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Effect of trap-assisted recombination on open-circuit voltage loss in phthalocyanine/fullerene solar cells

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ABSTRACT

Large energy losses in open-circuit voltage (V_{OC}) are still an issue for the photo-conversion efficiency of organic` solar cells (OSCs). We clarify the relationship between charge recombination and V_{OC} loss for phthalocyanine/fullerene planar heterojunction (PHJ) OSCs. We quantify the V_{OC} loss relative to the charge-transfer state energy by the temperature dependence of V_{OC}. The charge recombination order obtained from impedance measurements indicates the presence of trap-assisted recombination. Our results suggest that the V_{OC} losses are caused by the broad distribution of the tail state near the donor/acceptor (D/A) interface in the PHJ device. Thus, reducing the number of trap states near the D/A interface could lead to an increase in V_{OC}.

1. Introduction

Open-circuit voltage (V_{OC}) is an important parameter in determining the performance of organic solar cells (OSCs) [1]. It depends primarily on the energy level difference (E_{DA}) between the highest occupied molecular orbital (HOMO) of the electron donor material (D) and the lowest unoccupied molecular orbital (LUMO) of the electron acceptor material (A) [2]. However, the observed value of eV_{OC} (where e is the elementary charge) is always much lower than E_{DA} [3], and the consequent energy loss has been identified as a significant issue that hinders OSC performance.

In the open-circuit condition, the photo-generated charges are described as an equilibrium between the charge transfer and charge separated states at the donor/acceptor (D/A) interface [4]. The charge-transfer state energy (E_{CT}) is equal to E_{DA} minus the coulomb binding energy [4,5]. However, the photo-generated charges decay to the ground state through charge recombination, which causes a loss of energy between E_{CT} and eV_{OC}; therefore, the charge recombination process is important for estimating the V_{OC} loss. In ideal solar cells, the V_{OC} loss is solely due to bimolecular recombination [6]. However, in OSCs, trap-assisted recombination also causes additional V_{OC} loss [7,8].

In this study, we clarify the relationships between the V_{OC} loss and the charge recombination process. The V_{OC} loss relative to the E_{CT} is quantified in a phthalocyanine (H_2Pc)/fullerene (C_{60}) planar-heterojunction (PHJ) cell that is a typical materials combination in OSCs. To investigate the origin of the V_{OC} loss in H_2Pc/C_{60} devices, we estimate the ideality factor (n), which indicates the charge recombination type. In addition, we observe the temperature dependence of the charge recombination behavior by impedance spectroscopy. Finally, we propose a way to decrease the V_{OC} loss based on these experimental results.

2. Results and discussion

The PHJ device was fabricated by thermal evaporation under high vacuum, and had an ITO/MoO_3/H_2Pc/C_{60}/BCP/Al structure (Fig. 1(a)). An atomic force microscopy (AFM) image of H_2Pc surface is shown in Fig. 1(c). The arithmetic mean roughness (R_a) of the film surface was 1.65 nm. We measured a V_{OC} of 0.47 V, short-circuit current (J_{SC}) of 2.84 mA cm^{-2}, fill factor of 0.59, and power-conversion efficiency of 0.78% at room temperature under simulated solar illumination (AM 1.5, 100 mW cm^{-2}). These values are similar to those reported in previous studies [9,10].

We estimated the V_{OC} loss relative to the E_{CT} values obtained from the temperature dependence of the $J–V$ characteristics (Fig. 2(a)). Since the E_{CT} is a low temperature limit for the V_{OC}, we can extract the E_{CT} values as the intercept of the linear plots of V_{OC} as a function of temperature [5]. The temperature dependence of V_{OC} was plotted in Fig. 2(b). This shows that V_{OC} decreased from 0.54 to 0.42 V as the temperature increased from 275 to 317 K. The change in V_{OC} with temperature can be expressed as follows:

$$eV_{OC} = E_{CT} - nkT\ln\left(\frac{J_{00}}{J_{ph}}\right), \quad (1)$$

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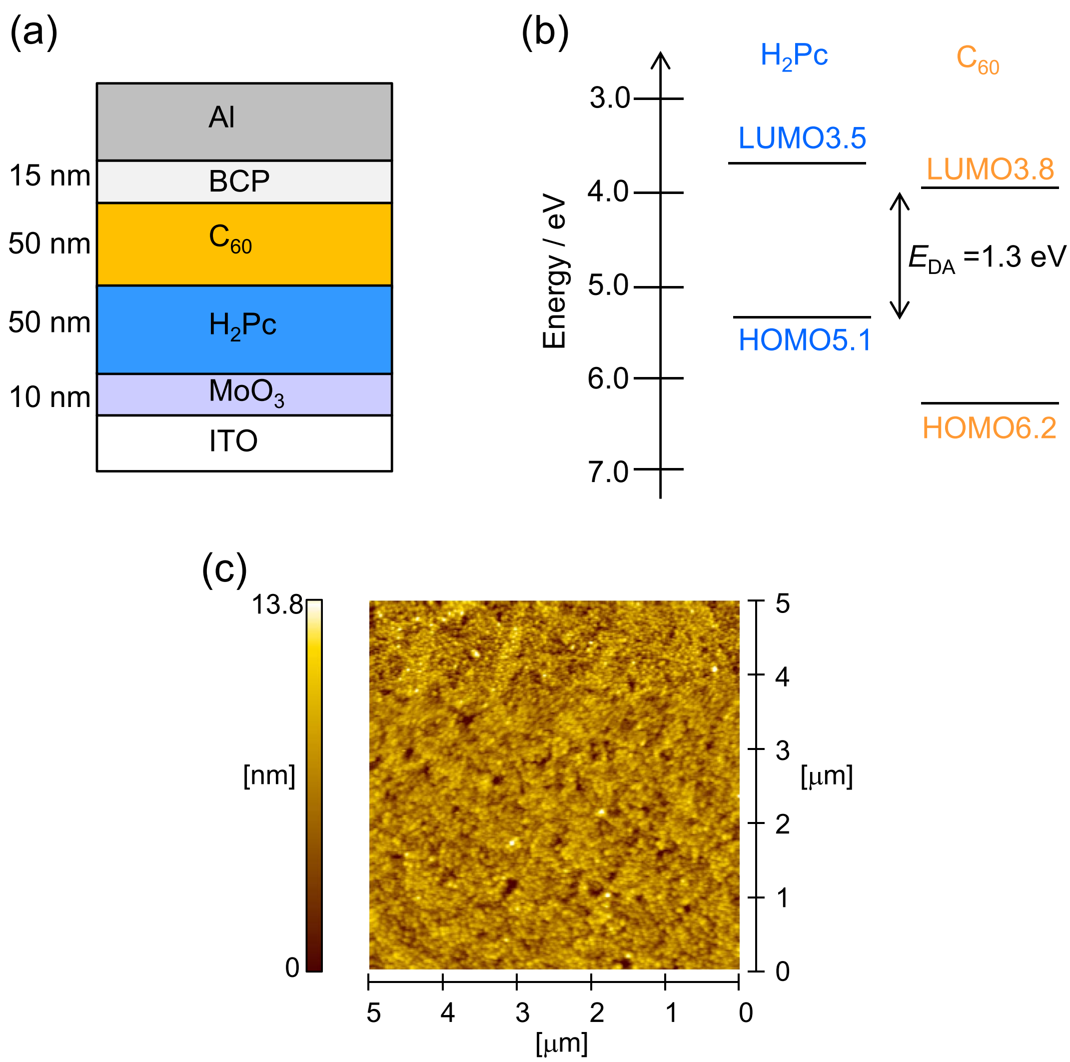

Fig. 1. Schematics of (a) the H_2Pc/C_{60} OSC device and the (b) H_2Pc and C_{60} energy levels. (c) AFM image of 50 nm thick H_2Pc film on ITO/MoO_3.

where k is Boltzmann's constant, T is the temperature, J_{ph} is the photogenerated current density, and J_{00} is the pre-exponential factor of the reverse saturation current density. For the results shown in Fig. 2(b), this gives an E_{CT} of 1.34 eV, which is roughly equal to the E_{DA} for H_2Pc/C_{60}. As the energy loss between E_{CT} and eV_{OC} at room temperature was 0.87 eV, more than half of the energy was lost owing to charge recombination.

Next, to identify the type of charge recombination occurring in the OSC, we estimated the ideality factor n from the light intensity dependence of the J–V characteristics shown in Fig. 2(c). Since the slope of the relationship between V_{OC} and the light intensity can be represented as nkT [11,12], we can extract n from the slopes of these plots. In ideal p–n junctions where recombination is dominated by bimolecular recombination, i.e., band-to-band recombination, n is equal to unity. However, in classical p–n junctions, n has been reported to increase owing to Shockley–Read–Hall (SRH) recombination [13]. An n value greater than unity also indicates the presence of trap-assisted recombination in OSCs [14,15]. The relationship between light intensity and V_{OC} is plotted in Fig. 2(d), which shows that V_{OC} increased from 0.34 to 0.53 V as the light intensity increased from 5 to 400 mW cm^{-2}. The slope of a linear fit to this data gives $n = 1.57$, thus indicating the occurrence of both bimolecular and trap-assisted recombination in this PHJ device. Eq. (1) expresses the energy loss between E_{CT} and eV_{OC} in terms of n, k, T, J_{ph}, and J_{00}. We calculated that $J_{00} = 7.19 \times 10^9$ mA cm^{-2} using the J_{SC} values for J_{ph}, obtained n values, and slope of the temperature dependence of V_{OC}. The value of J_{00} is related to the charge recombination rate [16]. The contributions of J_{00} and n to the V_{OC} loss are as follows [7]:

$$eV_{rec}\ \text{loss} = kT\ln\left(\frac{J_{ph}}{J_{00}}\right)\ \text{and}$$

$$eV_{trap}\ \text{loss} = (n-1)kT\ln\left(\frac{J_{ph}}{J_{00}}\right).$$

The J_{ph}/J_{00} ratio corresponds to the balance between the charge generation and recombination rates. V_{rec} represents the energy loss in the ideal case where n is unity and V_{trap} represents the additional loss when n is greater than unity, i.e., the contribution of trap-assisted recombination. The values of V_{rec} and V_{trap} were calculated to be 0.55 and 0.32 V, respectively (Fig. 2(e)).

To investigate the charge recombination process, we performed impedance spectroscopy to obtain the recombination lifetime τ and carrier density N for the PHJ device. Cole-Cole plots were measured under various light intensities from 10 to 400 mW cm^{-2} with DC voltages equal to V_{OC} applying to the device, and the results are shown in Fig. 3(a). The observed capacitive semicircles are fitted using simple parallel RC elements as the active layer and a direct R as the contact resistance (Fig. 3(a), bottom) [17,18]. The fitting results are consistent with the experimental data. The recombination lifetime τ was calculated from the RC constant, and its light intensity dependence is shown