Ligand Effect of Zinc Oxide Nanoparticles on Photovoltaic Performance of Polymer Hybrid Solar Cells

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Thin-film making process for highly efficient poly(3-hexylthiophene)-2,5-diyl (P3HT) and zinc oxide (ZnO) nanoparticles hybrid solar cell was optimized with or without ligand of indoline dye as the dispersing agent for ZnO. Increment of the short circuit current density was observed after the addition of the ligand to the mixture of P3HT and ZnO. Further quenching of the emission of P3HT by ZnO with the ligan than that without the dye was also observed. It was found the 1.5 times enhancement of power conversion efficiency by addition of the dispersing agent. Impedance analyses to evaluate parallel resistance (R_p) and series resistance were investigated and found thickness dependence of the R_p. Current density of P3HT-ZnO hybrid system is crucially affected by the interfacial resistance of the grain boundaries of ZnO.

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Polymer based organic thin-film solar cells have attracted much attention for next-generation photovoltaic devices with several specific properties being light-weight, fabricated onto a flexible plastic substrate, and easily applicable to large-area processing combined with printing and coating technologies. There have been numerous reports on electron transporting ZnO-layer inserted polymer solar cells in order to rectify the directions of charge transport1 and stabilize the interfacial resistance of the grain boundaries of ZnO.

In spite of the remarkable progress of the power conversion efficiencies (PCEs) from 1% to over 10%,4–8 tuning of the thin-film making process is still uncertain in terms of desirable charge transport and collection through the photovoltaic performance. In this context, we newly investigated appropriate ligand as the dispersing agent with indoline dye of 5-[[4-[[4,2,2-Diphenylethenyl]phenyl]-1,2,3,4,5,6,7,8-hexahydrocyclopenta[d]indol-7-yl]methylene]-2-(3-ethyl-4-oxo-3-thiazolidinylidine)-4-oxo-3-thiazolidineacetic acid (D149) for inter-diffusion of ZnO nanoparticles in the active layer of conducting polymer, P3HT as the organic-inorganic hybrid solar cells for optimization of highly efficient photovoltaic performance as compared with that of the conventional organic thin-film device with [6,6]-phenyl C61 butyric acid methyl ester (PCBM) and P3HT as the active layer of bulk heterojunction cell.

Experimental

Preparation of ZnO nanoparticle.—Zinc acetate dihydrate (0.298 g) was dissolved in methanol (10 g) and stirred for 3 min with heating up to 65°C. 5 g of 3 wt% KOH in methanol was poured into the above solution and stirred for 2.5 h. After the centrifugation at 20,000 rpm for 15 min and the removal of the supernatant, the crude precipitates were dispersed in 150 g of methanol through the sonication. Thereafter, another centrifugation at 20,000 rpm for 30 min and the removal of the supernatant, the purified precipitates were dispersed again in 0.5 g of CHCl3 as ZnO nanoparticles homogeneously dispersed solution.

Preparation of mixed solution of ZnO with P3HT, and PCBM with P3HT.—0.5 wt% of indoline dye D149, purchased from Mitsubishi Paper Mills Limited was dissolved in CHCl3, ZnO and P3HT (Aldrich) were added to the above D149 solution, which were adjusted to 2wt%, respectively. On the other hand, PCBM (American Dye Source) and P3HT were dissolved as 3 wt%, respectively in chlorobenzene.

Preparation of organic-inorganic hybrid solar cell.—In the preparation of solar cell devices, indium-tin oxide (ITO) coated glass substrates (Geomatec, 10 Ω cm−2) were firstly patterned by etching and then cleaned thoroughly with a sequence of solvents: detergent, deionized water, acetone and isopropanol, for 10 min each in an ultrasonic bath. The cleaned substrates were purified further by oxygen plasma treatment for 10 min. The substrates were then spin coated with a 0.45 μm filtered poly (3, 4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) solution (DENATRON NCX), purchased from Nagase Chemtex Corporation, at 4,000 rpm for 60 s to produce a 50 nm thick layer. Thereafter, 2 wt% of ZnO dispersed P3HT solution in ethanol was spin coated onto the above PEDOT:PSS layer at 3,000 rpm, resulted a 100 nm thick layer of ZnO including P3HT. Thereafter buffer layer of ZnO was spin-coated. Subsequently the device was pumped down in vacuum (5 × 10−3 Pa), and a ~100 nm thick Al electrode was deposited by thermal evaporation followed by the annealing at 110°C for 5 min. Meanwhile, conventional organic thin-film solar cell was prepared by spin coating of PCBM-P3HT mixture onto the glass-ITO/PEDOT:PSS at 1,500 rpm followed by the annealing at 150°C for 5 min. In the case of PCBM-P3HT based device, 0.5 wt% of titaniumtetraisopropoxide in ethanol was spin coated at 4,000 rpm as the precursor of the buffer layer of TiOx.

Evaluations of photovoltaic performance.—The photovoltaic characteristics were measured under AM1.5 (100 mW cm−2) simulated illumination using a Bunkoh-Keiki CEP-2000 with a 1,000 W xenon arc lamp. TEM observation was performed with JEOL FE-TEM: JEM-2010F at 200 kV of accelerating voltage. Photoluminescence studies from 600 nm to 800 nm were carried out using HITACHI Fluorescence Spectrometer F-2700 at the excitation wavelength at 450 nm. Electrochemical impedance spectroscopy (EIS) measurement was performed with a frequency response analyzer of Solartron ELECTROCHEMICAL INTERFACE SI1287, FREQUENCY RESPONSE ANALYZER 1255B. The frequency range was from 100 Hz to 1 MHz under the illuminated conditions of 100 mW cm−2.

Results and Discussion

Inclusion of ZnO instead of PCBM to P3HT.—TEM images of the ZnO nanoparticles were shown in Figure 1. The diameter was approximately 5 nm. It was confirmed by the observation of the lattice image that each particle forms single crystalline.

Photovoltaic performance of the 3:1 (w/w) P3HT-ZnO based hybrid solar cell (viz. without using the dispersing agent) was examined and compared with that of the conventional bulk heterojunction (BHJ) organic thin-film device with P3HT-PCBM. The current density (J)-voltage (V) curves are shown in Figure 2. Open circuit voltage (Voc)
of P3HT-ZnO based cell was higher than that of P3HT-PCBM one. While, short circuit current density ($J_{sc}$) of P3HT-ZnO based device was lower than that of P3HT-PCBM one. Higher $V_{oc}$ was ascribed to the shallower conduction band (CB) edge of ZnO as compared with the lowest unoccupied molecular orbital (LUMO) level of PCBM. On the other hand, Figure 3 shows optical microscope images of P3HT-PCBM based cell (left) and P3HT-ZnO one (right). No aggregates are observed in the case of P3HT-PCBM based cell. While, aggregates can be observed in the case of P3HT-ZnO even in the resolution of $\sim$1–10 um. This result implies that the extent of agglomeration of P3HT-ZnO is much higher than that of P3HT-PCBM, though the ZnO nanoparticles themselves are in the range of 5–10 nm as indicated in Figure 1. Therefore, lower $J_{sc}$ was attributed to the insufficient dispersion of ZnO nanoparticles in the P3HT layer (Figure 3), which brought lower efficiency of charge separation.

**Addition of dispersing agent to the mixture of ZnO and P3HT.**—Indoline dye, D149 was used as the dispersing agent for ZnO nanoparticle in the mixture of 3:1 (w/w) P3HT-ZnO. The $J$-$V$ curves of the P3HT-ZnO based hybrid cell with several amounts of D149 were shown in Figure 4. The weight ratios of D149/P3HT were 0.003, 0.01, 0.1, 0.2, and 0.3, respectively. The $J_{sc}$ increased with increasing the amount of D149. This might be ascribed to the improvement of the charge separation by the addition of the dispersing agent. Meanwhile approximately the same $V_{oc}$ of 0.6 V was obtained though the value jumped up to 0.8 V when the weight ratios of D149/P3HT increased up to 0.3. This result might be elucidated by the following mechanisms as shown in Figure 5: When the ratio of D149 (= D149/P3HT) was low (that is less than 0.2), photogenerated holes from P3HT and/or D149 pass through the P3HT to the PEDOT:PSS/ITO. On the contrary, when the ratio of D149 was high (more than 0.3), some portions of the photogenerated holes from D149 directly go to PEDOT:PSS/ITO though the rest of them still pass through the P3HT.

In order to clarify the extent of the improvement of the charge separation process by the addition of the dispersing agent, photoluminescence study was performed. Figure 6 shows the emission spectra of P3HT film, P3HT-ZnO film without D149, P3HT-ZnO film with D149, and P3HT-PCBM film. Emission peak at around 700 nm was observed in the case of P3HT film since the photogenerated exciton gradually reduces with no charge separation. While, there is no emission peak at around 700 nm in the case of P3HT-ZnO film because the exciton immediately charge separates at the interface of P3HT and PCBM. On the other hand, P3HT-ZnO film without the dispersing agent shows some extent of the reduction of the emission intensity at around 700 nm, but it still remains. On the contrary, the addition of D149 to P3HT-ZnO resulted the remarkable decrease of the emission intensity at around 700 nm. This result indicates that the efficient dispersion of ZnO nanoparticles in the P3HT layer makes the efficient charge separation due to the improvement of the dispersed state of ZnO.
charge separation occurs by the improvement of the dispersion of ZnO nanoparticles.

**Photovoltaic performance of organic-inorganic hybrid solar cell.**—The $J$-$V$ curves of 3:1 (w/w) P3HT-ZnO with D149 (D149/P3HT = 0.2) based hybrid cell and BHJ device with PCBM-P3HT were shown in Figure 7. $PCE$ of 1.4% was attained with P3HT-ZnO cell and $PCE$ of 2.5% was obtained with P3HT-PCBM based one. Most apparently different profile between the two $J$-$V$ curves in Figure 7 is series resistance ($R_s$). The $R_s$ value of P3HT-ZnO cell was 720 ohm, and that of P3HT-PCBM one was 224 ohm, respectively.

In order to elucidate the origins of $R_s$, EIS measurement was performed and compared. Cole-cole plots of the P3HT-PCBM based cell with three different thicknesses of the active layers of 100 nm, 150 nm and 200 nm were shown in Figure 8. There is no remarkable changes of the semicircles even when the thickness of the active layer was changed from 100 nm to 200 nm. Since the major part of the internal resistance in this case includes the factor of the capacitance, most plausible factor of the resistance in the BHJ P3HT-PCBM system is the interfacial resistance. In addition, since these values are independent from the thickness of the active layer, the origins of the resistance came from the interlayer resistance between the electrode and the buffer layer, and/or the buffer layer and the active layer. The bulk resistance of the active layer was estimated to be 10 ohm, while the interfacial resistance was relatively larger as 500 ohm. It can be concluded that depletion of the interlayer resistance will be required for further improvement of the cell performance.

On the other hand, the cole-cole plots of the P3HT-ZnO with D149 based device with three different thicknesses of the active layers of 100 nm, 150 nm and 200 nm were shown in Figure 9. Much larger semicircles were obtained in the case of P3HT-ZnO with D149 based device as compared with those of P3HT-PCBM ones. Furthermore, the active layer-thickness dependence was also confirmed: Thicker layer resulted the larger semicircle. In this context, the most plausible origins of the internal resistance of the P3HT-ZnO system was interfacial resistance. It is also assumed that the thickness dependence is assigned to the increment of interfacial resistance from the inside of the active layer. Since P3HT is the same component as the case of P3HT-PCBM system, major factor of the interfacial resistance is speculated to be ZnO. Frequency dependence was observed in Figure 9 and this result also supports the resistance is ascribed to the grain boundaries in ZnO. Consequently, it was found that the loss of the current density of P3HT-ZnO system as compared with the case of P3HT-PCBM is derived from the interfacial resistance of the grain boundaries of ZnO.

**Summary**

We could demonstrate that the effect of ligand as the dispersing agent for sufficient dispersion of ZnO nanoparticles into the P3HT layer for the improvement of the photovoltaic performance of the hybrid solar cell. Photoluminescence measurements revealed that the almost perfectly charge separation was achieved with P3HT-ZnO by the addition of ligand. Further enhancement of the $PCE$ will be possible if we succeed to reduce the interfacial resistance of the grain boundaries of the nanostructured ZnO.
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