Thin Films of Copper Indium Selenide Fabricated with High Atom Economy by Electrophoretic Deposition of Nanocrystals Under Flow

Andrew D. Dillon, Long Le Quoc, Mustafa Goktas, Borirak Opananont, Subham Dastidar, Shawn Mengel, Jason B. Baxter, Aaron T. Fafarman*

*Corresponding author: fafarman@drexel.edu

Electrophoretic deposition (EPD) of colloidal nanocrystals (NCs) under flow is explored as a general method for the fabrication of semiconducting thin films. For photovoltaic applications, a low process voltage is highly desirable to avoid damaging the accreting semiconductor. Here we report a continuous flow reactor design that can operate at reduced voltage compared to a traditional batch reactor while preserving the electrophoretic velocity of the NCs by utilizing narrow electrode spacing. In a batch reactor, the low ratio of reactor volume to electrode surface area dictated by such a narrow spacing of the electrodes would impose a limit on the mass of nanocrystals that are resident in the reactor and therefore the thickness of the films that can be deposited. By continuously flowing the colloidal dispersion of NCs this limitation is obviated and thick films can be deposited. Through modeling and experiment we demonstrate the process parameters necessary to completely utilize the NCs in the feed solution, thereby achieving nearly 100% atom economy in the deposition process. The reactor design is compatible with large area substrates and is specifically designed to enable continuous, high-rate fabrication of the active layer of photovoltaic cells.

Keywords: EPD, thin film, quantum dot, flow microreactor

1. Introduction

A solar panel fabricated entirely at low temperature from liquid starting materials on a flexible plastic sheet could be made at extremely low cost, in a process akin to printing a newspaper. Colloidal dispersions of semiconductor nanocrystals (NCs) in solvent are a widely pursued class of such 'inks' for printing the photoactive layer of a photovoltaic cell. (Gur et al., 2005; Huynh et al., 1999; Tang et al., 2011) Colloidal NCs can be synthesized with high chemical and crystal-phase purity and a narrow size distribution (Murray et al., 1993). When assembled into functional optoelectronic thin films these attributes are necessary for good electronic performance. (Beverly, 2002; Choi et al., 2012; Gao et al., 2013; Koh et al., 2011; Mićić et al., 2001; Nelson and Zhu, 2012). Solar cells utilizing colloidal NC solids as the active layer have exhibited solar power conversion efficiency greater than 10% (G.-H. Kim et al., 2015; Chuang et al., 2014; Ning et al., 2014) while examples that use NCs as building-blocks for sintered thin films have achieved efficiencies of 10-12%. (Cao et al., 2012; Panthani et al., 2014) However, these results have relied on spincoating to deposit the ink, a process with limited yield and scalability.

As an alternative, electrophoretic deposition (EPD), has been in commercial practice since the 1940s, and is employed to coat products as large as automotive body parts, at sufficiently low cost to justify its use in commodity products like enameled tableware. (Boccaccini et al., 2002; Corni et al., 2008; Der et al., 1943; Lesley, 1949; Van der Biest and Vandeperre, 1999). In the EPD process, charged particles dispersed in a solvent drift in an externally applied electric field (electrophoresis) and accumulate on the oppositely charged electrode as a dense film of particles. EPD has been studied for the synthesis of superconductors (Closset et al., 2014; Greci et al., 2006) and biocomposite implants. (Sun et al., 2009).

Continuous flow microreactors have also been explored for manufacturing. While many different groups have reported using them to make liquid and gas products including dyes and pharmaceuticals, (Kiwi-Minsker and Renken, 2005; Watts and Haswell, 2005, 2003; Watts and Wiles, 2007; Wille et al., 2004) microreactors have only recently been used to deposit solid materials on surfaces. (Opasanont et al., 2014; McPeak et al., 2013; Chang et al., 2009; Choi et al., 2013; Jung et al., 2008; Mugdur et al., 2007; Su et al., 2013). Recently there has been a report of combining the two concepts and using EPD to deposit metal nanoparticles in a flow reactor. (Koenen et al., 2015)

However, semiconductor film fabrication presents formidable challenges for EPD, and on the commercial scale it has been applied only to insulators and conductors thus far. Semiconductor NCs have been deposited by EPD in batch reactors previously using applied bias typically in the range of hundreds of volts. (Islam et al., 2004; Islam and Herman, 2002; Krejci et al., 2012; Mainz et al., 2014; Singh et al., 2013; Wong and Searson, 1999). For functional semiconductors, low deposition voltage is beneficial to avoid undesirable electrochemical side-reactions that could otherwise degrade the accreting semiconducting film. However, low voltage operation presents a significant mass transport challenge for conventional EPD; given the typical centimeter-scale electrode spacing, low voltage equates to a small electric field, reducing the electrophoretic velocity of the particles and, hence, the deposition rate. In a batch system, it is not feasible to raise the electric field magnitude by reducing the electrode spacing because the film thickness is limited by the initial number of particles between the electrodes. In this work we employ a simple reactor design to demonstrate that flowing fresh NC suspension between two closely spaced electrodes in a continuous flow reactor can overcome both the mass transport limitation of low voltages and the total mass limitation of a confined volume to enable high deposition rate and large film

thickness. By comparing the products of the reactor to the predictions of a simple convection-migration model, we have elucidated the relationships between process parameters such as voltage, flow rate, and particle mobility and process objectives including film thickness, uniformity, deposition rate, and feed utilization, under the conditions of laminar flow. We show that the process is compatible with flexible conductive substrates such as foils and metalized plastic sheets. In light of these results, EPD under flow could be a uniquely efficient manufacturing platform for the fabrication of thin-film semiconductors by continuous, high-rate processes such as roll-to-roll manufacturing, as discussed below.

2. Experimental Methods

2.1 Materials

Oleylamine (OLAm, 70% technical grade), Selenium powder (Se), diphenylphosphine (DPP) were purchased from Sigma-Aldrich; Copper (I) Chloride (CuCl) from Strem Chemicals; Indium (III) Chloride (InCl_3) from Acros Organics, toluene and acetonitrile from Fisher Scientific, and 200 proof ethanol from Decon Labs.

2.2 Copper Indium Selenide (CIS) NC Synthesis

For the present work, we employ colloidal NCs of copper indium selenide (CIS), a promising photovoltaic material. (Gillespie et al., 1999; J.-Y. Kim et al., 2015; Panthani et al., 2013, p. 2) The CIS NCs are synthesized by previously established methods, (Panthani et al., 2013) in which a diphenylphosphine selenide precursor is injected into a hot solution of copper and indium salts in oleylamine, resulting in NCs that are coated with a layer of oleylamine surface capping groups as follows. In a N_2 filled glovebox, 99 mg of CuCl and 221 mg of InCl_3 were mixed in a three-neck flask with OLAm, which had been degassed at 110°C under vacuum for >2 hours. This mixture was transferred to a

Schlenk line and heated to 110°C under vacuum for 30 minutes. Afterwards, the solution was placed under N₂ and heated to 145°C. Separately, 553 mg of Se powder was combined with 1.2 mL of DPP and 17.5 mL of degassed OLAm in a N₂ filled glovebox. Upon the CuCl and InCl₃ solution reaching 145°C, 5 mL of DPP-Se solution was injected. The reaction was allowed to continue at 145°C for 1 hour, after which the solution was cooled.

After cooling, CIS NCs were washed with 25 mL of ethanol to flocculate the NCs. The suspension was then centrifuged at 4200 RCF for 5 minutes, and the resulting supernatant discarded. The NC pellet was then redispersed in 5 mL of toluene. This washing procedure was repeated twice, reducing the amount of ethanol to 5 mL. The resulting dispersion of CIS NCs in toluene was then stored until further use.

2.3 CIS Characterization Methods

In order to measure the NC synthesis yield, half of a normal yield was separated after washing and precipitated with excess ethanol and centrifuged at 4200 RCF for 5 minutes. The resulting pellet was dispersed in minimal toluene. This resulting solution was dropcast at 70°C onto a 1x1 inch glass slide of known weight, dried overnight under vacuum, and the mass of the added NCs determined. Electrophoretic mobility measurements were performed using a Brookhaven Instruments *Nanobrook Omni* in Phase Analysis Light Scattering Mode with alternating voltage at 200 V. Nanocrystal dispersions were filtered twice with 0.2 µm PTFE filters and then 0.02 µm Anotop (Whatman) filters prior to electrophoretic mobility measurements. All absorbance measurements were performed using a PerkinElmer LAMBDA 35 UV-vis spectrophotometer. To measure the relative concentration of the EPD reactor effluent as a function of time, a reference sample was first collected before voltage was applied. Subsequently for each time point, 0.2 mL was collected over two minutes and diluted in

2.4 mL of the appropriate toluene-ethanol mixture in a cuvette and the absorbance determined at 500 nm. Samples for TEM were prepared on carbon-coated copper grids by dropping a dilute dispersion of CIS NCs in toluene over an acetonitrile droplet. The droplet was then siphoned off, leaving CIS NCs deposited onto the copper grid below.

AFM measurements were performed using Veeco (Bruker) Metrology, Inc., Multimode Nanoscope IIIa Scanning Probe Microscope System in contact mode. Additionally, the transmittance of the deposited films was measured because the logarithm of transmittance is approximately proportional to film thickness; by calibrating this proportionality, transmittance measurements can serve as a convenient proxy for thickness. To achieve this calibration the thickness of a set of films was measured by AFM and plotted against the log of absorbance at 500 nm, yielding a linear least squares fit with the equation $\log(T_{500}) = (1.2 \pm 0.1) \times 10^4 \text{ cm}^{-1} \cdot t + (-0.03 \pm 0.03)$, where $\log(T_{500})$ is the log of the transmittance at 500 nm and t is the film thickness in centimeters. To measure film thickness as a function of position in the microreactor, the spectrometer beam was masked to an aperture of approximately 1 mm and the substrate placed at different positions relative to the center of the aperture. Scanning electron microscopy micrographs of EPD-deposited films were taken using a Zeiss Supra 50VP. CIS films were measured on an X-Ray Diffractometer (Rigaku Smartlab), using a Cu anode X-ray tube, $\text{Cu}_{K\alpha} = 0.154 \text{ nm}$.

2.4 Electrophoretic Deposition

The EPD microreactor is comprised of a conductive base plate and conductive substrate separated by an insulating spacer of 2.5 mm thickness, as seen in Figure 1a. Horizontal convective flow through the 34 mm long rectangular channel is driven by a syringe pump and a DC voltage applied across the two electrodes drives vertical electrophoretic transport (See Scheme in Figure 1b).

Figure 1. Continuous flow reactor. (a) Picture showing the stainless steel and ITO electrodes. (b) Scheme of cross section of reactor with continuous flow from left to right, and the applied electrical field perpendicular to the flow (negatively charged particles move in the opposite direction of the applied field).

In a typical deposition, 1 mL of 42 mg/mL CIS NC solution was mixed with 5 mL of a toluene-ethanol mixture such that the resulting solution had the desired volume fraction of ethanol (typically 0, 0.17 or 0.25). The flow cell was prepared such that the spacing between electrodes was uniformly 2.5 mm. Prior to supplying voltage to the cell, the flow cell was filled with NC solution and a syringe pump was used to flow the solution at 0.1 mL/min. After flowing NCs under solution for the desired time, an appropriate NC-free ethanol-toluene mixture was flowed through the cell at 0.4 mL/min for 3 minutes to clear any undeposited NCs from the cell. Afterwards, pure ethanol was flowed through the cell at 0.4 mL/min for 3 minutes to improve film drying. Lastly, air was flowed through the cell to displace any remaining liquid.

2.5 EPD Transport Modeling

To illustrate the dependence of the deposition process on a few key experimental parameters, we develop a simple convection-migration model for particles transiting the

reactor. With a Reynolds number under typical conditions of 0.3, the convective flow profile is that of a typical Poiseuille (pressure-driven) flow between parallel plates, resulting in a parabolic flow profile in the horizontal direction (x , Figure 1b). Migration in the vertical direction (y) is due to electrophoresis. Thus for particles, the sum of convection and migration results in a constant v_y driven by the electric field while v_x is a quadratic function of y (Figure 1b). Equations 1 and 2 describe the velocity profile, with $y=h$ at the top surface of the flow cell where deposition occurs and $y=0$ at the bottom.

$$v_x(y) = \frac{6Q}{wh} \left(\frac{y}{h} - \frac{y^2}{h^2} \right) \quad (1)$$

$$v_y = uV/h \quad (2)$$

Q is the volumetric flow rate of solution, w is the width of the deposition cell, h is the height of the cell, u is the electrophoretic mobility, and V is the applied voltage. Figure 2 shows the trajectory of NCs entering the cell at different heights following the laminar flow profile, $v_x(y)$, and electrophoretic drift, v_y . This model neglects diffusion and assumes that the adsorption reaction at the surface is sufficiently fast that the deposition rate is limited by the arrival rate of particles. To judge the relative importance of migration versus diffusion in the bulk of the channel, we can construct an electrophoretic Péclet number, $v_y h / D$, where D is the particle diffusion constant. Under typical conditions, the value of this dimensionless scaling factor is greater than 10^3 . However, if the adsorption reaction was slow compared to the arrival rate, or if the particles slowed appreciably as they approach the electrode due to viscous forces, then the resulting mass transport boundary layer would render diffusion more relevant. We note that both the bulk electrophoretic velocity and the surface reaction rate are expected to be proportional to the applied field, so this simple model can be considered the ‘high field’ limit.

Figure 2. Modeled trajectory of particles entering the flow cell at various heights.

As a consequence of neglecting diffusion, the particle trajectories are deterministic. As an example, using the measured negative electrophoretic mobility of these NCs in a solution with 0.25 volume fraction ethanol with a flow rate of 0.1 mL/min (mean linear velocity of 0.04 mm/s) and applied bias of 150 V, a particle entering the cell at the negative electrode will take 48 seconds to deposit, in which time it will travel laterally 1.9 mm –only 5% of the length of the cell. After an initial start-up phase, the model predicts a uniform deposition flux equal to $c_0 v_y$, where c_0 is the starting concentration of particles. This flux remains constant from the inlet up to a distance $L_{\max}$ along the length of the reactor, after which it abruptly stops (See Figure 2). The profile would become more graded as diffusion and boundary layer effects increase in relative magnitude.

Additionally, in the development of the model, we have approximated the electrophoretic mobility as a single value when in fact experimental particles exhibit a distribution of values. To refine the model, we employed a simulation that randomly assigned each particle an electrophoretic mobility according to a normal distribution. We can then use a deterministic simulation of an ensemble of particles, randomly assigning

each particle a starting position, x_0 and y_0 , and an electrophoretic mobility, u , following the normal distribution. Each particle can then be tested to see where it will deposit or if it will exit the cell. From this simulation, both the film thickness profile and effluent concentration can be calculated.

3. Results and Discussion

3.1 CIS NC Characterization

Transmission electron microscope (TEM) images, X-Ray diffraction (XRD) and UV-vis absorbance of representative NCs are shown in Figure 3. TEM images (Figure 3a) show NCs with a typical diameter of 4 nm. This is in agreement with the crystal grain size estimated from the linewidth of the XRD peaks (Figure 3b) according to the Scherrer equation. XRD confirms that dropcasted, as-synthesized NCs are chalcopyrite-phase CuInSe_2 . The small diameter of the crystals results in a quantum confinement effect that increases the band gap to 1.4 eV, (Panthani et al., 2013) as can be seen in the inset to Figure 3c, compared to the bulk CIS value of 1.0 eV.

Figure 3. Characterization of CIS NCs. (a) TEM image of representative CIS NCs. Inset shows closer image of NCs. (b) XRD of thin films of NCs deposited by dropcasting on glass (blue) or EPD on FTO-coated glass (red). Database values for CIS (black) and

FTO (green) are shown. (c) UV-Vis absorbance spectrum of as-synthesized CIS dispersed in toluene. Inset shows the same data plotted using the axis conventions known as a 'Tauc plot,' used to determine the band gap of a semiconductor (Tauc et al., 1966). The band gap is given by the intercept of a linear fit to the low energy edge of $(\alpha h\nu)^2$ (dashed line).

3.2 Electrophoretic Deposition Under Flow

A critical objective of our process optimization is the complete or near complete utilization of the NCs in the feedstock. This makes efficient use of the valuable indium and selenium elements with the added benefit of rendering the solvent suitable for recycling. A fixed flow rate of 0.1 mL/min was selected, yielding a residence time of 15 min in the reactor. By measuring the reactor effluent absorbance at 500 nm, the relative concentration of the NCs after deposition was calculated. This serves as a metric of the fractional utilization of the feed; in an optimized process, its value would be zero. In a typical run, a solution with NC concentration of approximately 8 mg/mL was used. At a fixed deposition voltage of 150 V (0.6 kV/cm) and using pure toluene as the solvent, deposition of the predominantly negatively charged NCs occurs. For times greater than the residence time (or equivalently, a feed volume greater than the reactor volume), the system approaches steady state, at which point the NC concentration in the effluent has dropped by 30% (Figure 4a, green curve).

Figure 4. Results of EPD under flow. (a) Effluent concentration versus time after applying 150 V using a NC solution with ethanol volume fraction (f_{EtOH}) of 0 (green), 0.17 (blue), and 0.25 (red). (b) Effluent concentration versus time using a NC solution with ethanol volume fraction of 0.17 after applying a voltage of 100 V (purple), 150 V (blue), and 200 V (black). (c) Thickness versus position along the length of the reactor from the inlet for films deposited over one hour at 150 V, showing decreasing film thickness along the length of the film. Thickness calculated from measured visible light transmission using the linear calibration described in Experimental Methods. NC dispersion was 0.5 mg/mL with a 0.17 volume fraction of ethanol, and the flow rate was 0.1 ml/min. Inset: photograph of representative CIS film deposited by EPD.

To improve upon the utilization of the NCs in the reactor feed, we first consider the electrophoretic forces acting on them. Frequently in the EPD of surfactant-capped colloidal NCs such as these, a quantity of an anti-solvent is added to facilitate deposition. (Bass et al., 2011; Jia et al., 2008; Kornhuber et al., 2013). The addition of anti-solvent has been shown to increase the electrophoretic mobility of NCs (Bass et al., 2011). Similarly to Bass et al, we speculate that the polar anti-solvent facilitates partial dissociation of the positively charged oleylamine ligands from the nanocrystal surface, resulting in a greater net negative charge on the particles. This would be in accordance

with well-studied cadmium selenide nanocrystal system, where it has been directly observed that addition of alcoholic anti-solvents causes a similar partial dissociation of cadmium-ligand complexes from the nanocrystal surface.(Anderson et al., 2013) For this reason we added varying amounts of ethanol to the purified dispersion of NCs, keeping the volume fraction below the threshold that would cause visible flocculation of the particles. For an ethanol volume fraction of 0.25, we observed an average electrophoretic mobility of $(-9\pm2)\times10^{-10}$ m²/V·s (Table 1). A dispersion of NCs in this solvent was used as the reactor feed and 150 V bias was applied. Under these conditions the effluent exiting the reactor was depleted of 94% of the original NCs within the first 5 minutes after the voltage was applied (Figure 4a, red squares). A lower ethanol volume fraction of 0.17 resulted in an electrophoretic mobility of $(-4\pm2)\times10^{-10}$ m²/V·s (Table 1) and utilization of only 78% of the original NCs in the feed by the time that steady state is achieved (Figure 4a, blue squares). The deposition rate could also be tuned by changing the applied voltage, as seen in Figure 4b. With a fixed volume fraction of ethanol of 0.17, deposition under reduced voltage resulted in less deposition (70% deposition at 100 V), while deposition at increased voltage improved the atom economy (88% deposition at 200 V). In summary, either increasing the voltage or increasing the ethanol content makes it possible to almost completely utilize the NCs in the feed at a flow rate of 0.1 mL/min.

Table 1. Electrophoretic mobility of CIS NCs dispersed in a toluene-ethanol mixture.	
Ethanol fraction	Electrophoretic mobility (m ² /V·s) [#]
0.10	$-(0.2\pm0.4)\times10^{-10}$
0.17	$-(4\pm2)\times10^{-10}$
0.25	$-(9\pm2)\times10^{-10}$
[#] Error shown is the standard deviation between 10 measurements.	

To understand the variability of the rate of deposition along the length of the reactor and hence the achievable uniformity of the deposited film, the film thickness was

measured as a function of distance from the reactor inlet. Relative changes in the absorbance are conveniently measured by transmission spectroscopy and are proportional to changes in film thickness. Therefore film absorbance was measured along the reactor length and translated into thickness using a quantitative calibration (see Experimental Methods). Films were prepared by flowing a 0.5 mg/mL NC solution of 0.17 ethanol fraction by volume for one hour under 150 V so that the majority of the deposition occurs under steady-state conditions. The films' absorbance at 500 nm was measured at 5 mm intervals, providing a metric of the relative deposition rate across the film, shown in Figure 4c. Under the conditions explored here, the film is highly non-uniform, with more deposition occurring near the inlet. Due to the effect of the irregular flow at the inlet and outlet, absorbance values were not measured within 5 mm of these positions in the reactor. Film uniformity on the microscale is shown via scanning electron microscopy (SEM) and atomic force microscopy (AFM) in Figure 5. Here it should be noted that there has been no optimization of drying conditions to reduce cracking, as is typically necessary for EPD films (Boccaccini et al., 2002). XRD of the deposited films show that the chalcopyrite CIS phase is preserved through the EPD process.

Figure 5. SEM micrograph of CIS film deposited by EPD at 150 V. The CIS concentration was 0.5 mg/mL with a 0.17 volume fraction of ethanol and the flow rate

was 0.1 ml/min. Inset shows AFM micrograph of the same film. RMS surface roughness was 19 nm.

3.3 Modeling EPD Under Flow

To understand the experimental deposition profiles and feedstock utilization experiments in Figure 4, a simple deterministic convection-migration model was developed, neglecting diffusion and boundary layer effects and employing experimentally measured electrophoretic mobility values (Table 1). After an initial start-up phase, the model predicts a uniform deposition flux, up to a position in the reactor determined by the linear flow rate and the electrophoretic velocity; beyond this position the flux is zero. Experimentally no such flat deposition profile is observed (Figure 4). One way to improve the model is to consider the fact that the NCs exhibit a range of electrophoretic mobilities, rather than a single value. To provide a rough approximation of the distribution of these values, we use the standard deviation of the measured mobilities in Table 1. The trajectories are then calculated for an ensemble of particles whose mobility values are assigned according to a normal distribution and from this both the film thickness and reactor effluent concentration can be calculated as a function of time. The results are shown in Figure 6.

Figure 6. Results of modeling the EPD flow cell. (a) Relative effluent concentration versus time for model (black diamonds) and experiment (red squares). Conditions of the run are flow rate of 0.1 mL/min, concentration of 8 mg/mL, ethanol volume fraction of 0.25 and 150 V applied bias. Time $t=0$ corresponds to the moment the voltage is applied. (b) Model results for deposition rate along the length of the reactor. Deposition was modeled at 150 V using NCs with experimental distribution of electrophoretic mobilities, u , for CIS NCs in 0.25, 0.17 and 0.1 ethanol volume fraction, in red, blue and green, respectively. Flow rate of 0.1 mL/min, except for the high Q example, which is 2.25 mL/min (dashed line).

Figure 6a shows a comparison of modeled and experimental effluent concentration versus time. Although the experimentally determined time required to reach an effluent concentration $<10\%$ of the original concentration is double that of the model results, the model does predict the shape of the data and the effluent concentration at short times. The model also predicts that the depositing flux is thickest at the inlet, dropping off with increased distance from the inlet, in qualitative agreement with the experimental thickness profile in Figure 4c. In this model, the distribution of electrophoretic velocities directly results in a decay in the deposition profile. The model predicts a brief plateau of uniform deposition rate (solid lines) that can be extended by increasing the flow rate (dashed line). However the plateau region is not reflected in the experimental data. We speculate that this discrepancy arises from neglecting diffusion and boundary layer effects. Nonetheless, a salient conclusion from the model is that better uniformity would result from a narrower distribution in electrophoretic mobility.

3.4 Prospects for Manufacturing

While these results demonstrate conditions of flow, voltage, electrode spacing and co-solvent to achieve high utilization of the NC feedstock, uniformity is also a

concern. For this objective, our results indicate the importance of limiting the variance in the mobilities exhibited by the NCs, which has not previously been an objective in NC synthesis. Also concerning uniformity, a key advantage of EPD under flow is that, by shaping the counter electrode, it is possible to design a reactor where the electric field operates only in the areas of the reactor where uniform laminar flow is established. The uniformity could also be enhanced by employing faster flow rates, but with increased waste in the effluent. Alternatively, it would be possible to segment the counter electrode to vary the voltage along the length of the reactor to enhance uniformity. Among the options for high-rate production of semiconductors such as photovoltaics, there are significant advantages to roll-to-roll fabrication schemes (Andersen et al., 2014; Krebs et al., 2010) for which EPD under flow is remarkably well suited. We have shown that EPD can produce adherent films on flexible substrates (Figure 7). To be industrially feasible, roll-to-roll fabrication requires rapid deposition processes. The EPD rate scales with the electric field, which, for a fixed voltage, is inversely proportional to the electrode spacing. Here we have demonstrated how convective flow can be used to overcome the film thickness limitations that would otherwise accompany such a confined reactor volume, thereby enabling both high deposition rates and relatively thick films. The only critical reactor dimension for EPD under flow therefore is the electrode spacing, rendering it scalable to the limits of the width and length of the web used in the roll-to-roll process. Looking toward the future, we speculate that the uniformity of the deposit as a function of position along the reactor length would be improved if the substrate were also translating while flow is occurring.

Figure 7. Film deposited via EPD onto flexible ITO-coated PET substrate.

4. Conclusion

The use of EPD under flow represents a novel method for preparing uniform semiconducting films on a wide variety of conductive substrates, including flexible foils or ITO-coated polymers. Herein we have shown how the deposition voltage can be decreased from typical batch-reactor designs by using narrow electrode spacing, thereby making the process relevant for semiconductor particles such as the CIS NCs used here. We show how continuous flow can be used to surmount the film thickness limitations that would be inherent to a narrow-channel batch reactor. Process parameters of voltage, solvent and flow rate are described for the near complete utilization of the NC feedstock. Low voltages combined with low waste gives flow cell EPD potential for continuous, high-rate fabrication of thin-film semiconductors in scalable roll-to-roll manufacturing schemes.

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Graphical Abstract