

Improved Power Conversion Efficiency of Organic Photovoltaic Cell Fabricated by Electro spray Deposition Method by Mixing Different Solvents

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A smooth surface of the poly(3-hexylthiophene) (P3HT)-doped-(6,6)-phenyl-C61-butyric acid methyl ester (PCBM) thin film was achieved by mixing different solvents for the electro spray deposition method. As a result, the high power-conversion efficiency (PCE) of the bulk-heterojunction organic photovoltaic cell (OPV) was comparable to that obtained in the case of the spin-coating method. By optimizing the additional solvent in *o*-dichlorobenzene, the P3HT/PCBM active layer with the root-means-square roughness of 2.23 nm and the PCE of 2.2% was fabricated employing acetonitrile as the additional solvent.

1. Introduction

Organic photovoltaic cells (OPVs) have been of interesting owing to their special advantages over Si-based photovoltaic cells, such as flexibility, controllability of the absorption spectrum, large device area, and the possibility employing of the roll-to-roll printing process.¹⁾ Nowadays, several groups have demonstrated a bulk-heterojunction structure with donor and acceptor organic materials,^{2,3)} and the power conversion efficiency (PCE) has been rapidly improved by optimizing molecular structures of the organic materials used.^{4,5)} In particular, many near-infrared-sensitive organic materials have been investigated to expand the spectral sensitivity, resulting in improved PCE. In addition, the fabrication process is an important issue for printable OPVs.^{6,7)} Thus far, several solution processes have already been demonstrated for fabricating organic devices.⁸⁻¹¹⁾ In addition, several spray methods have also been investigated for organic light-emitting diodes (OLEDs), such as the evaporative spray deposition from ultradilute solution,¹²⁾ screen printing,¹³⁾ and the painting method.¹⁴⁾

Our research group has also investigated an efficient solution process, called the electro-spray deposition (ESD) method.¹⁵⁻¹⁸⁾ The OPV,¹⁵⁾ the organic photoconductive device,¹⁶⁾ and the OLED¹⁸⁾ have already been demonstrated fabricated by the ESD method. In this process, a high voltage of 2 to 15 kV is applied to the polymer solution, which is then divided into several particles with diameters of the order of 1 to 5 μm .^{19,20)} As a result, most of the

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solvent evaporates before reaching the substrate owing to the large surface area. This fact indicates a multilayer structure can be deposited without dissolving the underlying organic layer. Therefore, p-n and p-i-n structures can be realized using arbitrary solutions. Another important advantage of the ESD method is the direct fabrication of nano particle and nano fiber structures by optimizing fabrication conditions, such as the viscosity of the polymer solution, the applied voltage, and the vapor pressure of the solvent.²¹⁻²³⁾ Therefore, the surface area at the organic/organic interface can be drastically increased, and this interesting merit will cause an improved PCE of the OPV.

Recently, Kim et al. reported an OPV fabricated by the ESD method.²⁴⁾ The reported device performance is almost same as that of the reference device fabricated by the spin-coating process. However, the solvent vapor soaking technique is necessary to reduce the surface roughness of the poly(3-hexylthiophene) (P3HT)-doped-(6,6)-phenyl-C61-butyric acid methyl ester (PCBM) layer. This fact indicates that the nano structure is difficult to fabricate by the reported technique. Another approach to reducing the surface roughness of the organic thin film is the mixed organic solvent technique. In a previous paper, Ju et al. demonstrated that the surface roughness of the organic thin film (poly(2-methoxy-5-(2-ethylhexoxy)-1,4-phenylenevinylene) was improved through the addition of *N,N*-dimethylformamide (DMF) in toluene at different vapor pressures, and an OLED was fabricated by the ESD method.¹⁰⁾ In addition, we also demonstrated the reduced surface roughness of the P3HT:PCBM thin film using acetone as the additional solvent because of its high relative dielectric constant, and a high photovoltaic performance was achieved by optimizing the concentration of acetone.¹⁵⁾ However, further improved device performance has been required for practical applications.

In this study, we investigated the optimal additional solvent for fabricating the ESD-based bulk-heterojunction OPV. The spray diameter, the supply speed, and the surface roughness of the P3HT:PCBM thin film were investigated for the ESD process with the solvent mixture (*o*-dichlorobenzene (*o*-DCB)/additional solvent). Finally, we also estimated the device performance of the OPV fabricated by the ESD method with the mixed solvent technique, by changing the additional solvent.

2. Experimental Procedure

First, P3HT (1.2 mg) and PCBM (1.0 mg) were mixed into *o*-DCB (1 ml). Then, the additional solvent was also added into the resulting solution. The concentration of the additional solvent was 10 vol.%. The additional solvents used were dimethyl sulfoxide (DMSO), DMF, and acetonitrile. The relative dielectric constants of DMSO, DMF, and acetonitrile are 47.0, 36.7, and 35.7, respectively. The high relative dielectric constant of the solvent is an important factor in spreading the spray diameter in the ESD process,¹⁸⁾ and the surface roughness of the organic thin film can be drastically reduced by optimizing the fabrication condition by the mixed solvent technique.¹⁵⁾ Therefore, we selected the above-mentioned additional solvents to

achieve the improved photovoltaic performance of the ESD-based OPV.

Figure 1 shows the experimental setup for the ESD process. We used a glass capillary for the ESD process because of the controllability of its diameter, which leads the smooth surface roughness of the organic thin film.¹⁵⁾ The glass capillary was fabricated using a puller (PC-10, Narishige) and a microforge (MF-900, Narishige). The inner diameter of the glass capillary was approximately 50 μm . A positive high voltage was applied to a copper wire in the P3HT:PCBM solution in the glass capillary using a high-voltage source (HJPQ-30P1, Matsusada Precision). The earthed line was connected to a patterned indium tin oxide (ITO) layer on top of the glass substrate.

We investigated the spray diameter and the supply speed of the ESD process using a charge-coupled device (CCD) camera (Watec, WAT-902B).¹⁸⁾ The distance from the glass capillary to the substrate was 10 cm, and the applied high voltage was changed from 5.5 to 11 kV. The surface roughness of the fabricated P3HT:PCBM thin film was estimated using an atomic force microscope (AFM) (Seiko, SPA-300) and the scanning electron microscope (SEM) (Hitachi Science Systems, S-4100).

An OPV was fabricated in a subsequent process. An ITO-coated glass substrate was cleaned in solvent (isopropyl alcohol, acetone, and ethanol) and deionized water under ultrasonic waves, and it was treated by ultraviolet ozone cleaning for 20 min. After spin-coating PEDOT:PSS (Clevious PH500) at 5000 rpm for 1 min, the sample was annealed at 140 °C for 10 min in nitrogen atmosphere. The P3HT:PCBM layer was deposited by the ESD method in air, and the Al electrode (130 nm) was successively thermally evaporated in a vacuum chamber. The additional solvents were DMSO (device A), DMF (device B), and acetonitrile (device C). The deposition time in the ESD process was fixed at 60 min for all ESD processes. Finally, the fabricated device was annealed at 140 °C for 25 min in nitrogen atmosphere to form the bulk-heterojunction structure. The distance from the glass capillary to the glass substrate was 10 cm, and the applied high voltage was 4 kV. The applied voltage was changed from the above-mentioned deposition condition to measure the spray diameter and the supply speed. This is because the PEDOT:PSS layer causes a change in the electric field around the ITO-coated glass substrate. Therefore, we changed the deposition condition to realize the same spray diameter and supply speed as in the above-mentioned ESD process. In addition, the reference device was also fabricated by the spin-coating process. The P3HT:PCBM layer was spin-coated at 2000 rpm for 1 min in nitrogen atmosphere, and the other processes were the same as in the above-mentioned fabrication process. Current density-voltage characteristics of the OPV were measured using a Keithley series 2400 digital source meter under the standard solar spectrum (AM 1.5G, 100 mW/cm²).

3. Results and Discussion

Figure 2(a) shows the influence of the high voltage applied during the deposition of the P3HT:PCBM layer on the spray diameter 6 mm from the tip of the glass capillary. Our previous study revealed that the spray diameter was directly proportional to the dielectric constant of the solvent, even though the viscosity, the surface tension, and other solvent parameters were changed by changing the solvent.¹⁸⁾ This result indicates that the dielectric constant is the dominant factor in determining the spray diameter of the ESD process. Since the spray diameter was less than 1 mm without mixing the additional solvent (in the case of *o*-DCB only), this result shows the spray was drastically spread by adding a solvent with a high relative dielectric constant.¹⁸⁾ The maximum spray diameter was realized when DMSO was used as the additional solvent. This is because the high relative dielectric constant of the additional solvent causes the spread of the spray diameter owing to Coulomb repulsion.¹⁸⁾ The dielectric constants of DMF and acetonitrile are almost the same; therefore, the difference in the spray diameter was considered to be caused by the difference in the viscosity, surface tension, and other parameters of DMF and acetonitrile. In addition, the maximum spray diameter was observed at 6 kV for all the cases of additional solvents. This result indicates that a stable Taylor cone was formed at the tip of the glass capillary when the applied voltage was 6 kV, and this fact causes the maximum spray diameter under this deposition condition.^{25,26)} In addition, the spray diameter decreased with increasing applied voltage over 6 kV for all solvents. This is because the electric field between the glass capillary and the ITO-coated glass substrate increased with increasing applied voltage. Therefore, the droplet velocity increased with increasing applied voltage, resulting in a narrow spray diameter.^{27,28)}

Figure 2(b) shows the relationship between the applied voltage and the supply speed of the P3HT:PCBM solution. The supply speed was estimated from the movement of the liquid level in the glass capillary. The supply speed increased with increasing applied voltage owing to the high electric field under the high-applied-voltage condition.²⁷⁾ Moreover, the minimum supply speed was observed when DMSO was used as the additional solvent.

Figure 3 shows the SEM images of the P3HT:PCBM thin films deposited by the ESD process with different additional solvents in *o*-DCB. The additional solvents used were DMSO [Fig. 3(a)], DMF [Fig. 3(b)], and acetonitrile [Fig. 3(c)]. The fiber like structure with the diameter of 500 to 700 nm was obtained for all the cases of additional solvents when the applied voltage was 5.5 kV. Since the supply speed decreased with decreasing applied voltage, the solvent of the droplet was easily evaporated before reaching the ITO-coated glass substrate under the low-voltage condition. The most likely cause of this result is that the fiber-like structure was formed owing to the high concentration of P3HT:PCBM in *o*-DCB. This is because the viscosity of the droplet became high with the evaporation of the solvent, causing the fiber like structure in the deposited thin film.^{29,30)} On the other hand, the fiber like

structure was not observed at voltages over 6.0 kV when DMF and acetonitrile were used as the additional solvent. Since DMSO has a higher relative dielectric constant (47.0) than DMF (36.7) and acetonitrile (35.7), a large spray diameter and slow supply speed were realized in the case of DMSO. Therefore, the evaporation speed of the droplet increased with increasing relative dielectric constant of the additional solvent. This fact indicates that the evaporation speed of the P3HT:PCBM droplet with DMSO was higher than those of other additional solvents (DMF and acetonitrile). As a result, the fiber like structure was obtained when DMSO was used as the additional solvent because of the dried droplet, which was caused by the high relative dielectric constant.

The vapor pressure of solvent is an important factor in forming the fiber like structure. This is because the evaporated solvent causes the increased concentration of P3HT:PCBM in the droplet. Since the ratio of additional solvent was 10 vol% under this experimental condition, the vapor pressure of additional solvent does not affect the evaporation speed of the P3HT:PCBM droplet. As a result, the number of fiber like structures increased with decreasing spray diameter due to the high droplet speed toward the substrate, as shown in Fig. 2(a). In any case, a low surface roughness was realized at an applied voltage of over 6.0 kV when DMF and acetonitrile were used as the additional solvent.

Figure 4 shows the root-mean-square (RMS) roughness of the P3HT:PCBM thin film fabricated by the ESD method with different additional solvents as a function of the applied voltage. The RMS roughness decreased with increasing applied voltage owing to the smaller number of fiber like structures on top of the P3HT:PCBM layer, as shown in Fig. 3. The dried droplet of P3HT:PCBM forms the fiber like structure before reaching the substrate at 5.5 kV, resulting in a rough surface. On the other hand, the almost dried droplet was deposited at 6.0 kV, and the nano structure was formed without dissolving the underlayer. In addition, the droplet shape is almost circular because of the isotropic force of the charged droplet. The RMS roughness was drastically reduced using DMF and acetonitrile compared with DMSO, and the minimum RMS roughness of less than 10 nm was achieved. Even though the RMS roughness was reduced at an applied voltage over 7 kV, a cast like P3HT:PCBM thin film was formed. The insets of Fig. 4 show photographs of the deposited P3HT:PCBM thin film. The patchy thin film (the cast like P3HT:PCBM films.) was formed when the applied voltage was over 7 kV. Therefore, the optimal applied voltage for forming the smooth P3HT:PCBM thin film is 6 kV .

Figure 5 shows the current density-voltage characteristics of devices A, B, and C fabricated by the ESD process with different additional solvents and of the reference device fabricated by the spin-coating process. The high voltage applied to fabricate the OPV was 4.0 kV; however, the optimal voltage for forming the smooth P3HT:PCBM thin film on the glass substrate was 6.0 kV. This is because the PEDOT:PSS layer causes a reduced applied high voltage

owing to the higher conductivity of PEDOT:PSS compared with that of the glass substrate. The voltage applied to fabricate the OPV was determined from the measured spray diameter and supply speed, which were the same values as those under the optimized conditions in Fig. 2 when the P3HT:PCBM thin film was deposited on the glass substrate. The measured thicknesses of the P3HT:PCBM layers were 50 nm (device A), 100 nm (device B), 150 nm (device C), and 130 nm (reference device). The difference in the thickness of P3HT:PCBM layers was caused by the difference in the spray diameter and the supply speed, as shown in Fig. 2.

Table I summarizes the PCE, the short-circuit current density (J_{sc}), the open-circuit voltage (V_{oc}), and the fill factor (FF) of the fabricated OPVs. Both surface roughness and the thickness of the P3HT:PCBM layer affect the photovoltaic performance. Since the thickness of the P3HT:PCBM layer was changed because of the difference in the spray diameter upon changing the additional solvent, we cannot discuss the influence of the surface roughness on the photovoltaic performance. However, this result indicates that the photovoltaic performance of the ESD-based OPV was improved by using the additional solvent technique. The highest photovoltaic characteristics of the ESD-based OPV were achieved when acetonitrile was used as the additional solvent (device C). The P3HT:PCBM layer of device C showed a smooth surface roughness owing to the optimized evaporation speed of the droplet, as shown in Fig. 4. The calculated series resistances were 23.0, 18.4, and 14.8 Ω for devices A, B, and C, respectively. In general, the series resistance tends to increase with increasing thickness of the active layer. This result indicates that the series resistance decreased with increasing surface roughness of the P3HT:PCBM layer deposited with different additional solvents. Therefore, the reduced surface roughness of the P3HT:PCBM layer causes the low series resistance, resulting in improved J_{sc} and FF, which in turn cause the high PCE of device C fabricated by the ESD method using acetonitrile. On the other word, the fiber like structure causes the decreased carrier transport path from the active layer to the electrode, resulting in the low PCE. Furthermore, a higher V_{oc} was realized for the ESD-based OPV compared with the reference device. One possible hypothesis of the improved V_{oc} is the crystallization and the stacking structure of P3HT and PCBM. In a previous paper, Ali et al. reported that the absorption spectrum of P3HT neat film deposited by the ESD method is changed by adjusting the supply speed, as a result of the change in the stacking structure of P3HT.³¹⁾ This result indicates that the energy level of ESD-based P3HT:PCBM film is shifted, resulting in the improved V_{oc} .

Figure 6 shows the spectral sensitivity of the OPVs. The peak-spectral sensitivities of all the devices were approximately 580 nm, corresponding to the absorption of P3HT. This result indicates that an efficient bulk-heterojunction structure was formed by the ESD method, and the photo induced carriers were efficiently dislocated in the P3HT:PCBM layer. The spectral

selectivity was measured by irradiating monochromatic light with the optical intensity of 0.5 mW/cm^2 ; the photovoltaic performance of OPV is influenced by the optical intensity of irradiated light. Therefore, the spectral sensitivity does not directly indicate the photocurrent density measured using the standard solar spectrum.

4. Conclusions

We achieved a smooth surface of the P3HT:PCBM thin film and improved photovoltaic performance of the ESD-based OPV using an additional solvent with a high relative dielectric constant. We found that acetonitrile is the most suitable additional solvent for reducing the surface roughness of the P3HT:PCBM thin film, and results in the high PCE of the bulk-heterojunction OPV. The highest PCE was 2.22 % .

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Table and Figure captions

Table 1. Photovoltaic characteristics of ESD-based OPVs fabricated using different additional solvents.

Figure 1 Experimental setup for ESD method.

Figure 2. (a) Spray diameter 6 mm from glass capillary as a function of applied high voltage. (b) Influence of applied voltage on supply speed of P3HT:PCBM solution.

Figure 3. SEM images of P3HT:PCBM thin films fabricated by ESD with different solvents and applied voltages. Additional solvents were (a) DMSO, (b) DMF, and (c) acetonitrile.

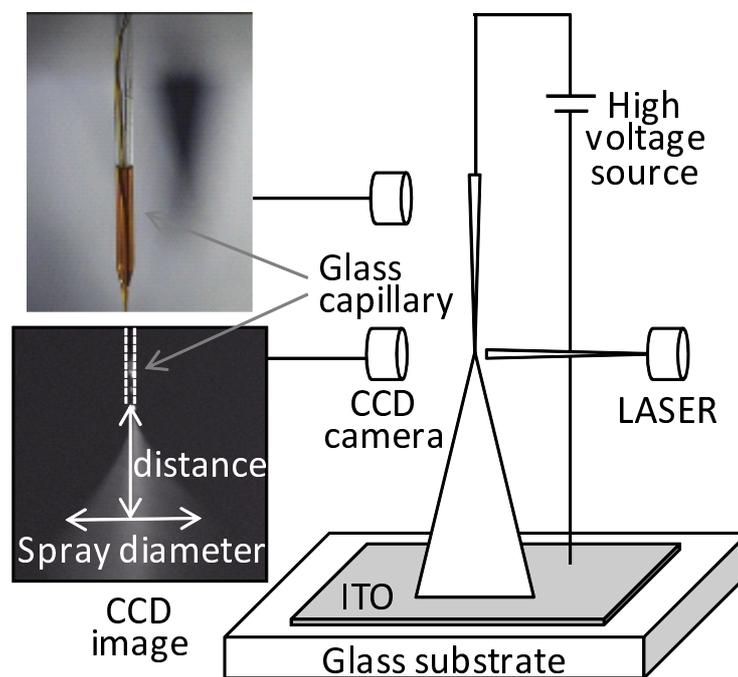
Figure 4. Relationship between applied voltage while depositing P3HT:PCBM thin film and RMS roughness estimated from AFM image.

Figure 5. Current density-voltage characteristics of OPVs fabricated by ESD with different additional solvents in *o*-DCB.

Figure 6. Spectral sensitivity of OPV fabricated by ESD and the conventional spin-coating process. Additional solvents were DMSO, DMF, and acetonitrile.

Table I. Photovoltaic characteristics of ESD-based OPVs fabricated using different additional solvents.

device name	solvent	PCE (%)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	thickness (nm)
A	DMSO	1.30	6.15	0.59	0.36	50
B	DMF	2.14	7.08	0.62	0.49	100
C	acetonitrile	2.22	7.42	0.59	0.49	150
reference	-	2.67	8.56	0.57	0.57	130

**Fig. 1.** Experimental setup for ESD method.

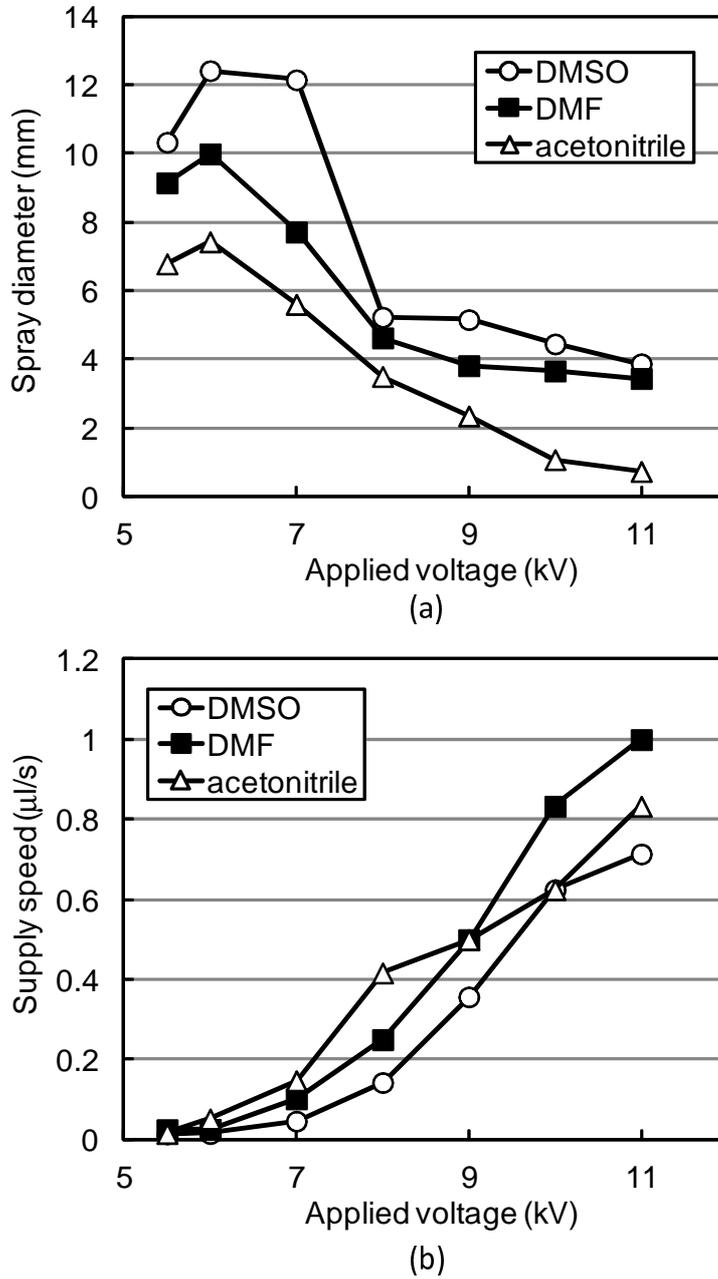


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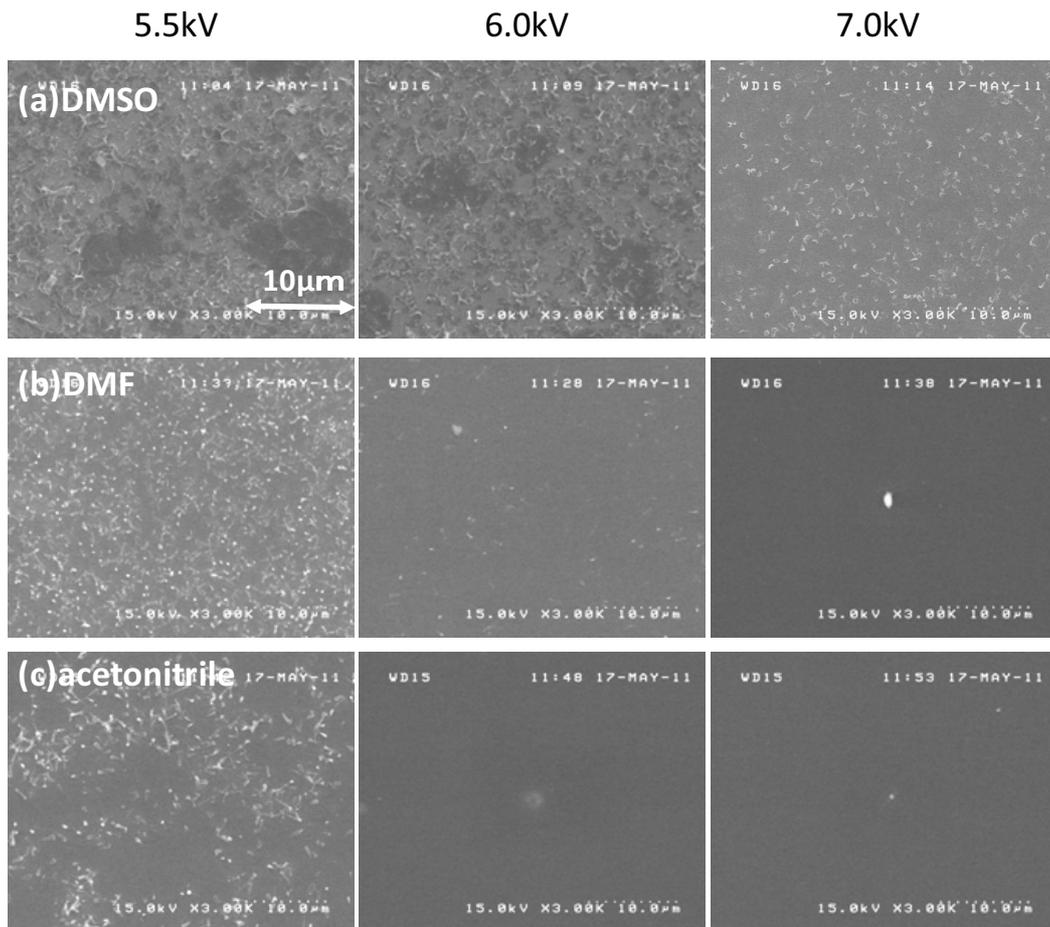


Fig. 3. SEM images of P3HT:PCBM thin films fabricated by ESD with different solvents and applied voltages. Additional solvents were (a) DMSO, (b) DMF, and (c) acetonitrile.

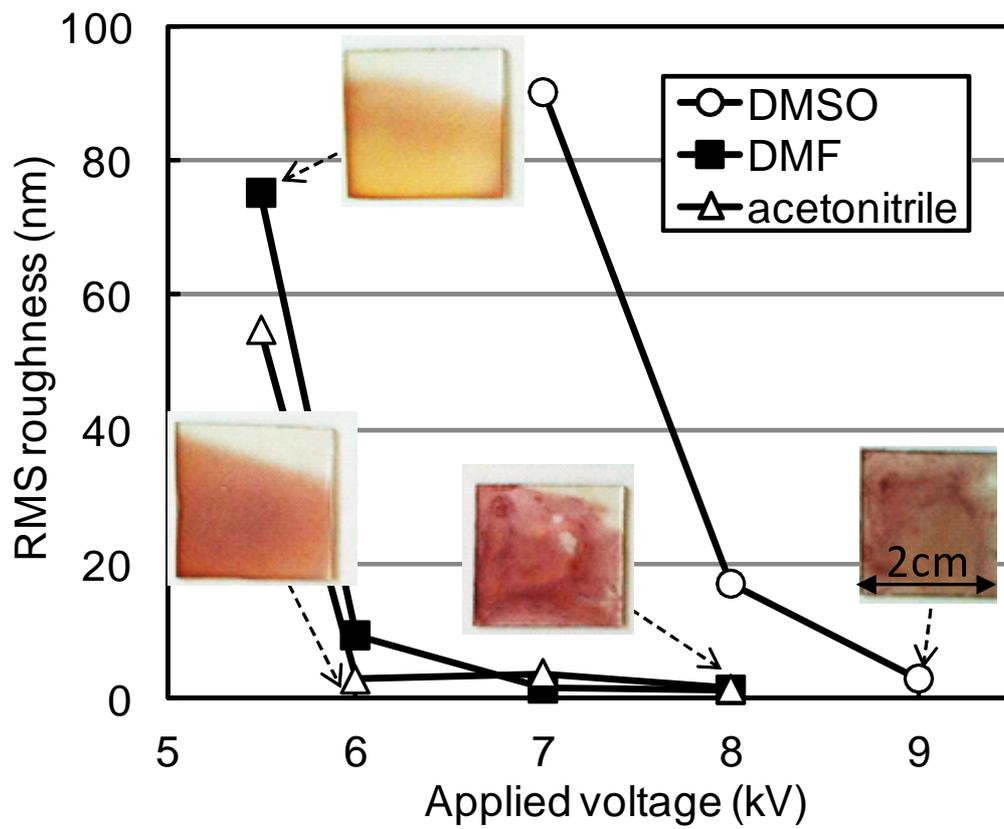


Fig. 4. Relationship between applied voltage while depositing P3HT:PCBM thin film and RMS roughness estimated from AFM image.

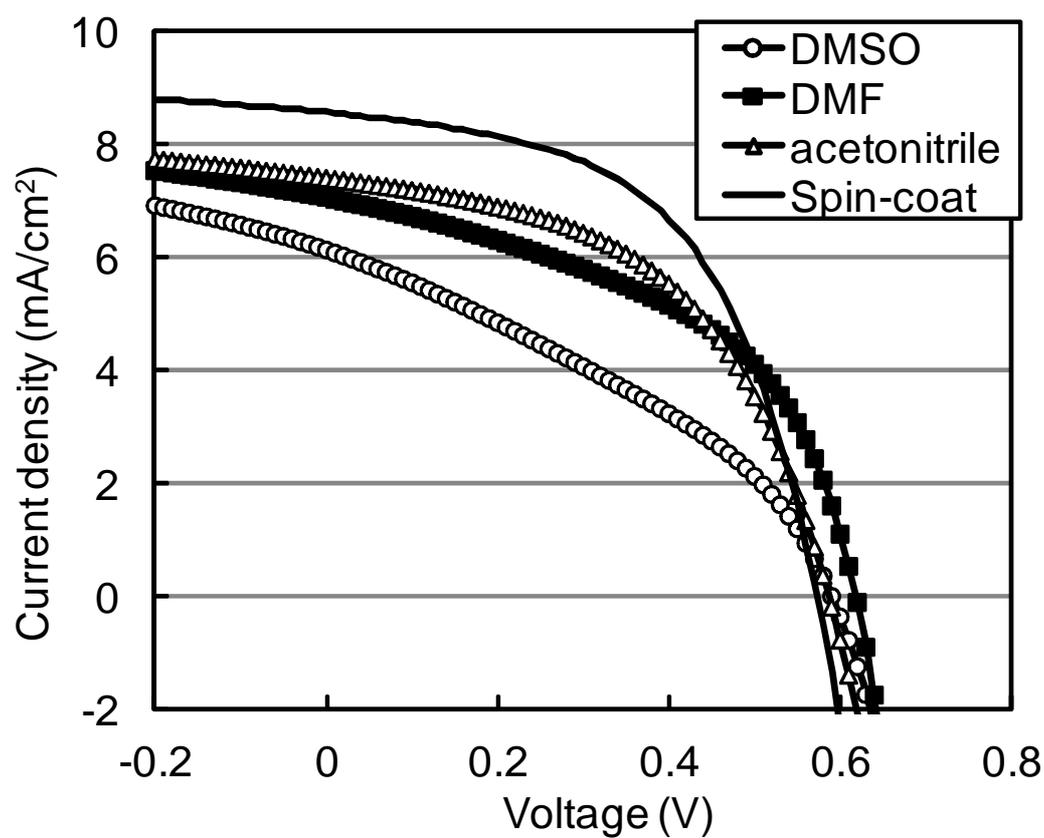


Fig. 5. Current density-voltage characteristics of OPVs fabricated by ESD with different additional solvents in *o*-DCB.

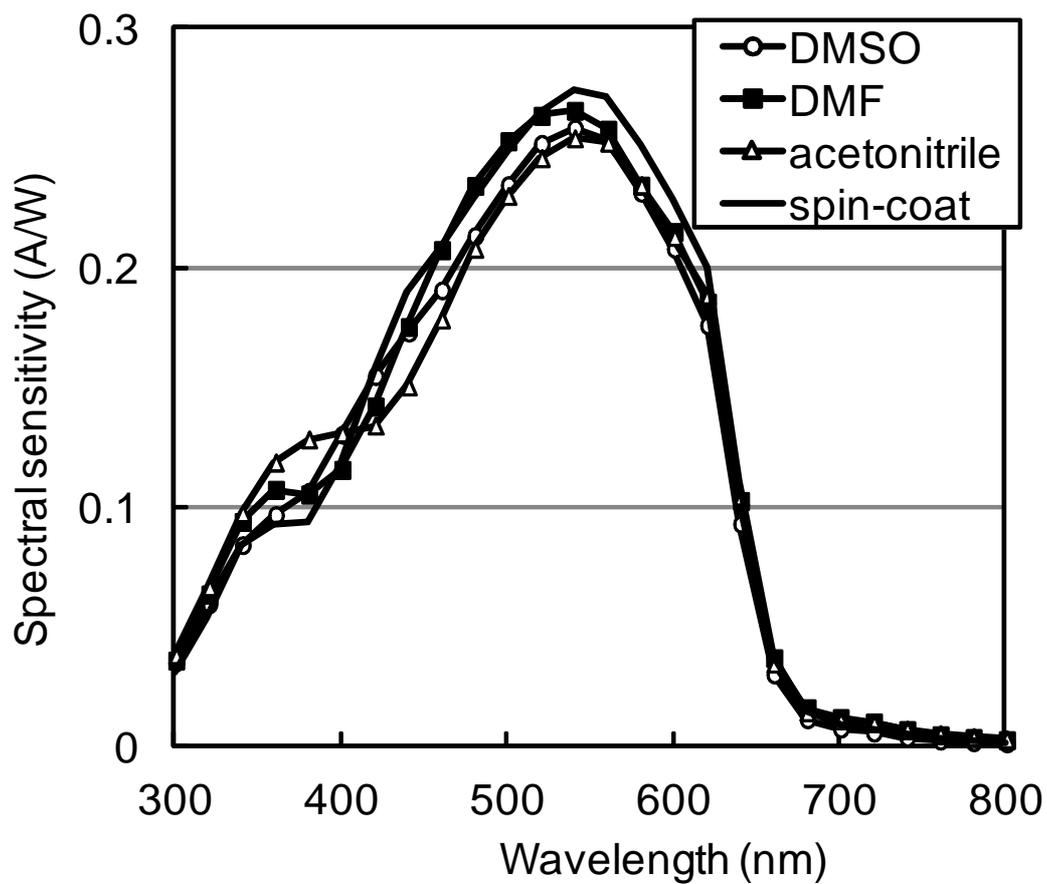


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