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Preparation and characteristics of hybrid ZnO-polymer solar cells

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Abstract We demonstrate a hybrid solar cell which was made by blending nanocrystalline ZnO (nc-ZnO) and conjugated polymer regioregular poly(3-hexylthiophene) (P3HT) as the active layer of the solar cell. It can be seen that the efficiency of this new type of solar cells obviously varied as the size and morphology of ZnO nanostructures. The short-circuit photocurrent, fill factor, and power conversion efficiency were enhanced while the smaller nc-ZnO was utilized in such a device.

Introduction

Organic photovoltaic devices have attracted much interest these days due to their potential for the production of flexible and large-area solar cells at low cost [1]. Polymer or organic solar cells often utilize a nanostructured interpenetrating network of electron-donor and electron-acceptor materials [2–6]. In other word, so-called hybrid polymer solar cells use a blend of conjugated polymer and inorganic material to convert sunlight into charges [5]. Moreover, it can be expected that such a devices will integrate the advantages of two materials—high electron mobility of inorganic semiconductors and photosensitivity, and high hole mobility of conjugated polymers [7]. However, currently the power conversion efficiency (PCE, η) of the hybrid polymer photovoltaic devices is still very low due to the poor interfacial junction between the organic and inorganic materials. Hence, many investigations on improving the heterojunction between the two materials has been reported [7–10].

Since a conjugated polymer can provide exciton (bound electron–hole pair) rather than free charges by photoexcitation, it is very critical that the use of two materials with complementary p and n type electronic properties in the operation of a hybrid polymer solar cell. The exciton may be dissociated efficiently at the interface of organic–inorganic materials via a hole or electron transfer to generate the photocurrent. In addition, the exciton in conjugated polymers has a short lifetime ($\sim$sub-nanosecond) and a correspondingly small diffusion range (<10 nm), hence many organic solar cells are designed to have a large area interface at short distances (nanometer) from anywhere within two materials by either using a bulk heterojunction, or via a nanoporous structure in which the two materials are mixed on a nanometer scale. On the other hand, both the p and n type materials should offer continuous interpenetration pathways to transport the photocurrent to the electrodes for an efficient photovoltaic device [11–14].

In this work, we blended nanocrystalline ZnO (nc-ZnO) and regioregular poly(3-hexylthiophene) (P3HT) as an active layer of the hybrid bulk heterojunction solar cells, where two different morphology of nc-ZnO were employed in solution processes. No additional surfactants or ligands were needed to disperse the nc-ZnO in P3HT solvent [5]. Here, inorganic semiconductor ZnO was used as the n-type material in combination with the p-type conjugated polymer P3HT. Size effects of the nc-ZnO can be observed by measuring current density–voltage (*J*–*V*) under AM 1.5

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(AM = air mass) illumination with light intensity of 100 mW/cm^2 in our investigation.

Experimental

Materials employed in this work were P3HT, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), and Al. nc-ZnO were prepared by sol–gel processes, the related synthesis methods can be found everywhere [15]. For device fabrication, indium tin oxide (ITO) glass substrates with a sheet resistance of 10 Ω/sq were cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol. A transparent bilayer electrode comprising PEDOT:PSS as hole collection was prepared on the ITO glass by spin-coating method. Then, P3HT was first dissolved in chlorobenzene (CB) to make 30 mg/mL solution, followed by blending with 70 mg of nc-ZnO, the ratio of P3HT/ZnO was estimated to be 3/7. Note that two kinds of nc-ZnO were used in the study, including ZnO nanodots and nanorods. Composite layers of P3HT and ZnO as the active layer of solar cells were 3,000 rpm spin-coated on ITO glass substrates with PEDOT:PSS layers, and baking at 120 °C for 10 min. Finally, 100-nm-thick Al was evaporated on the top of cells as electrodes. All the device fabrication were performed in a N_2 atmosphere glove box (both [O_2] and [H_2O] were <0.1 ppm). Active area of the device was estimated to be 0.35 cm^2. Figure 1 shows the layout of the hybrid polymer solar cell.

Surface morphologies of samples and size distribution of the nc-ZnO were characterized by a JEOL JSM-6700F field-emission scanning electron microscope (FESEM), operated at 3 keV. The absorption spectrum of hybrid active layers was carried out by Hitachi U-3310 ultraviolet–visible (UV–vis) spectrophotometer. All electrical measurement were taken in air using a calibrated solar simulator with AM 1.5 illumination and light intensity of 100 mW/cm^2. Current density–voltage characteristics of solar cells were realized by a Keithley 2400 source meter.

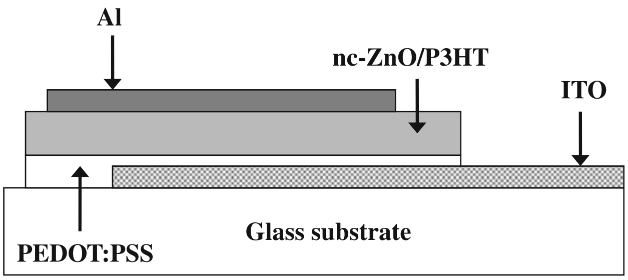

Fig. 1 Device structure consists of an active layer of nc-ZnO/P3HT (with 70 wt% nc-ZnO) sandwiched between Al electrode and conducting electrode of PEDOT:PSS on an ITO glass substrate. The active area of the device is 0.35 cm^2

Results and discussion

We introduce nc-ZnO as the n-type semiconductor in hybrid bulk heterojunction solar cells, the morphology for different size of the nc-ZnO as shown in Fig. 2. Figure 2a shows the ZnO nanodots with a typical diameter of 10 nm, it can be seen that the distribution of the size is very uniform. On the other hand, the rod-like ZnO with bigger size are not uniform in size distribution as shown in Fig. 2b, we can see the typical diameter and length of a ZnO nanorod are about 80 and 300 nm, respectively. In addition, it was also found an aggregation phenomenon in Fig. 2b. Note that the ZnO nanodots are more than 10 times the total surface area of the ZnO nanorods in the same wt%. It is possible that the surface area of the inorganic nanostructures will affect the performance of hybrid polymer solar cells. Figure 3 shows the UV–vis absorption spectra for ZnO nanodot/P3HT blend film, it can be seen that the absorbance peak of nc-ZnO is located at 375 nm while the π–π* band of P3HT is in the 400–650 nm region [6].

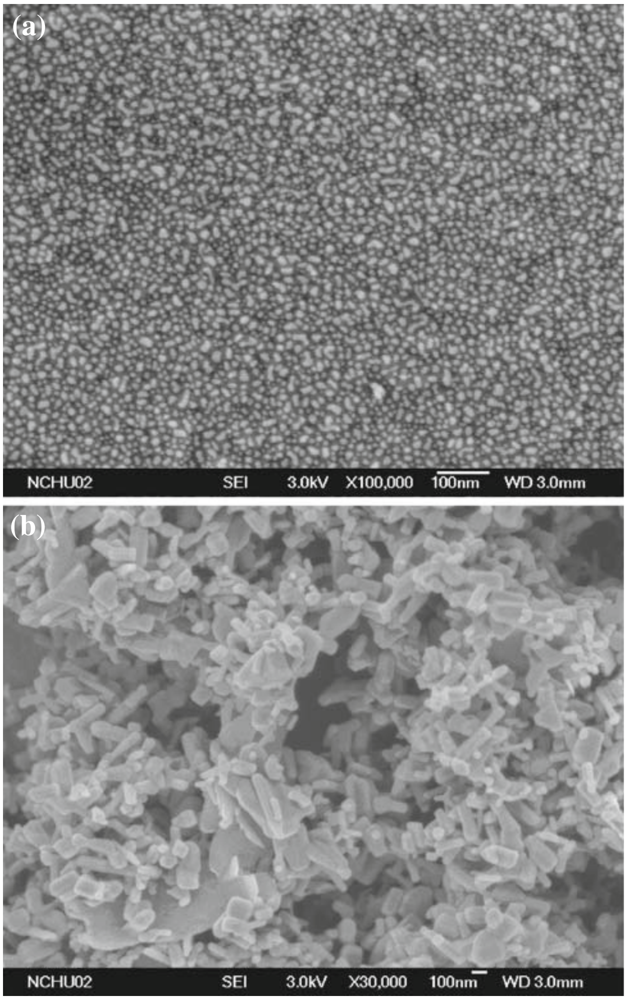

Fig. 2 FESEM images of **a** ZnO nanodots and **b** ZnO nanorods

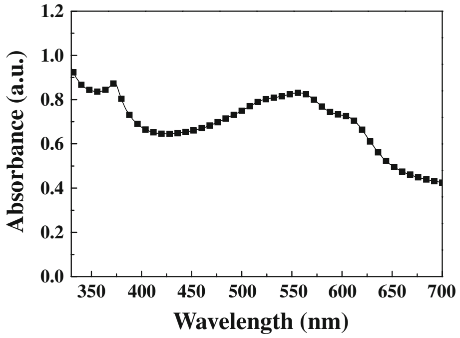

Fig. 3 Absorption spectrum of ZnO nanodot/P3HT spin-coated on ITO glass

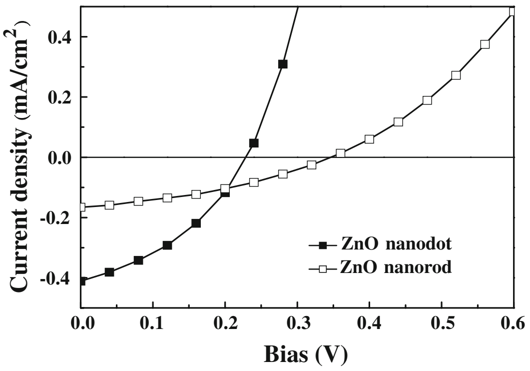

Fig. 4 Current density–voltage (*J–V*) characteristic of nc-ZnO/P3HT solar cells under a simulated AM 1.5 illumination with light density of 100 mW/cm^2

Figure 4 shows the current density–voltage characteristics for the fabricated solar cells constructed using ZnO nanodot and nanorod carried out under a simulated AM 1.5 illumination with light density of 100 mW/cm^2. The PCE η and fill factor FF were evaluated by the following relations:

$$\eta = \frac{J_m \times V_m}{P_{inc}} \tag{1}$$

$$FF = \frac{J_m \times V_m}{J_{sc} \times V_{oc}} \tag{2}$$

where J_{sc} is the short-circuit photocurrent density, V_{oc} is the open circuit voltage, and P_{inc} is the incident light power. J_m and V_m represent the maximum current density and voltage, respectively [16].

The J_{sc}, V_{oc}, J_m, V_m, FF, and η derived from the *J–V* curves for both hybrid polymer solar cells based ZnO nanodots and nanorods are indicated in Table 1. By Table 1 and Fig. 4, we can see that the short-circuit photocurrent and fill factor of the hybrid bulk heterojunction solar cell with ZnO nanodots ($J_{sc} = 0.4$ mA/cm^2, $J_m = 0.26$ mA/cm^2, and FF = 41%) are superior to that of the cells with ZnO nanorods ($J_{sc} = 0.16$ mA/cm^2, $J_m = 0.083$ mA/cm^2, and FF = 39%). While the former is smaller than the later by V_{oc} and V_m comparison (V_{oc}: $0.22 < 0.32$, V_m: $0.14 < 0.24$). Since much increased photocurrent J_{sc}, it can be seen that nanodot-based polymer solar cell produced a total PCE η of 0.036% while nanorod-based cell merely showed a lower η of 0.020%. The former is about 1.8 times the PCE of the later. These results could be attributed to the increment of the charge separation interface between P3HT and nc-ZnO.

As a result, the increase in short-circuit photocurrent for composite blend based device is due to efficient photo-induced charge transfer between donor (P3HT) and acceptor (ZnO). In other words, the ZnO nanodots are more than 10 times the total surface area of the ZnO nanorods in the same solution process, the increased short-circuit photocurrent in this device is due to the increased surface area of the dissociation interface which leads to higher charge extraction from the device and a subsequent decrease in charge recombination [12, 17].

Conclusions

In summary, a hybrid solar cell was fabricated by blending nc-ZnO and a conjugated polymer P3HT as an active layer, where we used two different morphology of nc-ZnO to mix with P3HT. The ZnO nanodots are more than 10 times the total surface area of the ZnO nanorods in the same wt%. It can be seen that the efficiency of this new type of solar cells obviously varied as the size of ZnO nanostructures. The J_{sc}, fill factor, and conversion efficiency is enhanced while the smaller nc-ZnO was utilized in such a device. As a result, we can attribute the improvement in short-circuit photocurrent to the increment of interfacial area between nc-ZnO and P3HT, which leads to higher charge extraction from the device and a subsequent decrease in charge recombination.

Table 1 Characteristics of the hybrid polymer solar cells under the illumination of AM 1.5 simulated solar light at an intensity of 100 mW/cm^2

Active layer	J_{sc} (mA/cm^2)	J_{max} (mA/cm^2)	V_{oc} (V)	V_{max} (V)	FF (%)
ZnO nanodot/P3HT	0.4	0.26	0.22	0.14	41
ZnO nanorod/P3HT	0.16	0.083	0.32	0.24	39

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