A simple encapsulation method for organic optoelectronic devices*

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The performances of organic optoelectronic devices, such as organic light emitting diodes and polymer solar cells, have rapidly improved in the past decade. The stability of an organic optoelectronic device has become a key problem for further development. In this paper, we report one simple encapsulation method for organic optoelectronic devices with a parafilm, based on ternary polymer solar cells (PSCs). The power conversion efficiencies (PCE) of PSCs with and without encapsulation decrease from 2.93% to 2.17% and from 2.87% to 1.16% after 168-hours of degradation under an ambient environment, respectively. The stability of PSCs could be enhanced by encapsulation with a parafilm. The encapsulation method is a competitive choice for organic optoelectronic devices, owing to its low cost and compatibility with flexible devices.

Keywords: organic optoelectronic devices, stability, encapsulation

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1. Introduction

The organic optoelectronic device has attracted more and more attention due to its unique features, such as cost effectiveness, flexibility, environmentally friendly, light weight, and easy fabrication.[1–3] However, the water and oxygen have serious negative effects on the stability of an organic optoelectronic device, especially under working conditions.[4,5] In order to keep organic optoelectronic devices performances, devices are encapsulated to avoid water and oxygen corrosion. Many methods of encapsulating organic optoelectronic devices have been reported. The inorganic thin-film deposited encapsulation is a common method by plasma-enhanced chemical vapor deposition (PECVD) or atomic layer deposition (ALD). Thin silica, silicon oxide, and silicon nitride layers are usually deposited by PECVD.[6–8] ALD is usually used to deposit thin zinc oxide, titanium oxide, and aluminum oxide layers.[9,10] Inorganic films are required to achieve adequate barrier performance for encapsulating organic optoelectronic devices, and it alone is not adequate due to its inevitable defects. Therefore, inorganic films must be alternated with polymer film into a multilayered film stack.[11] A laborious encapsulation technique is sealing a device in a glass ampoule under a vacuum with a tungsten feed through the pins for electrical connections.[12,13] While the complete glass seal works well, it is too complex with too many operations that may go wrong. A simple encapsulation technique employs a glass substrate and an aluminum backplate that is to be sealed through using a glass filled with thermosetting epoxy (prepreg).[12] The sealing procedure needs a mechanical pressure by placing a lead brick on the top of the assembly and a thermosetting time of 12 hours. The encapsulation technique could not be effectively applied to flexible devices. A solution process encapsulation method was reported by coating a ZnO layer on the top of a photoactive material and subsequent UV resin solution dropped.[14] The mixed solution is irritating to human skin and eyes, because it consists of acetone and UV resin. The UV resin coating should be repeated several times for a thick encapsulation layer.

In this paper, we report a new encapsulation method by using parafilm based on polymer solar cells. Recently, we reported that the performance of PSCs was improved through sensitization by doping a narrow band gap polymer.[15] Ternary bulk heterojunction polymer solar cells have been considered as the efficient way for expanding the absorption spectrum of active layers and improving PSC performance. 2,4-bis[4-(N,N-diisobutylamino)-2,6-dihydroxyphenyl] squaraine (DIB-SQ) has a high absorption coefficient, high charge carrier mobility, and intense absorption in the red and near infrared spectral ranges. The small molecular DIB-SQ is doped into poly 3-hexylthiophene (P3HT):[6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) as sensitization. All PSCs are fabricated and encapsulated by thermal treatment parafilm.

2. Experimental section

The indium tin oxide (ITO) glass substrates (sheet resistance 15 Ω/□) were cleaned consecutively in ultrasonic baths containing acetone, ethanol, and de-ionized water and dried by high pure nitrogen gas. The pre-cleaned ITO substrates were then treated by UV-ozone for 10 min in order to further

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clean the substrates and improve the work function of ITO substrates. The solution of poly-(3,4-ethylenedioxythiophene)-poly-(styrenesulfonate) (PEDOT:PSS) (purchased from H. C. Starck Co. Ltd.) was spin-coated on the ITO substrates under 5000 rounds per minute (rpm) for 40 s. Then PEDOT:PSS coated ITO substrates were dried in air at 120 °C for 10 min. The polymer P3HT and $PC_{71}BM$ were dissolved in 1,2-dichlorobenzene (36 mg/ml) with a weight ratio of 1:0.8. The DIB-SQ doping concentration in P3HT:$PC_{71}BM$ was 1.2 wt%. The mixed solution was spin-coated onto the PEDOT:PSS for preparing the active layers at a rate of 600 rpm in a high nitrogen glove box. The 1-nm LiF interfacial layer was deposited under a 10^{-4}-Pa vacuum condition, which was monitored by a quartz crystal microbalance. An aluminum cathode layer of about 100 nm was deposited on the active layer under 10^{-4}-Pa vacuum conditions. The vertical overlap of the ITO anode and Al cathode is defined as the active area (about 3.8 mm^2). The prepared PSCs were encapsulated by parafilm through thermal treatment.[16] Parafilm (produced by the Pechiney Plastic Packaging Company) is a plastic film with a paper backing. Parafilm becomes soft and sticky at about 70 °C, therefore the encapsulation process could be finished during the annealing treatment on PSCs. The prepared parafilm was flat on the top of the Al cathode to cover the active area. All PSCs experienced thermal annealing at 120 °C for 10 min in a high nitrogen glove box. Parafilm was spontaneously adhered to the device after cooling to room temperature, the overlap of parafilm and aluminum became more white and lost the sheen of aluminum, as shown in Fig. 1(c). All the PSCs were stored in culture dishes under dark-room conditions for lifetime measurements.

The absorption spectra of the films were measured with a Shimadzu UV-3101 PC spectrometer. The current–voltage (I–V) characteristics of PSCs were measured using a Keithley 4200 semiconductor characterization system and ABET Sun 2000 solar simulator. The chemical structures of used materials, the schematic diagram of PSCs and the figures of prepared PSCs with and without encapsulation are shown in Fig. 1.

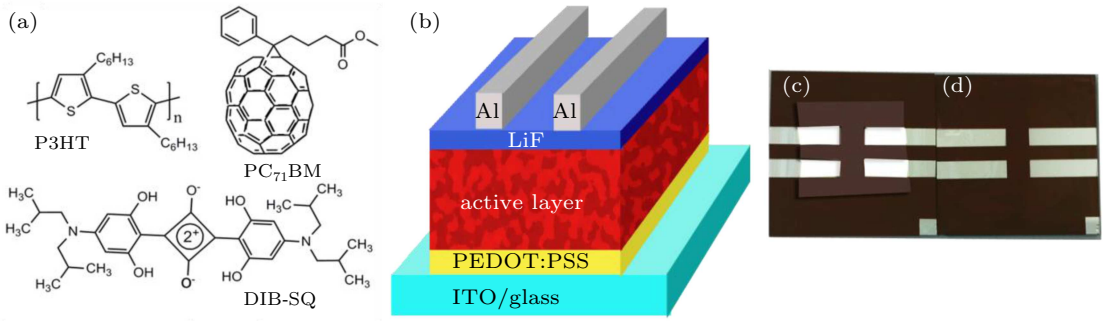


Fig. 1. (color online) (a) Chemical structures of organic materials P3HT, $PC_{71}BM$, and DIB-SQ; (b) schematic configuration of PSCs; (c) and (d) photo-images of PSCs with and without encapsulation.

3. Results and discussion

The absorption spectra of the neat P3HT, $PC_{71}BM$, DIB-SQ, and their blend films are shown in Fig. 2. Small molecule material DIB-SQ has an absorption peak at 690-nm accordant with its band-gap between the highest molecular occupied orbits (HOMO) and the lowest molecular unoccupied orbits (LUMO). Polymer P3HT has a widen absorption range from 400 nm to 650 nm, with two absorption peaks at 520 nm and 610 nm. There is a great complementary absorption spectrum between P3HT and DIB-SQ films. The absorption spectral range of ternary blend film can be extended from visible light to the infrared range. Material $PC_{71}BM$ has a larger absorption range with two apparent absorption peaks at 375 nm and 480 nm, which can harvest solar light photons for an improved performance of the PSCs. The DIB-SQ doping concentration should be balanced between photon harvest and charge carrier transport in the ternary blend films. Therefore, the optimized DIB-SQ doping concentration is about 1.2% based on our experimental results.

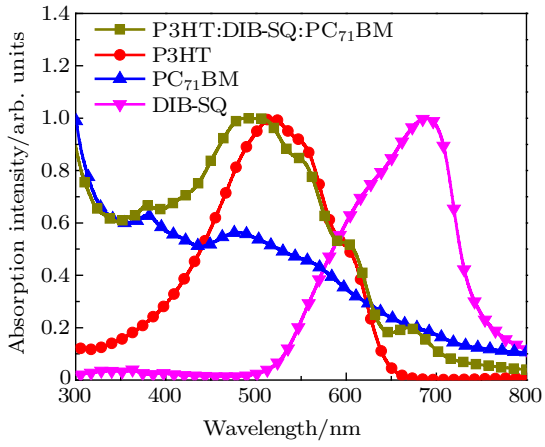


Fig. 2. (color online) Normalized absorption spectra of P3HT, $PC_{71}BM$, DIB-SQ, and P3HT:DIB-SQ:$PC_{71}BM$ films.

The initial current density–voltage (J–V) characteristics of binary PSCs and ternary PSCs with and without encapsula-

tion are measured under 100 mW/cm^2 of AM 1.5 G simulated solar spectrum irradiation, as shown in Fig. 3. The key photovoltaic parameters of binary PSCs and ternary PSCs with and without encapsulation are summarized in Table 1. It is apparent that the PCEs of two kinds of PSCs with encapsulation are better than those of PSCs without encapsulation, respectively. The PCE improvement of PSCs with encapsulation may be attributed to the effective protection Al cathode by parafilm away from air when the PSCs are taken out from the high nitrogen glove box. Meanwhile, the PCE of encapsulated PSCs is improved from 2.54% to 2.93% by doping DIB-SQ. In order to further confirm the effect of parafilm encapsulation on the stability of PSCs, the *J*–*V* curves of PSCs are measured after different storage times. The performance of PSCs with encapsulation shows a slow decay process relative to PSCs without encapsulation. Here, the *J*–*V* curves dependent on the storage time of ternary PSCs are shown in Figs. 4(a) and 4(b).

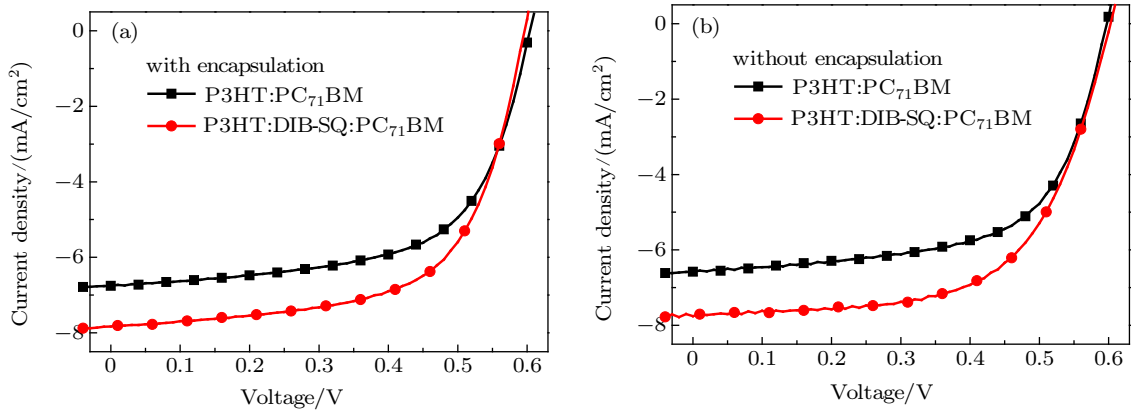


Fig. 3. (color online) Initial *J*–*V* characteristics of binary PSCs and ternary PSCs with and without encapsulation under illumination of AM 1.5 G, 100 mW/cm^2.

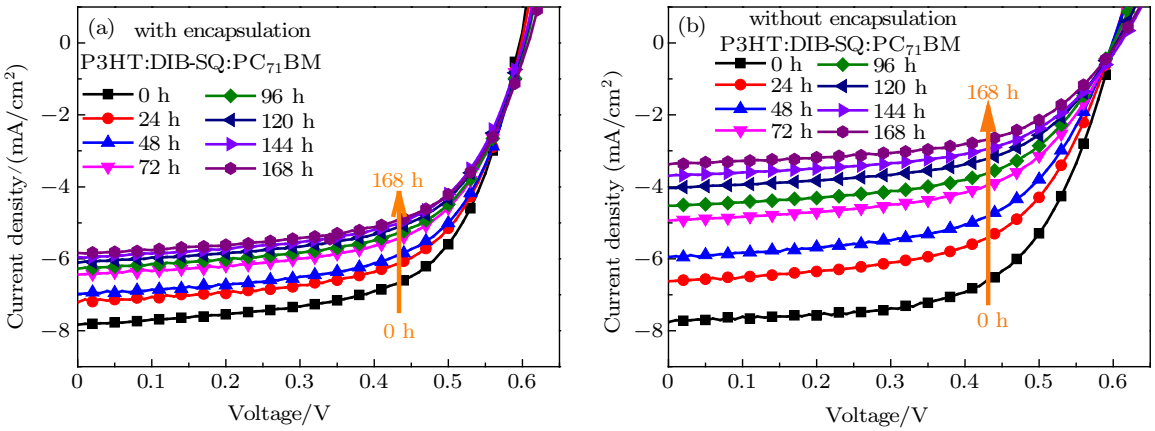


Fig. 4. (color online) Variation *J*–*V* characteristic of the ternary PSCs with and without encapsulation with storage time.

Table 1. Key photovoltaic parameters of PSCs and ternary PSCs with and without encapsulation under illumination of AM 1.5 G, 100 mW/cm^2.

Active layer	With encapsulation				Without encapsulation			
	J_{sc}/(mA/cm^2)	V_{oc}/V	FF/%	PCE/%	J_{sc}/(mA/cm^2)	V_{oc}/V	FF/%	PCE/%
P3HT:PC$_{71}$BM	6.76	0.60	62	2.54	6.58	0.60	62	2.46
P3HT:DIB-SQ:PC$_{71}$BM	7.83	0.60	62	2.93	7.76	0.60	62	2.87

According to the *J*–*V* curves dependent on the storage time, the key photovoltaic parameters of the ternary PSCs with and without encapsulation are summarized in Table 2. The values of the short circuit current (J_{sc}) of the ternary PSCs with and without encapsulation decrease from 7.83 mA/cm^2 to 5.8 mA/cm^2 and from 7.76 mA/cm^2 to 3.4 mA/cm^2 after 168 hours of ambient aging, respectively. For all the PSCs, the values of the open circuit voltage (V_{oc}) are kept constant until the PSCs experience 168-hour ambient storage. The fill factor (FF) of PSC with encapsulation shows a slow decay relative to that of the PSC without encapsulation. It is known that FF is determined by $P_{max}/(J_{sc}V_{oc})$, where P_{max} is the

maximum power of PSC, the decrease of FF might be caused by the increase of the series resistance of the device.[17] The improved stability of PSC with encapsulation should be attributed to keeping the active layer and cathode from air by parafilm, especially for the cells under working conditions. As we know, parafilm is commonly used for sealing or protecting vessels, and sealing a lidded container against moisture and air contamination for long term storage. The oxygen permeability of parafilm is 150 (cc/m^2)/day at 23 °C and 50% relative humidity (RH). The water vapor permeability of parafilm is 1 (g/m^2)/day at 38 °C and 90% RH. It is interesting that the oxygen permeability of parafilm could keep constant under different RH conditions.[18] Due to these features, parafilm is an ideal option for encapsulating organic optoelectronic devices.

The evolutions of J_{sc} and PCE of PSCs with and without encapsulation with storage time are depicted in Fig. 5. The decay curves of J_{sc} and PCE show a similar trend dependent on the storage time. The degradation of J_{sc} shows the two-stage degradation, a fast decay followed by a slow degradation. It is reasonable to deem that the fast decay is mainly due to the water and the slow decay is due to the oxygen.[19] The formed traps in the active layer by water permeation might establish a space charge, resulting in the decrease of J_{sc}.[20] Seemann *et al.*[21] reported that the diffusion of oxygen, combined with illumination, results in a strong decrease of the J_{sc} within minutes. The J_{sc} could partially be recovered by heating, which is taken as an indicator of the degradation occurring in the photoactive layer. The PCE of ternary PSC with encapsulation decreases from 2.93% to 2.17% after 168-hour ambient storage. The PCE of ternary PSC without encapsulation decreases from 2.87% to 1.16% after 168-hour ambient storage under the same conditions. The degradation of the performance of PSC with encapsulation is likely to be due to the chemical reactions of the active layer and/or electrodes under working conditions with current passing through the cells.[5] According to the experimental results, the parafilm encapsulation method can effectively prevent the water and oxygen from diffusing into cells, thus the stability of PSCs with parafilm encapsulation is improved compared with the that of PSCs without parafilm encapsulation.

Table 2. Key photovoltaic parameters data up to 168-hours storage for the ternary PSCs with encapsulation and without encapsulation.

Time/h	With encapsulation				Without encapsulation			
	J_{sc}/(mA/cm^2)	V_{oc}/V	FF/%	PCE/%	J_{sc}/(mA/cm^2)	V_{oc}/V	FF/%	PCE/%
0	7.83	0.60	62	2.93	7.76	0.60	62	2.87
24	7.21	0.60	62	2.69	6.62	0.60	59	2.34
48	6.98	0.60	62	2.60	5.95	0.60	58	2.08
72	6.44	0.60	62	2.39	4.94	0.60	58	1.72
96	6.28	0.60	62	2.33	4.52	0.60	58	1.56
120	6.11	0.60	61	2.25	4.03	0.60	57	1.39
144	5.95	0.60	61	2.19	3.69	0.60	57	1.27
168	5.84	0.61	61	2.17	3.37	0.60	57	1.16

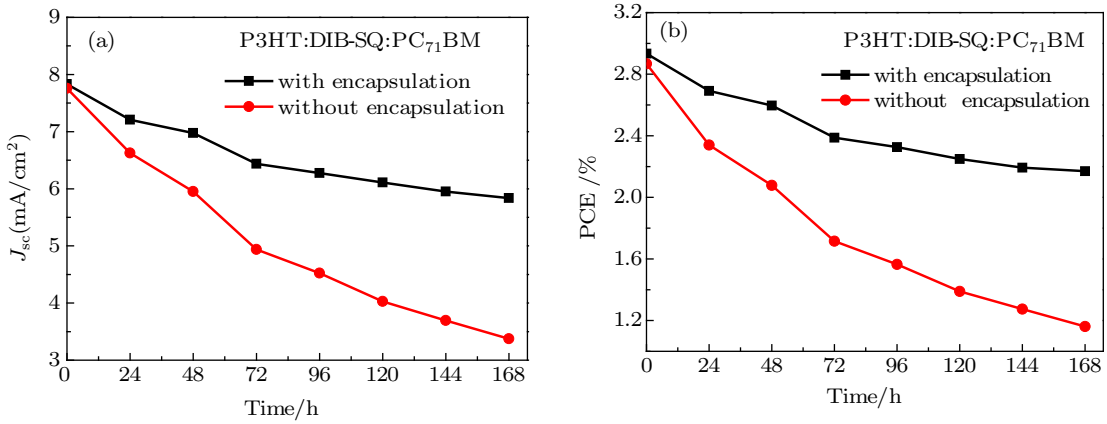


Fig. 5. (color online) Evolutions of key photovoltaic parameters of the ternary PSCs with and without encapsulation with storage time.

4. Conclusions

In conclusion, the encapsulation method by using parafilm can significantly increase the stability of PSCs. The PCEs of ternary PSCs with and without encapsulation decrease from 2.93% to 2.17% and from 2.87% to 1.16% after 168-hour degradation under a dark-room environment, respectively. The encapsulation method by using parafilm is a competitive choice for organic optoelectronic device encapsulation.

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