Photo-generated charge behaviors in all-polymer solar cells studied by Kelvin probe force microscopy

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ABSTRACT

Photo-generated charge behaviors in the bulk heterojunctions (BHJs) of all-polymer solar cells (PSCs) are studied by Kelvin probe force microscopy (KPFM). Root-mean-square deviations (RMSDs, R_q) of the contact potential difference (CPD) images are applied to quantitatively characterize the phase segregations of the BHJs. When the BHJs are illuminated, CPD values and R_q of CPD images are changed, which attributes to the photo-generated charge transfer and accumulation. Inner structures of the BHJ are thus extrapolated by studying the charge behaviors, demonstrating KPFM an effective technique to study the relationship between inner structures and photovoltaic activities in all-PSCs.

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1. Introduction

Increased research activities on polymer solar cells (PSCs) have been witnessed in the recent years due to their unique advantages such as low cost, light weight, mechanical flexibility, options for up-scaling and roll-to-roll printing [1,2]. So far, mixed bulk hetero-junction (BHJ) PSCs based on polymer/fullerene systems have been mostly studied and shown power-conversion efficiencies (PCEs) over 10% [3–6]. On the other hand, all-polymer solar cells (all-PSCs) [7], in which n-type semiconducting polymers are introduced instead of fullerene derivatives serving as electron acceptors have become attractive with rapidly improving PCEs [8]. With the ability of flexible molecular design of polymeric donors and acceptors, the energy levels can be well tuned and the absorption coefficient to visible light can be highly improved. Consequently, there is a high potential to reach even higher PCEs than fullerene-based PCSs.

Phase segregation with the size around 10 nm and bi-continuous interpenetrating network is a target for fabricating high performance PSCs [9]. The characterization of phase segregation is therefore of significant importance. Transmission electron microscopy (TEM) is a common technique to study phase segregation of polymer/fullerene BHJs [10,11], but it is not suitable for all-PSCs because of the weak contrast between the polymer components. Kelvin probe force microscopy (KPFM) [12,13], which measures the contact potential difference (CPD) between the KPFM tip and the sample [14–16], has been widely used to investigate the electronic properties in photovoltaic devices [17–20]. Recent work has demonstrated KPFM a powerful technique to characterize the phase segregation and visualize the bottom component distribution of the BHJs in all-PSCs [21]. The photovoltaic behaviors of all-PSCs, however, have rarely been studied by KPFM. Since charges existed in a sample can be reflected in CPD [22], photo-generated charge behaviors in all-PSCs are expected to be visualized in CPD images.

Here, we present a study on BHJs of all-PSCs consisting of poly [2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] (PTQ1) [23] and Poly{[N,N′-bis(2-octyldodecyl)-naphtha-lene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5′-(2,2′-bithio-phene)} (N2200) [24] by PeakForce KPFM (PF-KPFM) [22,25]. The chemical structures of PTQ1 and N2200 are presented in Fig. 1a. Solvent influence on phase segregation is firstly discussed. BHJs are then characterized in the dark and with illumination. Photo-generated charge behaviors are analyzed in view of inner structures in the BHJs.

2. Experimental details

Patterned indium tin oxide (ITO, 15 Ω sq^{-1}) coated glass

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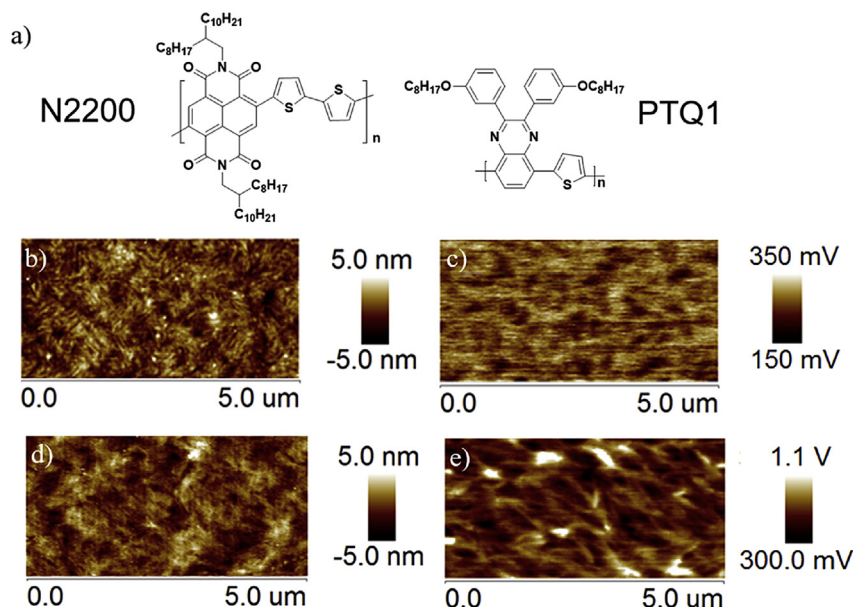 E-mail address: chilf@suda.edu.cn (L. Chi).

Fig. 1. a) Chemical structures of PTQ1 and N2200; b, d) topography and c, e) CPD images of BHJs spin-coated from chloroform (b, c) and chlorobenzene (d, e).

substrates were cleaned by ultrasonication in acetone and iso-propanol (10 min) sequentially, and organic residues on the ITO surfaces were then removed by oxygen plasma (2 min). A layer of poly (3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS; CleviosTMP VP AI4083, Heraeus) was spin-coated (4000 r.p.m., 30 s) on the ITO from a 1:1 water diluted solution, followed by thermal annealing (110 °C, 10 min) to remove the residual water. The PTQ1:N2200 BHJs were then spin-coated from chlorobenzene (18 mg/mL, 3000 r.p.m., 40 s) or chloroform (10 mg/mL, 3000 r.p.m., 40s) and thermally annealed (100 °C, 10 min). The component ratios of donor and acceptor (D:A) in BHJs are 2:1 if no special statement. For studying the influences of component ratios on the phase segregation, other D:A ratios were chosen as will be discussed below.

The PF-KPFM (Dimension Icon, Bruker) measurements were performed under ambient conditions with MESP-RC probes. All samples were stored in a glove box with nitrogen atmosphere before KPFM experiments. KPFM operates in lift mode, in which the topography is obtained at first scan by PeakForce tapping mode [26], and the cantilever is lifted at a constant height to measuring the CPD values by following the topography profile. During KPFM measurement, a dc-voltage (V_{dc}) is applied to the sample and is tuned to achieve equal potential between KPFM tip and sample. At the moment, the long-range electrostatic force between KPFM tip and sample is nullified, and the dc-voltage now is named as V_{null}. Thus, the CPD value is obtained: $V_{CPD} = V_{tip} - V_{sample} = V_{null}$, where V_{tip} and V_{sample} are the potential of tip and sample, respectively. Note here that the CPD value mirrors the surface potential of sample. For KPFM measurements with illumination, a halogen lamp was applied to generate the illumination.

3. Results and discussion

3.1. Solvent influence on phase segregation of BHJs

All-PSCs consisting of PTQ1 and N2200 are well studied systems and have shown high device performances with the BHJs spin-coating from chloroform [27]. Fig. 1b and c shows AFM topography and CPD images of the PTQ1:N2200 BHJ fabricated with

chloroform. The contrast in the CPD image is attributed to materials with different electronic properties. Therefore, it indicates the phase segregation of the BHJ. The weak contrast shown in Fig. 1c arises from the limitation of KPFM resolution and a well-mixed polymer blend. Typically, the solvent has a significant influence on the device performance of PSCs [28]. A solvent resulting in a well-mixed polymer blend with small domain size of phase segregation usually leads to a good device performance. A bad phase segregation with large domain size leading to reduced device performances, however, is easier to be measured and analyzed by KPFM. Fig. 1d and e shows the topography and CPD images of the PTQ1:N2200 BHJ made from chlorobenzene. Both the topography and CPD images are obviously distinguished from those of BHJs made with chloroform. The CPD image of Fig. 1e yields a much higher contrast compared to Fig. 1c, and BHJs studied in the following are thus fabricated with chlorobenzene as the solvent. The performances of devices made from chloroform and chlorobenzene are presented in Table 1.

3.2. KPFM results on BHJ with illumination

3.2.1. CPD value shift and bottom component distribution in the BHJ

For BHJs made from chlorobenzene, besides the microscopic phase segregation, macroscopic phase segregation with domain sizes of several micrometers usually appear in the CPD images, see Supporting Information Fig. S1. Fig. 2 presents CPD images (Fig. 2a, b) and the corresponding CPD value histograms (Fig. 2c) of a BHJ measured in the dark and under illumination. The whole area is divided into two parts: area A and B. The CPD values in area A are lower than those of area B when measured in the dark (blue curves in Fig. 2c). When the BHJ is illuminated, CPD values in the whole area are increased, and the values in area A and B increase by

Table 1
The photovoltaic parameters of devices made from chloroform and chlorobenzene.

Solvent	J_{SC} (mA/cm^2)	FF (%)	V_{oc} (V)	PCE (%)
Chloroform	6.6	558	0.82	3.1
Chlorobenzene	2.4	50	0.83	1.0