Increased photocurrent in bulk-heterojunction solar cells mediated by FeS$_2$ nanocrystals

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**Article info**

**Article history:**
Received 19 August 2010
Received in revised form 6 December 2010
Accepted 8 December 2010
Available online 6 January 2011

**Keywords:**
Organic solar cell
FeS$_2$
OPVs

**Abstract**

We found that the efficiency of bulk-heterojunction (BHJ) solar cells can be enhanced by incorporating a small amount of semiconductor FeS$_2$ nanocrystals (NCs) into the poly(3-hexylthiophene) (P3HT) and (6,6)-phenyl C$_{61}$-butyric acid methyl ester (PCBM) based active layer. Through optical and nanoscale structure measurements, it is evident that low-cost and non-toxic FeS$_2$ NCs in such devices can efficiently improve charge carrier transport and exciton dissociation. This simple approach for increasing the photocurrent by NCs will be useful for accelerating the development of practical applications using organic solar cells.

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1. Introduction

During the past decade, organic photovoltaics (OPVs) have attracted intense interest because of their unique advantages, including low-cost processes, high mechanical flexibility, and large-area fabrication [1–4]. In particular, much attention has been focused on bulk-heterojunction (BHJ) solar cells based on phase-separated blends of poly(3-hexylthiophene) (P3HT) as an electron acceptor and (6,6)-phenyl C$_{61}$-butyric acid methyl ester (PCBM) as an electron donor, because they provide a large interfacial area for efficient exciton dissociation [5–9]. Power conversion efficiencies of up to 5% under simulated solar irradiation have been achieved for P3HT:PCBM OPVs.

Compared to inorganic solar cells, one of the limiting factors of the efficiency of organic solar cells is the poor mobility of both electrons and holes in the composite matrix. Many techniques have been reported to improve the performance of P3HT:PCBM solar cells, including thermal annealing and growth ratio reduction [10,11], both of which have been linked to P3HT reordering and improvement of active layer morphology. Another important factor is the phase separation of constituent polymers, especially in BHJ cells. Under ideal conditions, the two phases of the polymers would uniformly interpenetrate one another to separate electrons and holes efficiently and transport them to the metal electrodes without recombination. Several approaches to obtain suitable phase separation have been reported, including the use of solvent variety and the donor/acceptor ratio [12,13]. Shaheen et al. [12] demonstrated that a chlorobenzene-based device exhibits a more than twofold increase in the short-circuit current density relative to a toluene-based device by changing the phase separation. In 2005, Kim et al. [13] reported excellent performance for the 1:1 (P3HT:PCBM) weight ratio composition by optimizing the morphology to enable close intermolecular packing of P3HT chains.

Alternatively, it is possible to provide direct and ordered transport pathways for carriers in BHJ structures with the assistance of ordered inorganic nanostructures such as ZnO nanofibers and TiO$_2$ nanorods [14,15]. However, although inorganic semiconductors have higher carrier mobilities and offer controllable transport pathways, the quality of the interface between organic and inorganic materials is very poor. The power conversion efficiency of hybrid inorganic/polymer blend photovoltaic devices is still lower than that of pure polymer devices. In addition, although several inorganic nanoscale materials, including CdSe and PbS nanorods, have also been tested in organic/inorganic hybrid solar cells, the toxicity of Cd and Pb poses limitations because of environment issues [16,17].

In this letter, we demonstrate a non-toxic and low-cost approach to improve the performance of OPVs based on FeS$_2$ nanocrystals embedded in a composite polymer. Given that FeS$_2$ is one of the most abundant materials on earth, it is a promising candidate for the development of practical applications of OPVs in the near future.

2. Experimental

The pyrite structure of semiconductor FeS$_2$ NCs was prepared by wet solution phase chemical syntheses. Initially, 63 mg of FeCl$_2$,
129 mg of 1,2-hexadecanediol and 10 mL of oleylamine were introduced to a three-necked round-bottom flask purged previously by N2 flow in order to remove oxygen and moisture inside the reaction system. The solution was heated at 100 °C to form the Fe–oleylamine complex. After a reaction time of 1 h, 5 mL of an oleylamine solution of sulfur was added to the above solution and the mixture was then heated to 220 °C for 1 h. Subsequently, the solution was cooled to room temperature and FeS2 nanocrystals with an average diameter of ~10 nm were synthesized. FeS2 NCs have a crystalline structure with clear lattice fringes as shown in Fig. 1(a), and disperse well in chloroform (CF) [18]. In our experiments, small amounts of FeS2 powder (0.1, 0.2, 0.3, and 0.4 mg) were added to a set of identical blend solutions to make P3HT:PCBM/FeS2 nanocomposite samples. The blend solutions were prepared by dissolving P3HT:PCBM (10 mg:10 mg) in 1 mL chlorobenzene (CB) and stirring at 50 °C for two days to form the active material. Solar cells with the structure ITO/P3HT:PCBM:FeS2 NCs/Al are schematically drawn in Fig. 1(b). The devices were fabricated on ITO-coated glass substrates (~15 Ω/sq.). After cleaning the substrate by sequential sonication in different solvents (detergent, DI-water, ACE, and IPA) for 20 min each and oxygen plasma treatment for 15 min, a 40-nm-thick layer of PEDOT:PSS was spin-coated onto the ITO glass as the hole transport layer and annealed at 140 °C for 10 min. Subsequently, active layers (~100 nm) with various weight percent (wt%) of FeS2 NCs were formed by spin-coating, and the substrates were transferred to a nitrogen-filled glove box and annealed at 110 °C for 10 min. Finally, the aluminum electrode (~100 nm) was deposited thermally on the devices, and a post-annealing treatment of 150 °C for 10 min was carried out to complete the photovoltaic devices. For device fabrication, all spin-coating processes were performed in an atmospheric environment.

3. Results and discussion

The current density–voltage (J–V) characteristics of the finished photovoltaic devices were measured under an illumination intensity of 100 mW/cm², as shown in Fig. 2. The measurements reveal that a small number of FeS2 NCs (0.1–0.3 wt%) inserted into the photoactive film results in a clear increase in the short-circuit current (Jsc) from 6.69 to 7.63 mA/cm², while Voc and FF remain nearly the same (0.66 V and 47%, respectively). The power conversion efficiency (PCE) of the devices is improved from 2.08% to 2.30%. However, when the concentration of FeS2 exceeds 0.3 wt%, the efficiency starts to decrease because of the increase in leakage current.

To assess the role FeS2 NCs in improving the photocurrent of the OPVs, we measured the incident photon-to-current efficiency (IPCE) of ITO/P3HT:PCBM/Al structures with and without FeS2 NCs (Fig. 3(a)). The IPCE data indicate that the main portion of the enhanced photocurrent is between the wavelengths of 380 and 650 nm, corresponding to the absorption of P3HT. The devices show a negligible infrared contribution from FeS2 NCs, which have a bandgap of about 0.95 eV. This behavior is most easily understood by assuming that the amount of NCs is too small to reveal the effect. Comparing the absorption spectra of P3HT:PCBM and P3HT:PCBM:FeS2 films, the devices show no difference (Fig. 3(b)). This indicates that the IPCE increment in the FeS2-incorporated device is due to superior exciton dissociation and carrier transport.

To further explore the reason for the photocurrent enhancement, we measured photoluminescence (PL) to examine exciton dissociation in the polymer film. Fig. 3(c) depicts the PL spectra for P3HT:PCBM and P3HT:PCBM:FeS2 NCs devices. Compared to the device without FeS2 NCs, the FeS2-incorporated device shows a lower PL intensity. This indicates clear evidence for enhanced exciton dissociation. The transmission electron microscopy (TEM) image of Fig. 1(b) shows that FeS2 NCs were sparse and uniform in the polymer film. The carriers are therefore difficult to transport...
across NCs in the composite. The situation is very different from the case of adding TiO$_2$ nanotubes to form carrier pathways and increase the carrier mobility of the devices [19]. Consequently, we surmised that the increased photocurrent comes from superior exciton dissociation caused by the enhanced phase separation of the constituent polymers due to the insertion of FeS$_2$ NCs.

To clarify this possibility, the film morphology was visualized through atomic force microscope (AFM) scanning in the tapping mode as shown in Fig. 4. The topography of the film with NCs is significantly rougher than the pristine ones, as shown by the increase in the area roughness value from 0.76 to 1.64 nm. Given that the FeS$_2$ NCs were uniformly distributed within the active layer, the roughness is assumed to be caused by severe interpenetration of the polymer materials. The extra-NCs are thought to serve as a medium for enhancing the interpenetration of PCBM and P3HT molecules in the composite film, leading to superior exciton dissociation. As a result of this superior exciton dissociation, the short-circuit current of BHJ solar cells is expected to increase, which explains our experimental results well. Finally, it is worth emphasizing here that although FeS$_2$ NCs cannot contribute to the photocurrent of OPVs by enhancing the infrared absorption, the concept of NC-mediated phase separation proposed in our study is beneficial for the performance of OPVs.

4. Conclusions

In conclusion, we have embedded inorganic semiconductor FeS$_2$ NCs in P3HT:PCBM OPVs to enhance solar cell performance. Through optical and nanoscale structural characterizations, we propose that the mechanism underlying the enhancement is an improved interpenetration of the constituent polymers, which leads to enhanced exciton dissociation and charge carrier transport. We suggest that the concept of NC-mediated phase separation developed on the basis of this study will be highly useful for the development of practical applications using organic solar cells.
Acknowledgments

This work was supported by the National Science Council and the Ministry of Education of the Republic of China.

References


