Controlled Electrophoretic Deposition of Smooth and Robust Films of CdSe Nanocrystals

Mohammad A. Islam,[†,‡] Yuqi Xia,[‡] Donald A. Telesca Jr.,[†,‡]
Michael L. Steigerwald,[‡] and Irving P. Herman*,[†,‡]

Department of Applied Physics and Applied Mathematics and Materials Research Science and Engineering Center, Columbia University, New York, New York 10027

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Controlled purification of the CdSe nanocrystal primitive solution critically affects the electrophoretic deposition of these nanocrystals. Film morphology is optimized after two precipitation steps with no TOPO/TOP added in either step. This suggests the need to minimize impurities in the solution or to remove a controlled, small fraction of the ligands on the nanocrystal surface. The smoothness of electrophoretically deposited nanocrystal films is excellent (<3 nm rms roughness) and the appearance of particulates of nanocrystals due to homogeneous nucleation is minimized, even during patterned deposition. Treating the films with cross-linker molecules makes the electrophoretically deposited films very resistant to dissolution and flaking in many solvents.

Introduction

Current interest in nanocrystals stems from the properties and applications of individual nanoparticles, in solution or as powders, and the use of these nanoparticles as building blocks of larger assemblies, such as nanowires and films. Such films can contain high densities of nanocrystals that are either isolated or coupled.[1−3] The properties and utility of nanocrystals and assemblies of nanocomponents − and any other material as well − usually hinge on the synthesis and fabrication details. Electrophoretic deposition of nanocrystals[4] has been shown to produce thick, high-density dot films (>100 dots thick) that are much more uniform than thick films formed by dry casting or spin casting,[5] and offers the possibility of patterned deposition.[4] (Of course, the monolayer films formed by very slow, controlled, dry casting are even more uniform locally.[6−8]) Important challenges in preparing such films suitable for applications are achieving a high degree of smoothness, freedom from particulates, and resistance to attack by common solvents (chemical robustness). This article demonstrates how these goals can be met.

We recently showed that CdSe nanocrystal films of controlled thickness can be fabricated by electrophoretic deposition from CdSe nanocrystals capped by TOPO (trioctylphosphine oxide) in hexane solution by using uniform dc electric fields.[4] Identical ~0.5-μm-thick films deposited on both the positive and negative electrodes, implying that there are both positively and negatively thermally charged dots in solution. These films do not redissolve in the hexane solvent, as do dry-cast and spin-cast films, but, as seen below, are unstable in other solvents such as methanol and chloroform; this makes lithographic patterning using wet etching methods difficult. Spatially patterned films were fabricated, down to the 1-μm dimensions of the smallest patterns tested, by prepatterning the Au electrodes. Particulates were seen on patterned and unpatterned films,[4] presumably due to the homogeneous nucleation of nanocrystals in solution. Two procedures are shown here to be critical in forming high-quality electrophoretic films. Controlled, several-cycle reprecipitation of the nanocrystals from the primitive preparation solution improves film smoothness and hinders particulate formation. Treating the films to cross-link the nanocrystals after electrophoretic deposition makes these films chemically robust. Neither procedure was used in preparing nanocrystal films in our previous work reported in ref 4.

Experimental Methods

Synthesis of Nanocrystals. CdSe nanocrystals of diameter ~3.6 nm capped by TOPO and TOP (trioctylphosphine) were synthesized by wet chemical methods[9,10] in which solutions containing the molecular precursors for Cd [dimethyl cadmium, $(CH_3)_2Cd$; 0.15 g] and for Se (trioctylphosphine selenide, TOPSe; 1.4 mL, 1 M solution), and TOP (6 mL) were injected into a heated solvent (12 g of TOPO at 360 °C). After being heated at 300 °C for 1 h, the mixture was cooled to room temperature. The resulting mixture contained CdSe nano-

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* Corresponding author. E-mail: iph1@columbia.edu.
[†] Department of Applied Physics and Applied Mathematics.
[‡] Materials Research Science and Engineering Center.

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crystals capped by TOPO, along with free TOPO and TOP. Because the TOPO/TOP mixture would otherwise solidify at room temperature, *n*-butanol was added as a cosolvent.

The excess TOPO and TOP (as well as other adventitious impurities) were removed by well-known methods used in the size selective precipitation: methanol (25 mL) was added slowly to 5 mL of the original reaction mixture, causing the nanocrystals to precipitate. The supernatant and the precipitate were separated by centrifugation. The supernatant, which has most of the unwanted species such as free TOPO, TOP, and butanol, was discarded. The precipitate was left to dry in air for a few minutes. This procedure is referred to as 1× treatment (leading to "1× treated dots").

Small amounts of hexane (4 mL) and chloroform (1 mL) were then added to redissolve the nanocrystals; subsequently methanol (25 mL) was added slowly to reprecipitate them. Once again, this mixture was separated by centrifugation, the supernatant was discarded, and the precipitate was separated and dried. This is called 2× treatment. Repetition of this redissolution/reprecipitation process gives a 3× treatment, and so on.

Electrophoretic Deposition. As in ref 4, a pair of parallel plate electrodes [150-nm-thick Au on 10-nm Ti on Si (100)] of lateral dimension ~2 cm and separated by ~2 mm was submerged in the CdSe nanocrystal/hexane solution (3.0×10^{14} dots/cc) in a beaker, and high dc voltage (~500 V) was applied across them in a dark room at room temperature. For IR transmission and cross-linker experiments, 0.1-μm-thick ITO-on-glass electrodes were used. Dc current was monitored during the runs.

Pre- and Postdeposition Treatment. The two techniques used to improve the integrity of dry-cast CdSe dot films[11,12] were tested here. At times, the electrode surfaces were pretreated by a drop of 1,6-hexanedithiol (for Au electrodes) or 3-mercaptopropyl trimethoxysilane (for ITO electrodes) followed by heating at 70 °C under N_2 flow for 30 min, to improve surface adhesion. At times, after electrophoretic deposition, the film was submerged in a 10 mM solution of 1,7-heptanediamine in methanol for 4 h, followed by heating at 70 °C under N_2 flow for 30 min to cross-link the dots.[11,12]

Film Analysis. The films formed on both electrodes were investigated after removal from the beaker using profilometry, scanning electron microscopy (SEM), visible microscopy, atomic force microscopy (AFM) (tip diameter ~10 nm), photoluminescence (PL) spectroscopy, and photoelastic-modulated Fourier transform infrared reflection absorption spectroscopy (PEM-FTIRRAS).[13] Profilometry traces were taken to determine film thickness. The thickness of the electrophoretically deposited films was targeted to be typically 0.5−0.7 μm (~30 min run), as it was shown previously that films thicker than 0.8 μm crack, likely due to stress relaxation.[4]

Results and Discussion

Treatment by Repeated Precipitation. Electrophoretic deposition on Au and ITO films was conducted with the CdSe/TOPO nanocrystals in hexane solvent, separately after either 1×, 2×, 3×, 4×, or 5× treatment. If the particles were treated more than five times they did not redissolve in hexane anymore. This suggests that the particles have lost most, if not all, of their capping TOPO/TOP, as is confirmed below. In fact, the 5×-treated particles precipitated from hexane after a day or two. Films were also formed by dry casting and spin casting after each precipitation cycle on the same type of substrate, and similarly analyzed. Results are first presented for films with no pre- or postdeposition treatments.

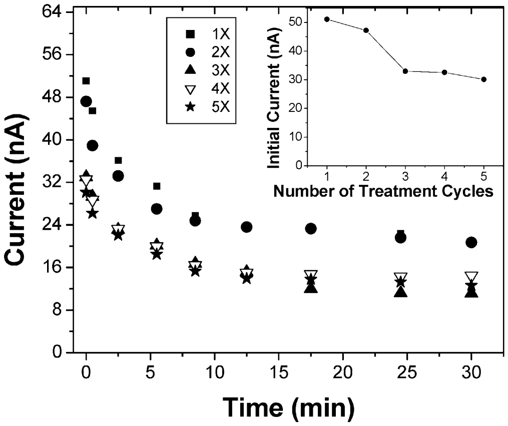

Figure 1. Current vs time during the electrophoretic deposition of films on Au electrodes using 1×−5× treated CdSe nanocrystals (with no added TOPO/TOP).

The initial dc current density during deposition was found to be a few tens of nA/cm^2 for 530 V applied (2.5×10^5 V/m) and 3.0×10^{14} dots/cc solution, as shown in Figure 1 for 1×−5×-treated particles. Without the dots, the current was ~100× smaller with the hexane solvent only.

Figure 2 shows SEM images and large-area visible micrographs of typical regions in the films electrophoretically deposited on the positive Au electrode from 1×−5×-treated nanocrystals. The morphology and other properties were the same for the corresponding films formed on the negative Au electrode, except for films made using 1×-treated dots. Film morphology was best after 2× treatment (Figure 2b); these films were very smooth, with ~2.2 nm rms roughness over 5 μm, as seen in Figure 3a. (The gold film electrode had ~2.5 nm rms roughness.) Smooth films were also formed on ITO electrodes. Although it is possible that some of the nanocrystals may reach the surface as agglomerates, this high degree of smoothness suggests that they are not agglomerates in the film. Films formed with 3×-treated particles had relatively good morphology, but were a bit rougher, as seen in the SEM image of Figure 2c. Large clumps or particulates are visible for 4×- and 5×-treated dot films. When the nanocrystals were precipitated just once, they formed clusters on the positive electrode − occupying 10−20% of the electrode area, with no observable deposit on the negative electrode. AFM images show these clusters of the nanocrystals are uniform in size and rhombohedral, ~0.5 μm on a side (inset of Figure 2a). The ratio of the number of nanocrystals deposited [as determined from the film thickness and estimated packing fraction] to the number of elementary charges collected [as calculated by integrating the current with time] depends on postsynthesis treatment, and is 0.7 for films formed using 1×-treated dots and 10 for films formed using 2×-treated dots.[4]

The morphology of the ~0.5−0.7-μm-thick films formed by dry casting and spin casting with 1×−5× treated dots was very poor, and much worse than that of electrophoretically deposited films with 2×-treated dots.

In a series of runs, TOPO, TOP, or TOPO/TOP was added (0.05%, 0.1%, 0.2%, or 1% by mass) to the CdSe nanocrystals/hexane/chloroform/methanol solution dur-

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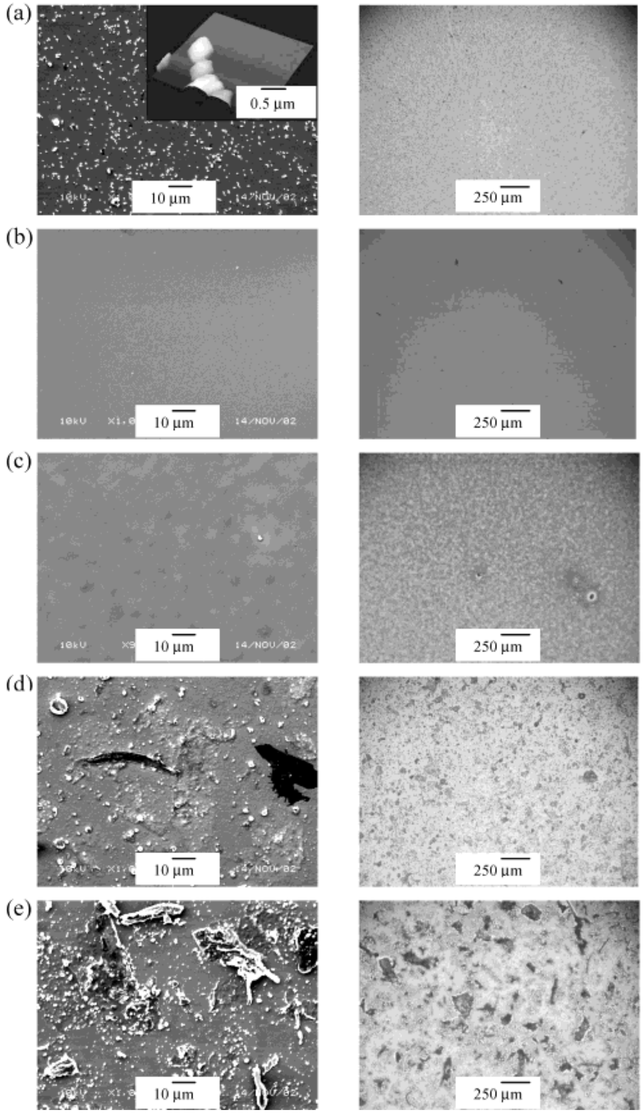

Figure 2. SEM images (left) and visible micrographs of ~0.25-cm lateral dimension (right) of the CdSe dot films formed by electrophoretic deposition on the positive Au electrode from the 1×−5× treated CdSe dots (with no added TOPO/TOP), in (a)−(e), respectively. The results for the films formed on the negative electrode are similar to those for the 2×−5× treated dots. For the 1×-treated dots, there was no deposition on the negative electrode and deposition occurred in rhombohedral-shaped islands on the positive electrode, as seen from the AFM image of the inset to (a).

ing the second to fifth reprecipitation cycles, and electrophoretic films were formed using these dots. (In size-selective precipitation of CdSe/TOPO nanocrystals, it is standard practice to add ~1% TOPO/TOP during each precipitation cycle to replenish the loss of capping TOPO/TOP.) Film smoothness and freedom from particulates monotonically improved with decreasing additions, and were optimized with no additions. Adding 1% TOPO/TOP in the second treatment step increased the rms roughness from 2.2 to 15 nm as seen in Figure 3b. In fact, there was little electrophoretic deposition when only free TOP was added. TOPO and TOP were not added during the preparation of the dots used to make the films discussed below.

Films were electrophoretically deposited using the "best" particles (2×-treated, with no added TOPO/TOP) on patterned Au film electrodes on the SiO_2 on Si substrate. Figure 4 shows the patterned films were also of high quality, with very few of the large particulates that were seen in our earlier publication.[4]

The conductivity σ of the 2×-treated dot solution was measured using $\sigma_{\text{measured}} = J/E$, where J is the dc current density and E is the applied field. This is analyzed using the Einstein−Nernst equation: $\sigma_{\text{calculated}} = n_{\text{charged}}e^2/6\pi\eta R$, where n_{charged} is the density of charged CdSe dots, η is the viscosity of the solvent (3.26×10^{-4} N s/m^2), and R is the hydrodynamic radius of the spheres (2.35 nm for 3.6-nm core diameter CdSe dots with a 1.1 nm TOPO cap).[14] By comparing σ_{measured} with $\sigma_{\text{calculated}}$ it is found that only 0.22% of the 2×-treated dots were charged, if there were no other ions in the dot solution.[4] The initial dc current during electrodeposition decreased with the number of treatment cycles, as shown in Figure 1. This is consistent with fewer individual particles dissolving in solution [possibly due to more particle aggregation and seen by particulate formation (Figure 2e)] or a smaller fraction of dots that are charged (by up to a third in the 3×−5×-treated dots compared to the 1×−2×-treated dots, from Figure 1); these can result from the loss of ligands during successive precipitation cycles.

The PL peaks of the CdSe nanocrystals in solution shift to the red with several treatment cycles, from 580 to 582 nm for 1×-, 2×-, and 3×-treated dots to ~586 nm for 4×- and 5×-treated dots. The PL spectra of the electrodeposited films show a sharp peak at 582−583 nm for 1×-, 2×-, and 3×-treated dots and 590−592 nm for 4×- and 5×-treated dots. The sharp peaks indicate that the films are made of dense arrays of dots that are not greatly changed from the solution, aside from the redshift from the solution PL due to interdot radiative transfer between nearby dots to larger, lower band gap dots in the film.[15] There was strong PL from the electrophoretically deposited, dry-cast, and spin-cast films, with intensities that changed little with successive treatment cycles (when taking into account the small coverage during the electrophoretic deposition of 1×-treated dots).

The density of TOPO/TOP ligands in these electrophoretically deposited films was probed by PEM-FTIR-RAS, as shown in Figure 5. The CH_2 symmetric and antisymmetric stretches and the CH_3 antisymmetric stretch are at 2856, 2926, and 2956 cm^{-1}, respectively. The integrated area of the CH_2 antisymmetric stretching peak in the 2919 cm^{-1} to 2939 cm^{-1} region is largest for the best electrophoretically deposited film (2×-treated). [The integrated area of the IR peak for the films made from 1×-treated dots on the positive electrode is smaller than that of 2×-treated dots because of the low film coverage (10−20%).] The integrated area decreases monotonically with the number of treatment cycles (2×−5×) for these electrophoretically deposited films and for the dry- and spin-cast films. This also indicates that the number of capping ligands on the nanocrystals decreases with each treatment cycle, which is not surprising. Because of the change in coverage between electrophoretic films made from 1×- and 2×-

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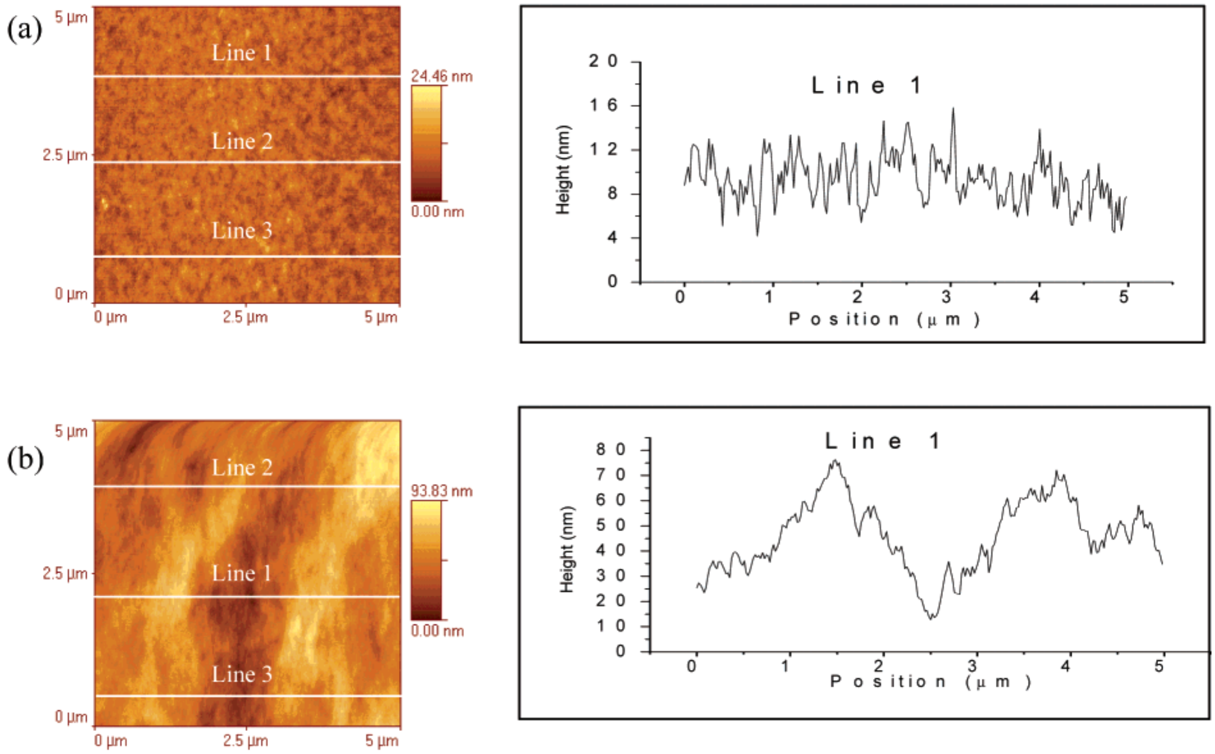

Figure 3. AFM images of the films formed on the positive Au electrode from (a) 2×-treated dots with no TOPO/TOP added, and (b) 2×-treated dots with 1% TOPO/TOP added in step 2. The surface profile to the right of each AFM image shows the morphology and roughness of each film. In each figure, the three traces show similar roughness.

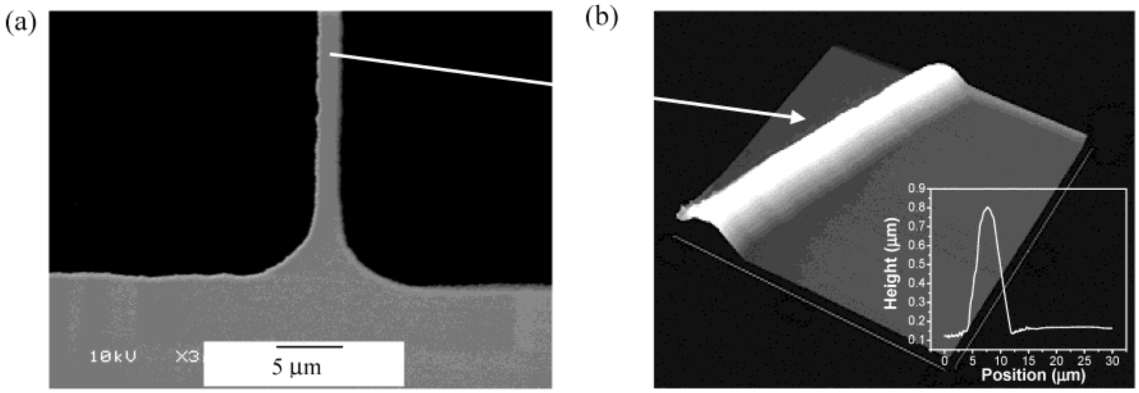

Figure 4. (a) SEM and (b) AFM images of a CdSe dot film electrophoretically deposited on a 2-μm-wide, 0.15-μm-thick patterned Au line electrode on a 0.2-μm-thick SiO_2-on-Si substrate (dark regions in SEM), using 2×-treated dots with no TOPO/TOP added. The inset to (b) shows a height of ~700 nm: ~150 nm from the Au electrode and ~550 nm from the CdSe dot deposition. The dimensions of the AFM image are 30 μm × 30 μm.

treated dots, the change in ligand coverage was checked in the dry- and spin-cast films. There is no apparent decrease in the CH_2 antisymmetric stretch peak height in dry-cast (Figure 5 inset) and spin-cast films made from 2×-treated dots relative to those made from 1×-treated dots, suggesting that ligand coverage is about the same. Unlike some other ligands, TOPO binds strongly and loss of ligands is not due to the volatility of the capping ligands in the dried nanocrystal films.[16,17]

The TOPO ligand peaks in the best electrophoretically deposited dot films (2×-treated dots) are the same for films on the positive and negative electrodes. The CH_2 stretches are about 6−9 cm^{-1} lower than those in neat TOPO and 7−9 cm^{-1} higher than those in dry-cast and spin-cast CdSe dot films. This suggests a greater degree of bonding between the TOPO in adjacent CdSe/TOPO dots in electrophoretically deposited films, these dots are closer together than in dry-cast and spin-cast films, or possibly the effect of film strain.

PEM-FTIRRAS probes only the region near the surface of the film. Transmission FTIR measurements integrating the thickness of the whole film could not be made for films deposited on the Au electrodes. Qualitatively similar results − weaker TOPO peaks with more treatment cycles − were seen by transmission FTIR when the films were formed electrophoretically, by dry-casting or by spin-casting on transparent ITO-on-aluminosilicate glass electrodes.

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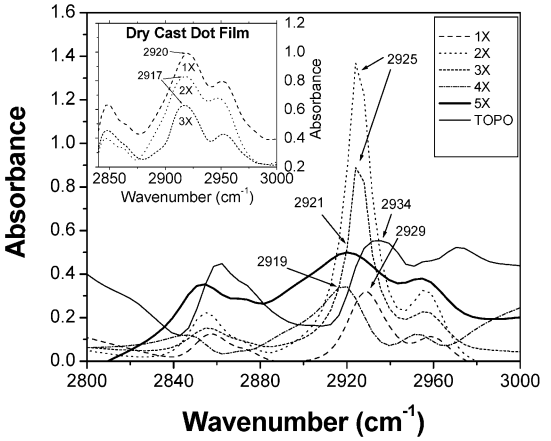

Figure 5. PEM-FTIRRAS spectra of the electrophoretically deposited films formed on the positive Au electrode from 1×–5×-treated CdSe dots with no added TOPO/TOP. Results for the films electrophoretically deposited on the negative electrode (except for the 1×-treated dots, for which no film forms) and for the dry-cast and spin-cast films are similar. The inset shows the PEM-FTIRRAS spectra of the dry cast films formed on Au films from the 1×–3×-treated CdSe dots with no added TOPO/TOP.

The number of treatment cycles does not seem to have a big impact on the density of charged dots in solution or charge transfer at the electrode. It clearly impacts the sticking of dots on the surface and homogeneous nucleation of particulates of dots. The improvement in film morphology when the component dots were treated for the second time is consistent with a decrease in impurities in the solution. Because some of these "impurities" could be TOPO/TOP and the TOPO/TOP in solution is in equilibrium with that on the dots, this improvement could also be caused by the concomitant small decrease in the number of TOPO/TOP ligands on the dot surface (smaller than that observable in the IR spectra here). Good packing or adhesion of dots on the dot films during electrophoretic deposition could be, in fact, assisted by the creation of some reactive surface sites not bound by ligands in the second precipitation. These bare sites may assist by enabling some interdot bonding – possibly helped by charge transfer during deposition – or by enabling the dots to come closer, making a more tightly bound assembly. Either is suggested by the upshift in TOPO CH_2 stretching mode frequencies in electrophoretic dot films relative to dry- and spin-cast dot films. Because of the rapid equilibrium between TOPO/TOP in solution and on the dot surface, it is difficult to distinguish between a mechanism in which the existence of impurities between the depositing dots hinders deposition and one in which the creation of some empty sites on the surface actually assists the deposition process. Both mechanisms are consistent with the worsening morphology when more TOPO or TOP was added during the reprecipitation steps. The worsening of the morphology of electrophoretic films composed of dots prepared with more precipitations, from 2×- to 5×-treatment, may be due to the excessive loss of TOPO ligands on the dot surface and homogeneous formation of clumps of these dots. The concomitant dot size selection with successive precipitation is not likely to be a factor in film morphology.

Pre- and Posttreatment of the Films. Films electrophoretically deposited from 2×-treated CdSe dots do not dissolve in hexane, but they do deteriorate (flake off, dissolve, etc.) after extended soaking in chloroform, acetone, methanol, or chlorobenzene. After deposition, these dot films were treated with a 10 mM solution of 1,7-heptanediamine in methanol and heated (as detailed in the Experimental Methods section). The PL peak energy and the local roughness of the CdSe dot films electrophoretically grown were the same for the untreated and treated films. These treated CdSe dot films retained their integrity after sitting for 30 min in hexane, chloroform, methanol, acetone, chlorobenzene, and the electrolyte solution tetrabutylammonium perchlorate (TBAP) in dimethyl formamide. They did not dissolve or flake off, as confirmed by optical microscopy, and their roughness did not change after sitting in these solvents, as determined by AFM. The amine groups in 1,7-heptanediamine apparently cross-link adjacent CdSe nanocrystals, either at bare sites or sites where TOPO was initially bound. Lack of reactivity to these solvents was the same with or without use of the adhesion promoter (1,6-hexanedithiol for Au electrodes and 3-mercaptopropyl trimethoxysilane for ITO electrodes) prior to electrophoretic deposition. Untreated films and those treated with the adhesion agent both passed the "scotch tape" adhesion test. The adhesion layer did not affect the current during deposition.

Combining the electrophoretic deposition and cross-linking steps into one step was tested by adding the cross-linker to the nanocrystal solution during electrophoretic deposition and then heating the dried film – as during postdeposition cross-linking, with no adhesion pretreatment. Addition of 0.1–10 mM 1,7-heptanediamine decreased the dc current from ~50 nanoamps to 1–3 nanoamps and enhanced the rate of dot deposition up to 2-fold, as determined from the loss of dots in solution. After heating, these films also had strong PL, but were very rough and readily dissolved in chloroform and flaked off in acetone, methanol, and the TBAP solution. With successively lower concentrations of the cross-linker molecule added during deposition, from 0.01 to 0.001 to 0.0001 mM, the current increased from 20 to 44 to 53 nA, the current with no added cross-linker, and the film deposition rate and morphology transitioned to those with no added cross-linker. In no case were the films resistant to chemical attack after the heating step. The film deposited with 0.0001 mM of the cross-linker was chemically robust only after postdeposition cross-linking.

Apparently, the 1,7-heptanediamine does not cross-link the nanocrystals during dot deposition. It may promote the homogeneous formation of particulates of these dots that are deposited but not strongly bound to each other in the film. The cross-linker may enhance the net flow of nanocrystals to the surface, but either interferes with the charge-transfer process at the surface or produces large clusters of dots with low charge. This decrease in collected current with increased deposition rate is in contrast to changes when other "impurities" are added during electrophoretic deposition, such as TOPO, for which the current is not affected and the deposition rate decreases under some conditions.[4] According to the above mechanism, the poorer film morphology could also be due to attachment of the cross-linkers to vacant ligand sites.

Concluding Remarks

In conclusion, controlled treatment of the CdSe nanocrystal primitive solution critically affects the electrophoretic deposition of these nanocrystals. The smoothest films are formed using dots with 2×-treatment with no TOPO/TOP added in either precipitation step. This suggests that the key to the formation of high-quality films is either the need to minimize impurities in the solution (while maximizing the TOPO/TOP ligands on the nanocrystal surface) or the loss of a controlled, small fraction of the ligands on the nanocrystal surface. Also, the appearance of clumps of nanocrystals due to homogeneous nucleation is minimized, even during patterned deposition. Adding free TOPO/TOP, TOPO, or TOP during reprecipitation clearly hurts the electrophoretic deposition process. Treating the films with cross-linker molecules improves the chemical, and presumably mechanical, robustness of the electrophoretically deposited films. Without this purposeful cross-linking, the nanocrystals are likely bound together by van der Waals forces between the ligands and cores of neighboring dots; with cross-linking, however, the dots are more strongly bound to one another via the diamines that act as directly bridging ligands − one amine terminus of the cross-linker bonding strongly to one dot and the other terminus bonding to a neighboring dot. Introducing the cross-linker molecules during electrophoretic deposition does not lead to cross-linked films. Even though the properties of the cross-linked films were very good here without the use of an adhesion-promoter before deposition, adhesion may have been improved with the promoter.

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