Spontaneous phase separation for efficient polymer solar cells

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Inducing self-organized phase separation in polymer-fullerene blends by using patterned substrates to modify surface energies improves the performance of organic photovoltaics.

Polymer solar cells offer a potentially inexpensive way to produce electricity from sunlight and are therefore receiving an increasing amount of attention. Many of these cells have a ‘bulk heterojunction’ structure, which is produced by blending conjugated polymers with the spherical carbon molecules known as fullerenes (C_{60}). The conjugated polymers and fullerenes have different electrical properties. The polymer is a p-type conductor, with positive ‘holes’ as its major charge carrier, while the fullerenes are an n-type conductor, with negative electrons as their major charge carrier. These two materials naturally form a randomly interpenetrating network with a large interfacial area, which ensures the highly efficient dissociation of excitons. These are electron-hole pairs that form when a photon of light hits the solar cell. They subsequently separate into individual holes and electrons when they encounter a junction between the two types of conductors.

Because the separated electrons and holes must then move through two different materials to the electrodes—the polymer for the holes and the fullerenes for the electrons—the precise structure of the polymer-fullerene blend plays an important role in determining the efficiency of the solar cell. Ideally, the conjugated polymer and fullerenes would be vertically separated, with an average interspacial distance that is equal to or less than the exciton diffusion length (10–20nm). Furthermore, the polymer-fullerene blend should be aligned perpendicular to the electrodes to provide direct pathways for efficient charge transportation.

Several research groups have attempted to fabricate polymer solar cells that possess this kind of vertical separation between the conjugated polymer and the fullerenes. The group of Arias reported that organic solvents with high boiling points enhanced the vertical phase separation of a polymer mixture. Kim and colleagues used an imprint method to generate an ordered structure on a polymer thin film. By depositing an n-type conductor onto the artificial structure, the researchers managed to induce vertical separation.

Recently, we reported an effective method for inducing self-organized phase separation in polymer solar cells, leading to an ideal structure and an improved power conversion efficiency. This phase separation was achieved by using microcontact printing (µ-CP) to pattern the device buffer layer into two regimes with different surface energies.

Pattern-directed spinodal decomposition has been reported in polymer blends with patterned surfaces of self-assembled monolayers (SAMs). These SAM materials can modify the surface energy of the substrate, which controls local boundary interactions between the polymer blends and the substrate, resulting in directed phase separation. In other words, phase separation in the polymers can be induced by patterning the substrates.

Continued on next page
Figure 2. Tapping mode AFM images of the self-assembled monolayer (SAM)-patterned PEDOT:PSS films (a, c, e) and the P3HT:PCBM layer on the SAM-patterned PEDOT:PSS films (b, d, f). The grating sizes were 1.00 µm in (a) and (b); 0.75 µm in (c) and (d); and 0.50 µm in (e) and (f).

Figure 1 illustrates the process. Using µ-CP, a polydimethylsiloxane mold produces a defined pattern in a SAM prepared from 3-aminopropyltriethoxysilane on a layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), which has been deposited on an indium tin oxide (ITO) substrate.

To produce the active layer, poly(3-hexylthiophene) (P3HT) and the fullerene derivative (6,6)-phenyl-C_{61}-butyric acid methyl ester (PCBM) (1:1, w/w) are dissolved in 1,2,4-trichlorobenzene. This solution is then spin-coated onto the SAM-patterned PEDOT:PSS layer. After spin coating, the active layer is spontaneously dried to induce lateral phase separation, and the polymer film is then heated at 110°C for 15min to remove the residue solvent. Finally, aluminum and calcium are deposited onto the active layer to form the cathode.

We first examined the SAM grating pattern on the PEDOT:PSS layer using an atomic force microscope (AFM). Figure 2, panels (a), (c), and (d) show AFM images of SAM patterns of varying sizes. When the grating size was 0.5 µm, the edge of the grating was slightly unclear due to defects in the template. After coating the P3HT/PCBM blend onto the patterned surface, phase separation clearly occurred in line with the grating pattern, as shown in Figure 2(b), (d), and (f). It appears that the underlying pattern induced the self-organized phase separation.8 Driven by the two different surface free energies on the PEDOT:PSS layer, P3HT and PCBM adhered spontaneously and selectively onto their preferred individual surfaces.

Figure 3 displays the electrical characteristics of devices incorporating the various grating patterns, showing that the device efficiency increases as the grating size decreases. The device covered with the SAM with no patterning showed poor performance, with a calculated power conversion efficiency (PCE) of 1.43%. For grating diameters of 1.00 and 0.75 µm, the PCE values increased to 2.22 and 2.41%, respectively. At a grating spacing of 0.5 µm, the PCE improved to 2.47%.

We are now exploring a number of different approaches for further improving the efficiency of these devices. These include reducing the dimensions of the grating to the diffusion length of excitons in order to suppress exciton quenching. We also plan to use a dot-like pattern, rather than the striped patterns that we employed here to demonstrate the concept. With such a 3D interpenetrating structure, a dot-like pattern would increase the area of the p-n junctions and might further improve the efficiencies of charge separation and transportation. In addition, inserting hole- and electron-blocking layers between the cathode and anode, respectively, and the active layer might inhibit the recombination of charges at the electrodes.2

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References