SPECIAL TOPIC — Physical research in liquid crystal

Fullerene solar cells with cholesteric liquid crystal doping*

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This paper reports the doping effect of cholesteric liquid crystal 3β-Hydroxy-5-cholestene 3-oleate on polymer solar cells composed of the poly 3-hexyl thiophene and the fullerene derivative. With a doping ratio of 0.3 wt%, the device achieves an ideal improvement on the shunt resistor and the fill factor. Compared with the reference cell, the power conversion efficiency of the doped cell is improved 24%. The photoelectric measurement and the active layer characterization indicate that the self-assembly liquid crystal can improve the film crystallization and reduce the membrane defect.

Keywords: liquid crystal, cholesteryl oleatea, polymer solar cells, active layer optimization

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1. Introduction

Solar cell with high power conversion efficiency (PCE) is expectant in the last decade because of the increasing cost in natural energy and stronger environmental protection concern.[1–5] The bulk-heterojunction (BHJ) polymer solar cells (PSCs) have attracted substantial interests due to the potential characters of the low cost, light weight, flexibility, and reel-to-reel coating application in largearea manufacturing.[6–8] However, the lower PCE of PSC is a major obstacle in the commercial utilization. Therefore, it is one of the most important topic to improve PCE for many scientific researchers.

As an ideal active layer material, the mixture of poly(3-hexylthiophene) (P3HT) which serves as electron donors and [6, 6]-phenyl-C61-butyric acid methyl ester (PC61BM) which acts as electron acceptors has been well studied. Aiming some key factors, numbers of the researcher have made many exciting jobs in materials, film growth control, hole/electron modifying layer, electro-optic properties of the interface, electrode, and so on.[9–13] On the manufacture process of the cell active layer, the solid and solvent doping are the most common and an effective options; while the annealing processes, including thermal, solvent vapor, and the electromagnetism annealing, are also wildly reported.[14–17] For BHJ PSCs, the exciton diffusion length of the efficient charge generation is strongly dependent on the crystallization of the active layer molecules with high order. In other word, the active layer molecules with higher crystalline order can improve the exciton dissociation and carrier transport, and then achieve the perfect cell performance.[18–20]

Considering the molecular order, liquid crystal (LC) material is firstly to be thought because LC molecular order can be controlled to repair the structure defects in the bulk and at the interface with a molecular level.[21] LCs can be employed as an organic semiconductor, interface modifying, or a doping material in manufacturing photo-voltaic device.[22–25] As an electron donor, it has been reported that a new nematic LC material which possesses a high charge carrier mobility and makes the solar cell reach a maximum PCE of 9.3%.[25] As the simple and effective method, doping LC into organic BHJ can induce a significant enhancement of PCE of PSCs.[26–28] In a device fabricated from P3HT:C60 bilayer, a smectic phase LC is applied as the doping to result in a substantial improvement in short circuit current density (J_{sc}) and PCE.[26] It is trustworthy that the doping LC can prevent the penetration of C60 through P3HT layer, therefore improve the morphology of the active layer. Using discotic LCs, the charge transport in BHJ can be enhanced obviously.[29–31] As the interface modifying layer, both J_{sc} and fill factor (FF) were increased without open-circuit voltage (V_{oc}) sacrifice by introducing the discotic LC between the hole transporting layer and the active layer made of P3HT:PC61BM. A maximum increase of 43% in PCE was obtained.[31]

For different liquid crystalline phases, the electro-optic property of the material possesses great difference. The above investigations aimed mainly at the modification work on PSCs using nematic, smectic, and discotic LC phase materials, respectively. As a doped material, the main purpose is to increase the crystalline order of the active layer using LC's self-organization function. Cholesteric LC (CLC) is a kind of liquid crystalline material with chiral nematic phase which the molecules can self-organize to form a macroscopic he-

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licoidal structure. In our previous study, a cholesteryl chloride LC was doped into BHJ made of P3HT and indene-C60 bisadduct to investigate the crystallization effect.[32] The result indicated that PCEs of the devices were improved effectively because of the increased V_{oc}. As a preliminary attempt, a compound 3β-Hydroxy-5-cholestene 3-oleate (HCO) was introduced into P3HT:PC61BM active layer to improve the cell performance.[33] It is found that HCO can improve the performance of PSCs effectively. In this work, the detailed experimental on the material doping is proposed, and the physical mechanism will be discussed.

2. Experiments

2.1. Materials

Indium tin oxides (ITO) (thickness 180 ± 25 nm, resistance ≤ 10 Ω/□) glasses were purchased from Kaivo. The hole transport layer poly(3,4-ethyleneoxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) was purchased from Bayer AG, P3HT (98% region regularity) and the active layer materials PC61BM (P3HT:PC61BM = 1:1, 8 mg/8 mg, solvent 0.5 ml) were purchased from Luminescence Technology Corp. Unless stated otherwise, all the solvents used in this study were reagent grades as received. HCO was purchased from Beijing Lark Chemical Reagent Co., LTD and used without further purification. The proportions of HCO are 0.1%/0.3%/0.5%/0.7%/0.9%, which were stirred 24 h on magnetic stirring apparatus until solution dissolved completely. Figure 1 shows the molecular structure of HCO and other materials used in this work.

2.2. Device preparation

ITO was patterned by etching for extracting electrode, the substrates were cleaned as follows: detergent, deionized water, NaOH solution, acetone, ethanol and deionized water by ultrasonic cleaner 15 min. The hole transport layer PEDOT:PSS was prepared by spin-coating (2500 r/min for 15 s and 3000 r/min for 45 s) on the substrate, then dried at 140 °C for 30 min. The mixture of P3HT:PC61BM:HCO was spin-coated on PEDOT:PSS layer (800 r/min for 1 min) and annealed 140 °C for 30 min. Al cathode (180 nm and size 0.04 cm^2) was evaporated on the active layer in the condition of pressure 10^{-4} Pa. Figure 2 shows the structure sketch map of the device with or without HCO doping.

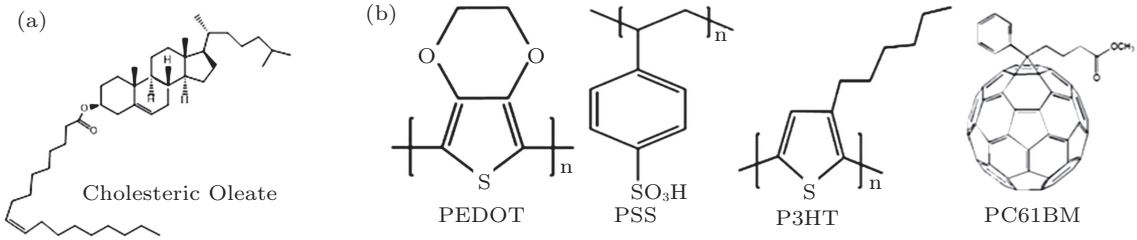


Fig. 1. Chemical structure of (a) HCO and (b) other materials used in this work.

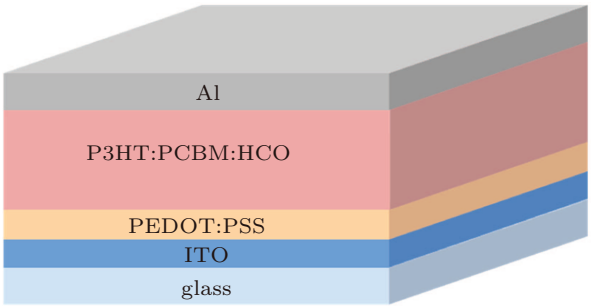


Fig. 2. (color online) Device structure of PSC, ITO/PEDOT/P3HT:PCB-61BM (with or without HCO)/Al.

2.3. Characterization

The current-voltage characteristic was measured with a solar simulator system (1000 W Xenon lamp simulator source AM 1.5 G, 100 mW/cm^2). The surface topography of active layer film was recorded using tapping mode Atomic Force Microscopy (AFM, Veeco Nano Scope 3D).

3. Results and discussion

To confirm the effect of HCO on crystallization condition of active layer membrane, x-ray diffraction (XRD) measurements were conducted and compared in Fig. 3. The peak intensities of the films with HCO are slightly higher than that of the reference film. Especially for the proportion of 0.3%, the crystallization is shown to be better than that of others.

Figure 4 displays the current voltage (J–V) characteristics, and Table 1 summarizes the parameters of the same devices. One can find that HCO doping leads to the drop of J_{sc} because of the lower light absorption which is caused from the Bragg reflection of the helix pitch of HCO.

According to the basic theory of PSC devices, V_{oc} is not only determined by HOMO and LUMO of the active materials, but also affected by the ratio of the optical current (I_{ph}) and dark current (I_o), i.e.,[34]

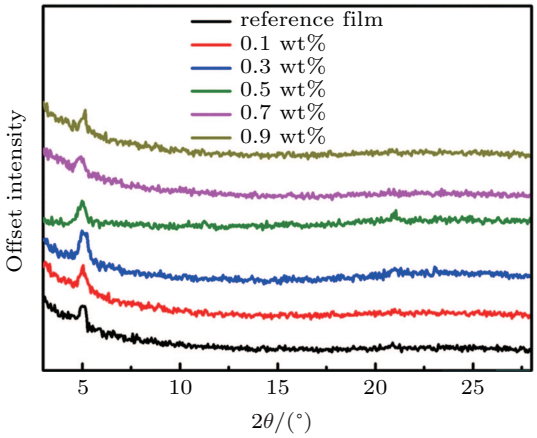


Fig. 3. (color online) XRD spectra of the active layer films with and without HCO doping under the same standard (the ordinate increased a certain values).

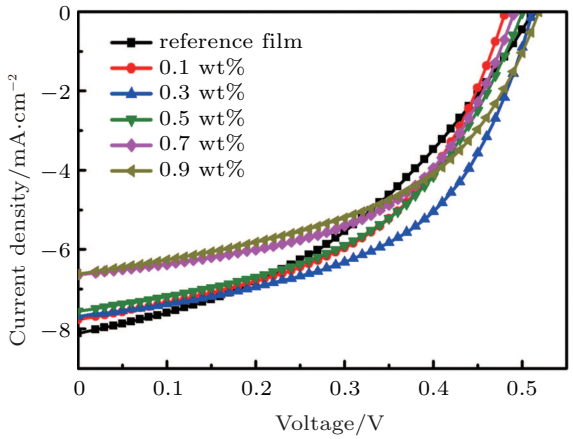


Fig. 4. (color online) J–V characteristics of the cells with different doping proportions of HCO in the light.

Table 1. Performance parameters of the devices with different HCO proportions.

HCO/wt%	J_{sc}/mA·cm^{-2}	V_{oc}/V	FF	R_s/Ω	R_{sh}/Ω	PCE/%
0	8.122	0.512	0.399	545.88	3280.03	2.49
0.1%	7.773	0.481	0.491	350.53	3996.08	2.76
0.3%	7.692	0.511	0.523	329.36	5438.79	3.09
0.5%	7.224	0.517	0.454	478.03	4137.12	2.55
0.7%	6.636	0.498	0.488	422.29	4709.03	2.56
0.9%	6.619	0.518	0.487	480.81	4661.13	2.51

$$V_{oc} = \frac{\mathrm{HOMO}_{donor} - \mathrm{LUMO}_{acceptor}}{e} - 0.3, \quad (1)$$

$$V_{oc} = \frac{KT}{q} \ln\left(\frac{I_{ph}}{I_o} + 1\right). \quad (2)$$

HCO doping does not contribute to the energy levels of the donor and acceptor; while as an ordered impurity, it has a great effort on the dark current of the devices. According to the change of I_{ph}, a comprehensive influence results in the uncertainty on V_{oc}, just as shown in Fig. 4.

As a complex and important parameter in PSCs, the series resistor (R_s) of the cell is composed of the contact resistance between metal and modified layer, active layer resistance. HCO molecules make the active layer molecule crystallize more orderly, i.e., the regular lattices, who reduces the membrane defects and the active layer resistance R_s. The shunt resistor (R_{sh}) describes the ability of carriers to recombine or capture, which is determined by the membrane defects of the active layer. Therefore, the nice active layer membrane reduces the carriers recombine center, and hence the larger R_{sh}.

Although both V_{oc} and J_{sc} do not increase, the devices possess some special performances because of HCO doping, especially for 0.3%, whose PCE was improved significantly. The fine cells are profited from their nice fill factor (FF), which is shown in Fig. 4 and listed in Table 1. Generally, a nice cell FF indicates that the device possesses a good condition, which includes the fine active layer membrane, less defects and carriers recombination centers, lower R_s and dark current, and with a high R_{sh}. Compared with the reference cell, the largest PCE was improved from 24.9% to 3.09% with the doping ratio 0.3%

Figure 5 shows J–V characters of the devices with different HCO doping at dark condition. Being the good agreement with the larger R_{sh} mentioned above, HCO doping shows that the ordered molecules can reduce the leakage currents under the reverse bias in the cells. Furthermore, the slight scale doping of HCO can increase the dark current linearly under the forward direction voltage, which reflects the fine membrane and the little R_s.

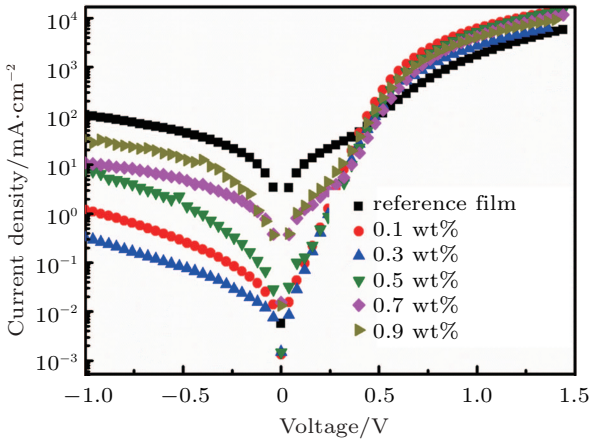


Fig. 5. (color online) Current density–voltage characteristics of PSCs with different doping proportions of HCO in the dark.

The membrane morphology feature of the active layer with and without HCO was also characterized using AFM, and the results are shown in Fig. 6. The data of the Root mean square (R_{ms}) roughness of the films are measured and listed in the figure caption. The doping of HCO are in favor of reducing the molecular clusters in film crystallization, and therefore to promote the order degree of the membrane molecules.

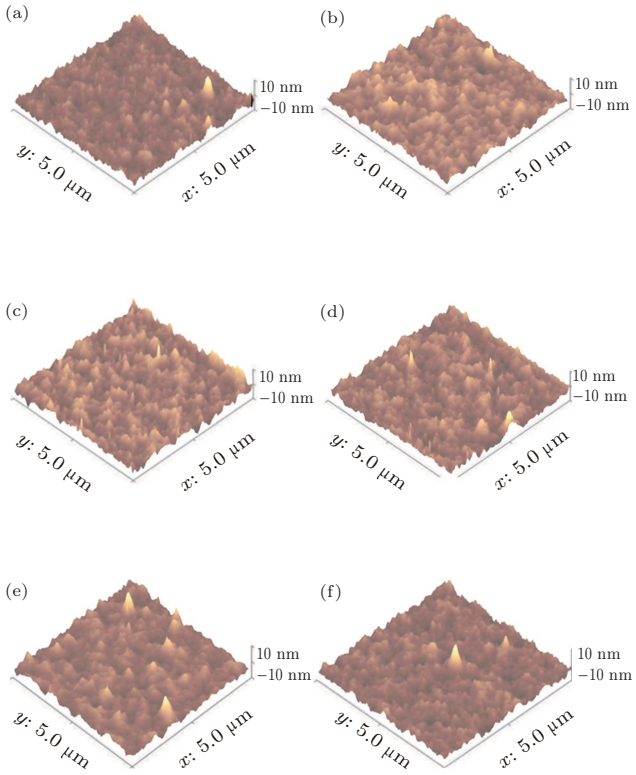


Fig. 6. (color online) The morphology features of the active layer with and without HCO. (a) The reference film, $R_{ms} = 1.14$; (b) 0.1%, $R_{ms} = 0.87$; (c) 0.3%, $R_{ms} = 1.01$; (d) 0.5%, $R_{ms} = 0.94$; (e) 0.7%, $R_{ms} = 0.97$; (f) 0.9%, $R_{ms} = 1.07$.

4. Conclusion

In summary, the photo-voltaic property of PSCs with HCO doping is discussed. For the proper doping concentration of 0.3%wt, the cell FF was improved remarkably, which yielded a superior enhancement of 24% on PCE compared with the reference cell. It is concluded that the slight doping of cholesteric LC on the active layer can improve the film crystallization and reduce the membrane defect, and therefore result in the enhancement on physical parameters, such as FF, R_{sh}. And hence an interesting effect on cell PCE. As a unique LC phase, the order influence should be compared with other LCs.

Because the helix pitch of CLC and the wavelength of the visible light have Bragg relationship on light reflection, the doping of CLC brought the decrease of the light absorption in BHJ. It is an interesting subject to compare the different functions brought from the nematic, smectic and discotic phase LCs. A potential application, for instance, the possible light-scattered effect induced by the light reflection inside the active layer PC61BM:P3HT:CLC, should be a future research subject.

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