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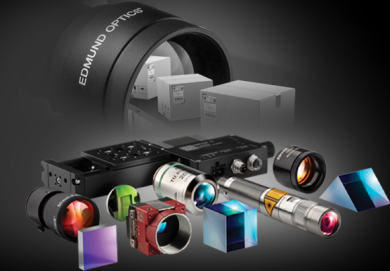
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Improved efficiency of zinc phthalocyanine/C₆₀ based photovoltaic cells via nanoscale interface modification

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The photovoltaic performance of zinc phthalocyanine (ZnPc)/C₆₀ heterojunctions is improved by alternately depositing ultrathin active layers between the two bulk layers. Using a proper multilayer structure, a 60% improvement in conversion efficiency under AM1.5 illumination is obtained, in comparison with that of flat heterojunctions. Transmission electron microscope investigations reveal an effective phase separation of ZnPc and C₆₀ and a high degree of crystalline ordering of C₆₀ in this system. The authors propose that an interpenetrating interface is formed, which facilitates both exciton separation and charge transport, and enhances the photocurrent from ZnPc due to an extended photoactive region. © 2007 American Institute of Physics. [DOI: 10.1063/1.2739364]

Organic solar cells have recently attracted much attention¹ due to their advantages such as easy preparation, low-cost materials of tunable band gap, compatibility with large-area flexible substrates, etc.

In spite of the extremely efficient exciton dissociation occurring at adjacent organic donor and acceptor sites,^{2,3} only a small number of excitons generated near the active interfaces contribute to the photocurrent (J_{ph}) in flat heterojunction (HJ) due to the short exciton diffusion length (L_D) in organic thin films, usually on the order of 10 nm.³ The bulk HJs enable sufficient donor-acceptor (D-A) contact and hence facilitate the exciton dissociation.^{2,4} The negative aspects are low charge carrier mobilities and considerable recombination of photogenerated carriers in the blend films.^{5,6} Such shortcomings are less pronounced in polymer-based photovoltaic (PV) cells, since phase separation of polymers and fullerene derivatives forms networks which efficiently transport charge carriers. Consequently, recent studies have addressed the morphology control to optimize transport and suppress recombination.⁷⁻¹¹

Bulk HJs based on small molecule materials are usually formed by D-A codeposition. The two species of molecules can be compiled randomly to form amorphous films or nanocrystals, depending on the growth modes.³ Such D-A contacts at a molecular level enable efficient exciton dissociation. However, charge transport in the blend layers is not as efficient as in neat films due to low mobilities. The morphology can be improved in terms of charge transport properties by a variation of deposition conditions, such as substrate temperature,¹¹ growth rates,¹² etc.

In this letter, we report a zinc phthalocyanine (ZnPc)/C₆₀ multilayer structure, which features efficient exciton dissociation and J_{ph} extraction. The significantly improved PV performance is explained by the formation of an interpenetrating interface through alternating deposition of ultrathin active layers with suitable configuration. Consequently, the contribution from ZnPc is increased, accounting

for the enhanced J_{ph}. The charge recombination which dominates the J_{ph} loss in the bulk HJs is effectively suppressed. A morphological analysis by high resolution (HR) transmission electron microscope (TEM) indicates that crystalline structures of photoactive materials are formed. As a result, the overall power conversion efficiency (η_p) is improved.

Solar cells are constructed on cleaned indium tin oxide (ITO) coated glass substrates with sheet resistance of 30 $\Omega/\square$ by thermal deposition at 5×10^{-6} Pa. ZnPc, C₆₀, and 4,7-diphenyl-1,10-phenanthroline (BPhen) are purified by vacuum sublimation. Deposition rates of organic layers and aluminum cathode are 0.5 and 15 Å/s, respectively, except for the *p* dopant [either 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄-TCNQ) or NDP2 from Novaled, giving identical results¹³] and the ultrathin interlayers, which are deposited at a rate of 0.05 Å/s. The current-voltage (*I*-*V*) characteristics are recorded with a source measurement unit (Keithley-236). A sun simulator (Hoenle AG) is used as a light source. Different incident light densities are obtained by using neutral filters. Short circuit current (I_{sc}) under monochromatic illumination is measured to characterize external quantum efficiency (EQE). All electrical mea-

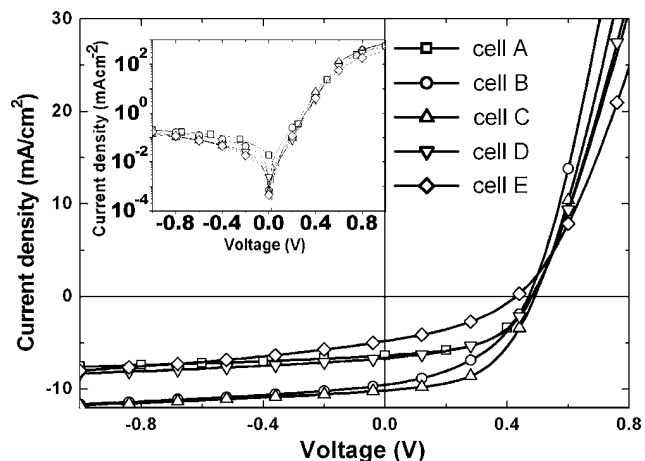


FIG. 1. *I*-*V* curves of cells A, B, C, D, and E under 115 mW cm⁻² AM1.5 illumination. Inset: Dark *I*-*V* curves of the five cells.

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TABLE I. Cell structure and key parameters under 115 mW cm^{-2} AM1.5 illumination. Each cell has the common parts, i.e., ITO/NDP2(1 nm) as the anode contact and BPhen(8 nm)/Al(60 nm) on the cathode.

Structure	V_{oc} (V)	I_{sc} (mA cm^{-2})	FF	η_p (%)	R_s (Ω)	R_p ($10^5 \Omega$)	Saturation factor
A: ZnPc(20 nm)/C ₆₀ (40 nm)	0.48	6.33	0.51	1.3	16.2	1.67	1.18
B: ZnPc(14 nm)/ZnPc:C ₆₀ (1:1, 12 nm)/C ₆₀ (34 nm)	0.47	9.52	0.44	1.7	11.6	1.37	1.23
C: ZnPc(14 nm)/[C ₆₀ (1, 2, 3)/ZnPc(3, 2, 1)]/C ₆₀ (34 nm)	0.49	10.13	0.51	2.2	15.0	2.18	1.17
D: ZnPc(14 nm)/[C ₆₀ (3)/ZnPc(3)] $\times$ 2/C ₆₀ (34 nm)	0.43	4.79	0.37	0.6	27.3	2.33	1.67
E: ZnPc(14 nm)/[C ₆₀ (2)/ZnPc(2)] $\times$ 3/C ₆₀ (34 nm)	0.48	6.64	0.48	1.3	16.5	2.03	1.25

measurements are carried out in a nitrogen-filled glovebox. Film morphologies are characterized by HRTEM.¹⁴

Five different cell structures are fabricated. We start from cell A, i.e., ITO/NDP2(1 nm)/ZnPc(20 nm)/C₆₀(40 nm)/BPhen(8 nm)/Al(80 nm). To form an Ohmic contact between ITO and ZnPc, a neat layer of F₄-TCNQ or NDP2, strong acceptors that enhance the *p*-type conductivity when mixed into a hole conducting matrix, is inserted, inducing a hole accumulation layer in ZnPc by electron transfer to the *p* dopant. Cells B–E contain either a mixed layer or a multilayer system of ZnPc and C₆₀. Table I summarizes the PV parameters of the five cells. The ultrathin interlayers are implemented, for example, in cell C, by successively depositing 1 nm C₆₀, 3 nm ZnPc, 2 nm C₆₀, 2 nm ZnPc, 3 nm C₆₀, and 1 nm ZnPc on the top of 14 nm ZnPc layer. After that, 34 nm C₆₀ is deposited. The total thicknesses of ZnPc and C₆₀ layers in all cells are 20 and 40 nm, respectively. The total thicknesses of interlayers or blend layer are kept at 12 nm to allow a comparison.

As shown in Fig. 1, cell A has a I_{sc} of 6.33 mA cm^{-2} , open circuit voltage (V_{oc}) of 0.48 V, and fill factor (FF) of 0.51 under 115 mW cm^{-2} AM1.5 illumination, and therefore a η_p of 1.3%. With a 12 nm ZnPc:C₆₀ (1:1 by volume) blend layer, η_p can be improved to 1.7%; however, only I_{sc} is increased to 9.52 mA cm^{-2} , and both V_{oc} and FF are reduced. The saturation factor (ratio of J_{ph} at -1 V to I_{sc}) of 1.23, compared to 1.18 of cell A, suggests strong field-dependent recombination, which dominates the J_{ph} loss in cell B.

Cell C with an asymmetric multilayer configuration offers the best PV performance among all cells. Cell C has a V_{oc} of 0.49 V and FF of 0.51, almost equal to those of cell A, while the significant improvement in η_p is solely due to the enhanced I_{sc} , being 60% higher than that of cell A. The de-

pendence of the key PV parameters in cells A and C on incident light intensities from 0.45 to 115 mW cm^{-2} is given in Fig. 2. As the V_{oc} increases logarithmically with light intensity, FFs exceed 0.50 under illumination densities above 10 mW cm^{-2} , which are similar to cell A. Light scattering and thus excessive absorption in the multilayer, another possible reason for improved J_{ph} , is ruled out by absorption measurements.

Figure 3 shows a difference in the EQE spectra of cells A, B, and C in the wavelength range $>550 \text{ nm}$, which corresponds to the photoresponse of ZnPc. It is clear that both blend layer and multilayer structures generate more J_{ph} from ZnPc than the flat HJ, while the contribution from C₆₀ in the short wavelength range is similar.

The introduction of the ultrathin ZnPc and C₆₀ multilayer structure aims not only to provide an intimate D-A contact for exciton separation but also to form a continuous connection of islandlike nanocrystals,¹² to facilitate the collection of photogenerated charge carriers.

In cell A, the photoactive zone in the flat HJs is determined by the L_D of active materials. For C₆₀, with a L_D of $\sim 40 \text{ nm}$ (Ref. 3) comparable with the thickness of C₆₀ film, the majority of the excitons in the layer contribute to the J_{ph} . On the other hand, L_D in ZnPc layer is estimated to be 6 nm,⁴ which means that only a small amount of excitons within L_D can be converted into charge carriers. As illustrated in the inset of Fig. 3, it is supposed that an interpenetrating interface is formed in cell C, considering the similarity of PV behavior of cells A and C. For ZnPc interlayers with a total thickness of 6 nm, the thickness of photoactive zone in ZnPc is almost doubled. This is consistent with the EQE measurement in Fig. 3, showing that the peak value of

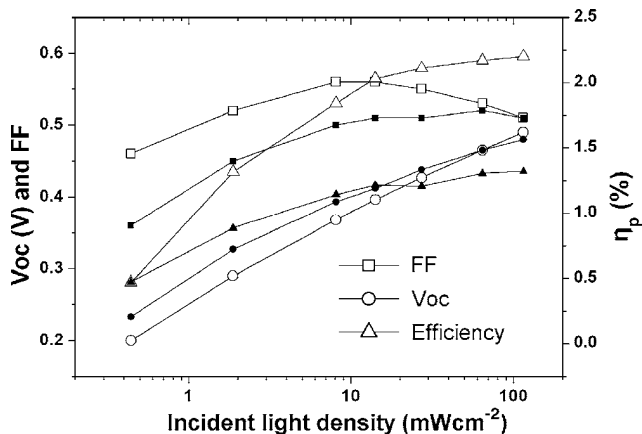


FIG. 2. V_{oc} , FF, and η_p of cells A (solid) and C (hollow) vs illumination intensity.

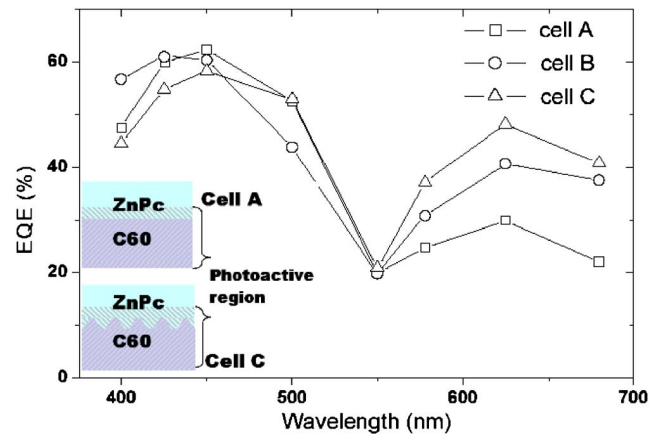


FIG. 3. (Color online) EQE outlines of cells A, B, and C. Inset: Illustration of the interfacial structure in cells A and C.

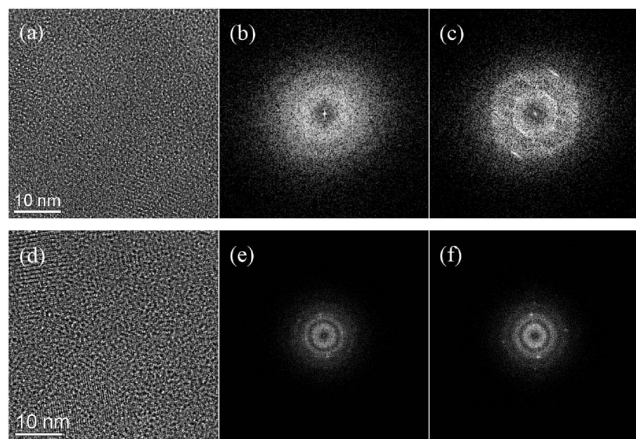


FIG. 4. (a) HRTEM image of 1:1 mixture of C_{60} and ZnPc. It shows partial crystallinity as visualized by the FFT images [(b) and (c)]. The right upper part (b) is amorphous, whereas the right bottom (c) clearly displays (111) crystal lattice reflections of C_{60} . (d) HRTEM image of the $C_{60}(1,2,3)/ZnPc(3,2,1)$ multilayered system, showing highly mosaic crystal domains of C_{60} . (e) FFT shows strong (202) C_{60} crystal reflections. (f) FFT of the left upper part of (d) indicates a single crystalline domain.

the EQE corresponding to ZnPc absorption increases from 30% for cell A to 50% for cell C.

The morphologies of the mixed and interlayer structures are analyzed by electron bright field imaging. Figure 4(a) shows the HRTEM image and the corresponding fast Fourier transform (FFT) patterns with (b) amorphous and (c) crystalline regions of the ZnPc: C_{60} 1:1 mixture layer, about 12 nm thick. It proves this system has a major amorphous fraction with a small amount of crystalline ZnPc and C_{60} .

In contrast, the multilayer system has highly crystalline structures as shown in Fig. 4(d), mostly consisting of crystalline C_{60} domains with 50–80 nm diameter. In Fig. 4(e), we find crystalline reflections (111), (202), (222), (204), and (224) corresponding to 8.6, 5.07, 4.14, 3.15, and 2.84 Å of C_{60} . Figure 4(f) displays the single crystalline C_{60} domain from the top left of the image in Fig. 4(d). We conclude that in the multilayer system, a higher amount of crystalline structures of C_{60} exists, compared to the mixed layer, implying a tendency of demixing of the constituents in the multilayer system, namely, the regions with crystalline C_{60} and amorphous ZnPc.

The illuminated I - V curves of cells D and E in Fig. 1 indicate that an equal thickness of interlayers in the multilayer structure exhibits no or a negative influence on the PV performance. With 3 nm interlayers in cell D, V_{oc} , I_{sc} , and FF all decrease considerably, and hence an η_p of 0.6% is observed. Decreasing the thickness of interlayers to 2 nm in cell E gives rise to an η_p similar to that of cell A. In the multilayer structure, the grain size of ZnPc and C_{60} should be much smaller than the L_D , and efficient exciton separation is expected. Thus, the charge transport in the multilayer structure is the controlling step according to the different PV performances observed from different multilayer cells. The poor η_p and saturation factors of cells D and E could be attributed to insufficient connection between the nanocrystals formed by the same materials in the multilayer. The J_{ph} loss with increasing bias in cell D indicates that charge accumulation leads to a significant reduction in V_{oc} and I_{sc} .

Fitting the dark I - V curves of the cells to the modified diode equation gives series and parallel resistances (R_s and

R_p) in Table I. Cell B with mixed D-A layer has the smallest R_s , while cell D has the largest, resulting in the lowest current density of cell D (as shown in Fig. 1) under forward bias. Since interfacial recombination dominates the dark current, this is another evidence for the insufficient connection. Meanwhile, comparing with other cells, R_p of cell D which is the highest in the dark becomes the smallest (not shown) upon illumination, implying significant recombination of photogenerated charge carriers. Small changes in the structure of the interlayer system lead to strong influence on PV performance. The interlayer system could be a test bed to quantify the effects of interfacial morphologies on PV cells.

Depositing interlayers at a rate of 0.5 Å/s rather than at the very low rate otherwise used for the interlayer growth influences the PV performance in a similar way to the 3 nm interlayers in cell D. Growth on lateral surface at high deposition rates may surpass that on the vertical direction, not suitable to form an effective interpenetrating interface between ZnPc and C_{60} , and hence block charge transport. Both exciton separation and charge recombination are strongly affected by interfacial structures of D-A contact. Likely, our results suggest that recombination loss is not proportional to D-A contact area, but sensitive to the nanoscale morphology. That gives further space for modifying organic interfaces to improve the efficiency.

In conclusion, we have demonstrated an ultrathin multilayer structure in which an interpenetrating contact between ZnPc and C_{60} is formed. TEM results show highly crystalline C_{60} in the multilayer system in contrast to amorphous ZnPc: C_{60} mixed layers. This structure improves the J_{ph} by extending the photoactive zone, and overcomes, to some extent, the limit of L_D on light-to-electricity conversion in organic small molecule solar cells.

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