Current Mode Atomic Force Microscopy (C-AFM) Study for Local Electrical Characterization of Conjugated Polymer Blends

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Abstract A blend of regioregular poly(3-hexylthiophene) (P3HT) and poly{[*N,N'*-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)} (P(NDI2OD-T2)), which has the potential for polymer solar cells application, was prepared for current mode atomic force microscopy (C-AFM) measurements in this study. Phase-separated domains and the local electrical characteristics of P3HT/P(NDI2OD-T2) blends were investigated by the C-AFM.

Keywords Current mode AFM · Polymer solar cells · Conjugated polymer · Polymer blends

INTRODUCTION

To utilize the energy of the sunlight and generate electricity without polluting the environment, solar cells are now widely investigated. Conjugated polymers that present light-harvesting and charge-transporting properties are one of the promising materials for use in solar cells (Inganäs et al. 2009; McNeill and Greenham 2009; Heeger 2010). Hole-transporting and electron-transporting polymers with different energy levels can be blended, causing charge separation at their phase-separated interface. To optimize device performance, the phase-separated domains and local electrical properties of conjugated polymer blends must be characterized since they are closely related to the charge separation and carrier transport. Current mode atomic force microscopy (C-AFM) is a powerful method for characterizing conductive thin films. This method can probe the overall microstructure of the thin film since the voltage is applied between the sample stage and the C-AFM cantilever to induce the current flowing across in the direction of the film thickness. With applying the voltage, the local current through the bulk can be

measured by C-AFM with the topographic scan. The greatest advantage of C-AFM is that it can efficiently examine the material functionality, and especially for its electrical properties. An addition of current mode to conventional AFM allows us to characterize the phase separation of conjugated polymer blends for polymer solar cells (PSCs). A C-AFM image presents a current contrast that results from the differences in semiconducting properties of the two polymers and is adopted to identify domain structure, size, and composition with high resolution. Moreover, measuring local current–voltage (I – V) characteristics using C-AFM can directly investigate the current-transporting properties in the confined domain or area, which is difficult to be examined by bulk I – V measurements.

In this study, a blend of regioregular poly(3-hexylthiophene) (P3HT, from Aldrich) and poly{[*N,N'*-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)} (P(NDI2OD-T2, from Polyera)) was prepared for C-AFM measurements. The blend shows high potential for PSCs application because of its wide-range absorption of visible light wavelengths and its high carrier mobility (Szendrei et al. 2010). *p*-Xylene was used as the solvent of P3HT and P(NDI2OD-T2). To prepare the sample, a PEDOT:PSS layer was first pre-coated on ITO glass and the P3HT/P(NDI2OD-T2) layer (50/50 by weight fraction) was then spin-cast on the pre-coated PEDOT:PSS. The commercial AFM (SPM-9600) from Shimadzu was employed. All the measurements were made using a conductive cantilever with Pt/Ir coating.

RESULTS AND DISCUSSION

Figure 1a displays a topographic image of the P3HT/P(NDI2OD-T2) = 50/50 blend; the difference in height was

Fig. 1 **a** Topographic image of P3HT/P(NDI2OD-T2) = 50/50 blends ($10\ \mu\text{m} \times 10\ \mu\text{m}$), **b** current image of P3HT/P(NDI2OD-T2) = 50/50 blends ($10\ \mu\text{m} \times 10\ \mu\text{m}$, applied voltage was 4.5 V at ITO side),

c energy level diagram of P3HT, P(NDI2OD-T2), ITO/PEDOT:PSS and Pt/Ir, **d** local *I*-*V* curve for P3HT domain by C-AFM, and **e** local *I*-*V* curve for P(NDI2OD-T2) domain by C-AFM

observed for the phase-separated domains. Current image with applying positive 4.5 V at the ITO substrate is demonstrated in Fig. 1b. The current distribution yielded a clear contrast, which could be correlated with the electric profiles of compositions. Figure 1c shows the energy level diagram of P3HT, P(NDI2OD-T2), ITO/PEDOT:PSS, and Pt/Ir. It shows that the difference between the HOMO level of P3HT and the Fermi level of the electrodes (ITO and Pt/Ir coated cantilever) is rather small, therefore, holes are easily injected from ITO to P3HT and electrons suffer a high energy barrier at the present cell configuration. A similar phenomenon was also studied in the other semiconducting polymer system (Alexeev et al. 2008). Injected holes (positive current) may preferentially flow through the hole-transporting polymer P3HT, and hence the current contrast in Fig. 1b can be attributed to the fact that P3HT phases have a higher positive current flow (red area) than the P(NDI2OD-T2) phases (blue area). The high-lying and low-lying structures in Fig. 1a can be related to the P3HT and P(NDI2OD-T2) phases, respectively. Accordingly, the compositions are identified by the current image.

Local electrical properties were determined from local I - V measurements by C-AFM. Figure 1d and e demonstrates the local I - V curves for the P3HT and P(NDI2OD-T2) domains in Fig. 1b, respectively. Figure 1d reveals a significant current response of P3HT domains to an applied voltage, which indicates that P3HT domains more effectively pass the local positive current. However, P(NDI2OD-T2) domains pass only very weak positive current since they respond negligibly to an applied voltage, as displayed in Fig. 1e. Different local I - V characteristics for P3HT and P(NDI2OD-T2) domains suggest that the positive current (hole) transports more effectively in P3HT domains than that in P(NDI2OD-T2) domains.

In this study, C-AFM was successfully adopted to detect phase-separated domains and the local electrical characteristics of P3HT/P(NDI2OD-T2) blends, since P3HT and P(NDI2OD-T2) have different current-transporting properties and I - V characteristics. In the future, local electrical properties of nano-structured polymer blends will be further examined with high resolutions of a few tens nanometers as the sensitivity of the current setup is increased. Thus, C-AFM is expected to be very useful for developing highly efficient PSCs.

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