

# Device performance enhancement of polymer solar cells by nanoparticle self-assembly

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## ABSTRACT

We show that it is possible to assemble a sparse mono-layer of Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs) at cathode interface of a polymer solar cell based on poly(3-hexylthiophene): [6,6]-phenyl-C<sub>60</sub>-butyric acid methyl ester (P3HT:PCBM) through the synergic effect of strong convective outflow, surface energy, Fe<sub>3</sub>O<sub>4</sub> NPs concentration and active layer thickness. When the distance between those Fe<sub>3</sub>O<sub>4</sub> NPs is smaller than the size of P3HT, the P3HT is excluded from the inter-particle space, and fullerene molecules fill in the space to build electron transport pathways improving charge transport and collection near cathode interface proved by transmission electron microscopy and X-ray photoelectron spectroscopy. The power conversion efficiency of the devices is improved up to 20%. The bulk morphology of light absorbing layers is not affected by the addition of Fe<sub>3</sub>O<sub>4</sub> NPs as demonstrated by neutron and X-ray scattering results.

## 1. Introduction

High interest has arisen in the field of organic solar cells during the past two decades, especially for polymer: fullerene solar cells because of their potential for low cost and fast roll-to-roll production on a flexible light weight substrate [1–3]. The sunlight shines through the transparent electrode to generate excitons, i.e., Coulomb-bound electron-hole pairs, in the polymer going to the interfaces of polymer and fullerene for separation to generate charge carriers. The charge carriers then transport to their electrodes respectively to output current. Because the diffusion length of these excitons is relatively short, approximately 10 nm, a less phase separated intimate mixing structure is preferred for efficient exciton separation [4]. However, sufficient charge transport requires a continuous pure electron donor and acceptor phase, so a trade off between exciton separation and charge transport must be taken into consideration.

Based on this, a vertical comb-like structure was proposed to be an ideal morphology for polymer: fullerene solar cells with a balanced weight ratio [5]. In this design, 5–10 nm thick layer of pure polymer and fullerene is adjacent to anode and cathode respectively. The sandwich layer between these two is composed of interdigitated polymer and fullerene with 10–20 nm width to ensure efficient exciton diffusion and avoid the trap of free charge carrier in each phase due to

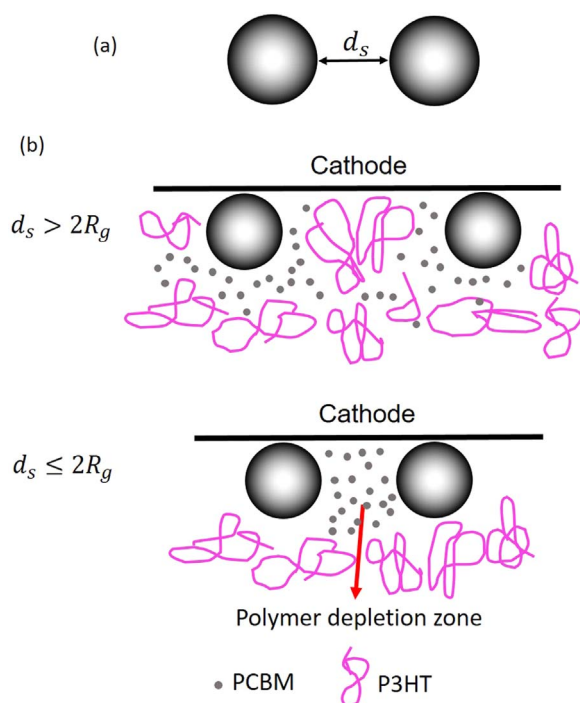
the lack of long-range order in organic materials. To obtain such a delicate structure on nanometer scale is always challenging. Therefore, in practice, the polymer and fullerene are blended to form a phase separated interpenetrating structure at nanometer scale creating the so called bulk-heterojunction (BHJ) to harvest the light [6]. The resulted morphology is usually vertical symmetric and homogeneous, so one deviation from the ideal design is no pure material phases formed at the contact interfaces, which is not beneficial to charge collection [7].

To break this morphological symmetry to improve the device performance, polymer rich layer needs to be formed near anode side, and fullerene rich layer, cathode side. For the well-studied system of poly(3-hexyl thiophene):[6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (P3HT:PCBM), Germack et al. lowered the surface energy of the hole transporting layer to successfully increase P3HT volume fraction from 47% to almost 100% near anode [8]. However, no significant difference was observed in the device performance. To have a more delicate nanostructure, the nanoimprint lithography method was applied to produce P3HT nanopillar on the anode and deposit PCBM afterward to realize the comb-like morphology [9–11]. However, this method can only provide precise control of morphology above 50 nm length scale, which is not small enough for any significant efficiency improvement, and its complicated fabrication process appears challenging to be commercialized.

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**Fig. 1.** (a)  $d_s$  is the inter-particle distance between two nanoparticles; (b) when  $d_s$  is smaller than  $2R_g$  of P3HT, the polymer is excluded to have polymer depletion zone and PCBM molecules fill the space between the two particles so that more PCBM could be found near cathode.

Considering the difficulties in manipulating P3HT morphology near the anode and the non-significant device performance improvement even after obtaining such delicate nanostructure, an alternative approach would be to focus on modifying the PCBM morphology near the cathode. Previously, Kiel et al. used phase sensitive neutron reflectivity finding higher PCBM concentration near air interface (which is cathode side in the device structure) after thermal annealing due to their slightly lower surface energy compared with P3HT and the convective flow during spin coating process [12,13]. This morphology change was accompanied with a significant 140% enhancement in power conversion efficiency (PCE). However, since the P3HT crystallinity and PCBM agglomerates also evolved after thermal annealing to have higher degree of phase separation to benefit the device performance, it is unclear what the role of high PCBM concentration near cathode is in improving PCE [14]. So it is necessary to study this PCBM concentration effect near cathode without affecting the bulk morphology of the active layers.

Since the P3HT:PCBM active layer is a thin film composed of nanoparticle and polymer, we considered applying nanoparticle self-assembly to realize the objective morphology. In the process of self-assembly, some forces are usually involved, such as entropic, enthalpic and long-range dispersion forces. Some kinetic effects like jamming and self-assembly in drying are also needed to be considered when the complete system is at non-equilibrium status [15,16]. In this study, the depletion flocculation effect was used to obtain the desired morphology. This phenomenon was originally observed in colloidal dispersions such as the aggregation of red blood cells in the polymer solution. Polymer molecules are excluded from the interstices between two particles forming polymer depletion zone of pure solvent, when the inter-particle distance is less than the diameter of the free polymer coil. The driving force for the formation of polymer depletion zone is the conformational entropy loss from the polymer coils since they lose more degrees of freedom than solvent molecules in the interstices between the particles [17,18]. Similarly, if nanoparticles were mixed into a blend of P3HT:PCBM, when the inter-particle distance is smaller than  $2R_g$  ( $R_g$  is radius of gyration) of P3HT, the polymer

depletion zone could be created for PCBM molecules to fill in acting as solvent molecules, since radius of PCBM ( $\sim 0.35$  nm) is much smaller than the  $R_g$  of P3HT, which is about 3–10 nm, considering it is polydisperse (PDI=1.4) [19,20]. By choosing particles with a lower surface energy than P3HT and PCBM, with the aid from a strong convective flow of spin coating, the segregation of them to the air interface could be obtained. Therefore a PCBM rich region could be formed building continuous electron pathways near cathode and further improving the charge collection. This process is shown in Fig. 1.

In this study, we mixed 11 nm diameter  $\text{Fe}_3\text{O}_4$  nanoparticles (NPs) into P3HT:PCBM system to investigate their impact on the morphology and device performance. Since these NPs do not scatter light, the optical effect like Mie scattering can be excluded to simplify the analysis. Moreover, these NPs are insulators so only morphological factor is needed to be studied.  $\text{Fe}_3\text{O}_4$  NPs vertical distribution in the P3HT:PCBM active layers were observed using transmission electron microscopy (TEM). Small angle neutron scattering (SANS) and grazing incidence X-ray diffraction (GIXRD) were used to characterize the morphological change of PCBM and P3HT. X-ray photoelectron spectroscopy (XPS) was used to study the composition of the active layers' top interface. Two different thicknesses of the active layers, and a series of  $\text{Fe}_3\text{O}_4$  NPs volume fraction addition was studied to find out the condition for optimum device performance.

## 2. Experimental section

ITO (indium tin oxide) coated one inch square glass (resistance of 8–12  $\Omega/\square$ , Delta technologies, LTD) was cleaned by ultrasonic treatment in acetone and isopropanol sequentially for 10 min. All the substrates were pretreated by ultraviolet ozone plasma for 15 min. This was followed by spin coating a 33 nm thick layer of poly(3,4-ethylenedioxythio-phenylene):poly(styrenesulfonate) (PEDOT:PSS, H.C. Starck, Al 4083) which was then transferred to an oven and annealed for 20 min at  $\sim 130$  °C. After this, the substrate was transferred to a nitrogen-filled glove box to fabricate solar cell devices. The solutions required for spin coating the active layer were prepared by dissolving P3HT (from Luminescence Technology Corp.,  $M_n=55,000$ g/mol, PDI=1.4) and PC<sub>61</sub>BM (from Nano-C) in di-ortho-chlorobenzene with specific  $\text{Fe}_3\text{O}_4$  nanoparticle concentrations in a nitrogen glove box to have 1:1 wt ratio P3HT:PCBM solution with 20 mg/ml concentration for each composition. A series of  $\text{Fe}_3\text{O}_4$  NPs (EMG1300, hydrodynamic diameter  $\sim 11$  nm, density 2.85g/cm<sup>3</sup>, from Ferrotec, size distribution is shown in Figure S1) volume fraction in solid content was obtained from 0 to 20 vol% (calculated by using each component's density and weight fraction). To have complete dissolution, the solution was stirred 24 h at 40 °C. A 0.45  $\mu\text{m}$  Teflon filter was used during the spin coating process. To investigate the thickness effect on the device performance, the solution was spin coated at 600 rpm for 60 s to obtain approximately 230 nm thickness and 1800 rpm 30 s for 90 nm thickness. The obtained thicknesses were controlled by the spin coating condition, not the amount of  $\text{Fe}_3\text{O}_4$  NPs. The spun-coated active layers were thermal annealed on a preheated hotplate at 110 °C for 10 min to obtain high degree of P3HT polycrystalline. Lithium fluoride (0.8 nm thickness) and aluminum (80 nm thickness) were sequentially thermal evaporated in a deposition chamber at a vacuum of  $2 \times 10^{-6}$  mbar. The working device area was approximately 0.1 cm<sup>2</sup>. The current-voltage curves were measured with a Keithley 2400 source meter, under illumination of 100 mW/cm<sup>2</sup> from 150 W solar simulator with AM1.5 G filters. 8 data points were collected for each sample from 8 different devices under the same condition. A 95% confidence interval was used when the collected data were averaged. All materials were used as received.

For characterizations other than the current-voltage test, the samples were prepared on soda-lime glass instead of ITO glass. To make cross-section images of thin films of P3HT:PCBM with  $\text{Fe}_3\text{O}_4$ , all films coated on glass were floated off in deionized water and then picked up by a piece of epoxy resin (Spurr's kit from Electron

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