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Rapid and multi-step, patterned electrophoretic deposition of nanocrystals using electrodes covered with dielectric barriers

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The rates of electrophoretic deposition (EPD) of CdSe nanocrystals (NCs) are approximately the same when powering electrodes on either the frontside or backside of thick dielectrics when the resistance of the NC colloid exceeds that of the dielectric barrier. Using electrodes with dielectric barriers enables conformal coverage over topography on the frontside. It also enables multistep processing when combined with powering patterned frontside electrodes for localized EPD. Powering patterned backside electrodes produces film features that are wider than the electrode dimensions, which is consistent with the results of modeling the electric field profile. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4863849]

Electrophoretic deposition (EPD) is a versatile method in which DC electric fields are used to fabricate a wide range of films,^{1,2} including those formed by depositing charged nanocrystals (NCs) from a colloid. EPD using colloids of charged NCs that are capped with organic ligands and in nonpolar solvents forms films of distinct NCs.^{2,3} This can be important for a range of applications, including the fabrication of light emitters and detectors, and photovoltaic devices with semiconductor nanocrystals. EPD of charged nanoparticles in polar solvents is often used to form films that are later densified to produce uniform and dense ceramics or composites.¹

During EPD, the conducting electrode is usually in contact with the colloidal solution (and so is on the "frontside" of the electrode substrate). However, recent work has demonstrated EPD where the conducting electrode is separated from the colloid by a dielectric barrier. In one study, the conducting pathway (a "buried" layer) was covered by a thin insulator, 30 nm thick polystyrene films on Si, to enable EPD of films of CdSe NCs.⁴ In another, the conducting electrode was fabricated on the "backside" of $100 \,\mu\text{m}$ thick polytetrafluoroethylene (PTFE) (and so was not in contact with the colloid) for EPD of poly-(3)hexylthiophene (P3HT) clusters on the frontside.⁵ EPD with such buried or backside conducting electrodes, sometimes called dielectric barrier EPD (DBEPD),⁵ has potential advantages of being able to deposit directly on dielectrics, avoiding the undesired electrochemistry and heating that can occur on conducting surfaces. EPD of nanoparticles (without molecular ligands) was demonstrated on insulating porous layers^{6,7} (and possibly also on insulating solid layers⁸). However, in this porous layer, the conductivity path to the underlying conducting electrode was maintained by charged species in the conducting solvent and not electron transport through the dielectric or "insulator," as in DBEPD.

While these previous studies demonstrated that DBEPD can occur, they did not address the key issues that can either

limit or expand near-term use of DBEPD. DBEPD would be expected to be very slow compared to EPD with frontside electrodes, because the large voltage drop across a dielectric barrier would make the particle drift speed (which is proportional to electric field and therefore the voltage drops across the colloid) small and therefore the deposition rate would be slow. The applied voltage and other conditions must be set so the voltage drop across the colloid is large enough for fast EPD, with the electric field in the dielectric being smaller than the breakdown limit. We show that DBEPD of colloidal NCs can be as fast as with frontside electrodes, even with quite thick insulators, for very common EPD experimental conditions. In addition, we show that this and the spatial resolution of patterned DBEPD can be understood by modeling the electric field in the colloid and dielectric. We also demonstrate versatile fabrication processes that utilize both frontside and backside electrodes.

CdSe nanocrystals of 3.8-5.1 nm diameter capped with phosphonates and trioctylphosphine oxide (TOPO) were synthesized using the procedure in Ref. 9 but with two precursor injections¹⁰ and were washed 3-5 times and then dispersed in hexane solvent before EPD, as in Ref. 11. CdSe NC diameters were determined using visible absorption spectroscopy, as has been confirmed by transmission electron microscopy.¹² The electrode substrates were highly insulating, 1.2 mm thick glass slides (Electron Microscopy Sciences). For the maximum voltage used here, 3000 V, the maximum electric field in the substrate $(3000 \text{ V}/1.2 \text{ mm} = 2.5 \times 10^6 \text{ V/m})$ was much smaller than the breakdown fields of glasses ($\sim 10^7 - 10^8 \text{ V/m}$). (No evidence of breakdown was seen.) The frontsides of the electrode substrates ($\sim 2 \text{ cm}$ lateral dimensions) were in contact with the colloid solution and separated by 2.5 cm by using a cylindrical teflon chamber of this length and 2 cm inside diameter; O-ring seals prevented leakage and contact of the solution with the backside of the substrate electrodes (Fig. 1(a)). Unpatterned backside electrodes for DBEPD were made by attaching $\sim 2 \text{ cm}$ square piece of Cu/Ni tape (Ted Pella) to the back of the glass. Unless otherwise specified, "Au" electrodes were formed by thermal evaporation of 10 nm Cr/50 nm Au, and the opposing electrode was an unpatterned frontside Au

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electrode. Patterned Au electrodes were fabricated by patterning photoresist (Heidelberg μ PG 101 Laser Writer), followed by metal deposition and then liftoff, to form centrally placed lines with the desired widths. EPD profiles were analyzed using scanning electron (SEM), optical, and atomic force microscopies and profilometry. SEM was used to examine the transverse profiles after cross-sectioning the samples (by cracking them).

As seen in Fig. 1(c), similar DBEPD CdSe NC films formed on the frontsides of both glass electrodes when 1000 V was applied for 30 min across unpatterned backside electrodes and the colloid solution (with a $\sim 1.2 \times 10^{15}$ /cm³ concentration of the 3.8 nm NCs, corresponding to 0.2 mg/ml). The circular shape of the films is determined by the teflon assembly and not the, larger, backside electrodes.

Figure 2 shows that EPD films with essentially the same thickness formed on both substrates when 1000 V was applied across either a pair of frontside Au electrodes, a pair of backside electrodes, or one frontside and one backside electrode (5.1 nm CdSe NCs, $\sim 5.0 \times 10^{14}$ /cm³, 0.2 mg/ml), so surprisingly, it did not matter whether the electrode was on the frontside or the backside of the substrate. It is not surprising that films with very similar thickness are formed on the positive and negative electrodes in each case (here and in Fig. 1(c)), since this has been seen and explained in past studies of CdSe NC EPD.³ However, the similarity of the films for these three types of electrode pairs was not expected since the voltage drop would normally be expected to occur across the thick insulating substrate; however, this is not the case here. The resistance of the colloid solution was $1.2 \times 10^{11} \Omega$ (conductivity is $6.8 \times 10^{-10} \Omega^{-1} m^{-1}$, using the initial EPD current of 8.5 \times 10 $^{-9}$ A) and that of the glass substrate was 3.7 \times 10 10 Ω (conductivity is $1.0 \times 10^{-10} \Omega^{-1} m^{-1}$, as obtained from separate I-V measurements). Consequently, most of the voltage drop was across the solution for each type of electrode pair: 1000 V, 610 V, 760 V, respectively, for the chosen resistivities and thicknesses of the colloid and substrate. (The small difference in electrode separations due the substrate thickness is not significant.) The growth of the EPD film itself should have



FIG. 1. (a) The EPD/DBEPD assembly used to prevent contact of the colloid solution with the backside electrodes; (b) schematic of the DBEPD process; (c) optical micrographs of the CdSe NC DBEPD films (with thickness \sim 505 nm on the positive electrode and \sim 565 nm on the negative electrode) with unpatterned electrodes on the backsides of the glass substrates.



FIG. 2. Thickness of CdSe NC EPD films formed on unpatterned positive ("P") and negative ("N") electrodes for a pair of frontside electrodes ("Au"), pair of backside electrodes ("Glass"), or a pair with one frontside (negative) and one backside (positive) electrode on the glass substrate, for a range of EPD durations, determined using atomic force microscopy. The specific electrode for the film is noted for each data point, along with the pair of electrodes. The solid line is the integrated current during the run with a pair of backside of electrodes, with a scale that enables comparison with the thickness data.

little effect on this, aside from the concomitant depletion of the NCs from the colloid leading to saturation effects (Fig. 2).

EPD requires transport of thermally charged NCs to the front of the electrode substrate, neutralization of the NCs, charge transfer to the conducting electrode, and sticking of the NCs to the substrate surface (or to the existing EPD film), and perhaps also clustering of NCs before deposition.¹³ Consequently, if limited by the first step, the EPD rate would be proportional to the drift velocity, which itself is proportional to the local electric field E. Assuming the DBEPD rate is proportional to the flux of charged NCs onto the substrate, this rate is $\propto V_a/(d_c/n_c e\mu_c + d_s/\sigma_s)$, where d_c , $n_{\rm c}$, $\mu_{\rm c}$ are the colloid layer thickness, concentration of charged NCs and NC mobility, d_s and σ_s are the thickness and conductivity of the substrate, e is the elementary charge, and $V_{\rm a}$ is the applied voltage. So, rapid DBEPD would be expected when $d_c/n_c e\mu_c$ is designed to be larger than, or at least not much smaller than, d_s/σ_s .

Figure 2 also shows that the film thickness increased approximately linearly with time, until saturation. Film thickness also increased with EPD voltage (until saturation) and NC concentration. The integrated current during EPD when the pair of backside electrodes was used and the thickness are seen to scale with time the same way in Fig. 2.³ These curves are similar for the other electrode pairs.

The prospects of using patterned electrodes for DBEPD was addressed in the study depicted in Fig. 3. This figure compares EPD using (a) backside and (b) frontside electrodes stripes with width 0.1 mm (\ll substrate thickness, 1.2 mm). 1000 V was applied for 30 min across the same colloid solution as used to obtain Fig. 2, and the Au counter electrodes were not patterned. Figure 3(a) shows that DBEPD using the patterned backside electrode produces an \sim 850 nm thick feature with \sim 1.8 mm full-width at half-maximum (FWHM). Figure 3(b) shows the lateral dimension of the EPD feature



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FIG. 3. Optical micrographs of CdSe NC EPD using 0.1 mm wide patterned line electrodes on the (a) backside and (b) frontside of the glass substrate (positive electrode), along with the profilometer trace and, for (a), the calculated electric field profiles on the frontside.

matches that of the patterned frontside electrode, as was also seen in earlier work³ down to a width of 1 μ m.

To understand Fig. 3(a), we modeled the electric field *E* on the top of the glass using a two-dimensional steady-state finite-difference model of Ohm's Law, $J = \sigma E$, and the continuity of current equation in steady state, $\partial \rho / \partial t = -\nabla \cdot J = 0$, where σ is the conductivity and ρ and *J* are the charge and current densities. This is justified because steady state current flow dominates essentially throughout EPD, since the RC constants of the colloid and glass substrate are relatively short, ~ 0.024 s and 0.58 s, respectively (using the dielectric constants for the hexane solvent, 1.8, and the glass electrode, 6.7).

Figure 3(a) shows that the profiles of the normal components and magnitudes of *E* at the top surface of the glass slide ($E_{normal FWHM} = 2.2 \text{ mm}$, $E_{magnitude FWHM} = 3.7 \text{ mm}$). They are much broader than the electrode, as would be expected between line and plate electrodes in a line/plane capacitor. The *E* field profile widths match the EPD profile well, with the normal component fitting better, so this is consistent with the general mechanism of EPD. (With this approximately line-plane geometry, *E*, 3.6×10^4 V/m, exceeds that with an unpatterned backside electrode, 3.0×10^4 V/m, even though the voltage drop across the colloid, 170 V in the middle of the substrate, is smaller than that with an unpatterned electrode, 760 V.)

DBEPD can preserve pattern resolution only when the dielectric barriers are relatively thin. Calculations show that for a backside electrode feature of width $w = 0.1 \text{ mm} = 100 \,\mu\text{m}$, the FWHM of E_{normal} on the frontside increases linearly from $\sim 2w$ to 4w for (glass) dielectric thicknesses ranging from 0.5w to 2w (for this electrode arrangement). Also, pattern resolution cannot be preserved much better by changing colloid conductivity. Starting with the conditions of Fig. 3(a), this FWHM decreases to 2.1 mm (from 2.2 mm) when the conductivity is increased by either $10 \times \text{ or } 100 \times$; it increases with decreasing conductivity first slowly, to 2.7 mm when the conductivity is decreased by $10 \times$, and then faster to 13.2 mm when it is decreased by $100 \times$.

Conformal coverage of topography on the substrate frontside by DBEPD would add a new dimension to potential applications of EPD. Figure 4 demonstrates conformal coverage over two different types of 5 μ m wide lines on the substrate frontside, by using two different types of DBEPD processes, both with unpatterned backside electrodes and unpatterned frontside counter electrodes. The SEMs of the cross-sectioned samples in Figs. 4(b) and 4(c) show



FIG. 4. (a) Schematic of unpatterned CdSe NC DBEPD over frontside topography, a 350 nm thick, 5 μ m wide Cr/Au stripe, with scanning electron micrographs of the cross-sectioned substrate, showing blanketed conformal coverage by (b) ~360 nm and (c) ~1850 nm thick CdSe NC DBEPD films. (d) Schematic of local EPD of CdSe NCs on a patterned 350 nm thick, 5 μ m wide Cr/Au stripe, followed by unpatterned DBEPD of P3HT over this frontside topography, with (e) scanning electron micrograph of the cross-sectioned substrate, showing a ~1200 nm thick DBEPD P3HT film conformally covering a ~300 nm thick local EPD deposit of CdSe NCs atop the 5 μ m wide Cr/Au stripe. (The film asymmetry was caused by the patterning step.)

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blanketed, conformal coverage over \sim 350 nm high frontside topography (300 nm Cr/50 nm Au stripe) on the positive electrode by relatively thin (\sim 360 nm) and thick (\sim 1850 nm) films of CdSe NCs, respectively, formed by using the approach illustrated in Fig. 4(a). This was done by using 4.0 nm CdSe NC colloids ($\sim 2.6 \times 10^{15}$ NCs/cm³, 0.5 mg/ml in (b) and $\sim 6.7 \times 10^{15}$ NCs/cm³, 1.3 mg/ml in (c)), with 1000 V applied for 30 min. The SEM of the cross-sectioned sample in Fig. 4(e) shows conformal coverage by $a \sim 1200 \text{ nm}$ thick P3HT film (from P3HT clusters¹⁴) by DBEPD, by using the unpatterned backside electrode, over $a \sim 300 \text{ nm}$ thick CdSe NC EPD film that had first been selectively deposited on \sim 350 nm high frontside topography (300 nm Cr/50 nm Au stripe), as is illustrated in Fig. 4(d). For the CdSe NC EPD, 300 V was applied for 3 min using the substrate as the positive electrode as in Figs. 4(b) and 4(c) (4.0 nm, 5.1×10^{15} NCs/cm³, 1.0 mg/ml). For the P3HT DBEPD, 3000 V was applied for 120 min powering the same substrate as negative electrode, as is necessary for P3HT, using 2.4 mg P3HT (from Lumtec (LT-S909, $MW > 45\ 000$ Daltons)) first dispersed in 30 ml toluene, and then diluted with 20 ml hexane.

Because of this conformal coverage, a combination of an unpatterned backside electrode and several distinct patterned frontside electrodes can be the building blocks for fabricating discretionary 3D, multi-layer structures of different NCs (or materials such as conducting polymers) by alternately powering one of a series of electrodes with different solutions present, as is illustrated in Figs. 4(d) and 4(e).

In conclusion, DBEPD rates can be fast with carefully designed geometry and colloid conditions, and the coverage is conformal. 3D multi-level discretionary structures can be fabricated using multi-step EPD, by alternately powering patterned frontside, and patterned or unpatterned backside electrodes for a variety of dielectrics, including flexible substrates. More functionality can be added by utilizing several existing techniques, such as those used in the EPD of mixtures of different NCs^{15,16} and of functionally graded

materials.¹⁶ Transfer of these findings from nonpolar to polar and aqueous colloid solutions requires the use of lower voltages (on the order of volts) to avoid solution electrochemistry; with the much higher conductivity of these solutions, the fields in the colloids would be much smaller.

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