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Bulk heterojunction organic solar cells fabricated by oblique angle deposition

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Abstract

Bulk heterojunction organic solar cells based on small molecules are often fabricated by co-deposition of donor and accepter materials on substrates placed horizontally. An intimate blend of donor and accepter molecules is the common product in as-prepared samples. Using metal phthalocyanine as the donor and fullerene as the accepter, we tilt the substrate to deposit the active layer. Both short circuit current density and open circuit voltage increase obviously in bulk heterojunction organic solar cells fabricated by oblique angle deposition. Analysis of the active layer reveals that phase segregation occurs in obliquely deposited bulk heterojunction layer. The mechanism of phase segregation is discussed. A change of stacking style of fullerene molecules on metal phthalocyanine grains is proposed on the tilted substrate. This result provides a simple method to form phase segregation in bulk heterojunction layer.

Introduction

Bulk heterojunction structure, which blends donor and acceptor molecules intimately to produce molecular-scale donor/acceptor interfaces for exciton dissociation, is generally considered as the most promising strategy for high efficiency organic solar cells nowadays [1]. In polymer-based bulk heterojunction photovoltaic devices, it is found that proper phase segregation in the blend film is one key factor to obtain a high power conversion efficiency, which brings less charge loss and more optical absorption [2]. Bulk heterojunction structure can be fabricated in small-molecule-based organic solar cells by co-deposition of donor and accepter materials [3]. However, although great efforts have been made to induce suitable phase segregation in donor-accepter blend film, only limited successes are reported in literatures. Post-annealing small molecule devices is detrimental sometimes because pinholes are created in the blend layer [4]. Some improvements are obtained in metal phthalocyanine-fullerene devices when substrates are heated during co-deposition of metal phthalocyanine and fullerene. Phase separation is observed in copper phthalocyanine (CuPc):C60 and zinc phthalocyanine (ZnPc):C60 blend layers grown on mildly heated substrates [5,6]. Up to date, the most efficient way to produce proper phase segregation in small molecule blend film is to grow a template layer on the substrate before co-deposition of metal phthalocyanine and fullerene. Tiny aggregate nucleates in the blend film due to the strong interaction between template and metal phthalocyanine molecules. Nonetheless, suitable template material is not easy to choose. For example, hexaazatriphenylene-hexacarbonitrile (HAT-CN) and copper iodide (CuI) are determined as the template material for CuPc and ZnPc [7,8], respectively, even though these two phthalocyanine molecules have similar structure and property. For other small molecule materials, there still remains a challenge to create suitable phase segregation by this template effect. Partly because of the weak effect of

substrates to produce phase segregation, a complex graded donor-accepter heterojunction has been prepared by adjusting donor/accepter evaporation rate in co-deposition process, resulting in a more efficient transport route in blend layer for both electrons and holes [9]. Recently, a large donor/accepter ratio (3:1) shows a obvious effect on phase segregation in CuPc:C60 bulk heterojunction [10]. It seems that some compelling forces outside the donor-accepter system, such as a higher substrate temperature, a template layer or a large donor/accepter ratio, are necessary to produce phase segregation in small molecule blend film.

Oblique angle deposition, in which the substrate is inclined at an angle relative to the incident beam (less than 90°), has been used to prepare metal phthalocyanine columnar structure via a self-shadowing effect [11,12]. Fullerene film is then coated on the columnar structure to construct interdigitated bulk heterojunction solar cells. However, these devices do not show high power conversion efficiency as expected. Large diameter of tilted columns (several hundred nanometers) and thick active layer (micron scale), which are typical sizes of the products obtained via the self-shadowing effect in oblique angle deposition, are proposed as the main obstacle for this unsatisfied behavior. Here, we present the results of small molecule solar cells prepared by oblique angle deposition. A small tilting angle (~ 55°) is used in our experiments. Higher power conversion efficiency is obtained due to phase segregation in obliquely co-deposited metal phthalocyanine:fullerene layer.

Experimental section

Cleaned indium tin oxide (ITO) glasses were used as the substrates in all devices. CuPc (Yannuo Chem., purity 99%) and ZnPc (Yannuo Chem., purity 99%) were used as donor materials, and C60 (Acros Organics, purity 99%) was used as acceptor material. Bathocuporine (BCP, J&K

Scientific LTD, purity 99%) was used as the buffer material. All above materials were used as received. The configuration of all devices is ITO/donor/donor:accepter/accepter/BCP/Al. The donor:accepter mixtures are all in weight ratio 1:1. The devices were fabricated in a commercial vacuum deposition system (ULVAC-KIKO VWR-400M/ERH). Organic materials were deposited onto ITO substrates successively at a rate of ~0.05 nm/s under a pressure of ~1×10^{-3} Pa. Aluminium was deposited at a rate of ~0.5 nm/s under a pressure of 5×10^{-3} Pa. The film thickness and deposition rate were monitored in situ using a quartz crystal oscillator. The area of a single device is 4 mm^2. A sunlight simulator (Newport Oriel 91160) was used to illuminate the sample with the power of 100 mW/cm^2. The current-voltage curves were measured by an electrochemical analyzer. All IV measurements were performed in air. Optical absorption was measured with a UV-Vis-NIR spectrophotometer (Cary 5000) in air. Monochromatic incident photon-to-electron conversion efficiency (IPCE) analysis was carried out in air (Newport 74125). Atomic force microscope (AFM, DI NanoScope) was used to scan the surface of organic films. Transmission electron microscope (TEM, FEI Tecnai F30) was used to observe phase segregation in organic films.

Two types of bulk heterojunction were prepared in our experiments. The first type was deposited by normal deposition, in which the evaporant flux reaches the substrate perpendicularly and then nucleates on the sample surface. For the second type, oblique angle deposition was used to deposit the active layer. Normal deposition was used to deposit BCP/Al layers in all devices. The angle of the substrate relative to the incident beam was tuned in the vacuum chamber *in situ* by manual operation. Tuning degree in present experiments was ~ 55°. Figure 1a and 1b show two types of deposition schematically. In order to verify the real thickness of organic layers deposited obliquely, controlled samples were fabricated and observed by scanning electron microscopy

(SEM). Typical thicknesses were calibrated in this way approximately and used in this work. The thicknesses of BCP(8 nm)/Al(100 nm) layers were used in all devices. Total thickness of active layer (donor/donor:accepter/accepter) kept the same value for both types of devices, which were 47 nm approximately. We think that in this device architecture, the difference of optical distribution between two types of device can be neglected. Therefore, we do not consider any effect of optical distribution in this work.

Results and discussions

We choose common donor (ZnPc and CuPc) and accepter materials (C60) to fabricate bulk heterojunction photovoltaic devices. Similar configuration and thickness are used in our devices according to Ref. 3. The bulk heterojunction layer is sandwiched between a thin donor and accepter layer. A series of devices prepared with ZnPc and C60 by normal (perpendicular) deposition or oblique angle deposition are compared. Thin films of ZnPc(12 nm), ZnPc:C60(25 nm), C60(10 nm), BCP, and Al are perpendicularly deposited on ITO substrate sequentially to construct a bulk heterojunction solar cell (device A). At least three devices are fabricated every batch and the best efficiency in every batch is analyzed in this work. Current density-voltage (J-V) curves of device A in the dark and under light illumination are drawn in Fig. 2a. Device B differs with device A on ZnPc/ZnPc:C60/C60 layers, which are deposited at a angle relative to the horizontal plane (~ 55°). J-V curves of device B are also shown in Fig. 2a. All measured factors of device A and B are listed in Table 1. More than doubled efficiency (1.82%) is obtained in device B. IPCE measurement confirms better performance of obliquely deposited device, which is shown in Fig. 2b. Higher conversion efficiency is measured in all range of wavelength from the device fabricated by oblique angle deposition. No obvious improvement is observed when only one organic layer is deposited obliquely.

The enhancement of both short circuit current density (J_{sc}) and open circuit voltage (V_{oc}) in device B reveals a beneficial effect of oblique angle deposition on bulk heterojunction devices. Because the buffer layer (BCP) and the cathode metal (Al) are the same for device A and B, we believe that the improved performance comes from obliquely deposited active layer. Morphology and structure of two kinds of bulk heterojunction are compared firstly to investigate the reason for the higher efficiency. SEM observation shows that oblique angle deposition makes a continuous film and no obvious fluctuation is found at the surface (shown in SI Fig. S3). No pin hole or void appears in samples with one/two/three layers fabricated by oblique angle deposition, indicting no self-shadowing effect in our experiments. XRD spectrum of bulk heterojunction prepared by oblique angle deposition demonstrates a small peak at 6.8° (the star mark in Fig. 2c), suggesting that tiny ZnPc grains (edge-on phase) form in the bulk heterojunction layer [6,8]. No obvious peak is observed in XRD measurement when only one organic layer is deposited obliquely.

A large increase of J_{sc} (device A: 4.75 mA/cm^2, device B: 8.18 mA/cm^2) is the main reason for higher efficiency of device B. This result is in accordance with IPCE measurement, which shows an enlargement of efficiency in all range of wavelength by tilting the substrate. This overall enlargement means the charge transport is improved and less charge loss happens in the active layer prepared by oblique angle deposition. In order to compare the charge transport in device A and B, device behavior is analyzed according to the common one-diode model [13]. R_s (series resistance), R_{sh} (shunt resistance) and n (ideality factor) are listed in Table 1. A reduction of series resistance (device A: 9.2 Ωcm^2, device B: 6.9 Ωcm^2) and an enhancement of shunt resistance (device A: 128 Ωcm^2, device B: 183 Ωcm^2) confirm better charge transport due to oblique angle deposition. Another possible reason for higher J_{sc} in device B is the enhanced

optical absorption. Optical absorption of ZnPc/ZnPc:C60 samples shows higher absorption in obliquely deposited sample. Normalized absorption spectra of two samples are shown in the inset of Fig. 2b. Two absorption peaks at 630 nm and 692 nm, which come from Q band absorption of ZnPc [14], are obvious in both samples. Higher absorption in the range of 400 – 550 nm appears in the sample prepared by oblique angle deposition. It is reported that C60 crystallites contributes more absorption than amorphous C60 film in this range [6]. Higher absorption suggests that some tiny C60 crystallites may form in obliquely deposited sample and contribute more enhancement of optical absorption than ZnPc, though no C60 peak is detected in XRD analysis.

 Above results reveal that both charge transport and optical absorption of ZnPc:C60 bulk heterojunction are improved by oblique angle deposition. In bulk heterojunction photovoltaic devices based on either polymer or small molecule, efficient charge transport and enhanced optical absorption are often found in bulk heterojunction with suitable phase segregation [2,8]. For ZnPc:C60 bulk heterojunction grown on a heated substrate, improved charge transport and higher optical absorption are obtained and proposed as a result of phase segregation [6]. We think that the improved performance of device B also comes from phase segregation caused by oblique angle deposition.

AFM and TEM are used to observe the nanoscale morphology of ZnPc/ZnPc:C60 film. Figure 3a and 3b show AFM images of two samples fabricated by perpendicular and oblique angle deposition, respectively. The values of RMS roughness in Fig. 3a and 3b are 2.25 nm and 3.48 nm. AFM observation reveals that the distribution of particles in Fig. 3b is not as uniform as those in Fig. 3a. Comparing with the self-shadowing effect in pervious literatures [11,12], coarse surface in Fig. 3b is similar to ZnPc:C60 bulk heterojunction with phase separation [6]. We use TEM to observe ZnPc/ZnPc:C60 film deposited on copper grid. Figure 3c and 3d show the

morphology of two samples fabricated by perpendicular and oblique angle deposition, respectively. Comparing with the featureless surface of the sample prepared by perpendicular deposition, some tiny particles are found in obliquely deposited film. These particles distribute uniformly in the film and have the size of less than 10 nm. More detailed characterization of phase segregation in ZnPc:C60 bulk heterojunction with different thickness is demonstrated in the supporting information. AFM and TEM observations show that some particles are formed on pre-deposited ZnPc layer even in a very thin ZnPc:C60 BHJ layer, and these particles may grow larger in the following process of oblique deposition. Above analysis proves that phase segregation occurs in ZnPc:C60 bulk heterojunction fabricated by oblique angle deposition, resulting in the improvement of charge transport and optical absorption.

We think that the phase segregation occurs in nanoscale during the period of obliquely co-deposition of ZnPc and C60. The growth of ZnPc film has been studied detailedly in previous literatures [15]. There are two common stacking styles for ZnPc, edge-on and face-on orientation (shown in Fig. 1a and 1c schematically). It is found that ZnPc in edge-on orientation grows on ITO substrate at room temperature, whereas face-on ZnPc grows on CuI coated ITO substrate due to the strong interfacial coupling [8]. Main difference between these two phases is the stacking angle of ZnPc molecule on the substrate, which is schematically shown in Fig. 1a and 1c. We believe that the different grain surface of ZnPc induces the phase segregation in our experiments.

In both types of devices, a thin layer of ZnPc is deposited on ITO substrate firstly. The growth of edge-on ZnPc grains occurs on both horizontal-placed and tilted ITO substrate (shown in Fig. 1a and 1b). Then ZnPc and C60 molecules are evaporated simultaneously and deposit on the surface of ZnPc grains. The difference of incident angle induces different stacking style for ZnPc and

C60 during this co-deposition period. An intimate mixture of ZnPc and C60 is produced in the configuration of perpendicular deposition because of weak interaction of randomly located ZnPc and C60 on top of edge-on ZnPc grains. In contrast, the exposed surface of ZnPc grains against the evaporant flux changes in oblique angle deposition (shown in Fig. 1b). Some side facets of edge-on ZnPc grains expose to evaporated ZnPc and C60 molecules in this case. The tilting angle brings some similar deposition facets as those in face-on ZnPc (shown in Fig. 1c) except a small deflection (9°). It is reported that ZnPc and C60 molecules are easy to nucleate on face-on ZnPc grains and grain boundaries, respectively [8]. We think that this kind of stacking style remains in our experiments of oblique angle deposition, resulting in the formation of ZnPc and C60 crystallites.

We employ this method to prepare CuPc:C60 photovoltaic cells because CuPc and ZnPc have similar structure and property. Similar thickness of organic layer is used in the structure of ITO/CuPc(12 nm)/CuPc:C60(25 nm)/C60(10 nm)/BCP/Al. The difference between perpendicular deposition and oblique angle deposition is investigated. Better result is also measured in obliquely deposited device. We find that the deposition angle of C60 film (perpendicular or oblique angle) on top of the bulk heterojunction layer does not show obvious influence on the device performance, which is in accordance with above conclusion of phase segregation in the period of co-deposition. Photovoltaic cells fabricated by perpendicular deposition and oblique angle deposition are called device C and D. J-V curves of device C and D in the dark and under light illumination are shown in Fig. 4. All measured and attracted factors of device C and D are listed in Table 1. Higher Jsc and Voc are obtained in obliquely deposited device. Then we adjust the thickness of bottom two organic layers. The optimized device (device E) has the structure of ITO/CuPc (18 nm)/CuPc:C60 (20 nm)/C60 (10 nm)/BCP/Al. J-V curves

of device E are shown in Fig. 4. All measured and attracted factors of device E are listed in Table 1. A significant reduction of the series resistance (device D: 21.5 Ωcm^2, device E: 10.8 Ωcm^2) reveals that charge transport is much more efficient in a thin CuPc:C60 layer. One possible reason for this phenomenon may be that CuPc bottom layer has less selective effect on CuPc and C60 molecules, and then, proper phase segregation occurs in a thinner bulk heterojunction layer. Our result shows that oblique angle deposition can produce phase segregation in metal phthalocyanine and fullerene mixtures naturally. We believe that this method may be used in other material system if there are different favorite depositing sites for different molecules. Selective deposition at different sites in one experiment may even be achieved with a dedicated setup to accurately adjust the tilting angle of the substrate.

Conclusions

In summary, we demonstrate a simple way to improve the power conversion efficiency of small molecule solar cells by oblique angle deposition. Both short circuit current density and open circuit voltage increase in obliquely deposited devices. Higher optical absorption and more efficient charge transport are observed in bulk heterojunction devices fabricated by oblique angle deposition. Phase segregation in the bulk heterojunction layer is found as the main reason for the improved performance. A change of stacking style of fullerene molecules on metal phthalocyanine grains is proposed on the tilted substrate. This method may be used in other material system if there are different favorite depositing sites for different molecules.

Table 1 Measured and extracted device parameters.

Device	Jsc (mA/cm^2)	Voc (V)	η (%)	FF	n	Rs (Ωcm^2)	Rsh (Ωcm^2)
A ZnPc:C60 perpendicular	4.75	0.47	0.85	0.38	1.1	9.2	128
B ZnPc:C60 oblique	8.18	0.57	1.82	0.39	2.76	6.9	183
C CuPc:C60 perpendicular	4.18	0.33	0.47	0.34	2.1	24	233
D CuPc:C60 oblique	4.45	0.37	0.59	0.36	2.74	21.5	209
E CuPc:C60 (thin) oblique	5.85	0.4	0.84	0.36	2.87	10.8	145

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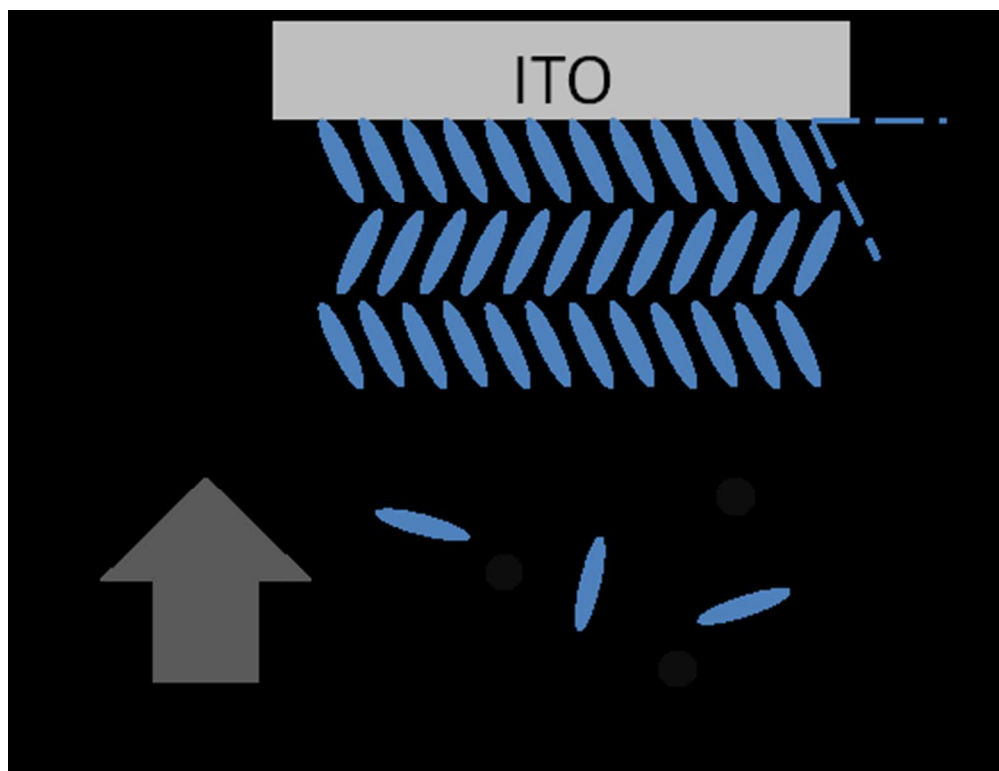
Figure captions

Fig. 1 Schematic demonstration of co-deposition of ZnPc and C60 on ZnPc coated ITO substrate, (a) horizontal substrate, and (b) tilted substrate. (c) face-on ZnPc grains grown on CuI coated ITO substrate. Blue ellipse and black dot stand for ZnPc and C60 molecule, respectively. In (a) and (b), edge-on ZnPc grains grow on ITO substrate at room temperature.
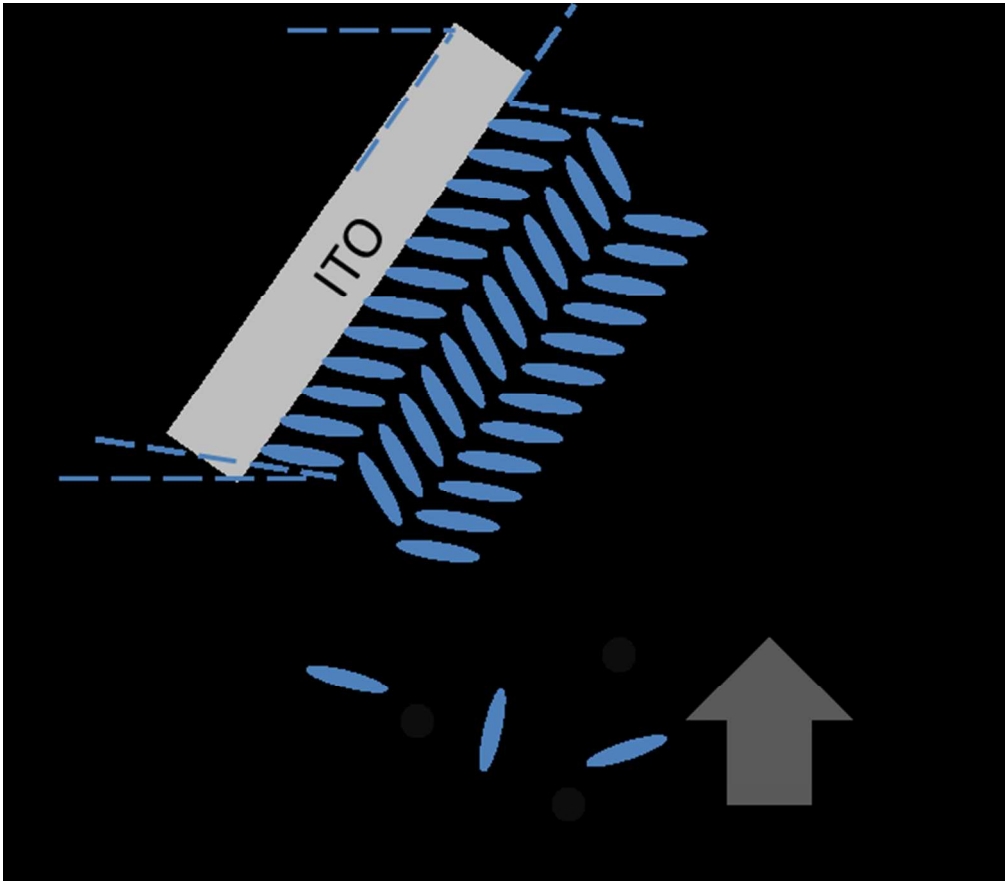
Fig. 2 (a) J-V curves of device A (perpendicular deposition) and B (oblique angle deposition). (b) IPCE spectrum of ZnPc:C60 bulk heterojunction device prepared by perpendicular and oblique angle deposition. Inset of Fig. 2(b): normalized optical absorption spectra of ZnPc:C60 bulk heterojunction device prepared by perpendicular (blue) and oblique angle deposition (red). (c) XRD spectrum of ZnPc:C60 bulk heterojunction prepared by perpendicular (red) and oblique angle deposition (blue), the star mark reveals the edge-on phase of ZnPc (Ref. 6 and 8).

Fig. 3 Nanoscale morphology of ZnPc:C60 bulk heterojunction sample. (a) AFM image, perpendicular deposition, (b) AFM image, oblique angle deposition, (c) TEM image, perpendicular deposition, (d) TEM image, oblique angle deposition. The area of square (a) and (b) is 800 nm $\times$ 800 nm.
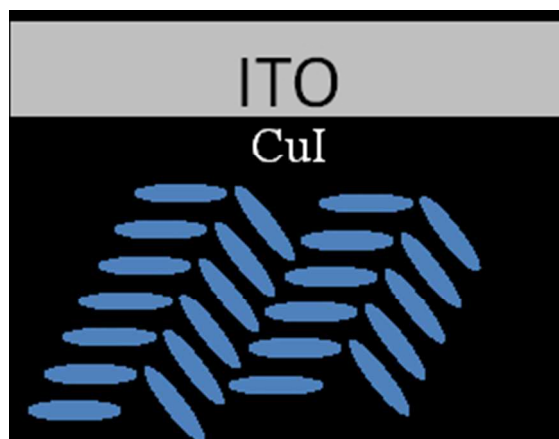
Fig. 4 J-V curves of device C (perpendicular deposition), D and E (oblique angle deposition).
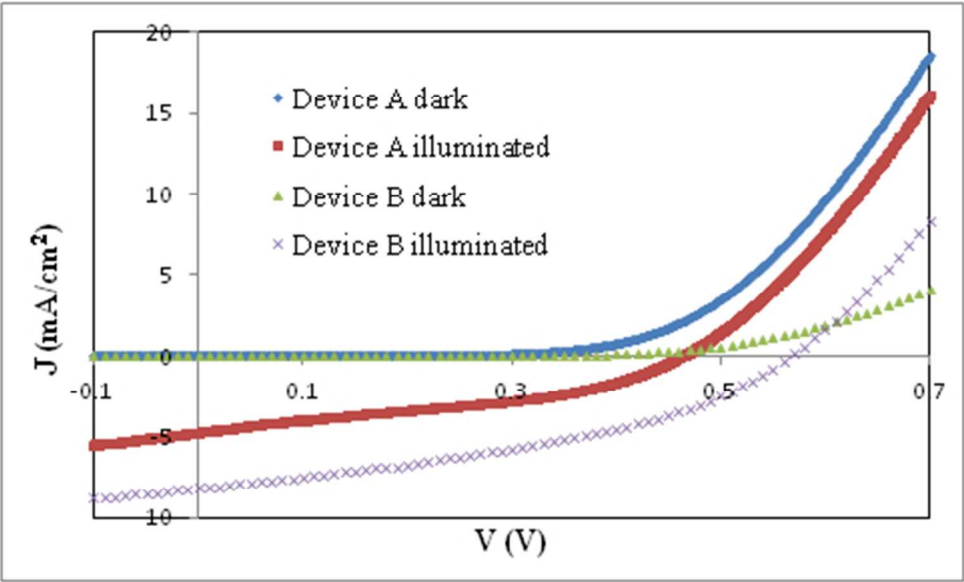
Schematic demonstration of co-deposition of ZnPc and C60 on ZnPc coated ITO substrate, (a) horizontal substrate
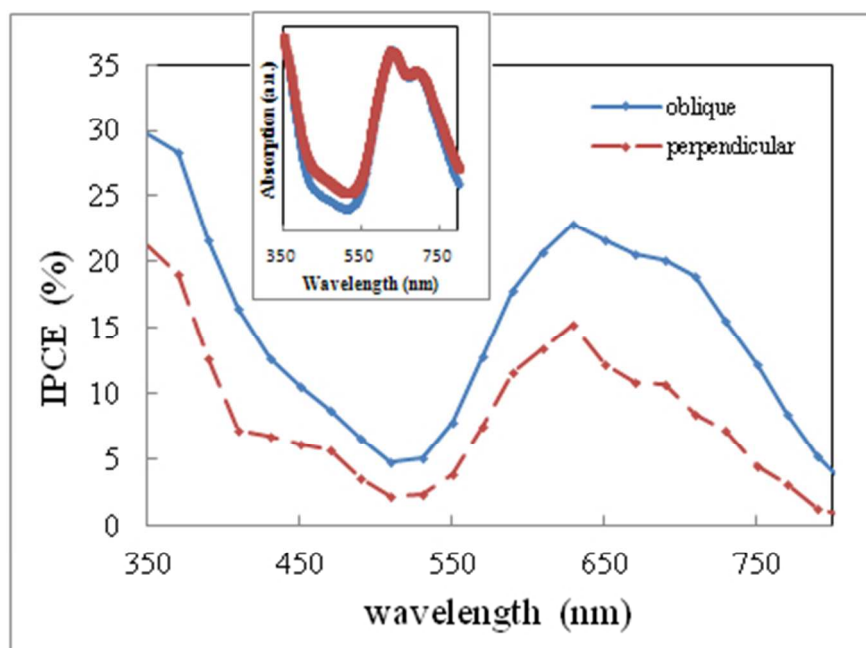87x67mm (150 x 150 DPI)

Schematic demonstration of co-deposition of ZnPc and C60 on ZnPc coated ITO substrate, (b) tilted substrate
107x94mm (150 x 150 DPI)

face-on ZnPc grains grown on CuI coated ITO substrate
47x36mm (150 x 150 DPI)

J-V curves of device A (perpendicular deposition) and B (oblique angle deposition)
171x103mm (72 x 72 DPI)

IPCE spectrum of ZnPc:C60 bulk heterojunction device prepared by perpendicular and oblique angle deposition. Inset of Fig. 2(b): normalized optical absorption spectra of ZnPc:C60 bulk heterojunction device prepared by perpendicular (blue) and oblique angle deposition (red).
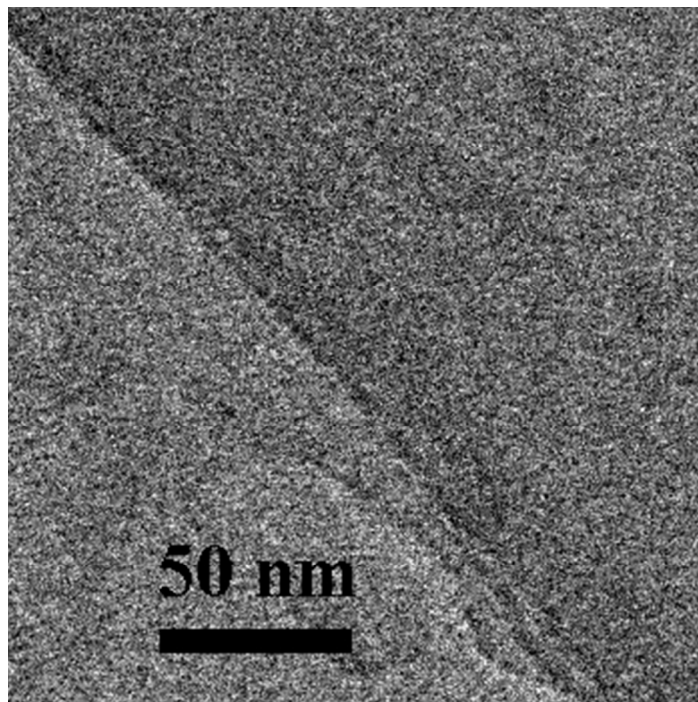154x114mm (72 x 72 DPI)
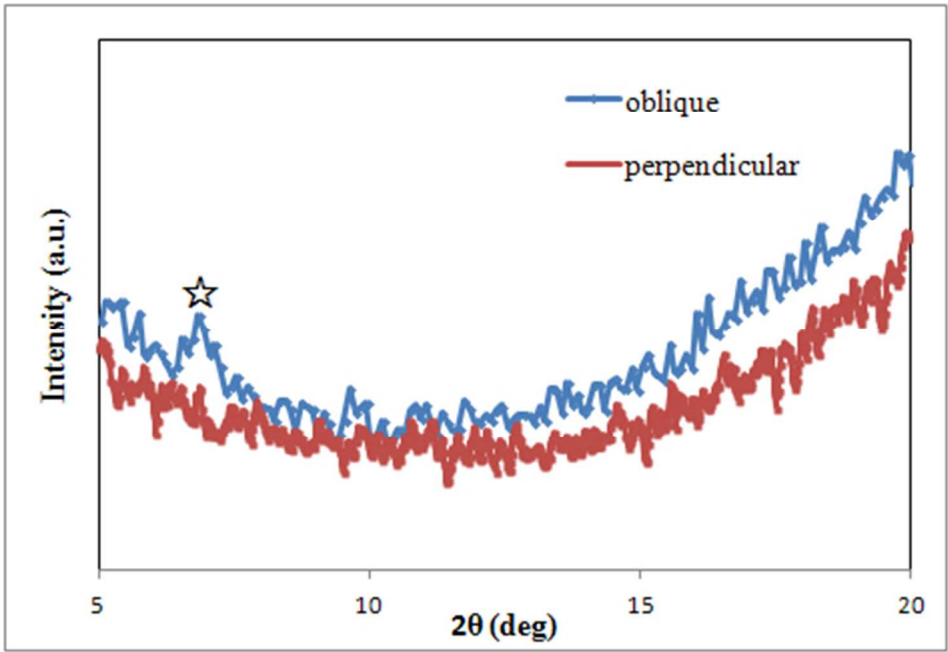
XRD spectrum of ZnPc:C60 bulk heterojunction prepared by perpendicular (red) and oblique angle
deposition (blue)
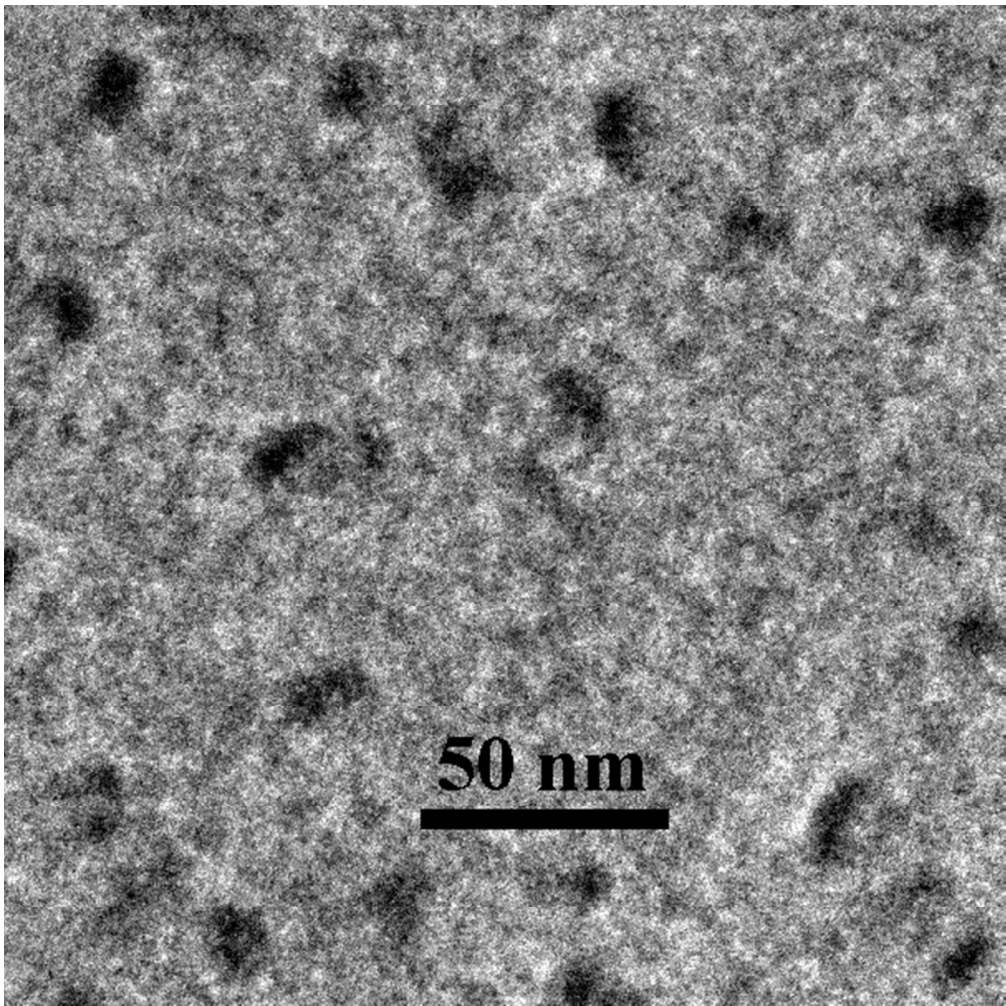166x114mm (72 x 72 DPI)
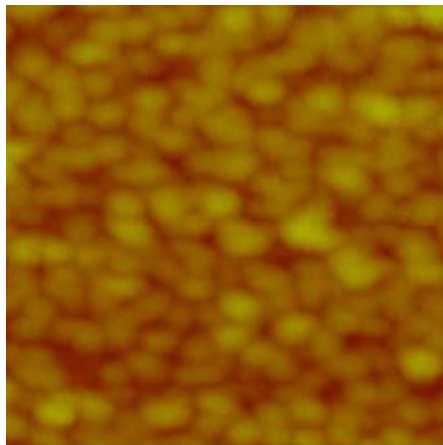
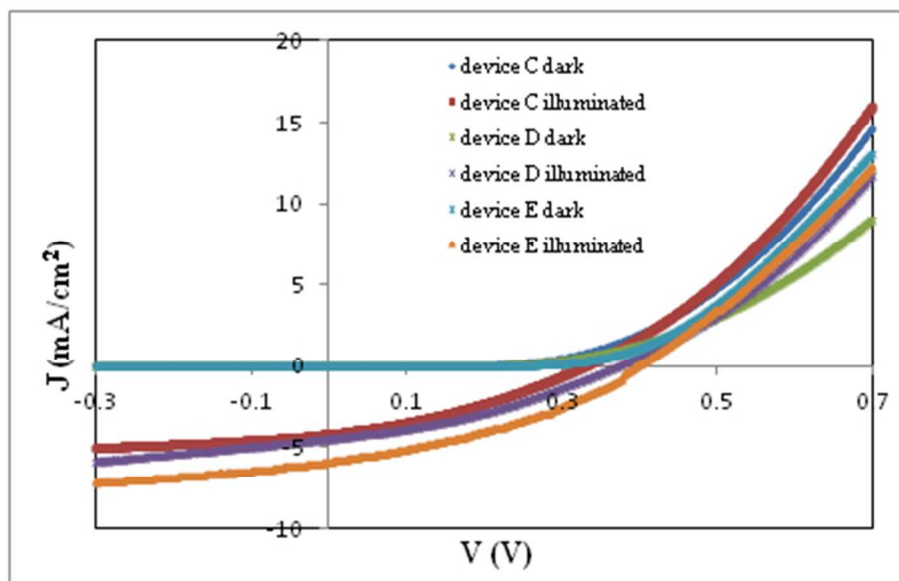AFM image, perpendicular deposition
77x77mm (72 x 72 DPI)
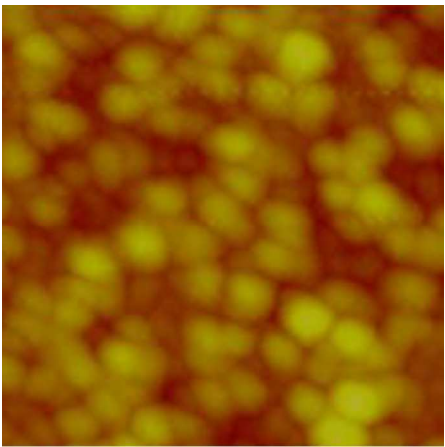
AFM image, oblique angle deposition
77x77mm (72 x 72 DPI)

TEM image, perpendicular deposition
122x122mm (72 x 72 DPI)

TEM image, oblique angle deposition
213x213mm (72 x 72 DPI)

J-V curves of device C (perpendicular deposition), D and E (oblique angle deposition)
160x103mm (72 x 72 DPI)