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Self-vertical phase separation study of nanoparticle/polymer solar cells by introducing fluorinated small molecules†

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A new approach to induce self-vertical phase separation of nanoparticle/polymer hybrid solar cells is reported by introducing fluorinated small molecules into the active layer. The formation of a vertically gradient structure improves not only polymer organization but also charge transport efficiency, thus increasing the photovoltaic cell performance by a factor of 5.

Polymer solar cells (PSCs) are known have the advantages of light weight, large area, low manufacturing cost and mechanically flexibility over the past decade.¹ In PSCs, bulk heterojunctions (BHJ) comprising a bi-continuous network of electron donating and electron accepting phases, achieve the highest power conversion efficiencies (PCE).² Promising power conversion efficiencies of 7–9% have been achieved on using blends of new conjugated polymers, such as PCPDTBT,^{3a} PSBTBT,^{3b} PTBs^{3c} and PBDTTTs^{3d} with fullerene derivatives.^{3e}

An alternative type of polymer solar cell including polymer and inorganic nanoparticles is appealing because of the relative high electron mobility and excellent physical and chemical stability of inorganic nanoparticles.⁴ Various inorganic nanoparticles, such as CdSe,^{4a,5a} PbS,^{5b} ZnO^{5c} and TiO₂,⁶ have been successful used in polymer/inorganic nanoparticles hybrid solar cells. The use of environmentally friendly materials of low toxicity is mandatory for the development of new energy technology; therefore, TiO₂ is a good candidate instead of CdSe or PbS nanoparticles. In addition, TiO₂ is a low cost material, which is synthesized by using a low energy consumption sol–gel process. In BHJ structures, separation and transport of charge carriers are critical factors on the performance of solar cells. In polymer/fullerene solar cells, several approaches including

annealing treatment^{7a,b} and adding additives,^{3a,7c–d} have been used to form a bi-continuous phase to facilitate the charge separation and charge transport and further enhance the performance. However, an effective approach to improve the nanoscale phase separation and charge generation in the polymer/inorganic nanoparticle hybrid solar cells is scant.

Recently, vertical phase segregation in BHJs with organic molecule semiconductors has been shown to improve the PCE of polymer solar cells.⁸ Hashimoto *et al.* investigated the blending of a polymer and fullerene derivative containing fluorocarbon side chains (F-PCBM) for high performance solar cells.^{8c} Due to the spontaneous vertical segregation, the fullerene derivative with fluorocarbon side chains formed a self-organized buffer layer at the interface between the active layer and metal cathode. The spontaneous formation of the buffer layer of F-PCBM noticeably improved the performance of the solar cells thereby improving the fill factor and series resistance.

In this work, we manifest a facile method to achieve vertical phase separation in hybrid photovoltaics by introducing fluorinated small molecules into the BHJs of poly(3-hexylthiophene) (P3HT) and TiO₂ nanorods. Two fluorinated small molecules, tris(perfluorophenyl)borane (B(C₆F₅)₃, BCF) and 2,6-(2,3,5,6-ditetrafluorobenzonitrile)-4,4'-dihexyl-4H-cyclopenta-[2,1-b:3,4-b']dithiophene (FBN-CPDT), were introduced into the blending of P3HT/TiO₂ nanorods. The two small molecules were chosen to have different characteristics in the blend. The BCF molecule is a potent Lewis acid that has been studied for band gap control in conjugated oligomers⁹ and found extensively as an activator in organic synthesis.¹⁰ FBN-CPDT is a small chromophore molecule derived from dihexyl carbon fused bithiophene.¹¹ In this study, we demonstrate an approach to facilitate charge transport by controlling the vertical phase separation between the polymer and inorganic nanoparticles.

The synthesis of TiO₂ nanorods and the fabrication of OPV cells are depicted in the electronic supplementary information (ESI†). The chemical structures and UV-Visible absorption spectra of the two fluorinated molecules are shown in Fig. 1. FBN-CPDT exhibits absorption in the wavelength of 400–500 nm and BCF has no absorption beyond 400 nm. Both compounds exhibit low surface energy due to the presence of fluorinated group. The matter of low surface energy prefers to migrate toward

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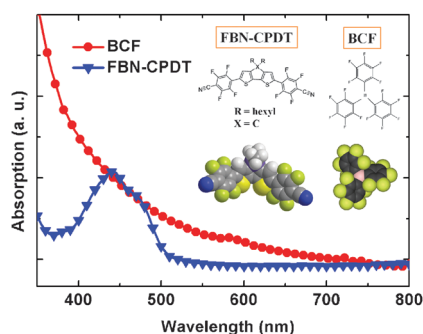


Fig. 1 Chemical structures and absorption spectra of fluorinated molecules which are used in the P3HT–TiO₂ hybrid system.

the air at the interface between liquid and air. If we add the fluoro molecule into the hybrid of P3HT and TiO₂ nanorods, we speculate that the fluorinated molecule will migrate towards the air and take the hybrid material upwards simultaneously during the film formation process.

To examine the changes in morphology upon the addition of either BCF or FBN-CPDT to the BHJ films, cross-sectional images of the hybrid films comprising P3HT, TiO₂ nanorods and the fluorinated molecule were taken by scanning electron microscopy. These thin films were fabricated from the ternary solution consisting of P3HT, TiO₂ nanorods and fluorinated molecule in a weight ratio of 46 : 53 : 1 respectively. Thus, the amount of the fluorinated molecule is very small as compared to that of P3HT and TiO₂ nanorods. Fig. 2 shows that the cross-sectional structure of the P3HT–TiO₂ active layer has a distinct vertical phase-separation when the layer contains either 1 wt% of BCF or FBN-CPDT. Fig. 2(a) indicates that the TiO₂ nanorods (some of them are shown in red circles for clarity) are distributed randomly in the active layer (P3HT–TiO₂) without the fluorinated molecules. However, the TiO₂ rich domain with the thickness of *ca.* 106 nm and 59.2 nm for BCF and FBN-CPDT respectively, is clearly observed for an active layer thickness *ca.* 180 nm as shown in the corresponding Fig. 2(b) and (c). Due to the strong electron withdrawing characteristics of the fluorine atom and the empty Pz-orbital on boron, BCF is considered as a strong Lewis acid; FBN-CPDT can be regarded as electron deficient small molecule. When we synthesized the TiO₂ nanorods, we modified the surface of TiO₂ with pyridine so they can be compatible with P3HT.¹² Thus, the acidic fluorinated molecule

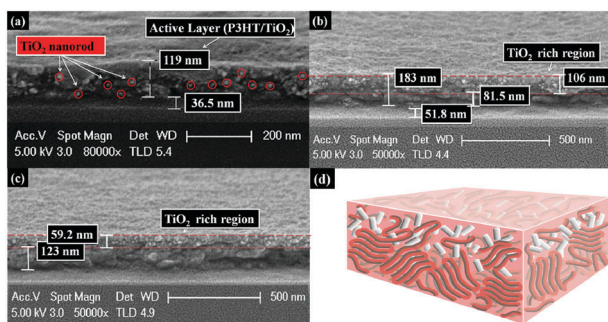


Fig. 2 SEM images of (a) P3HT–TiO₂ without fluorinated molecule, (b) P3HT–TiO₂ with 1 wt% BCF and (c) P3HT–TiO₂ with 1 wt% FBN-CPDT. (d) Schematic of the distribution of P3HT and TiO₂ in the active layer with the fluorinated molecules.

was naturally coordinated to the basic pyridine–TiO₂ as a complex while they were added to the blend of P3HT–TiO₂ nanorods. It is possible that the upward migration of the fluorinated molecules would induce both P3HT and TiO₂ nanorods to move upward as well. However, the TiO₂–fluorinated small molecule complex has higher upward tendency than P3HT which results in a spontaneous self-vertical phase separation between TiO₂ and P3HT during the spin coating process. The formation of a vertical phase separation facilitates the charge transport toward the corresponding electrode. The linear molecular conformation of FBN-CPDT is expected to have stronger vertical shear force than the spherical conformation of BCF because of the better contact of a linear molecule with TiO₂ nanorods (see Fig. 1 insets). The cross-sectional SEM morphology studies prove this interesting hypothesis as shown in Fig. 2a and b. The FBN-CPDT is indeed more effective in causing vertical phase separation and results in a thinner TiO₂ rich domain as compared with that of BCF (59.2 vs. 106 nm).

The P3HT dominates the absorption in the hybrid film of P3HT–TiO₂–fluorinated molecule because the concentration of the fluorinated molecules is quite low (~1% by weight). However, Fig. 1S (ESI[†]) shows a large increase in the absorbance per unit thickness of P3HT (400–650 nm) when the fluorinated molecule was added into P3HT–TiO₂. A stronger absorbance implies a higher short circuit current density (*J*_{sc}) of PSCs. Furthermore, the more prominent shoulder peaks at 600 nm indicates that the addition of fluorinated molecule results in a higher ordered crystal structure of the P3HT molecules. Fig. 1S(b) and 1S(c) (ESI[†]) illustrate how the fluorinated molecules affect the stacking of P3HT in the P3HT–TiO₂ hybrid film. Without the fluorinated molecules as sketched in Fig. 1S(b),[†] the P3HT molecules were dispersed evenly with the TiO₂ nanorods to form small size P3HT crystallines. With the fluorinated molecules, the reasons of improved P3HT absorption are that (1) P3HT molecules become more extended and exhibit good stacking of P3HT from the migration of fluorinated molecules and (2) TiO₂ nanorods segregate to the surface of the film forming a P3HT rich domain on the substrate. The P3HT-rich domain is likely to be organized to have higher crystallinity due to lower disruption from the TiO₂ nanorods as shown in Fig. 1S(c).[†] It is interesting to note that regardless of the different absorption behavior between BCF and FBN-CPDT, the increasing extent of absorption is about the same for both fluorinated molecules at 1 wt% addition. Thus, the P3HT is still the major light harvesting component in both cases. We deduce the increase in the absorption of P3HT is from its morphology changes with the addition of the fluorinated molecules in the P3HT–TiO₂ hybrid film.

Additionally, we examined how the vertical phase separation influences solar cell performance and charge carrier mobility. The solar cell performance was improved using the active layer of P3HT–TiO₂ hybrid containing fluorinated molecules as shown in Fig. 2S (ESI[†]) and the photovoltaic properties are summarized in Table 1S (ESI[†]). When we introduced 1 wt% of fluorinated molecules into P3HT–TiO₂ hybrid solution, the PCE was increased from 0.22 to 0.92% for BCF and to 0.78% for FBN-CPDT. The extent of increase in PCE is by a factor of ~4 which can not be explained by the increase in absorption alone. Interestingly, use of BCF results in a greater

increase in PCE than when FBN-CPDT is employed. According to our previous studies,⁸ the performance of the P3HT–TiO₂ nanorods hybrid system is limited by the low and unbalanced charge mobility between electron and hole. The changes in the morphology of the P3HT–TiO₂ hybrid by adding fluorinated molecules must play the vital role in the large increase of PCE. We speculate that the vertical phase separation of the hybrid has increased and improved the balance of charge mobility. First, the formation of a TiO₂-rich region next to the metal electrode is expected to increase the efficiency of charge transport. Second, the FBN-CPDT containing P3HT–TiO₂ hybrid has a thinner TiO₂ rich domain as compared with that of BCF (59.2 vs. 106 nm) which results in a lower PCE due to the lower amount of interface interactions between P3HT and TiO₂ for effective charge separation and transport. We measured the mobility of hole and electron of the device to prove our speculation. The space charge limited currents (SCLC) model method was used and the data are summarized in Table 1S (ESI[†]). The electron mobility of the device is indeed increased by an order of magnitude as compared with the device without the fluorinated molecules. Previous literature has indicated that hole mobility in P3HT–TiO₂ hybrid films is strongly related to the shape of TiO₂,¹³ which can be attributed to the improved crystallinity of P3HT and highly ordered orientation of the P3HT chains induced by TiO₂. Therefore, the hole mobility of the device is increased with more ordered P3HT. Thus, a balanced charge mobility is achieved in this new P3HT–TiO₂ hybrid system containing fluorinated molecules. Furthermore, we can improve the PCE of P3HT–TiO₂–FBN-CPDT solar cell by increasing the thickness of the TiO₂ rich domain. We increased the amount of TiO₂ from 53 to 60 wt% and FBN-CPDT from 1 to 3 wt% in the hybrid composition. The increase of FBN-CPDT serves two purposes: helping the phase separation of increased TiO₂ and compensating the decreased light harvesting from decreased P3HT. Consequently, the device fabricated from the active layer containing the weight ratio of P3HT, TiO₂ nanorods and FBN-CPDT in 37:60:3 exhibits the further improvement in the device performance as shown in the insert of Fig. 2S (ESI[†]). The PCE improved from 0.78 to 1.11% with Voc of 0.65 V, Jsc of 3.23 mA cm⁻² and FF of 0.53.

In conclusion, we have demonstrated an effective method to form a self-vertical phase separation in polymer/inorganic nanoparticle hybrid solar cells using fluorinated molecules such as BCF and FBN-CPDT. The self-vertical phase separation enhances the PCE of a P3HT–TiO₂ nanorod hybrid solar cell. These results are due to the improvement of P3HT crystallinity and the increase of charge mobility. The increase in performance is not sensitive to the type of fluorinated molecule. Thus this method should be available for a wide range of fluorinated molecules. This study provides a novel approach to control the nanostructure of polymer/inorganic nanoparticle hybrid materials and further to enhance the charge transport and the PCE of hybrid solar cells.

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