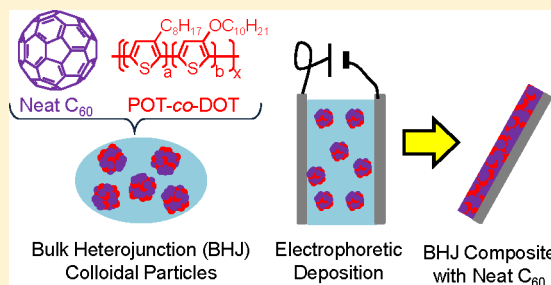


# Electrophoretic Deposition of the Thiophene-Based Copolymer and Its Composites with C<sub>60</sub>

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**ABSTRACT:** Electrophoretic deposition is a useful and efficient technique to deposit conjugated polymers, if suitable suspension of the target polymer is obtained. Unfortunately, neither general theory nor universal procedure for the preparation of a suspension suitable for electrophoretic deposition has seemed to be established yet. Thus, accumulation of individual knowledge is still important in this area. Here, the preparation of suspensions of a thiophene-based polymer poly(3-octylthiophene-2,5-diyl-co-3-decyloxythiophene-2,5-diyl) (POT-co-DOT) and their application to the electrophoretic deposition have been reported. The suspensions of POT-co-DOT with various good/poor solvents ratios were easily obtained by mixing a toluene solution of the polymer and acetonitrile. The composition of the dispersion medium significantly affects the surface morphology of the film prepared by the electrophoretic deposition in the suspension. Composite films consisting of POT-co-DOT and C<sub>60</sub> have also been successfully prepared by electrophoretic deposition. Because the optical absorption peak at 333 nm in C<sub>60</sub> showed neither significant broadening nor a red shift, C<sub>60</sub> molecules were expected to be well-dispersed in the composite films. A photovoltaic device with a composite film prepared from a POT-co-DOT/C<sub>60</sub> = 2:1 suspension showed 10 times larger short-circuit current density and 5 times larger power conversion efficiency than a device with pure POT-co-DOT, although further work is required to improve the device performance.



## 1. INTRODUCTION

Conjugated polymers are promising candidates for the conducting and semiconducting materials in printed electronic devices. In laboratories, the spin-coating technique is widely used for prototyping the electronic devices such as organic light-emitting devices, photovoltaic devices, and field effect transistors.<sup>1–3</sup> Although the spin-coating technique is quite easy to carry out at a relatively low initial cost, the operating cost is not cheap because most of the material placed on the substrate is blown away during the spinning, resulting in quite low material efficiency. Additionally, a relatively concentrated solution on the order of 10 g/L is required to obtain a film approximately 100 nm in thickness, which is suitable for the above-mentioned electronic devices. This hinders the application of the method to the low-solubility materials. Therefore, it is important to develop alternative coating methods that provide higher material efficiency and wider applicability than the spin-coating method.

Electrophoretic deposition is a classic coating technology, and numerous studies have been carried out on it.<sup>4–6</sup> However, the application of this method to the preparation of conjugated polymer films had not been reported until 2002.<sup>7</sup> Nowadays, this method is becoming popular in the field of organic functional materials.<sup>8–12</sup> According to the principle of the method, accumulation of the charged colloidal particles of the target material using an electric field, the film obtained is basically a porous film that is not suitable for the above-mentioned devices. Indeed, the electrophoretic deposition of conjugated polymer was originally proposed as a method to

obtain nanostructured films. In this context, a simple trick to obtain smooth and dense films by the electrophoretic deposition has been recently reported.<sup>13</sup> One of the most important features of this method is that a suspension prepared from relatively dilute polymer solution (~0.1 g/L) can be used for the film deposition. This makes it possible to prepare a film of low-solubility materials. It has also been reported that the material efficiency of the method reaches 90% under an appropriate condition.<sup>14</sup>

Polymer photovoltaic devices based on conjugated polymer–fullerene mixtures have been extensively studied for the past 2 decades.<sup>15–17</sup> The findings of photoinduced charge transfer between the conjugated polymer and the fullerene initiated the recent serious studies of polymer photovoltaic devices.<sup>18,19</sup> Typically, the energies levels of both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the polymers such as poly(3-hexylthiophene) are higher than those of the fullerenes such as C<sub>60</sub>. This type of energy-level configuration promotes transfer of the photoexcited electrons in the LUMO level of the polymer to the LUMO level of the fullerene, and holes in the fullerene are transferred to the polymer. In other words, the

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polymer and the fullerene work as an electron donor and acceptor, respectively.

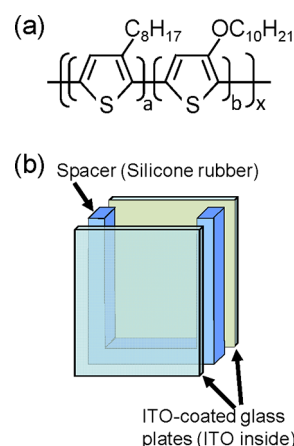
Although some experimental evidence of the photoinduced charge transfer such as drastic quenching of the photoluminescence and dramatic enhancement of photoconductivity of the polymer can be observed in polymer films doped with 1–5% fullerene, this system is not suitable for the photovoltaic devices because it lacks the pathway for the electrons. To install pathways throughout the composites for both carriers, so-called “bulk heterojunction composites,” which consist of equivalent amounts of the donor and acceptor materials, are used for the photovoltaic devices. Because the polymer–fullerene composites are usually prepared by mixing the solutions of the two components, neat fullerene such as  $C_{60}$ , which has relatively low solubility in common organic solvents (practically 2 g/L in toluene), is thought to be inadequate for this purpose. Instead, chemically modified fullerenes with high solubility such as [6,6]-phenyl- $C_{61}$ -butyric acid methyl ester ( $C_{60}$ -PCBM) are predominantly used for this purpose.<sup>20</sup> However, the synthesis and purification steps of the modified fullerenes are expected to elevate economic and environmental costs. Moreover, it is known that the modified fullerene shows smaller electron mobility than neat fullerenes.<sup>21,22</sup> Therefore, it seems important to develop a method to prepare bulk heterojunction composites consisting of conjugated polymers and neat fullerenes.

Recently, it has been reported that flat and dense films of composites consisting of conjugated polymers and a large amount of neat  $C_{60}$  can be prepared by means of electrophoretic deposition.<sup>23–25</sup> However, photovoltaic devices based on the composites showed very low power conversion efficiency (PCE) on the order of  $10^{-3}\%$ . It is known that conjugated polymers based on thiophene such as poly(3-hexylthiophene) have relatively high carrier mobility and are appropriate for the photovoltaic devices.<sup>15–17</sup> Here, the electrophoretic deposition of a thiophene-based copolymer and its composites with neat  $C_{60}$  is reported.

## 2. EXPERIMENTAL SECTION

Unfortunately, neither general theory nor universal procedure for the preparation of stable conjugated polymer suspensions without surfactants has been established. Therefore, our first task is to find a conjugated polymer, with which a stable suspension is easy to prepare, using a trial-and-error approach. In this study, a thiophene-based conjugated polymer poly(3-octylthiophene-2,5-diyl-*co*-3-decyloxythiophene-2,5-diyl) (POT-*co*-DOT), which was developed as a donor material in the photovoltaic devices,<sup>26</sup> was found to meet our request. The molecular structure of POT-*co*-DOT is shown in Figure 1a.

POT-*co*-DOT (Aldrich), poly(3,4-dioxythiophene)/poly(styrene sulfonate) salt (PEDOT, Aldrich),  $C_{60}$  (Nano-C), toluene (Wako), and acetonitrile (Wako) were used as received. Suspensions of POT-*co*-DOT were prepared by a method based on the reprecipitation technique. Typically, 9 mL of acetonitrile was mixed with 1 mL of a solution containing 1 g/L of POT-*co*-DOT to obtain a suspension in which 0.1 g/L of the polymer is dispersed in a medium of a acetonitrile/toluene = 9:1 (by volume) mixture. By changing the initial concentration of the toluene solution of the polymer and the volume ratio, suspensions with various acetonitrile/toluene ratios containing 0.1 g/L of the polymer were prepared. The suspensions of composites of POT-*co*-DOT and  $C_{60}$  were prepared by mixing the toluene solution containing the polymer and  $C_{60}$  with the same volume of acetonitrile.



**Figure 1.** (a) Molecular structure of POT-*co*-DOT and (b) scheme of the thin slab vessel used in this study.

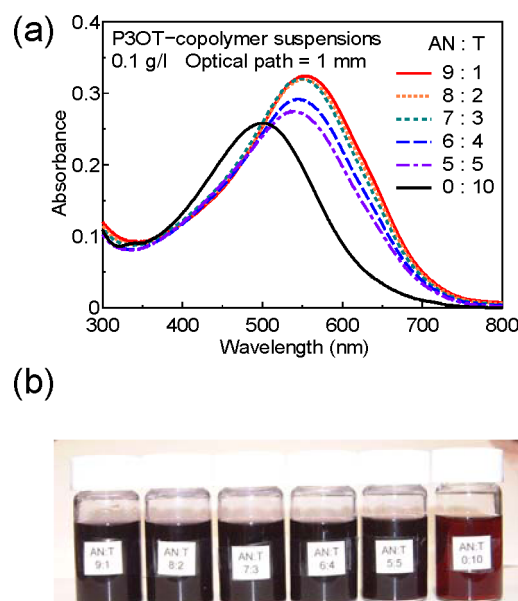
Electrophoretic deposition was carried out using thin slab vessels consisting of a silicone rubber spacer sandwiched between a pair of indium–tin oxide (ITO) electrodes coated on glass plates, as shown in Figure 1b. The electrode distance was varied by changing the thickness of the spacer. To make a photovoltaic device, a composite film of POT-*co*-DOT and  $C_{60}$  was deposited on a PEDOT film coated on an ITO electrode using the vessel with a 1 mm thick spacer. Then, an Al electrode was deposited on the composite film to complete the device with the active area of  $1 \times 1 \text{ cm}^2$ .

Optical absorption spectra were measured using a Shimadzu UV-1800 spectrophotometer. A glass cell with an optical path of 1 mm was used for liquid samples. Atomic force microscope (AFM) images were collected with a Burleigh Metris 2000 system in the noncontact mode. The photovoltaic devices were characterized using a Keithley 6517A electrometer under AM 1.5G  $100 \text{ mW/cm}^2$  (1 sun) illumination from an Asahi Spectra HAL-C100 solar simulator. All experiments were carried out in air.

## 3. RESULTS AND DISCUSSION

**3.1. Electrophoretic Deposition of POT-*co*-DOT.** Figure 2a shows optical absorption spectra of the suspensions containing 0.1 g/L of POT-*co*-DOT with various acetonitrile/toluene ratios and the toluene solution containing the same amount of the polymer. The absorption peak wavelength of the suspension with an acetonitrile/toluene = 5:5 medium is 539 nm, which is substantially longer than that of the toluene solution, 499 nm. The peak wavelength becomes longer as the acetonitrile concentration is increased and is 553 nm for the suspension with the acetonitrile/toluene = 9:1 medium. The differences in the optical absorption spectra between the suspensions and the solution can be easily observed by the naked eye, as shown in Figure 2b. This reflects that POT-*co*-DOT is solidified in the suspension. The lack of strong scattering in the visible to near-ultraviolet region suggests that the polymer is solidified as small particles whose diameters are less than such a wavelength.

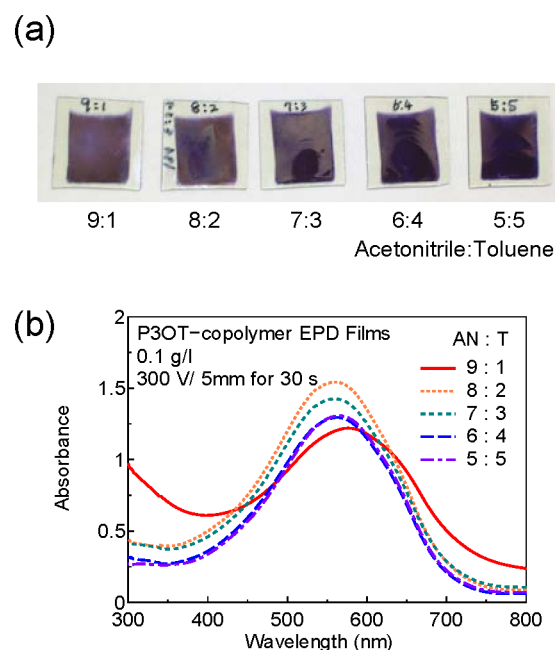
The films of POT-*co*-DOT were easily obtained by means of the electrophoretic deposition in the thin slab vessels filled with the suspensions. Typically, DC 300 V is applied between the electrodes placed 5 mm apart, and the deposition is completed within 15 s for all of the suspensions. In the present case, the deposition occurred on the negatively biased electrode,



**Figure 2.** (a) Optical absorption spectra and (b) photograph of the POT-*co*-DOT suspensions (0.1 g/L) with various acetonitrile/toluene ratios. The toluene solution of POT-*co*-DOT (0.1 g/L) is also shown for comparison. AN and T stand for acetonitrile and toluene, respectively.

indicating that the colloidal particles of POT-*co*-DOT are positively charged. Taking the fact that the colloidal particles of poly(3-octadecylthiophene) are also positively charged into account, it is speculated that thiophene-based conjugated polymers seem to have a tendency to be positively charged. However, this cannot be related to the fact that these polymers are electron-donor-type or p-type semiconducting polymers that are likely to be easily oxidized and carry positive charge because colloidal particles of a typical p-type conjugated polymer poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEHPPV) in suspensions generated in the same manner have negative charges.<sup>24,27</sup>

Figure 3a shows a photograph of POT-*co*-DOT films deposited from suspensions with various dispersion media compositions. While the deposition in a suspension with acetonitrile/toluene = 9:1 gives a film with a rough surface, a smooth film was deposited by using a suspension with acetonitrile/toluene = 5:5. These features are similar to those observed in the previous study using poly[(9,9-dioctyl-2,7-divinylfluorenylene)-*alt*-(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene)] (PDOF-MEHPV) and can be interpreted as follows.<sup>8</sup> A film obtained by the electrophoretic deposition is accumulated colloidal particles covered with a dispersion medium just after the deposition. In the present case, the dispersion medium consists of a poor solvent acetonitrile and a good solvent toluene. Because acetonitrile evaporates faster than toluene, toluene is concentrated on the film and dissolves the colloidal particles during the drying. If the amount of toluene on the film is enough to cover the entire film, the particles are completely dissolved to form a dense and smooth film. On the other hand, the initial morphology is kept in the film deposited from a suspension with a small amount of toluene because the dissolution is limited to the surfaces of the particles. Thus, the solubility of the material such as the rate of dissolution plays a key role in the determination of the surface morphology of the film.

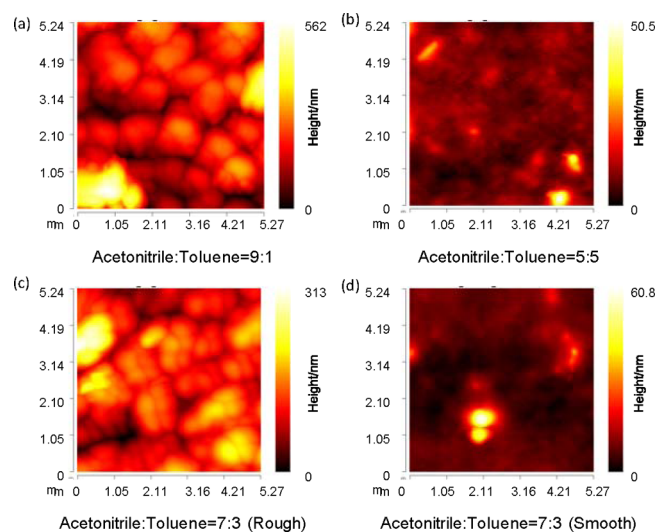


**Figure 3.** (a) Photograph and (b) optical absorption spectra of the POT-*co*-DOT films deposited from the suspensions with various acetonitrile/toluene ratios. The size of the glass substrates is approximately  $2 \times 2.5 \text{ cm}^2$ .

However, the morphological change in the intermediate compositions was different. In PDOF-MEHPV, the individual film was almost uniform, and the roughness of the polymer film almost monotonically decreased with decreasing acetonitrile concentration in the suspension. On the other hand, in the present POT-*co*-DOT case, the surface was not uniform, that is, smooth and rough regions distinctly appeared in a film, and the smooth area increased with decreasing acetonitrile concentration. The difference in the morphological change due to the composition of the dispersion medium seems to come from the difference in the solubility of the two polymers. The optical absorption spectra of the films are shown in Figure 3b. The optical absorption peak was 565 nm for the film deposited from a suspension with acetonitrile/toluene = 5:5. The peak slightly shifts toward shorter wavelength with increased acetonitrile concentration. The peak shift may arise from the light scattering in the rough area. The optical spectrum of the film from the suspension with acetonitrile/toluene = 9:1 is strongly modulated by the scattering.

Figure 4a shows the AFM images of a POT-*co*-DOT film deposited from a suspension with acetonitrile/toluene = 9:1. The surface of the film consists of relatively large particles approximately  $1 \mu\text{m}$  in diameter. However, because no strong optical scattering is found in the absorption spectra of the parent suspension, these particles are probably secondary particles, that is, particles formed by the aggregation of colloidal particles during the deposition and/or the drying processes. The root-mean-square (rms) roughness of the surface of the film was evaluated as 50 nm from a cross-sectional analysis of the image. On the other hand, the surface of the film deposited from a suspension with acetonitrile/toluene = 5:5 was relatively flat, as shown in Figure 4b, with the rms roughness evaluated as 2 nm. As mentioned above, a film from the suspensions with an intermediate composition consists of smooth and rough areas. Figure 4c and d shows the AFM images of the rough and smooth areas of a film deposited from a suspension with

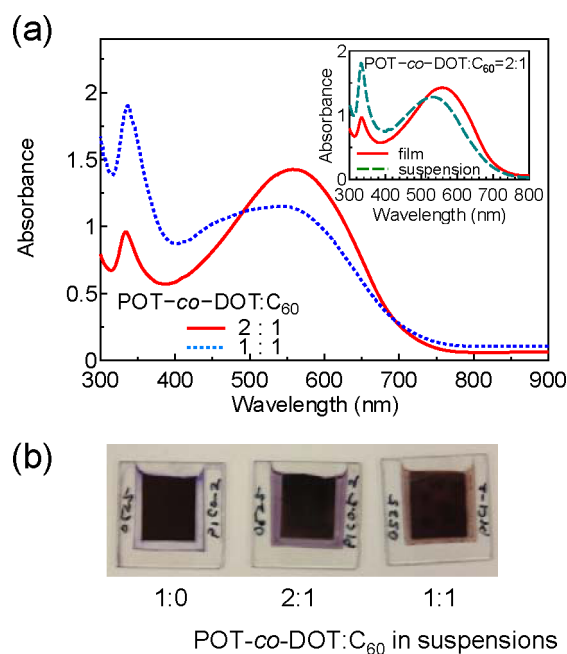




**Figure 4.** AFM images of the POT-*co*-DOT films deposited from suspension with (a) acetonitrile/toluene = 9:1 and (b) acetonitrile/toluene = 5:5. (c,d) AFM images of rough and smooth parts of the film from acetonitrile/toluene = 7:3, respectively.

acetonitrile/toluene = 7:3. Apparently, the surface morphologies of the rough and smooth areas are similar to those of the films from the acetonitrile-rich and the acetonitrile-poor suspensions, respectively.

**3.2. Electrophoretic Deposition of Composites Consisting of POT-*co*-DOT and C<sub>60</sub>.** Figure 5a shows the optical absorption spectra of the films deposited from suspensions of composites consisting of POT-*co*-DOT and C<sub>60</sub>. Because composites containing equivalent weights of a polymer and a



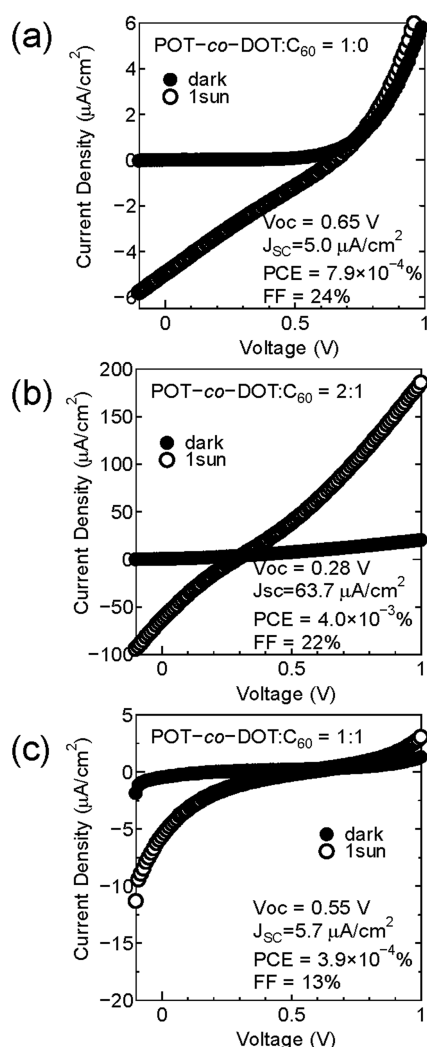
**Figure 5.** (a) Optical absorption spectra and (b) photograph of the POT-*co*-DOT/C<sub>60</sub> composite films. The size of the glass substrates is approximately 2 × 2 cm<sup>2</sup>. The POT-*co*-DOT/C<sub>60</sub> ratios indicated are those of suspensions from which the films were deposited. The inset in (a) shows the optical absorption spectra of a POT-*co*-DOT/C<sub>60</sub> = 2:1 composite suspension in a 1 mm thick glass cell and a film deposited from the suspension in the vessel with a 1 mm thick spacer.

fullerene are frequently used in the studies of polymer photovoltaic devices,<sup>15–17</sup> samples with POT-*co*-DOT/C<sub>60</sub> = 2:1 and 1:1 were prepared. Although colloidal particles of POT-*co*-DOT have positive charge and those of C<sub>60</sub> have negative charge,<sup>23,24,27</sup> the electrophoretic deposition of the POT-*co*-DOT/C<sub>60</sub> composite films occurred only on the negative electrodes for all cases tested in this study, indicating that the colloidal particles of the composites are positively charged. A sharp peak at 333 nm, which is not found in the pure POT-*co*-DOT film, is attributed to an allowed electronic transition in C<sub>60</sub>. It is known that the peak shifts toward longer wavelength and becomes wider upon increased aggregation degree of C<sub>60</sub>.<sup>28</sup> In the present case, the aggregation of C<sub>60</sub> is not pronounced, at least in the POT-*co*-DOT/C<sub>60</sub> = 2:1 sample. Because the solubility of C<sub>60</sub> in the acetonitrile/toluene = 1:1 mixture is much higher than that of POT-*co*-DOT, a film of the composite contains a much smaller amount of C<sub>60</sub> per polymer than its parent suspension. As shown in the inset, the concentration of C<sub>60</sub> in the film can be roughly estimated to be half of that in the suspension by comparing the ratios of the absorption peaks attributed to the polymer and the fullerene. Photographs of the samples deposited on the patterned ITO electrodes are shown in Figure 5b. There were no pinholes detectable by the naked eye.

As shown in Figure 6a, the device with pure POT-*co*-DOT shows a PCE of 7.9 × 10<sup>−4</sup>% under AM 1.5G 1 sun illumination. The short-circuit current density (*J*<sub>SC</sub>) of the device with a composite film prepared from a POT-*co*-DOT/C<sub>60</sub> = 2:1 suspension is 10 times higher than that of the pure POT-*co*-DOT device, resulting in a PCE of 4.0 × 10<sup>−3</sup>%, as shown in Figure 6b. This is probably due to the photoinduced charge transfer between the polymer and C<sub>60</sub>. However, both the *J*<sub>SC</sub> and PCE of the device prepared from a POT-*co*-DOT/C<sub>60</sub> = 1:1 suspension were much poorer than those of the POT-*co*-DOT/C<sub>60</sub> = 2:1 device, as shown in Figure 6c. This may come from the deterioration of the hole-transport pathways in the device due to the overloading of C<sub>60</sub>. A much smaller fill factor (FF) of the device than those of two former devices seems to support the interpretation. Because the devices prepared in the present study have a relatively thick active layer, a substantial improvement of the device performance is expected by careful tuning of the film thickness and the polymer/fullerene ratio.

## 4. CONCLUSIONS

In this paper, electrophoretic deposition of a thiophene-based polymer POT-*co*-DOT has been reported. The suspensions of POT-*co*-DOT with various good/poor solvents ratios were easily obtained by mixing a toluene solution of the polymer and acetonitrile. The composition of the dispersion medium significantly affects the surface morphology of the film prepared by the electrophoretic deposition in the suspension. Composite films consisting of POT-*co*-DOT and C<sub>60</sub> have been successfully prepared by electrophoretic deposition. Because the optical absorption peak at 333 nm attributed to C<sub>60</sub> showed negligible broadening or red shift, C<sub>60</sub> molecules were expected to be well-dispersed in the composite films. A photovoltaic device with a composite film prepared from a POT-*co*-DOT/C<sub>60</sub> = 2:1 suspension showed a 10 times larger *J*<sub>SC</sub> and a 5 times larger PCE than a device with pure POT-*co*-DOT, although the PCE remained on the order of 10<sup>−3</sup>%, much poorer than that of state-of-the-art polymer photovoltaic devices.



**Figure 6.** Current density–voltage characteristics of the photovoltaic devices using electrophoretically deposited films from suspensions of (a) pure POT-co-DOT, (b) the POT-co-DOT/ $C_{60}$  = 2:1 composite, and (c) the POT-co-DOT/ $C_{60}$  = 1:1 composite.

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### Notes

The authors declare no competing financial interest.

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