later it was thought that it

might be due to the variability of the composition of the purchased TOPO reagent, even the 90% pure reagent that had been used in previous studies. The phosphonic acid impurity in TOPO has long been known to be necessary to form high quality CdSe NCs. It is seen here that thick EPD films could be formed when tetradecylphosphonic acid is added during synthesis, and then the procedures of Refs. 3 (CdO precursor) and 4 (dimethylcadmium precursor) followed again , with multiple washings and so on.

CdSe NC Preparation

A solution of cadmium oleate was prepared by adding 0.2056 g (1.6 mmol) cadmium oxide, 4 mL of oleic acid (12.6 mmol) and 1 mL of octadecene to a 25 mL three-neck flask. The solution was degassed at 100°C for 30 minutes before heating to 240°C under nitrogen. Above approximately 200 °C the oleic acid complexes with the cadmium ions and the solution turns clear. The optically clear solution was held at 240°C for 10 min and then cooled to room temperature.

7 g of TOPO (90%) and 7 g of HDA (hexadecylamine) (90%) were added to the original flask containing the cadmium oleate. The solution was then degassed at 100°C for 2 h. In order to reduce the presence of water generated from condensation of excess oleic acid with TOPO and HDA, the solution was heated to 210°C under nitrogen for 5 min and then cooled to 100°C for an additional 1 h of degassing. Finally, the solution was heated to approximately 310°C before removing heat and allowing the solution to cool. As the solution passed through 300°C, 8 mL of TOP-Se solution was rapidly injected. Heat was applied to the solution immediately after injection of TOP-Se and after an initial temperature drop the temperature is raised to 280°C and the solution was held at this temperature for 8 min before cooling.

When the NC solution reached 60°C approximately 10 mL of toluene was added and the combined liquid was withdrawn and divided between two 50 ml centrifuge tubes, each containing 5 mL of butanol (to prevent solidification of the now cool NC solution). 10 mL of acetone and 10 mL of methanol were added to each tube and then centrifuged. The precipitate was redissolved in hexane and once again centrifuged. The supernatant was recovered and filtered through a 0.2 μm pore size PTFE filter and stored in a nitrogen filled glove box. The final diameter of the CdSe NCs was determined to be approximately 3.5 nm using UV-vis absorption spectroscopy. (For this size, the elastic modulus[5] is ~17 GPa.)

Immediately prior to deposition 5 mL of this solution was removed from the glove box and precipitated/dissolved in methanol/hexane eight additional times in order to create a solution of NCs that had been reprecipitated a total of nine times $(9\times)^1$. This number of washings was needed to observe EPD of thick films. The final CdSe/hexane solution transferred back to the glove box where it was combined with 45 mL of anhydrous hexane (this dilute CdSe solution was stable under dry conditions for up to one hour).

Electrophoretic Deposition Procedure

In the glove box, the washed and diluted CdSe solution was added to a sealed glass jar containing two electrodes. Each electrode consisted of a pre-scored ~7.6 cm × 2.5 cm silicon wafer with a 50 nm thick conductive film of thermally evaporated of Cr/Au. Both electrodes were attached to air-tight electrical feedthroughs which allowed voltage to be applied with the lid of the jar securely closed. The electrodes were parallel and separated by 26 mm. The sealed deposition jar containing electrodes and CdSe NC solution was removed from the glove box and a DC bias of 1000 V was applied to the two electrodes (via air-tight feedthroughs) for 20 min.

TOPO Treatment Procedure

Immediately after deposition, both positive and negative electrodes were quickly moved from the deposition solution to separate 30 mL baths of clean hexane. While fully submerged in hexane both electrodes were cleaved along preexisting score lines. The negative electrode was used for the companion study[2]. Individual pieces of the positive electrode, each measuring approximately 1 cm × 1 cm were rapidly moved from the clean hexane bath to new baths of 0 mM, 5 mM, 10 mM, 15 mM, 20 mM, 25 mM, 30 mM, and 40 mM TOPO in hexane. Each sample remained in its respective bath (covered to prevent evaporation) for 2 h. Each sample was then removed from its respective bath and allowed to air dry.

ii. Film Properties

Fracture was seen with treatment with the 0 and 5 mM TOPO solutions, but not with 10 mM and higher. The properties of the film fabricated in this run were similar to those presented in the main paper.

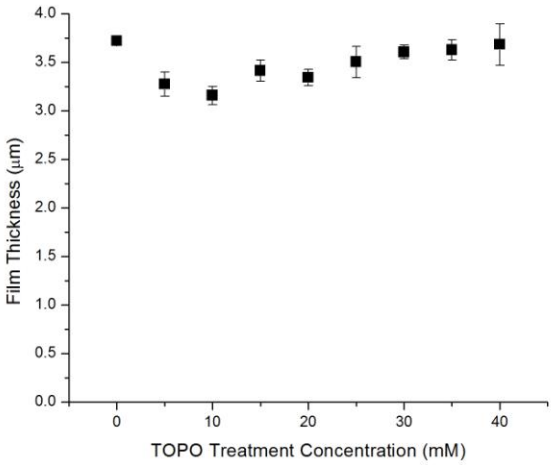

Figure S4. Thickness of the dried EPD CdSe NC film from the positive electrode in Run I vs. concentration of the TOPO solution used for treatment.

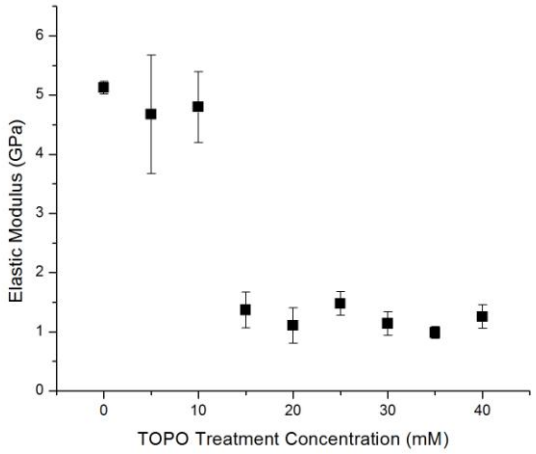

Figure S5. Elastic modulus of the dried EPD CdSe NC film from the positive electrode in Run I measured by nanoindentation vs. concentration of the TOPO solution used for treatment. The modulus of the as-deposited film (0 mM) measured here is smaller than the ~8-10 GPa values measured in the main paper, below, and in earlier studies[6] .

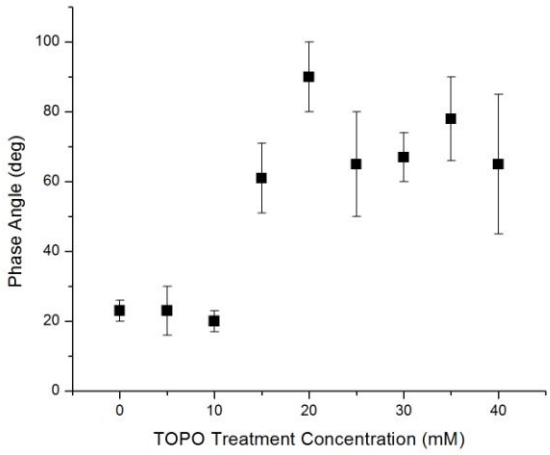

Figure S6. Phase angle of the dried EPD CdSe NC film in Run I from the positive electrode measured by nanoindentation vs. concentration of the TOPO solution used for treatment.

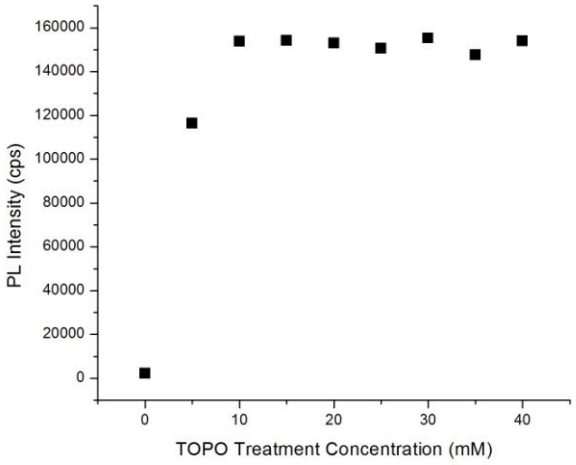

Figure S7. Photoluminescence of the dried EPD CdSe NC film from the positive electrode in Run I vs. concentration of the TOPO solution used for treatment.

B. Additional Run (II) With Tetradecylphophonic Acid Added During the Nanocrystal Synthesis

i. Film Preparation

In the Run III series presented in the main paper tetradecylphosphonic acid was added during CdSe synthesis and dimethylcadmium was used as the source of cadmium, and this was also done in the Run II presented here.

CdSe NC Preparation

6 g of TOPO (99%), 6 g of HDA (hexadecylamine) (90%), and 0.12 g of tetradecylphophonic acid were added to a 50 mL three-neck flask. The mixture was heated to 110°C for 2 h under vacuum to remove residual water and oxygen. Temperature was then increased to ~360°C under nitrogen. Heat was removed from the reaction flask and the reaction mixture was allowed to cool. As the solution cooled through 350°C, a mixture containing 4.986

g TOP, 1.555 g 1M TOP-Se, and 0.15 g dimethylcadmium was rapidly injected. Following injection the reaction temperature was allowed to reach 280°C where it was held for 20 min before cooling to room temperature. The final diameter of the CdSe NCs was determined to be approximately 3.2 nm using UV-vis absorption spectroscopy. (For this size, the elastic modulus[5] is ~14 GPa.)

When the NC solution reached 60°C approximately 10 mL of toluene was added and the combined liquid was withdrawn and divided between two 50 mL centrifuge tubes, each containing 5 mL of butanol (to prevent solidification of the now cool NC solution). 10 mL of acetone and 10 mL of methanol were added to each tube and then centrifuged. The precipitate was redissolved in hexane and once again centrifuged. The supernatant was recovered and filtered through a 0.2 μm pore size PTFE filter and stored in a nitrogen filled glove box.

Electrophoretic Deposition Procedure

2 mL of stock CdSe NC solution (1×) was combined with 3 mL of clean hexane and then precipitated/dissolved in methanol/hexane four additional times in order to create a solution of NCs that had been reprecipitated a total of five times (5×). The 5× solution (5 ml) was combined with 40 mL of clean hexane in a 60 mL beaker open to air. Two pre-scored silicon electrodes (~7.6 cm × 2.5 cm) coated with 50 nm Au and 10 nm Cr were immersed in the deposition solution and held 2 cm apart. A DC bias of 800 V was applied to the two electrodes for 10 min.

TOPO Treatment Procedure

Immediately after deposition, both positive and negative electrodes were quickly moved from the deposition solution to separate 30 mL baths of clean hexane. While fully submerged in hexane both electrodes were cleaved along preexisting score lines. Individual pieces of each electrode (~1 cm × 1 cm) were rapidly moved from the clean hexane bath to new baths of 0 mM, 5 mM, 10 mM, 15 mM, 20 mM, and 30 mM of TOPO in hexane. Each sample remained in its respective bath (covered to prevent evaporation) for 30 min. Each sample was then removed from its respective bath and allowed to air dry.

ii. Film Properties

The properties of the film fabricated in this run were roughly similar to those presented in the main paper. Fracture was seen with treatment with the 0 and 5 mM TOPO solutions, but not with 10 mM and higher.

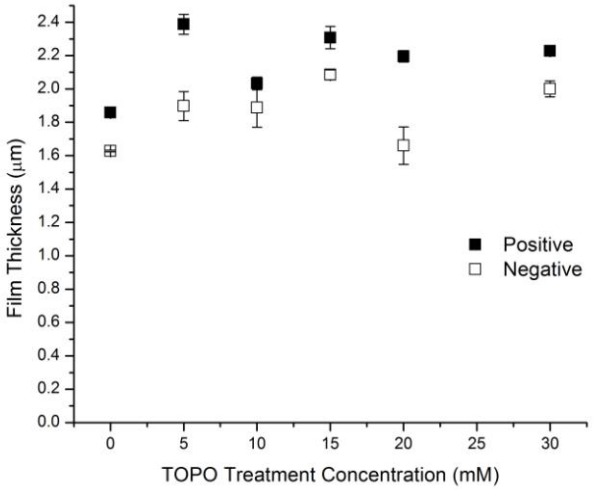

Figure S8. Thickness of the dried EPD CdSe NC film from both electrodes in Run II vs. concentration of the TOPO solution used for treatment.

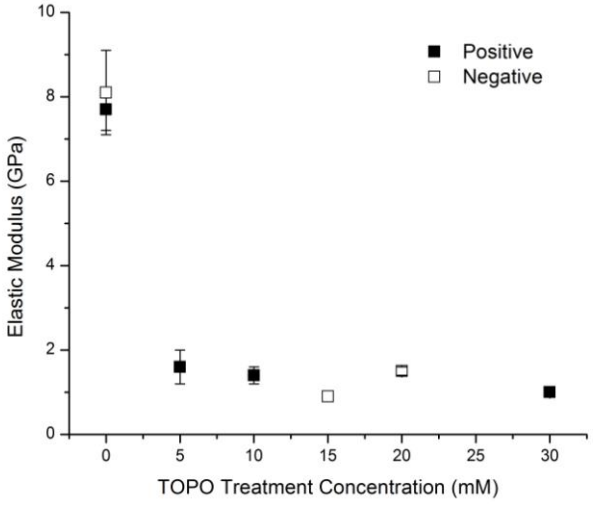

Figure S9. Elastic modulus of the dried EPD CdSe NC film from both electrodes in Run II measured by nanoindentation vs. concentration of the TOPO solution used for treatment. The modulus of the as-deposited film (0 mM) measured here and in the main paper is comparable to the ~8-10 GPa values measured in earlier studies[6].

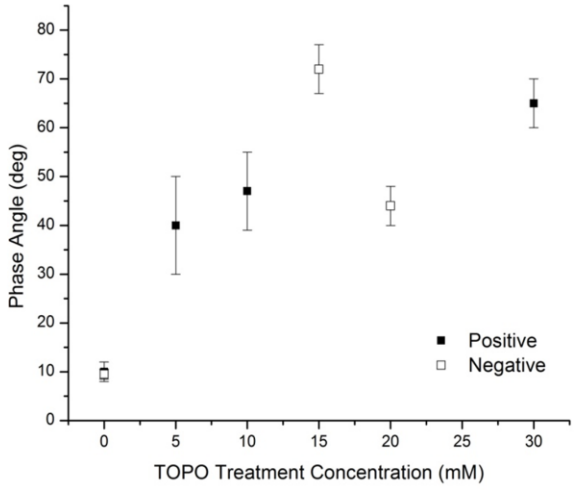

Figure S10. Phase angle of the dried EPD CdSe NC film from both electrodes in Run II measured by nanoindentation vs. concentration of the TOPO solution used for treatment.

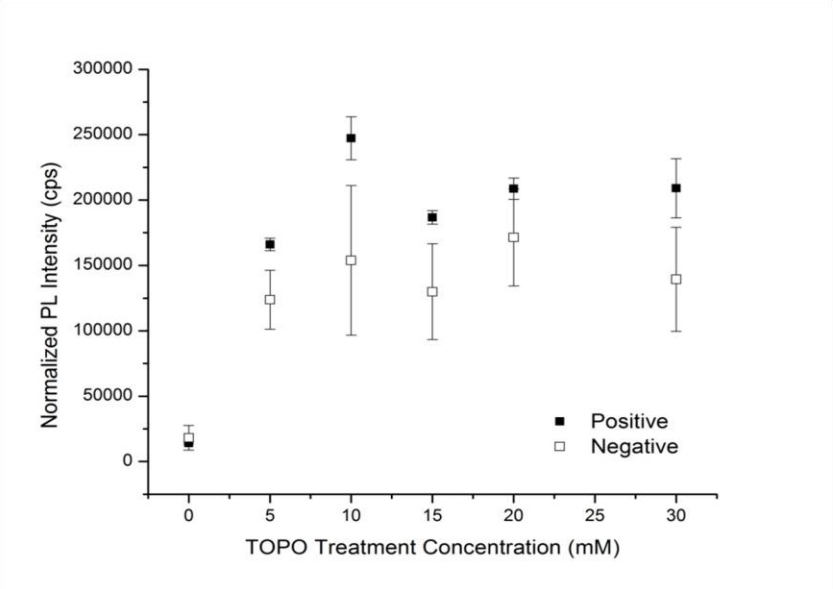

Figure S11. Photoluminescence of the dried EPD CdSe NC films from both electrodes in Run II vs. concentration of the TOPO solution used for treatment.

C. Additional Run (IV) With Tetradecylphophonic Acid Added During the Nanocrystal Synthesis

i. Film Preparation

One study was made with an EPD film from another run, which was also used in Run IV in the companion study[2]. It is similar to Run III used in the main paper. Dimethylcadmium was used as the source of cadmium, and this was also used in the Run II presented here.

In Run IV, CdSe NCs of 4.0 nm diameter were synthesized using a $Cd(Me)_2$ precursor, using 0.75 wt. % tetradecylphosphonic acid as ligand and 99% TOPO (and no HDA) as coordinating solvent. The NCs were washed to 4× prior to deposition. Film EPD was performed on a single set of ~7.6 cm × 2.5 cm electrodes, which were later diced. One piece from the

negative electrode was allowed to dry, and part of it was then soaked in 30 mM TOPO for 2 h and then dried in air again.

ii. Film Properties

The nanoindentation traces in Figure S12 are similar for the dried and cracked film and that soaked in 30 mM TOPO after drying and then dried. The film thickness appeared to decrease a little from ~1.46 μm for the dried, untreated film to ~1.19 μm after TOPO treatment and drying. Also, after treating the dried films, TOPO dendritic crystals appeared all over the surface. Note that after treating the still wet EPD films, TOPO crystals appeared on the surface after treatment only for 30 mM, and for that condition they were sparse.

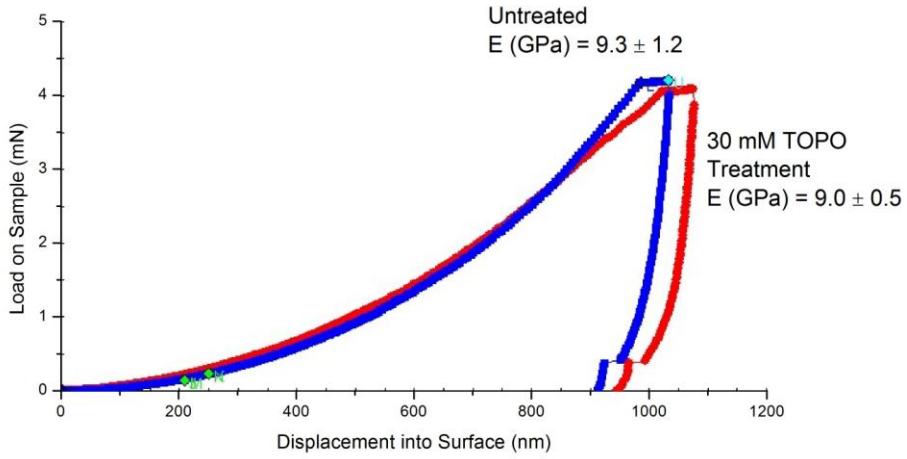

Figure S12. Nanondentation of the EPD CdSe NC film from the negative electrode in Run IV after drying; part of the sample was then treated with 30 mM TOPO solution treatment and then dried before measurement.

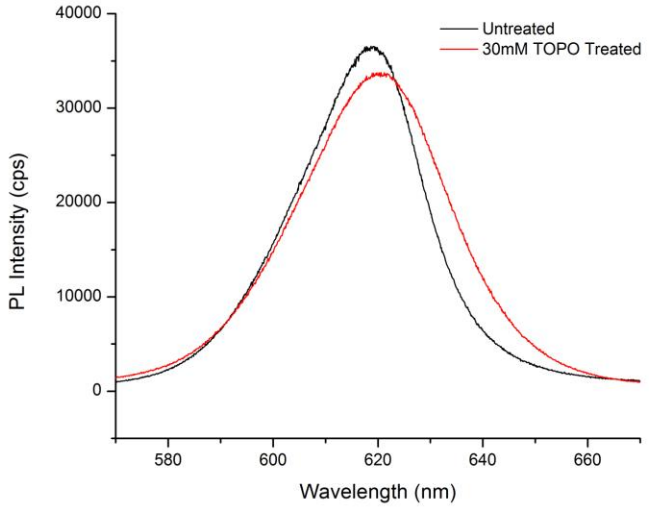

Figure S13. Photoluminescence of the EPD CdSe NC film from the negative electrode in Run IV after drying; part of the sample was then treated with 30 mM TOPO solution treatment and then dried before measurement.

3. Details of the Mean Field Theories of the Elastic Modulus

A. Micromechanics Models

Several models can be used to model the EPD CdSe NC films. The two-phase Halpin-Tsai model (below) modified for voids[7] is used in the main paper. One of alternative models, the three-phase Cohen-Ishai model[8], which includes an older and alternative way to account for voids, is also described below. Information about other models can be found in Ref. 9.

i. Halpin-Tsai Model

This two-phase model[10] predicts the bulk modulus K_{film} :

$$K_{film} = K_{TOPO}\frac{1+\xi_K\eta_K\Phi_K}{1-\eta_K\Phi_K}, \tag{S1}$$

where $\xi_K = 4G_{TOPO}/3K_{TOPO}$ [$= 2(1-2\nu_{TOPO})/(1+\nu_{TOPO})$ for particulate composites], $\eta_K = (m_K - 1)/(m_K + \xi_K)$, and $m_K = K_{CdSe}/K_{TOPO}$, and the shear modulus G_{film}:

$$G_{film} = G_{TOPO}\frac{1+\xi_G\eta_G\Phi_G}{1-\eta_G\Phi_G}, \tag{S2}$$

where $\xi_G = (7-5\nu_{TOPO})/(8-10\nu_{TOPO})$, $\eta_G = (m_G - 1)/(m_G + \xi_G)$, and $m_G = G_{CdSe}/G_{TOPO}$. (The notation is the same as in the main paper.)

From these the film elastic modulus E_{film} can be obtained:

$$E_{film} = \frac{9K_{film}G_{film}}{3K_{film}+G_{film}} \tag{S3}$$

This two-phase (CdSe cores/TOPO matrix) Halpin-Tsai model is then modified for voids[7] by using Equations 7 and 8 in the main text, where it is then called the three-phase Halpin-Tsai-Christensen model.

ii. Cohen-Ishai Model

In this three-phase model, the CdSe core filler phase is within an effective matrix medium, which consists of voids in the TOPO matrix. The composite elastic modulus *E* in the model[8] is bounded by the limits set by assuming as the model boundary condition of either uniform displacement

$$E_{film,1} = E_{TOPO,v,1}\left[1+\frac{c_{CdSe}}{\frac{m^*}{m^*-1}-{c_{CdSe}}^{1/3}}\right] \tag{S4}$$

$$E_{\mathrm{TOPO,v,1}} = E_{\mathrm{TOPO}}(1 - c_{\mathrm{v}}^{*2/3}) \tag{S5}$$

or uniform stress

$$E_{\mathrm{film,2}} = E_{\mathrm{TOPO,v,2}}\left[\frac{1 + (m^{*} - 1)c_{\mathrm{CdSe}}{}^{2/3}}{1 + (m^{*} - 1)(c_{\mathrm{CdSe}}{}^{2/3} - c_{\mathrm{CdSe}})}\right] \tag{S6}$$

$$E_{\mathrm{TOPO,v,2}} = E_{\mathrm{TOPO}}\frac{1 - c_{\mathrm{v}}^{*2/3}}{1 - c_{\mathrm{v}}^{*2/3} + c_{\mathrm{v}}^{*}}, \tag{S7}$$

where c_{v}^{*} is the volumetric fraction of voids in the porous matrix (ligand matrix + voids) system ($= c_{\mathrm{void}} / c_{\mathrm{TOPO}} + c_{\mathrm{void}}$ in the text), c_{CdSe} is the volumetric fraction of core filler in the entire three-phase system, E_{TOPO} is the TOPO matrix elastic modulus, $E_{\mathrm{TOPO,v}}$ is the reduced modulus of the porous matrix for the respective model, and $m^{*} = E_{\mathrm{CdSe}} / E_{\mathrm{TOPO,v}}$ is ratio of moduli of the filler core E_{CdSe} and that of the porous matrix. This treats porosity differently than in the Christensen model[7] (Equations 7 and 8 in the main paper). The average $E_{\mathrm{film}} = (E_{\mathrm{film,1}} + E_{\mathrm{film,2}})/2$ can be used as a measure of the elastic modulus. This model gives higher elastic moduli than the more-widely-used Tsai-Halpin model.

iii. Representative Results

Representative results of the models of the effective elastic modulus of dried, TOPO-treated EPD CdSe NC films are given in Table S1, for 4 nm diameter (r = 2 nm) CdSe cores (E_{CdSe} = 21.5 GPa) for E_{TOPO} = 0.8 GPa. All Poisson ratios are set equal to 0.18. Loose packing of the cores is assumed (f = 0.58), with minimum void fractions, as described in the main paper. Because the two-phase Halpin-Tsai model does not include the effect of the voids that exist for l = 0.1, 0.2, and 0.3 nm, the corresponding entries in the table are blank. The

Halpin-Tsai-Christensen model includes the effect of voids in the limit of small void fractions (Equation 1). The modulus predicted by the Cohen-Ishai model decreases with increasing void fraction much faster than this, and is likely less accurate.

Ligand shell thickness, l (nm)	CdSe volume fraction, c_{CdSe}	TOPO volume fraction, c_{TOPO}	Void volume fraction, c_{void}	Halpin-Tsai model, E_{film} (GPa)	Halpin-Tsai-Christensen model, E_{film} (GPa)	Cohen-Ishai Model, $E_{film,1}$ (GPa)	Cohen-Ishai Model, $E_{film,2}$ (GPa)	Cohen-Ishai Model, E_{film} (GPa)
0.6	0.46	0.54	0	1.97	1.97	2.15	2.88	2.51
0.5	0.51	0.49	0	2.25	2.25	2.52	3.26	2.89
0.4	0.58	0.42	0	2.66	2.66	3.06	3.80	3.43
0.3	0.58	0.30	0.12	-	2.53	1.87	2.74	2.30
0.2	0.58	0.19	0.23	-	2.44	1.14	1.67	1.40
0.1	0.58	0.09	0.33	-	2.50	0.53	0.74	0.63

Table S1: Representative model results. The two-phase Halpin-Tsai model does not include the effect of the voids that exist for l = 0.1, 0.2, and 0.3 nm, and these results are not given.

B. Re-analysis of the Previous Use of Micromechanics Models

Using Raman scattering and fracture patterns, in the Supporting Information of Ref. 11 we found the elastic modulus of 3.2 nm diameter CdSe NC EPD films to be 6.8-12.4 GPa (for ν_{film} ranging from 0.5 to 0.1) using the CdSe bulk elastic modulus of 41.5 GPa. The elastic modulus of these NCs has recently been measured[5] and is now known to be 14 GPa; using this new modulus changes the range of E_{film} from that study to 2.4-4.3 GPa, which is a bit below that measured for (untreated) EPD CdSe NC films. Also, in that study we used micromechanics models to estimate the elastic modulus of TOPO from the film modulus, which was found to be 2.45-4.41 GPa, for ν_{TOPO} ranging from 0.5 to 0.1. In this revisited analysis, E_{TOPO} now ranges from 0.9-1.5 GPa, which is closer to the values used in the model in the current study.

Note that in Equation 7 of the Supporting Information to Ref. 11 E_{film} should be E_{CdSe}. Moreover, note that the given Halpin-Tsai equations (Equations 6 and 7 there) are presented here in a more accurate manner.

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