

Optimization and degradation of rubrene/C₇₀ heterojunction solar cells*

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Small molecule organic solar cells (OSCs) with the structure of indium tin oxide (ITO)/molybdenum trioxide (MoO₃) (5 nm)/rubrene (x nm)/fullerene (C₇₀) (y nm)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) (6 nm)/aluminum (Al) (150 nm) are fabricated. The thickness of active layer for the devices is investigated in details. The results show that the optimum thicknesses of rubrene layer and C₇₀ layer are 30 nm and 25 nm, respectively. The degradation of the device is also investigated. The result indicates that the open-circuit voltage (V_{oc}) does not change, while the short-circuit current density (J_{sc}), fill factor (FF) and power conversion efficiency (PCE) decrease continuously with time. The degradation can be attributed to the oxygen in ambient diffusing and infiltrating into the active materials and reacting with C₇₀ in cells, which can result in the increase of interfacial series resistance.

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Organic solar cell (OSC) is a promising candidate for generating renewable energy due to its advantages of mechanical flexibility, light weight, low cost, and easy scale-up^[1-4]. Great progress in the power conversion efficiency (PCE) of organic solar cells has been achieved in recent years^[5-9] since the first double-layer structure OSC was introduced by Tang^[10]. The highest reported efficiency for organic solar cells has recently risen above 8%.

C₆₀ fullerene is a common acceptor material used in small molecule solar cells due to its high electron affinity and good stability. However, its low absorption in most of the solar spectrum range ultimately limits its potential. Because the visible light absorption of C₇₀ fullerene is significantly enhanced compared with that of C₆₀, C₆₀ as acceptor in OSCs is replaced by C₇₀ recently^[11,12]. In addition, the critical issue stunting the practical use of OSCs is their short lifetime, especially for those unencapsulated ones^[13,14]. The reasons for the limited lifetime of OSCs are still unclear, and they might be the degradation of organic materials under light irradiation with temperature increasing^[15,16], the decrease in conductivity of organic materials upon oxygen or water absorption^[17], and the infiltration of indium (In) into active layer^[18,19].

In this paper, we combine rubrene as donor and C₇₀ as

acceptor to fabricate heterojunction solar cells. The thickness of active layer is optimized to make the best use of the absorbed photons. The degradation of OSCs is also investigated.

The OSCs with the structure of indium tin oxide (ITO)/molybdenum trioxide (MoO₃)/rubrene/C₇₀/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP)/aluminum (Al) are fabricated on pre-cleaned glass substrates coated with transparent conducting ITO. The device structure is shown in Fig. 1. The sheet resistance of ITO is about 10 Ω /sq. The devices were fabricated in the following way. The ITO glass substrates were sequentially cleaned by ultrasonication in acetone, detergent, ethanol and deionized water, and then dried by N₂ gas. MoO₃, rubrene, C₇₀, BCP and Al were successively deposited in a thermal evaporator under a pressure of 9.0×10^{-4} Pa. All organic materials were used without further purification. The deposition rates of MoO₃, rubrene, C₇₀, BCP and Al are 0.5-1.0 \AA /s, 0.6-1.5 \AA /s, 0.8-1.5 \AA /s, 0.1-0.4 \AA /s, and 10-40 \AA /s, respectively. The thickness of rubrene layer is x nm ($x=20, 25, 30, 35, 40$), and the thickness of C₇₀ layer is y nm ($y=15, 20, 25, 30, 35, 40, 45$). The thicknesses of MoO₃, BCP and Al are 5 nm, 6 nm and 150 nm, respectively. The thicknesses of the deposition layers are determined by a quartz oscillator thickness monitor

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(XTM/2, INFCON) and verified by a surface profiler (XP-2, Ambios). The active area of the device is 5 mm×6 mm. The current density-voltage ($J-V$) characteristics of the device under air mass (AM) 1.5 (100 mW/cm²) solar-illuminated condition were measured at room temperature using a Keithley 2400 source measurement unit. All the measurements were carried out in air without encapsulation.

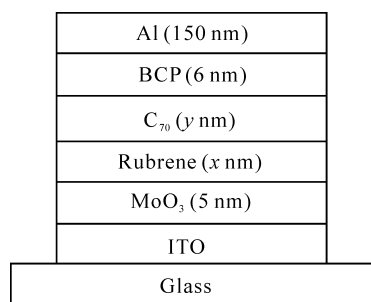


Fig.1 Schematic diagram of OSC structure

Fig.2 shows the absorption spectra of C₇₀, C₆₀, rubrene and rubrene/C₇₀. The observed enhancement in the absorption spectrum is due to the presence of the C₇₀ fullerene layer, and it may be widely used for improving the efficiency of OSCs. Moreover, the absorption spectrum of rubrene/C₇₀ is very similar to that of C₇₀ except for the weak absorption peaks at 495 nm and 529 nm, which correspond to the absorption peaks of rubrene. We can conclude that the absorption of C₇₀ is dominant in rubrene/C₇₀ layer, and the photons are mainly absorbed by the acceptor (C₇₀). Although the absorption of rubrene is weak in rubrene/C₇₀ layer, it has a significant effect on the charge separation in donor/acceptor interface. The open-circuit voltage (V_{oc}) of rubrene/C₇₀ is 0.82 V, which is larger than that of C₇₀:ZnPc^[11] and CuPc/C₇₀^[12], leading to the superior performance of the device.

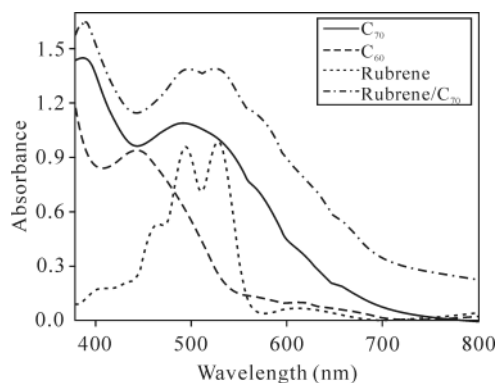


Fig.2 Absorption spectra of C₇₀, C₆₀, rubrene and rubrene/C₇₀

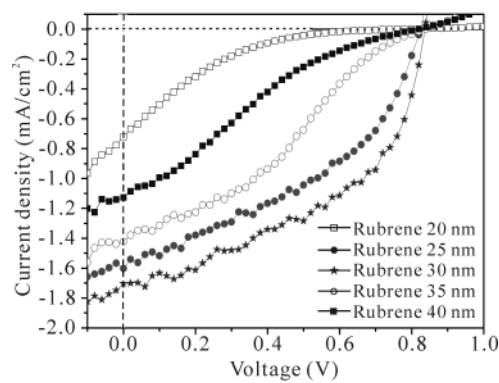
To investigate the dependence of $J-V$ characteristics on the thickness of rubrene layer, the devices with variable

rubrene layer thickness and an invariable C₇₀ thickness of 35 nm are fabricated. In Fig.3(a), the short-circuit current density varies with the increase of the thickness of rubrene layer, while the open-circuit voltage is almost fixed. In Fig.3(b), the variation of V_{oc} is only about 4.9% (from 0.78 V to 0.82 V). The V_{oc} is determined by the difference between the highest occupied molecular orbital (HOMO) level of the donor (rubrene) and the lowest unoccupied molecular orbital (LUMO) level of the acceptor (C₇₀). Indeed, V_{oc} obeys the following empirical equation^[20] with an additional loss of 0.3 V due to the influence of the dark current and the field-driven photocurrent in practical devices,

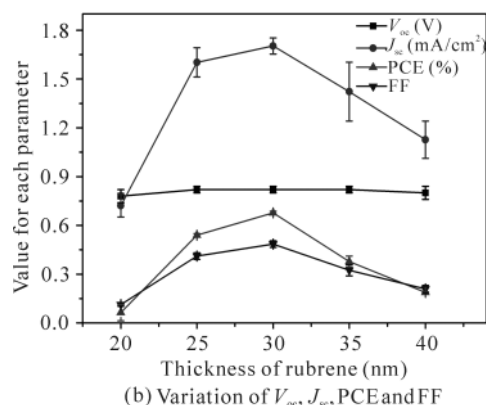
$$V_{oc} = \frac{1}{e} (|E_{HOMO}^{Donor}| - |E_{LUMO}^{Acceptor}|) - 0.3 \quad , \quad (1)$$

where E_{HOMO}^{Donor} is HOMO level of the donor, and $E_{LUMO}^{Acceptor}$ is LUMO level of the acceptor.

Although the thickness of rubrene layer varies, the energy gap between the HOMO level of rubrene and the LUMO level of C₇₀ is fixed. For this reason, V_{oc} is constant. However, the J_{sc} , FF and PCE are sharply improved with the increase of the thickness of rubrene layer up to 30 nm, and then decreased with the continuous increase of thickness, as shown in Fig.3(b). The optimum thickness of rubrene layer is 30



(a) $J-V$ curves



(b) Variation of V_{oc} , J_{sc} , PCE and FF

Fig.3 Photovoltaic performance of the OSCs with varying thickness of rubrene layer

nm. The active layer needs to be thin enough to shorten the distance for charge carrier transport and eventually reduce the probability of charge recombination. However, when the thickness of the active layer reduces, the number of the photons absorbed by the active material decreases, and thus less photocurrent is generated.

To study the dependence of J - V characteristics on the thickness of C_{70} layer, the devices with variable C_{70} layer thickness and an invariable rubrene thickness of 30 nm are fabricated. Fig.4 indicates the thickness of C_{70} layer does not influence the V_{oc} . However, the J_{sc} and PCE are drastically increased with the increase of the thickness of C_{70} layer up to 25 nm, and then abruptly decreased with the further increase of C_{70} layer thickness. The optimum thickness of C_{70} layer is 25 nm. The difference between optimum thicknesses of C_{70} layer and rubrene layer originates from the difference between the electron mobility in the C_{70} layer and the hole mobility in the rubrene layer. C_{70} electron mobility is determined by organic field effect transistor (OFET) measurement to be $\mu_e = 1.3 \times 10^{-3} \text{ cm}^2/\text{Vs}^{[11]}$, while rubrene hole mobility is $13 \text{ cm}^2/\text{Vs}^{[21]}$.

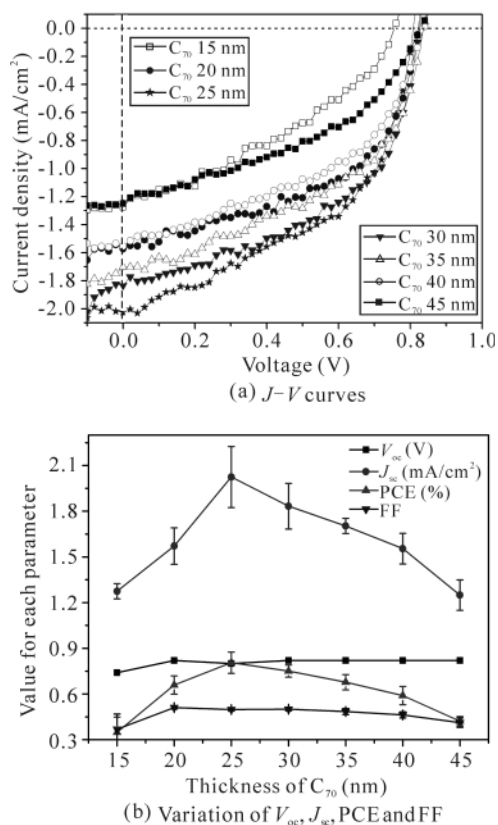


Fig.4 Photovoltaic performance of the OSCs with varying thickness of C_{70} layer

The degradation of OSCs which are exposed in air for 240 h after fabrication without encapsulation is investigated. All the photovoltaic characteristics are measured under the

illumination of $100 \text{ mW}/\text{cm}^2$ with an AM 1.5 G solar simulator. Between two measurements, the device is exposed in air without illumination, while the temperature is kept at $25 \text{ }^\circ\text{C}$, and the relative humidity is below 50%.

We can see in Fig.5(a) that the V_{oc} almost doesn't change with time (from 0.82 V to 0.8 V), while the J_{sc} decreases continuously with the increase of the time (from $1.54 \text{ mA}/\text{cm}^2$ to $0.36 \text{ mA}/\text{cm}^2$). In Fig.5(b), the V_{oc} almost doesn't vary with the increase of time, because the energy gap between the HOMO level of rubrene and the LUMO level of C_{70} is fixed. The J_{sc} , FF and PCE are continuously decreased over time. The decreases of J_{sc} and FF are caused by increase of the series resistance of the device. Fig.6 shows the series resistance is continually increased over time (from $60 \text{ } \Omega/\text{cm}^2$ to $3500 \text{ } \Omega/\text{cm}^2$). The increase of the series resistance is mainly due to both the decrease in carrier mobility of the organic layer and the deproavation of electrode/organic interfaces. As we all know, oxygen and H_2O vapor in ambient are two of the most important factors causing the degradation of OSCs. It is found that pure oxygen does not seem to speed up degradation, while the humidity profoundly influences the stability and leads to rapid degradation^[22,23]. However, Xi et al found that oxygen is the major factor in their work^[12]. Rusu et al found that the OSCs degradation under continu-

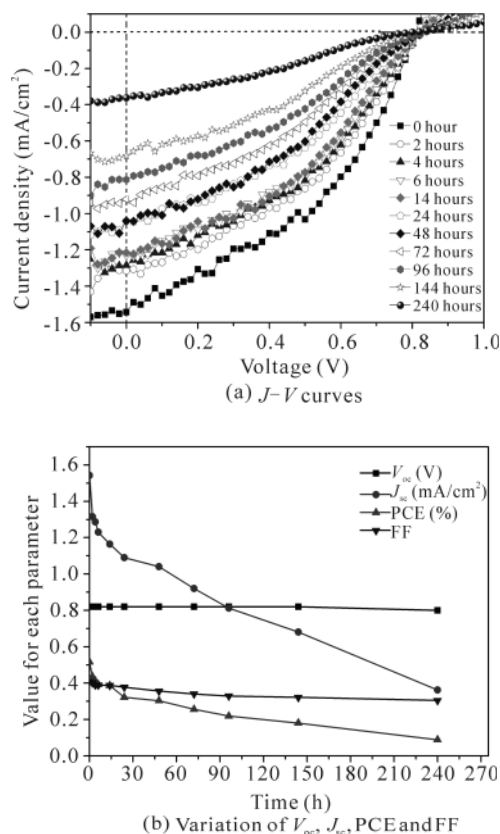


Fig.5 Photovoltaic performance of the OSCs over time

ous white-light illumination is mainly induced by the changes in the C_{60} electrical properties and at the CuPc/ C_{60} interface due to photo-assisted diffusion of O_2 ^[24]. We think that under an ambient condition, oxygen can diffuse and infiltrate into the active materials in cells, and may react with C_{70} in cells. The reaction causes electron traps in the lattice of C_{70} molecules, which increases the series resistance and leads to the degradation of cells. Moreover, the reaction of oxygen with the active materials should be fastened under illumination. More oxygen molecules diffuse and infiltrate into the acceptor layer, more electrons can be recombined, which can lead to the increase in interfacial series resistance and worse OSCs performance.

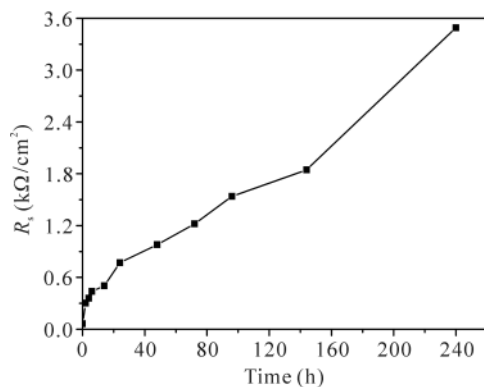


Fig.6 Variation of the series resistance over time

The optimization of rubrene/ C_{70} heterojunction solar cells is investigated. The results indicate the thicknesses of the donor (rubrene) and the acceptor (C_{70}) do not change the V_{oc} . However, J_{sc} and PCE are increased along with rubrene layer thickness up to 30 nm, and then abruptly decreased as the continuous increase of the thickness of rubrene layer. Likewise, J_{sc} and PCE are increased with C_{70} layer thickness up to 25 nm and then suddenly decreased with the further increase of thickness of C_{70} layer. Therefore, the optimum thicknesses of rubrene layer and C_{70} layer are determined as 30 nm and 25 nm, respectively. The PCE of the optimum device is 0.81%. The degradation of rubrene/ C_{70} heterojunction solar cells is also investigated. The result indicates the V_{oc} does not change over time. However, oxygen in ambient can diffuse and infiltrate into the active materials in cells, and may react with C_{70} in cells, which could result in the increase of interfacial series resistance. The J_{sc} and FF are decreased continuously over time, which can lead to the continuous decrease of the PCE.

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