Plasmon-Enhanced Polymer Photovoltaic Device Performance Using Different Patterned Ag/PVP Electrospun Nanofibers

Jung-Yao Chen, Hung-Chin Wu, Yu-Cheng Chiu, and Wen-Chang Chen*

Significant enhancement of P3HT (poly(3-hexylthiophene)):PC_{61}BM ([6,6]-phenyl C61-butyric acid methyl ester) photovoltaic devices using different patterns of electrospun Ag/PVP composite nanofibers, including nonwoven, aligned, and crossed patterns, is reported. The composite electrospun nanofibers are prepared using in situ reduction of silver (Ag) nanoparticles in Ag/poly(vinyl pyrrolidone) (PVP) via a two-fluid coaxial electrospinning technique. The composition, crystalline orientation, and particle size of Ag are manipulated by controlling the core/shell solution concentration. The smallest diameter of the composite nanofibers leads to the highest orientation of the Ag nanoparticles and results in the largest conductivity due to geometric confinement. Such composite nanofibers exhibit the surface plasmon resonance (SPR) effect, which provides near-field enhancement of electromagnetic field around active layer. Additionally, composite nanofibers with the crossed or nonwoven patterns further enhance high carrier mobility, compared to that of the aligned pattern. It leads to the 18.7% enhancement of the power conversion efficiency of photovoltaic cell compared to the parent device. The results indicate that the high conductivity and SPR effect of the Ag/PVP electrospun nanofibers can significantly improve the photocurrent and PCE, leading to promising organic solar cell applications.

1. Introduction

Large-area solution-processible organic photovoltaic (OPV) devices have attracted extensive scientific interest for renewable energy conversion due to the advantages of inexpensive, low fabrication temperature, and mechanical flexibility.\(^1\)–\(^7\) Currently, the power conversion efficiency (PCE) of polymer-fullerene bulk-heterojunction OPVs over 9–10% are reported for single-junction devices\(^8\) and for tandem solar cells.\(^9\)–\(^11\) However, photoactive polymers with comparatively low charge carrier mobility (usually less than \(10^{-4}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\)) could result in the poor quantum efficiency of the OPV. Thus, it is common to use a thinner polymer film for preventing the exciton recombination, leading to higher internal quantum efficiency.\(^12\)–\(^13\)

The minimized photoactive layer, however, is required to harvest sufficient incident photons. Therefore, it remains challenging to use thin polymer films to create a more efficient light trapping and coupling environment for high performance OPV devices.\(^14\)–\(^15\)

A light trapping method based on the surface plasmon resonance (SPR) effect has been widely used to enhance OPV device performance. Metallic nanostructures such as Au,\(^16\)–\(^21\) Ag,\(^22\)–\(^24\) or Al\(^25\) were employed to improve OPV PCE in the range of 10–25% via the enhancement of localized surface plasmon resonance (LSPR) near field absorption. Additionally, several studies have reported that the LSPR from metallic clusters would exhibit stronger local electrical field compared to isolated particles due to the collective SPR with interparticle plasmon coupling.\(^26\)–\(^28\) In addition, AuAg alloy\(^29\) or silica-coated noble metal nanoparticles\(^30\),\(^31\) used in the photoactive layer recently resulted in a 14–30% improvement in PCE. In particular, a silica shell layer of the metal/SiO\(_2\) core/shell nanoparticles was enabled to act as an electrically insulating interface that would not interfere with the exciton generation and transport into the photoactive polymer layer.\(^30\) To further improve the electrical conductivity, metallic nanoparticle assemblies formed supplemental charge transportation networks.\(^32\)

Electrospinning (ES) is a high-throughput processing technique to fabricate micro- or nanofibers from polymer solutions.\(^13\) The nonwoven or well-aligned nanofibers prepared from semiconducting materials could be produced by the ES technique and were used for optoelectronic devices (field-effect transistors,\(^14\),\(^15\) OPVs,\(^36\) and memory\(^37\) applications). The geometry confinement provided by the nanofiber could manipulate the nanostructure growth and resulted in control over the optical and electrical properties of the electroactive materials. For example, the plasmonic nanoparticle-incorporated electrospun fibers enabled unique 1D metallic nanoparticle assemblies into the OPV system for light trapping. Kim,\(^38\) Yu,\(^39\) and co-workers showed Au and Ag nanoparticles that were co-spun with polyethylene and poly(vinyl alcohol), respectively, with the encapsulated aggregates of plasmonic nanostructures. Au
nanorods were incorporated into poly(acryl amide) uniaxially aligned ES fibers for waveguiding applications with photon-to-plasmon conversion efficiency of 70%.\textsuperscript{[40]} However, the applications of such nanofibers in bulk-heterojunction OPV devices have not yet been explored, as far as we know. In addition, the effect of the fiber architecture on the OPV performance has not been investigated.

Here, we explore the morphology and electrical performance of the ES Ag/poly(vinyl pyrrolidone) (PVP) nanofibers with different patterns (nonwoven-, aligned-, and crossed-arrangement) and diameter for the performance of P3HT (poly(3-hexylthiophene)):PC$_{61}$BM ([6,6]-phenyl C$_{61}$-butyric acid methyl ester) OPVs. The nanofibers were prepared from the coaxial core-sheath ES technique with Ag(NH$_3$)$_2^+$ and PVP as core and shell solutions, respectively. The Ag nanoparticles were in situ reduced after the ES process. The PVP component not only provided appropriate viscoelastic properties for fabricate align- or crossed-patterns of the Ag/PVP nanofibers, but also prevented the direct contact of the Ag nanoparticles with the bulk-heterojunction layer to preserve the Ag SPR impression. The morphology of the prepared Ag/PVP ES nanofibers was characterized using field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and selected-area electron diffraction (SAED). The plasmonic textiles with non-woven, aligned, or crossed patterns were further incorporated into OPVs with a sandwich structure of indium tin oxide (ITO)/nanofibers/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)/P3HT:PC$_{61}$BM/Ca/Al for the enhancement of PCE with the SPR effect. The experimental results indicate the Ag/PVP plasmonic ES nanofibers with tunable morphology and patterning can significantly enhance OPV device characteristics.

2. Results and Discussion

2.1. Morphology of the Ag/PVP ES Nanofibers

With the merits of the ES technique, we can easily prepare various architectures of Ag/PVP nanofibers, as is schematically illustrated in Figure 1. Three types of composite nanofibers, AgF-1, AgF-2, and AgF-3, were fabricated via a coaxial ES technique for manipulating nanostructure and electrical conductivity; they consisted of a Ag(NH$_3$)$_2^+$ complex ion core and a PVP shell. The morphology of Ag/PVP composite nanofibers were characterized using both FE-SEM and TEM. The as-spun AgF-1, AgF-2, and AgF-3 ES textiles with average fiber diameters of 800, 350, and 285 nm, as shown in Figure 2a–c, respectively, are smooth and uniform without Ag nanostructures on the surface. This indicates that the PVP shell can completely cover the Ag-based core of nanofibers. It suggests that we can control the diameter of the nanofiber by varying the shell and core concentration. Note that the Ag theoretical values of in AgF-1, AgF-2, and AgF-3 are 1.39, 0.36, and 0.07%, respectively. Moreover, the fused crossed-junction of AgF-1 is confirmed by the SEM image after thermal annealing (200 °C for 20 min) and water-etching (Figure S1 in Supporting Information). It was reported that the melt junctions between nanowires or nanofibers would possess lower junction resistances, leading to the improved electrical conductivity.\textsuperscript{[41,42]} Thus, the prepared plasmonic nanofibers with the fused joint structure could provide enhanced charge carrier mobility for enhancing the OPV performance.

To characterize the Ag nanostructures in the composite nanofibers, the PVP part was removed by vacuum calcination at 400 °C for 2 h. The Ag structure in AgF-1, AgF-2, and AgF-3 is spherical, with average diameters of approximately 20 nm (Figure 2d), 16 nm (Figure 2e), and 5 nm (Figure 2f). This result is consistent with the SPR signal of the spherical Ag nanoparticles in the UV-visible spectra of composite nanofibers, as discussed later. To confirm the spherical morphology and the distribution of Ag nanostructures inside the fibers more directly, the TEM and SAED analyses (Figure 3) were performed. The Ag nanoparticles are well-dispersed in AgF-3 with an uniform size, as exhibited in Figure 3b. Nevertheless, the TEM image of AgF-1 (Figure 3a) only displays a full darkness result, which might be attributed to the large electron density of the Ag atom using the high concentration of the Ag precursor within the ES process. On the other hand, the TEM image of AgF-2 shows scattered Ag nanoparticles in the edge and full darkness in the middle (Figure S2a, Supporting Information). This agrees with the trend of the core concentration on the TEM image. The orientation of Ag nanoparticles was recognized from the SAED patterns, which were obtained by directing the electron beam
perpendicular to the studied nanofibers. From Figure 3c, diffraction rings with different Ag packing structures is obtained from the SAED pattern of AgF-1. Compared to AgF-1, AgF-3 (Figure 3d) shows the hexagonal symmetry of diffraction spots, indicating that the Ag nanoparticles in AgF-3 are highly oriented with the face-centered cubic crystalline structure. The smaller diameter of AgF-3 probably provides the severe geometrical confinement on the Ag growth and leads to the higher orientation than that of AgF-1. Similar orientation character is also presented in AgF-2 (Figure S2b, Supporting Information) with a smaller fiber diameter compared to that of AgF-1. The highly orientated Ag nanoparticles in AgF-3 could result in higher charge carrier mobility for the device applications.

To track the Ag reduction as well as morphological evolution in the Ag/PVP textiles, UV-visible absorption spectra were recorded because different shapes of Ag nanostructures exhibited SPR bands at variant frequencies. As shown in Figure 4a, the conspicuous SPR peak at 425 nm indicates the existence of Ag nanoparticles in AgF-1, even though the as-spun nanofibers are stored at room temperature. As shown in the figure, a red-shifted and stronger SPR signal (~427 nm) is observed after 4 days under ambient environment without thermal treatment, demonstrating the continuous growth of Ag nanoparticles. The intensity of SPR signal of AgF-1 nanofibers annealed at 200 °C abruptly increases and slightly red-shifts to 431 nm, showing that more Ag ions are reduced and the Ag nanoparticles have continued growing with increased annealing time. It indicates the Ag nanoparticles embedded plasmonic ES nanofibers can be directly manufactured via thermal treatment. In addition, the temporal optical absorption spectra based on the non-woven AgF-2 (Figure S3a, Supporting Information) also show the same trend. However, no obvious signal in the UV-visible spectra of AgF-3 (Figure S3b, Supporting Information) is observed due to the extremely low Ag concentration. Note that...
the optical absorption spectrum of the parent PVP ES nanofibers (Figure S3c, Supporting Information) exhibits no characteristic peak in the same wavelength range, suggesting the effect of Ag nanoparticle. The abundant nitrogen atoms of PVP are not only employed to coordinate with Ag, but also create a Ag network in the Ag/PVP composite nanofibers. Therefore, the composited nanofibers exhibit an excellent physical property to resist water or even other organic solvent. The SPR signals are almost the same in different fiber architectures, as shown in Figure 4b, indicating a similar SPR effect.

2.2. Electrical Properties of Electrospun Nanofibers

The electrical characteristics of the Ag/PVP composite nanofibers were performed using two-terminal electrical measurements with the Au electrodes. Figure 5 shows the electrical characterizations of AgF-3 where the nonlinear current–voltage (I–V) curve at the lower bias shown in the inset probably results from the intergrain boundary of Ag nanoparticles or the PVP component blocks the electron transportation in a low voltage bias; additionally, at a higher bias, the nanofiber becomes conductive. In the case of AgF-1 and AgF-2, the I–V curves also display the similar characteristic (Figure S4, Supporting Information). The calculated conductivities of AgF-1, AgF-2 and AgF-3 are $1.20 \times 10^4$, $3.81 \times 10^5$, and $5.60 \times 10^5$ S m$^{-1}$, respectively. AgF-3 achieves the highest conductivity among the three Ag/PVP composite nanofibers, mainly because of the higher degrees of Ag nanoparticle crystalline orientation, as evident from the SAED results.

2.3. Confocal Images of the Ag/PVP ES Nanofibers

ES is a versatile assembly method for fabricating uniform and ultrafine nanofibers with different patterning via various geometric collectors for example: nonwoven or uniaxially aligned arrangements. For the studied Ag/PVP plasmonic nanofibers, the macroscopic distribution of Ag nanoparticles could be extracted from the confocal images based on the photoluminescence character of Ag. Figure 6 shows the confocal images of AgF-3, which emit a blue color within the entire composite nanofibers, implying the Ag nanoparticles are well-dispersed. Indeed, the images reveal different patterns of Ag/PVP fibers, including nonwoven mats, uniaxially parallel array, and biaxially crossed pattern, as shown in Figure 6a–c.

2.4. OPV Cell Characteristics with Ag/PVP Nanofibers

Here, the different patterned Ag/PVP ES nanofibers are incorporated into the OPV devices with the sandwich configuration...
of ITO/composite nanofibers/PEDOT:PSS/P3HT:PC$_{61}$BM/Ca/Al, as shown in Figure 6, to investigate the effect of ES plasmonic nanofibers on OPV performance. The corresponding current density–voltage (J–V) characteristics of the devices with or without the Ag/PVP composite nanofibers are illustrated in Figure 7 and summarized in Table 1. All of the photovoltaic cells were measured at one sun intensity (100 mW cm$^{-2}$) under simulated AM 1.5G illumination. The controlled cell without the Ag/PVP nanofibers reaches a PCE of 3.53% with the open-circuit voltage ($V_{oc}$) of 0.64 V, short-circuit current ($J_{sc}$) of 8.54 mA cm$^{-2}$, and fill factor (FF) of 0.646. The AgF-1 nonwoven, aligned, and crossed ES nanofibers layer are introduced into the OPV cells and named N-AgF-1, A-AgF-1, and C-AgF-1, respectively. The PCEs show an obvious improvement from 3.53% (the reference cell) to 3.87% (N-AgF-1), 3.73% (A-AgF-1), and 4.03% (C-AgF-1) with the $J_{sc}$ values of 9.06, 8.68, and 9.63 mA cm$^{-2}$, respectively. After incorporating higher conductive AgF-2, the PCEs of N-AgF-2, A-AgF-2, and C-AgF-2 improve to 3.88, 3.86, and 4.14% with the $J_{sc}$ values of 9.22, 9.08, and 9.83 mA cm$^{-2}$, respectively. Furthermore, the OPVs with the highly conductive AgF-3 exhibit the PCEs of 3.77, 3.97, and 4.19% with the $J_{sc}$ values of 9.13, 9.39, and 9.87 mA cm$^{-2}$ for N-AgF-3, A-AgF-3, and C-AgF-3, respectively. Note that the $V_{oc}$ (generally 0.65 V) and FF (in a range of 0.63 to 0.66) of all nanofiber-containing OPVs show an insignificant difference. This suggests that the increase in the PCEs is mainly attributed to the improvement of $J_{sc}$ from the conductive nanofibers. Additionally, the performance of the device embedded with nonwoven pure PVP ES nanofibers is slightly inferior than that of the controlled cell (Figure S5, Supporting Information). This indicates that the presence of Ag nanoparticles in the composite nanofibers is the main contributor that improves the performance of OPVs.

The increases of the PCE and $J_{sc}$ values are caused by the enhancements in charge carrier mobility and the rate of exciton formation from the Ag/PVP plasmonic nanofibers. Since the charge transporting ability is essential for achieving high efficient OPV device, the space-charge-limited-current (SCLC) method was explored to elucidate the relationship between Ag/PVP ES nanofibers and hole or electron mobilities. Figure 8a,b show the $J^{0.5}$–V curves of the hole-only and electron-only devices, respectively, with nonwoven, aligned, and crossed AgF-3. The detailed fabrication and analysis method are also described in the Supporting Information. The hole mobilities of the reference cell, aligned, crossed and non-woven AgF-3 nanofibers-based device are 1.51 × 10$^{-4}$, 2.92 × 10$^{-4}$, 3.51 × 10$^{-4}$, and 6.50 × 10$^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively, while the electron mobilities are 4.36 × 10$^{-4}$, 5.17 × 10$^{-4}$, 8.04 × 10$^{-4}$, and 2.16 × 10$^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$. We also investigate the device structure of ITO/composite nanofibers/PEDOT:PSS/Au to explore the effects of fiber patterns on the electrical properties of the interface layer (Figure S6, Supporting Information). The electrical resistance of the reference device without nanofibers was 13.47 Ω mm$^{-2}$, but
Improved to 8.84, 9.85, and 9.20 Ω mm² after incorporating the interlayer of the nonwoven, aligned, crossed, and AgF-1 nanofibers, respectively. This suggests the significance of the enhancement on the conductivity using the ES nanofibers as the interlayer. The above results indicate the incorporation of Ag/PVP ES nanofibers in P3HT:PC₆₀BM OPV system can improve the charge drift velocity and further reduce the electrical resistance, especially for the composite nanofibers with fused joints (i.e., non-woven and crossed patterns). Thus, the OPVs with the cross-patterned Ag/PVP nanofibers exhibit the largest improvement in $J_{sc}$ as well as PCE and decrease in electrical resistance as compared to that of align-patterned nanofibers-based devices. The optimal PCE of photovoltaic devices with cross-patterned AgF-1, AgF-2, and AgF-3 nanofibers exhibit a PCE of 4.03, 4.14, and 4.19%, which are 14.2, 17.3, and 18.7% improvement, respectively, compared to the reference device (PCE = 3.53%) without composite nanofibers.

To elucidate the decreased PCE in the devices using non-woven fibers, the surface structure of PEDOT:PSS cast on different nanofiber patterns were characterized using SEM and atomic force microscopy (AFM; Figure S7, Supporting Information). The nonwoven-patterned AgF-1 exhibits the largest amount of fused joints per unit area due to the randomly deposited process and leads to the larger AFM surface roughness of the PEDOT:PSS layer near the nonwoven nanofibers compared to the aligned nanofibers. The fiber diameter also affects the surface structure. For example, the AgF-2 fibers with diameter of 350 nm could be fully sheltered by PEDOT:PSS (50–60 nm) plus P3HT:PC₆₀BM (250–280 nm) layer, but not for the case of the AgF-1 with the diameter of 800 nm (Figure S8, Supporting Information), leading to larger surface roughness near the fibers than that of AgF-2 or AgF-3. The high density fused points or large fiber diameter results in the high surface area near the fiber and probably leads to the large phase separation and inferior device performance.

Figure 9 shows the external quantum efficiency (EQE) results of the studied OPV devices for investigating the SPR effect of Ag/PVP ES nanofibers. The EQEs for all OPVs are increased after employing the Ag/PVP nanofibers covering a wide-range wavelength from 300 to 800 nm. Furthermore, the integrated photocurrent densities from the EQE spectrum of the reference, N-AgF-3, A-AgF-3, and C-AgF-3 are 8.40, 9.12, 9.24, and 9.65 mA cm⁻², respectively. The enhancement is a consequence of the improved charge carrier mobility and the exciton generation rate due to the SPR effect from the studied ES nanofibers. All the integrated current density values are in a good agreement with the measured photocurrent densities (within 5% error), indicating that the photovoltaic results are reliable. In addition, the extinction coefficients and EQE of the P3HT/PC₆₁BM device is significantly enhanced after incorporating the ES nanofibers (Figure S9, S10, Supporting Information). As shown in Figure S9 (Supporting Information), two highly enhanced absorption region are observed at 300–400 nm and 600–800 nm, which is comparable with the SPR signal of Ag nanoparticles and the enhancement region could be attributed to the refractive index change sensed by the Ag nanoparticles in different medium or environments. The above results demonstrate that the Ag/PVP plasmonic nanofibers are a promising candidate for enhancing the OPV performance.

2.5. Radiative Energy Transfer from Plasmonic Ag/PVP Nanofibers to the Photoactive Layer

The luminescence of the Ag metal was first observed by Moordadian, and it was generally attributed to electronic transitions
between the upper d orbital and the conduction sp band. The Ag luminescence can be induced by irradiating the metal surface or film with the emission source in a range of 320–520 nm.\textsuperscript{51} The photoluminescence (PL) spectra (Figure 10) were explored to investigate the interaction between the Ag/PVP ES nanofibers and P3HT:PC\textsubscript{61}BM photovoltaic layer. Figure 10a shows the PL spectra of AgF-3 with or without the P3HT:PC\textsubscript{61}BM film. Pure AgF-3 shows a clear emission peak at 390 nm with a 325 nm photoexcitation power signal. However, the PL intensity of the composite nanofibers with the P3HT:PC\textsubscript{61}BM layer is abruptly quenched almost 90\%. On the other hand, the emission signal of P3HT:PC\textsubscript{61}BM film (\textasciitilde550–800 nm) after incorporating the AgF-3 is enhanced, as shown in Figure 10b. The significant changes in the PL intensity of Ag/PVP nanofibers and P3HT:PC\textsubscript{61}BM film suggest the energy transfer between the Ag and photoactive layer. This energy transfer effect could be further confirmed by confocal images, as depicted in Figure 10c,d. There are two parts in the confocal image of Figure 10c: pristine AgF-3 nanofibers (top right side) and AgF-3 embedded in P3HT:PC\textsubscript{61}BM film (bottom left side). It could be clearly observed that the PL intensity of AgF-3 is sharply quenched after incorporating the photo-active film. Figure 10d shows the confocal images of pure P3HT:PC\textsubscript{61}BM region (top right side, region 1) and composite area of P3HT:PC\textsubscript{61}BM with AgF-3 (bottom left side, region 2). The mean PL intensity of regions 1 and 2 is 54.62 and 72.09 a.u., respectively, demonstrating that the emission in photoexcitation intensity of P3HT is enhanced after incorporating the Ag/PVP nanofibers. It should be noted that radiative energy transfer from the metal SPR to the semiconductor can take place through near-field electromagnetic and resonant photon-scattering mechanisms.\textsuperscript{52} Therefore, the PL change is attributed to the fact that radiative energy transfers from the excited plasmonic Ag nanoparticles to the nearby photoactive P3HT, and then increases the P3HT PL emission. The above result demonstrates the enhancement on the PCE of the P3HT:PC\textsubscript{61}BM photovoltaic cells through the plasmonic ES nanofibers.

3. Conclusions

We have successfully prepared Ag/PVP electrospun nanofibers with nonwoven, aligned, and crossed patterns using a two-fluid coaxial electrospinning technique. The Ag ions in the as-spun nanofibers were in situ reduced in the nanofiber with thermal treatment. The smallest diameter of the composite nanofibers led to the highest orientation of the Ag nanoparticles and resulted in the largest conductivity, comparable to that of ITO, due to the geometrical confinement. The composite nanofibers showed a surface plasmon resonance (SPR) effect, evident from the absorption peak around 425 nm. The incorporation of Ag/PVP ES nanofibers into the P3HT:PC\textsubscript{61}BM OPV cells improved the charge drift velocity and further reduced the electrical resistance, particularly for the composite nanofibers with fused joints, such as non-woven and crossed patterns. Additionally, the radiative energy transfer from excited plasmonic Ag/PVP electrospun nanofibers to the nearby active layer enhanced the exciton generation of P3HT. The P3HT:PC\textsubscript{61}BM OPV cell exhibited a PCE of 4.19\% using the cross-patterned AgF-3, which was an 18.7\% enhancement compared to the parent device with PCE of 3.53\%. The results suggest that the Ag/PVP electrospun nanofibers can potentially be used in advanced plasmonic solar cell devices.
4. Experimental Section

Materials: Silver oxide (Ag$_2$O, >99.99% trace metals basis), ammonium hydroxide solution (ACS reagent, 28.0–30.0% NH$_3$ basis), PVP (Mw ≈ 1 300 000), methanol (anhydrous, 99.8%), and o-dichlorobenzene (DCB, anhydrous, 99%) were purchased from Sigma-Aldrich (MO, USA) and used as received. Tetrabutylammonium perchlorate (TBAP, TCI (Tokyo, Japan)), P3HT (Mw ≈ 50 000, 90–95% regioregular, Reike Metals Inc. (Lincoln, NE)), and PC$_{61}$BM (99.7%, Nano-C (MA, USA)) were used without further experiment.

Preparation of Ag/PVP Electrospun Nanofibers: A two-fluid coaxial ES technique with modified collector was employed to produce aligned core/shell nanofibers, similar to previous reports. [34,35] Two syringes containing core and shell solutions were connected to a separate needle, and the needle was placed one inside the other to form a two-fluid coaxial ES system. The core and shell polymeric solutions were fed into the coaxial capillaries by two syringe pumps (KD Scientific Model 100, USA). In order to manipulate nanostructure and electrical conductivity of the Ag/PVP composite nanofibers, three different diameters of nanofibers were used.

Table 1. P3HT:PC$_{61}$BM OPV characteristics with or without the Ag/PVP composite nanofibers.

<table>
<thead>
<tr>
<th>Device</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>FF</th>
<th>PCE$^a$ [%]</th>
<th>$R_s$ [Ω cm$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference$^b$</td>
<td>0.64</td>
<td>8.54 ± 0.04</td>
<td>0.646 ± 0.005</td>
<td>3.53 ± 0.03</td>
<td>14.77</td>
</tr>
<tr>
<td>N-AgF-1</td>
<td>0.65</td>
<td>9.06 ± 0.09</td>
<td>0.657 ± 0.001</td>
<td>3.87 ± 0.04</td>
<td>13.89</td>
</tr>
<tr>
<td>A-AgF-1</td>
<td>0.65</td>
<td>8.68 ± 0.06</td>
<td>0.660 ± 0.001</td>
<td>3.73 ± 0.02</td>
<td>14.29</td>
</tr>
<tr>
<td>C-AgF-1</td>
<td>0.65</td>
<td>9.63 ± 0.07</td>
<td>0.644 ± 0.003</td>
<td>4.03 ± 0.03</td>
<td>13.12</td>
</tr>
<tr>
<td>N-AgF-2</td>
<td>0.65</td>
<td>9.22 ± 0.05</td>
<td>0.648 ± 0.007</td>
<td>3.88 ± 0.05</td>
<td>12.52</td>
</tr>
<tr>
<td>A-AgF-2</td>
<td>0.65</td>
<td>9.08 ± 0.03</td>
<td>0.654 ± 0.002</td>
<td>3.86 ± 0.07</td>
<td>13.73</td>
</tr>
<tr>
<td>C-AgF-2</td>
<td>0.65</td>
<td>9.83 ± 0.06</td>
<td>0.648 ± 0.005</td>
<td>4.14 ± 0.02</td>
<td>12.51</td>
</tr>
<tr>
<td>N-AgF-3</td>
<td>0.65</td>
<td>9.13 ± 0.08</td>
<td>0.636 ± 0.021</td>
<td>3.77 ± 0.09</td>
<td>13.84</td>
</tr>
<tr>
<td>A-AgF-3</td>
<td>0.65</td>
<td>9.39 ± 0.05</td>
<td>0.651 ± 0.002</td>
<td>3.97 ± 0.03</td>
<td>13.45</td>
</tr>
<tr>
<td>C-AgF-3</td>
<td>0.65</td>
<td>9.87 ± 0.02</td>
<td>0.653 ± 0.007</td>
<td>4.19 ± 0.03</td>
<td>12.29</td>
</tr>
</tbody>
</table>

$^a$The average value of PCE is calculated from at least 10 cells; $^b$The reference device is the device without ES nanofibers. The abbreviations of N-, A- and C- are the ES nanofibers with the architectures of nonwoven, aligned, and crossed patterns.

Figure 8. Measured $J-V$ characteristics under dark for a) hole-only and b) electron-only devices. The effective voltage can be corrected by subtracting the built-in voltage $V_{bi}$, arising from difference in the work function of the contacts, [49] and the voltage drop due to substrate series resistance ($V_{es}$) from the applied voltage ($V_{appl}$), such that $V = V_{appl} - V_{es} - V_{bi}$. The solid lines represent the fitting curves.

Figure 9. EQE measurements of all OPV devices with or without the Ag/PVP nanofibers.

4. Experimental Section

Materials: Silver oxide (Ag$_2$O, >99.99% trace metals basis), ammonium hydroxide solution (ACS reagent, 28.0–30.0% NH$_3$ basis), PVP (Mw = 1 300 000), methanol (anhydrous, 99.8%), and o-dichlorobenzene (DCB, anhydrous, 99%) were purchased from Sigma-Aldrich (MO, USA) and used as received. Tetrabutylammonium perchlorate (TBAP, TCI (Tokyo, Japan)), P3HT (Mw = 50 000, 90–95% regioregular, Reike Metals Inc. (Lincoln, NE)), and PC$_{61}$BM (99.7%, Nano-C (MA, USA)) were used without further experiment.

Preparation of Ag/PVP Electrospun Nanofibers: A two-fluid coaxial ES technique with modified collector was employed to produce aligned core/shell nanofibers, similar to previous reports. [34,35] Two syringes containing core and shell solutions were connected to a separate needle, and the needle was placed one inside the other to form a two-fluid coaxial ES system. The core and shell polymeric solutions were fed into the coaxial capillaries by two syringe pumps (KD Scientific Model 100, USA). In order to manipulate nanostructure and electrical conductivity of the Ag/PVP composite nanofibers, three different diameters of nanofibers
were prepared and named AgF-1, AgF-2, and AgF-3. 30 mg, 5 mg, and 1 mg Ag₂O were added into 1 mL ammonium hydroxide solution to form Ag(NH₃)₂⁺ complex ion as the core solutions<sup>49</sup> of AgF-1, AgF-2, and AgF-3, respectively. 200 mg mL⁻¹ of PVP dissolved in methanol was the shell solution in AgF-1 while the shell solution in AgF-2 and AgF-3 was 100 mg mL⁻¹ PVP dissolved in methanol with 30 wt% of TBAP added to increase conductivity and then stabilize the cone-jet. The tip rate of Ag(NH₃)₂⁺ solution (core flow) was fixed at 0.1 mL h⁻¹ while the PVP solution (shell flow) was operated at 1.0 mL h⁻¹. The tip of the core needle was connected to a high-voltage power supply (chargemaster CH30P SIMCO, USA). The spinning voltage was set at 14–15 kV and the working distance (the distance between tip of the needle and collector) was fixed at 13 cm. The stable cone-jet spinning mode in the ES process was monitored by charge-coupled device (CCD) camera (Xli 3M USB2.0 CCD camera, USA) and macro video zoom lens (OPTEM MVZL, USA) to obtain uniform and aligned nanofibers. All ES experiments were carried out in air. Except for the randomly oriented structures in the form of nonwoven mats, the nanofibers could be stretched across the collector gap (4 cm in length and gap width of 1 cm) to form a parallel array and crossed pattern by transferring two layers of uniaxially aligned composite nanofibers onto the same substrate, as shown in Figure 1. The as-spun nanofibers were further annealed at 200 °C for 20 min to reduce Ag ions with the help of NH₄OH where the nitrogen atom can provide unpaired electron. Subsequently, the Ag/PVP composite nanofibers were immersed in water for 1 h to etch the excess PVP and then dried at 80 °C under vacuum.

**Characterization:** The morphology of the studied nanofibers was characterized by the following: FE-SEM images were taken using a microscope (JEOL JSM-6330F) operated at an accelerating voltage of 10 kV. Fluorescence optical microscope images were obtained by using two photon laser confocal microscopes (Confocal) (Leica LCS SP5). UV-Visible absorption spectra and steady-state photoluminescence (PL) spectra were recorded on a Hitachi U-4100 spectrophotometer and Horiba Fluorolog-3 spectrofluorometer (Jobin Yvon), respectively. TEM images were taken by using a microscope (FEI Tecnai G2 20) operated at 200 keV to observe the distribution and crystallographic orientation of nanostructural Ag particles in Ag/PVP ES nanofibers. AFM images were obtained with a Nanoscope 3D Controller AFM (Digital Instruments, Santa Barbara, CA) operated in tapping mode at room temperature.

**Electrical Characterization of Ag/PVP Nanofibers:** To measure the two-terminal resistances of Ag/PVP ES nanofibers, aligned composite nanofibers were prepared from the above ES process and deposited on the silicon wafer with 200 nm-thick SiO₂ layer. The wafer was first cleaned with toluene, acetone, and isopropyl alcohol, and then dried by N₂ steam. Top-contact electrodes were defined by 100 nm-thick of Au through a regular shadow mask with channel length 2.5 mm. The electrical conductivity of the nanofibers was calculated from the slope of the I–V curve by using Keithley 4200-SCS semiconductor parameter analyzer (Keithley Instruments Inc., Cleveland, OH, USA), with a remote PreAmp (4200-PA) in a N₂-filled glove box at room temperature. The scanning voltage was applied from −50 V to 50 V with the stepwise of 1 V.

**Fabrication and Characterization of P3HT/PCBM Photovoltaic Cells using the ES Composite Nanofibers:** All the bulk heterojunction photovoltaic cells were prepared using the same preparation procedures and device fabrication procedure, described in the following. The glass-ITO substrates (obtained from Luminescence Technology Corp., Taiwan, 7 Ω sq⁻¹) were first patterned by lithograph, then cleaned with detergent, and ultrasonicated in acetone and isopropyl alcohol, then subsequently dried on a hot plate at 120 °C for 5 min. Ag/PVP ES nanofibers from above preparation method were deposited on ITO substrates with the rectangular metal gap, preparing non-woven, aligned, or cross patterned ES nanofibers. PEDOT:PSS (Baytron P VP AI4083) passed through a 0.45 µm filter and then spin-coated at 3500~5000 rpm on ITO/nanofibers and dried at 140 °C for 20 min under ambient environment. The active layer of the P3HT:PC61BM blend (1:0.8, w/w) in anhydrous DCB (17.5 mg mL⁻¹) was followed by spin-coating at 1000 rpm on top of the

**Figure 10.** a) PL spectra of AgF-3 before and after spin-coating P3HT:PC₆₁BM film. b) PL spectra of P3HT:PC₆₁BM layer before and after incorporating AgF-3. c) Confocal image of AgF-3 and spin-coated P3HT:PC₆₁BM film with collected emission bandwidth from 470 nm to 550 nm. d) Confocal image of AgF-3 and spin-coated P3HT:PC₆₁BM film with collected emission bandwidth from 550 nm to 790 nm.
PEDOT: PSS layer. These as-cast films were kept in petri dish to control the drying rate under nitrogen atmosphere. After that, the device was annealed at 140 °C for 10 min in a N₂-filled glove box. Subsequently, the device was deposited Ca (30 nm) and Al (100 nm) by thermal evaporation of under high vacuum (<<10⁻⁶ Torr) with the active area of 4 mm². The I–V measurements of the photovoltaic devices were conducted using a computer-controlled Keithley 2400 (Keithley Instruments Inc., Cleveland, OH, USA) source measurement unit (SMU) with a Pecell solar simulator under the illumination of AM 1.5 G, 100 mW cm⁻². The illumination intensity was calibrated by a standard Si photodiode detector with KG-5 filter. In addition, the EQEs were measured by using a Xe lamp in combination with a monochromator (Oriel Inc., USA).

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
The financial support from the National Science Council of Taiwan is highly appreciated. The authors thank Mr. Ying-Chiao Wang, Dr. Shao-Sian Li, and Prof. Chun-Wei Chen in Department of Materials Science and Engineering, National Taiwan University, for facilitating the EQE experiments. Additionally, the authors gratefully acknowledge the Instrumentation Center (sponsored by National Science Council, Taiwan) and Technology Commons in College of Life Science, National Taiwan University for the confocal experiment.

Received: November 1, 2013
Revised: December 5, 2013
Published online: January 27, 2014