# Improving the performance of polymer solar cells by adjusting the crystallinity and nanoscale phase separation*

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In this paper, we report a high-performance P3HT/PCBM bulk-heterojunction solar cell with a power conversion efficiency of 4.85% fabricated by adjusting the polymer crystallinity and nanoscale phase separation using an ultrasonic irradiation mixing approach for the polymer. The grazing incidence X-ray diffraction, UV/Vis spectroscopic, and atomic force microscopic measurement results for the P3HT/PCBM blend films reveal that the P3HT/PCBM film fabricated by ultrasonic irradiation mixing of the P3HT and PCBM solutions for 10 min has a higher degree of crystallinity, a higher absorption efficiency, and better phase separation, which together account for the higher charge transport properties and photovoltaic cell performance.

**Keywords:** crystallinity, polymer solar cell, ultrasonic irradiation, nanoscale phase separation

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## 1. Introduction

The polymer solar cell is a new type of promising photovoltaic conversion device with the advantages of low weight, large area, flexible substrate, and low-cost production. It can be fabricated using the convenient well-developed solution processed thin film deposition technology.[1−3] Despite the significant advances that have been made to improve the technology and the performance of polymer solar cells over the past decades,[4−11] the power conversion efficiency (PCE) of the device needs to be further improved before any practical applications can be realized. Blends of regioregular poly(3-hexythiophene) (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) are among the most promising materials used for realizing highly efficient polymer photovoltaic applications. Kim *et al.*[12] reported that the degree of crystallinity of P3HT in the P3HT/PCBM blend is much lower than that in the pristine P3HT film, resulting in a poor charge transport property. Increasing the degree of crystallinity of P3HT in the blend film is instrumental in improving the charge carrier property and the power conversion efficiency of the photovoltaic cell.[13] Annealing treatments including thermal annealing,[14] solvent-assisted annealing,[15] and additive-assisted annealing[16−19] have been developed to increase the degree of crystallinity of the P3HT/PCBM blend film. However, most of these treatments may cause the degradation of the device and increase the cost and the complexity of the fabrication process.[17]

Ultrasonic irradiation technology is widely applied in organic photovoltaic cells to dissolve the organic material in solvent.[19] Aiyar *et al.*'s work showed that ordered supramolecular precursors at the P3HT solution obtained under low intensity ultrasound can survive at the thin films fabricated with

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spin coating, resulting in a dramatic increase in the degree of crystallinity of the thin film.[20] According to the semiconductor physics principle, increasing the degree of crystallinity can reduce the trap number in a semiconductor thin film and improve the charge carrier mobility (holes for P3HT). In the bulk-heterojunction organic solar cell, the space-charge limit effect hinders the increase of charge collection efficiency at the device electrodes.[21] Increasing hole mobility can reduce the influence of the space-charge limit effect in a way and improve the charge collection efficiency, resulting in an increase in the power conversion efficiency of the photovoltaic cell. In this work, considering the fact that low-intensity ultrasonic irradiation can keep the degree of crystallinity of the P3HT thin film fabricated with spin coating, we present an ultrasonic irradiation mixing approach, by which the degree of crystallinity of the P3HT/PCBM blend film can be effectively retained compared with that of the pristine P3HT film. This approach can also form a nanoscopic separation of the P3HT and PCBM phases. An optimal photovoltaic cell fabricated in an ultrasonic irradiation mixing time of 10 min with a high short-circuit current density ($J_{\rm SC}$) of 13.47 mA/cm$^2$, an open-circuit voltage ($V_{\rm OC}$) of 0.62 V, a fill factor (FF) of 58%, and a PCE of 4.85 % can be obtained.

## 2. Experimental details

The polymer photovoltaic cells were fabricated by spin-coating a blend of P3HT/PCBM solution with 1:1 weight ratio as the active layer on a pre-cleaned glass substrate coated with 30 Ω/sq indium tin oxide (ITO) as the anode, and a 1 nm LiF layer and a 100 nm Al layer were deposited as the cathode by thermal evaporation (Edwards AUTO 500) through a shadow mask with an active device area of 0.099 cm$^2$. The deposition rate was monitored by a quartz oscillating crystal and fixed at 0.4–0.5 nm/min for LiF and 0.1–0.2 nm/s for Al. P3HT (51000 g/mol, Regioregular) and PCBM were purchased from American Dye Source, Inc. DCB (99%) was purchased from Alfa Aesar. Solid samples of the P3HT and PCBM were ultrasonically dissolved in 1,2-dichlorobenzene (DCB), respectively, each with a concentration of 30 mg/mL. When the P3HT solution colour was changed to bright orange, the PCBM solution was added into it, and the mixed solution colour was immediately changed to dark purple. Then the mixed solutions of P3HT and PCBM, with mixing times of 10 min (device A) and 10 h (device B) were ultrasonically irradiated. A control sample (device C) was also fabricated according to the method (active layer thickness $\sim$ 100 nm) given in Ref. [22]. The current density–voltage ($J$–$V$) characteristics of the as-fabricated devices were measured without any annealing treatment in the dark and under AM 1.5G solar illumination at an intensity of 100 mW/cm$^2$ with an Oriel 150 W solar simulator using a programmable Oriel mode 69907 power source and a current–voltage measurement system (2400 Sourcemeter, Keithley Instruments Inc.) at room temperature under ambient atmosphere. The light intensity was measured with an ultraviolet-visible-near infrared (UV–Vis–NIR) radiant power meter (Gigahertz-Optik Puchheim, Germany, P-9710 with an RW-3703-2 illuminance detector). For the monochromatic incident photo conversion efficiency (IPCE) measurement, a system combining a UV–Vis light source and a grating monochromator (1/8 m, Spectra-physics 74000) with a hand controller (Spectra-physics 74009) was used to provide the monochromatic light. The intensity of the monochromatic light was measured using an optical power meter (Newport 1930-C) with a low-power silicon photo detector (Newport 918-SL). UV–Vis spectral measurements of the as-fabricated P3HT/PCBM films on quartz were performed using a Perkin-Elmer Lambda 900 UV–Vis–NIR spectrophotometer with a 1.0 nm slit width. The thickness of the film was measured using a Dektak3 ST Surface Profiler. Grazing incidence X-ray diffraction (GIXRD) patterns of the as-fabricated P3HT/PCBM blend films on the $SiO_2$/Si substrates were recorded using a Bruker D8 Advance ($\theta/\theta$) diffractometer with a Göbel mirror attachment and an X-ray source operating at the tube voltage and 40 mA tube current. The irradiation of the Cu $K_{\alpha 1,2}$ X-ray beam ($\lambda$ = 1.5418 Å) was fixed at a grazing incident angle of 1.000°, and the detector was independently moved to collect the diffraction data in a $2\theta$ range of 3°–20° with a step size of 0.02° at a fixed speed of 10 s/step. Atomic force microscopy (AFM) measurements were performed on a Veeco diMultiMode V at the tapping mode under ambient atmosphere. The charge mobility of the as-fabricated P3HT/PCBM blend films was examined using a bottom-contact field-effect transistor (FET) configuration.[23]

## 3. Results and discussion

The performances of the three devices, A, B, and C, are summarized in Table 1, where $\mu_{\rm h}$ is the hole

mobility, and $R_s$ is the series resistance. For photovoltaic application, a higher charge carrier mobility is essential to ensure efficient charge extraction. The hole mobility and the series resistance of device C are $1.08\times10^{-3}$ cm$^2$/V·s and 20.8 Ω·cm$^2$, respectively. The photovoltaic cell of device C shows $J_{SC}$, $V_{OC}$, FF, and PCE of 7.76 mA/cm$^2$, 0.47 V, 42%, and 1.53%, respectively, which are compatible with the published values (7.85 mA/cm$^2$, 0.42 V, 41%, and 1.35%).[15] When the P3HT and PCBM solutions are mixed using an ultrasonic bath for 10 min, the mobility of as-fabricated device A increases to $2.51\times10^{-3}$ cm$^2$/V·s with a smaller series resistance of 11.9 Ω·cm$^2$, leading to a better photovoltaic cell performance ($J_{SC}$, $V_{OC}$, FF, and PCE of 13.37 mA/cm$^2$, 0.62 V, 53%, and 4.39%, respectively). However, with the ultrasonic irradiation mixing time further increasing to 10 h, the mobility of device B decreases to $1.78\times10^{-3}$ cm$^2$/V·s, and the series resistance increases to 20.9 Ω·cm$^2$. As a result, the PCE drops to 3.09%. The changing trend of field effect mobility as a function of ultrasonic irradiation time is consistent with Aiyar *et al.*'s result.[20] The best performance of an optimal photovoltaic cell with a PCE value of 4.85% can be achieved by spin-coating the ultrasonic irradiation mixing P3HT/PCBM solution on ITO glass with a resistance of 10 Ω/sq (Fig. 1).

**Table 1.** The device performances of the as-fabricated FET and photovoltaic cells.

| Device | $\mu_h/10^{-3}$ cm$^2$·V$^{-1}$·s$^{-1}$ | $R_s$/Ω·cm$^{-2}$ | $J_{SC}$/mA·cm$^{-2}$ | $V_{OC}$/V | FF/% | PCE/% |
|---|---|---|---|---|---|---|
| A | 2.51 | 11.9 | 13.37 | 0.62 | 53 | 4.39 |
| B | 1.78 | 20.9 | 12.91 | 0.57 | 42 | 3.09 |
| C | 1.08 | 20.8 | 7.76 | 0.47 | 42 | 1.53 |

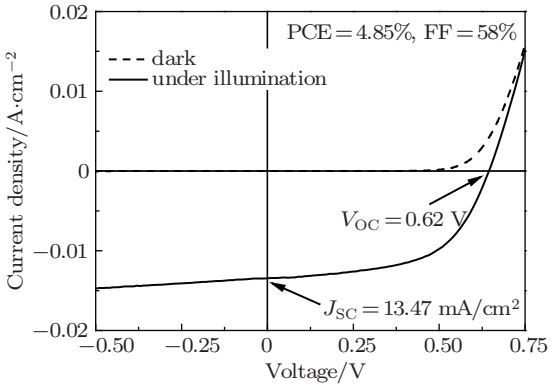



**Fig. 1.** The $J$–$V$ characteristics of the optimal device (P3HT and PCBM solutions are mixed by ultrasonic irradiation for 10 min, and then spin coated on ITO glass with a resistance of 10 Ω/sq ).

This result is consistent with the IPCE measurements on devices A and C. Figure 2 shows the IPCE patterns of the as-fabricated photovoltaic cells (devices A and C). The maximal IPCE of device C is ∼ 53% at a wavelength of 520 nm, which is significantly lower than that of device A (∼ 87% at 550 nm). We believe that the enhancement in IPCE can be attributed to the increases in the charge carrier mobility and the absorption efficiency in the active layer.

The UV–Vis absorption spectra of the three as-fabricated devices (A, B, and C) and the pristine P3HT film are shown in Fig. 3. The pristine P3HT film shows the highest absorbance, particularly at ∼ 600 nm, which appears as a shoulder peak and is attributed to the inter-chain interactions.[24] Compared with the pristine P3HT film, device C shares an absorption peak at ∼ 477 nm with a weaker shoulder at ∼ 600 nm. These spectral data are consistent with the previous result where P3HT and PCBM each act as heavily doped impurities of their counterparts and both inhibit the formation of a crystalline structure with a 1:1 weight ratio blend.[22] For devices A and B fabricated with ultrasonic irradiation treatment, the intensities of their absorption peaks at ∼ 520 nm are much stronger, and the vibronic absorption shoulders (∼ 550 nm and ∼ 600 nm) are much more pronounced, similar to the case for the pristine P3HT film. This result reveals that the ultrasonic irradiation mixing process can produce a higher degree of structural ordering in the P3HT/PCBM blend film,[15] and that the self-organization of P3HT molecules is still effective even in the presence of 50 wt.% PCBM.

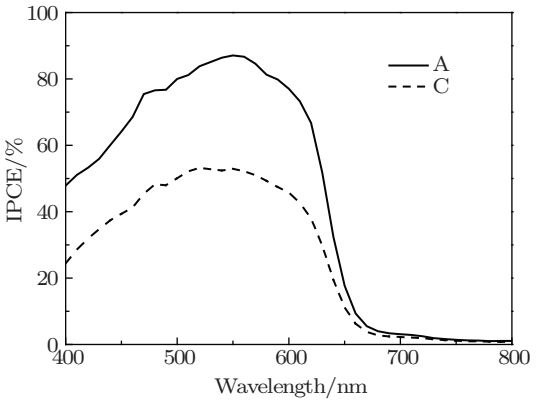



**Fig. 2.** The IPCE patterns of as-fabricated devices A and C.

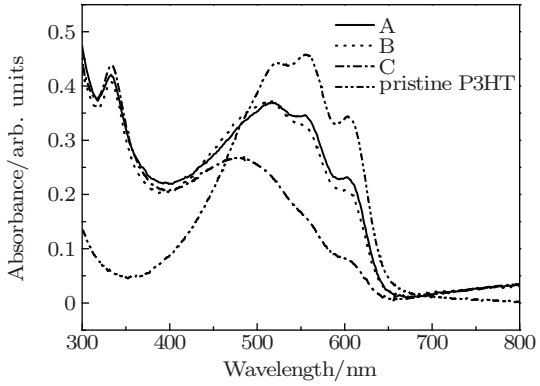



**Fig. 3.** The absorption spectra of the P3HT:PCBM blend films and the pristine P3HT film (film thickness ∼100 nm).

The degrees of crystallinity of the as-fabricated P3HT/PCBM blend films are also examined by the GIXRD measurement. As depicted in Fig. 4, all the devices show one strong diffraction peak and one weak diffraction peak with $2\theta$ values of 5.32°–5.37° and 10.68°–10.87°, respectively. These two peaks are indexed as [100] and [200] reflections with $d$ spacing values of 16.39 Å and 8.27 Å, respectively, which are comparable to the intra-chain separation distances of the adjacent P3HT molecules in the films.[12] It is noteworthy that the increase in the intensity of the diffraction peak at the $2\theta$ value of $\sim 5.3°$ for devices A and B consistently points to an increase in the degree of crystallinity of the P3HT/PCBM blend films. The much more highly ordered structures in devices A and B indicate that more nanocrystalline structures in the films are probably connected with each other, which enhances the device mobility. The inference can be verified from the hole mobility measurement results in the blend films listed at Table 1. On the other hand, the absorption characteristics of devices A and B are better than those of device C, as seen from the absorption spectra in Fig. 3. The phenomenon further indicates that increased ordering can increase inter-band absorption. To our best knowledge, the power conversion efficiency of organic photovoltaic cells is proportional to the product of absorption efficiency, exciton diffusion efficiency, and charge collection efficiency at the device electrodes. As the device structure is bulk-heterojunction, its exciton diffusion efficiency can be regarded as 100%. Obviously, the higher ordered characteristics in devices A and B cause the absorption efficiency and the charge collection efficiency to increase, thus improving the power conversion efficiency. Device A has the best characteristic among devices A, B, and C.

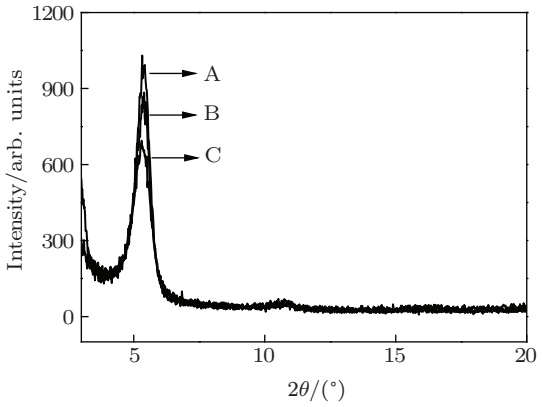



**Fig. 4.** The GIXRD patterns of P3HT:PCBM films (film thickness ∼ 100 nm).

Besides the degree of crystallinity, the extent of phase separation and the surface morphology of the film also play important roles in optimizing the power conversion efficiency.[25,26] Figure 5 depicts the AFM height images and the phase images of P3HT/PCBM blend films under different treatments. As depicted in the height images of the P3HT/PCBM blend films (the first row in Fig. 5), the P3HT/PCBM blend film fabricated by ultrasonic irradiation mixing for 10 min reveals a more smooth and uniform microstructure compared with devices B and C. The phase images reveal that only device A forms PCBM domains ($<\sim$ 200 nm in size) that are separated from the P3HT phase. We suggest that fast ultrasonic irradiation mixing of the P3HT and PCBM solutions effectively assists the homogenous dispersion of the P3HT and PCBM phases to achieve nanocrystalline/nanoscale domains. However, increasing the mixing time or not undergoing ultrasonic irradiation treatment would cause the further aggregation of PCBM molecules and disturb the molecular packing arrangement of P3HT, leading to a coarser film morphology with poor phase separation. The higher degree of crystallinity of P3HT enables a well-defined molecular ordering with higher charge carrier mobility and optical absorption, while the ideal microstructure of the blend film with the P3HT and PCBM phase separation morphology can improve the charge transfer rate from P3HT to PCBM, resulting in better photovoltaic cell performance.

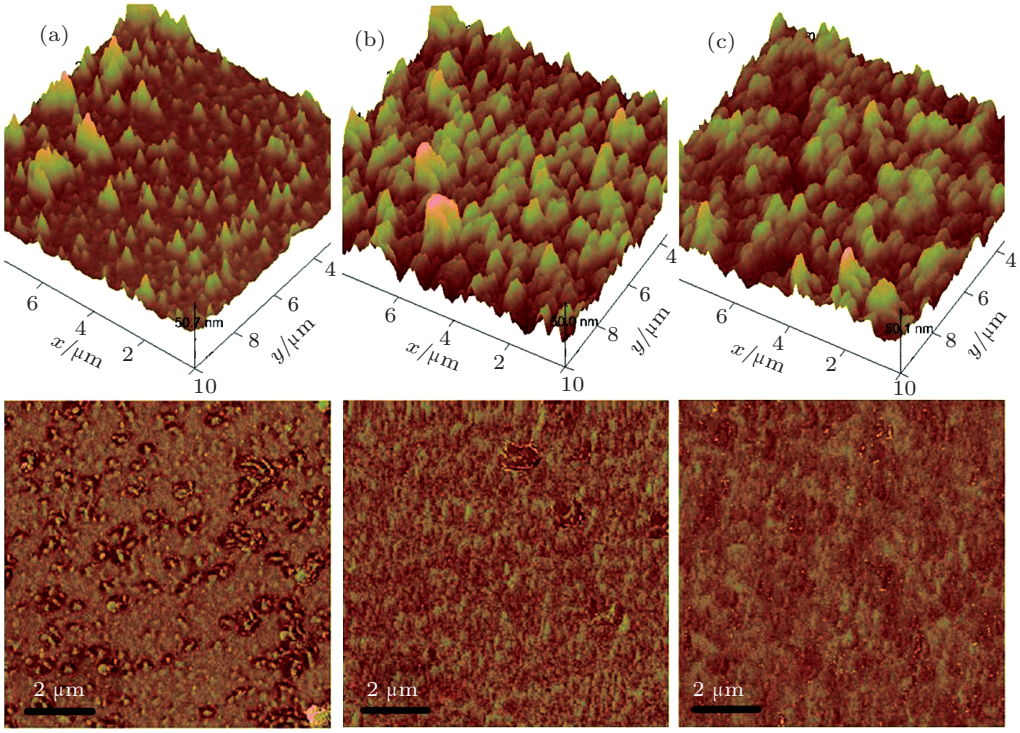



**Fig. 5.** (colour online) The AFM height images (top) and phase images (bottom) of devices (a) A, (b) B, and (c) C (film thickness ∼ 100 nm).

## 4. Summary

In this paper, we develop an ultrasonic irradiation mixing approach to fabricating a high-performance P3HT/PCBM-based photovoltaic cell with a PCE higher than 4.85%. Compared with the conventional process, the ultrasonic irradiation mixing approach within 10 min is effective in increasing the degree of crystallinity of the P3HT/PCBM blend film and introducing a nanoscale phase separation of the P3HT and PCBM in the blend film, leading to the improvement of its photovoltaic cell performance.

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