Applied Surface Science 257 (2010) 423–428

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Influence of interface modification on the performance of polymer/Bi_2S_3 nanorods bulk heterojunction solar cells

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ARTICLE INFO

Article history:
Received 23 December 2009
Received in revised form 20 May 2010
Accepted 1 July 2010
Available online 8 July 2010

Keywords:
Bulk heterojunction solar cells
Surface modification
Nanorods

ABSTRACT

In this paper, bulk heterojunction photovoltaic devices based on the poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV):Bi_2S_3 nanorods hybrid material were present. To optimize the performance of the devices, the interface modification of the hybrid material that has a significant impact on the exciton dissociation efficiency was studied. An improvement in the device performance was achieved by modifying the Bi_2S_3 surface with a thin dye layer. Moreover, modifying the Bi_2S_3 surface with anthracene-9-carboxylic acid can enhance the performance further. Compared with the solar cells with Bi_2S_3 nanorods hybrid with the MDMO-PPV as the active layer, the anthracene-9-carboxylic acid modified devices are better in performance, with the power conversion efficiency higher by about one order in magnitude.

1. Introduction

Recently, organic/inorganic bulk heterojunction (BHJ) photovoltaic devices that can be manufactured by the roll-to-roll or solution processed spin-coating technologies have attracted much attention, because of the advantages of low cost, ease in fabricating in large area and application on flexible substrates. Many inorganic nanocrystals have been used to compound with polymers in the fabrication of the BHJ solar cells, ZnO [1–3], TiO_2 [4,5], CdSe [6] and PbS [7–9] are utilized frequently. With a direct band gap of 1.3 eV [10], Bi_2S_3 is a promising candidate for photovoltaic application [11,12]. Moreover, an obvious thermoelectric effect has been detected in Bi_2S_3 [13,14]. As a result, it is possible to combine the photovoltaic and thermoelectric functions in a single device, which may utilize the solar energy in a high level.

For the hybrid solar cells, when the radiation enters the active layer, it can be absorbed by photo-excitation of the polymer, followed by the generation of an exciton, which has such a high binding energy as that the thermal energy at room temperature is not sufficient to dissociate it into free charge carriers. Only when the exciton diffuses to the interface with a second material, can it be dissociated into free charges that contribute to the current of the solar cells [15]. Furthermore, the exciton usually has a short diffusion length (<10 nm) and a corresponding short lifetime (often sub-nanosecond) [16]. If the excitons diffuse longer than the diffusion length, most of them will decay. Therefore, it is crucial to construct the BHJ and control the diffusion distance of excitons below the diffusion length for reducing the decay possibility and improving the dissociation possibility of the excitons. When the excitons diffuse to the interface of the polymer and the nanocrystal, due to the work function difference between the two materials, they can be dissociated into free charges. However, the contact quality of the two materials has a great effect on the exciton dissociation and the charge transport. Modifying the interface with a relatively charge conductive material can improve the performance of the solar cells obviously. Lin et al. [4] reported that for the TiO_2:poly(3-hexylthiophene) (P3HT) BHJ solar cells, an enhancement of about 5 times in power conversion efficiency can be achieved by replacing the insulating surfactant oleic acid on the TiO_2 nanorods surface with a more conductive ligand anthracene-9-carboxylic acid (ACA), the relatively high power conversion efficiency of 1.7% under simulated AM 1.5 illumination was achieved. The improvement in the device performance by modifying the nanocrystal surface has also been reported in the ZnO:P3HT [17] and PbS:poly[2-methoxy-5-(2′-ethylhexyloxy-*p*-phenylenevinylene)] (MEH-PPV) [7] solar cells.

In this paper, Bi_2S_3 nanorods with the diameter about 10 nm and the length about 100 nm were synthesized via the route reported by Sigman and Korgel [10]. Blending the Bi_2S_3 nanorods and the poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) as the active layer, BHJ solar cells were fabricated. To optimize the performance of the solar cells, the interface modification of the hybrid material was studied. A

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doi:10.1016/j.apsusc.2010.07.004

great improvement in device performance by modifying the hybrid material with a dye and the ACA was achieved, respectively.

2. Experimental

2.1. Nanorods synthesis

First, 0.23 g $Bi(NO_3)_3$ and 0.20 g $NaOOC(CH_2)_6CH_3$ were dissolved in 36 mL deionized water and 25 mL $CHCl_3$, respectively. Then, the two kinds of solution were mixed in a big beaker, under vigorous stirring. About 10 min later, 0.18 g elemental sulfur was added to the mixed solution. After that, the mixed solution was stirred for 60 min with the organic phase becoming faint yellow from white in color. The organic phase was separated and dried on a rotary evaporator to leave a bright yellow waxy solid. Then, 0.24 mL dodecanethiol was added to the solid with the color of the solid becoming black gradually in 1 h. The black solid was transferred into a tubular furnace, heated to 160 °C and kept for 1 h. After cooled to the room temperature, the product was dispersed in chloroform and precipitated by adding excess ethanol.

2.2. Surface modification of the product

To make sure that the surface modifiers are integrated with the nanorods closely, it is necessary to add a thin oxide layer on the nanorods before modification, because both the ACA and the dye (N719, *cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II)bis-tetrabutylammonium) have a strong affinity with the oxide due to the existence of the carboxyl. To achieve this, the nanorods were dispersed in a 70 mL KOH ethanol solution (10 mg/mL) under vigorous stirring. Then the solution was transferred to a Teflon-lined stainless steel autoclave, heated to 120 °C and maintained for 6 h. After cooled to the room temperature, the nanorods were centrifuged and washed with ethanol several times. To modify the nanorods with the N719, the nanorods with oxide layer were dispersed in the N719 ethanol solution at 60 °C. After vigorous stirring for 2 h, the N719 modified product was centrifuged and washed. The modification of the nanorods with ACA is similar to the above procedure, except the usage of the ACA pyridine solution at 80 °C.

2.3. Fabrication of the BHJ solar cells

In a typical procedure, the ITO-coated glass substrate was cleaned by detergent, deionized water, acetone and isopropyl alcohol sequentially, in an ultrasonic bath. A thin layer of PEDOT:PSS (Baytron 4083) doped with mannitol [17] was spin-coated to modify the ITO surface and annealed at 140 °C for 1 h. After cooled to the room temperature, the substrate was transferred to a nitrogen-filled glove box. MDMO-PPV (Aldrich) was first dissolved in chlorobenzene, followed by blending it with the nanorods chlorobenzene solution. The final concentrations of the MDMO-PPV and the nanorods were 6 mg/mL and 12 mg/mL, respectively. The blend was ultrasonicated for 1 h and stirred for 3 h, and then transferred to the nitrogen-filled glove box. The active layer was obtained by spin-coating the blend at 1500 rpm for 30 s. After that, an additional layer of ZnO nanoparticles sandwiched between the active layer and the aluminum electrode was spin-cast to act as a hole blocking layer [18] and also as an optical spacer [19]. The nanoparticle film can scatter more incident light than the continuous flat film, which can increase absorption efficiency of the active layer. The ZnO nanoparticles were prepared via the method reported by Liu et al. [20]. Finally, the Al electrode was deposited onto the ZnO nanoparticles layer by thermal evaporation in vacuum at pressure around 3×10^{-5} Torr. The BHJ solar cells containing the ACA or N719 modified nanorods hybrid with the MDMO-PPV as the active layer were fabricated in the same procedure and technical parameters as above. Fig. 1 shows the structure of the BHJ solar cells.

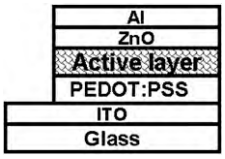

Fig. 1. The structure of the BHJ solar cells.

2.4. Characterization

High-resolution transmission electron microscope (HRTEM) for the Bi_2S_3 nanorods was performed using a JEM-2010 TEM equipped with a field emission gun operating at 200 kV accelerating voltage. Absorption spectrum was carried out by an UV-3100 UV–VIS–NIR recording spectrophotometer (Shimadzu). Photoluminescence (PL) spectrum was carried out at the room temperature under the excitation of 466 nm (Edinburgh Instruments Ltd., FLS 920). Time-resolved PL spectroscopy was performed by a lifespecred picosecond fluorescence lifetime spectrometer (Edinburgh Instruments Ltd.). The external quantum efficiency of the devices was measured using an integrated home-made system with a xenon lamp, a monochromator and an electrometer. *J–V* measurements were performed in forward bias with a computer-controlled Keithley 2400 Source Meter under ~100 mW/cm^2 illumination from a solar simulator. A 500 W xenon lamp served as the light source and the light intensity was calibrated using a standard silicon solar cell. In the *J–V* measurement process, the fill factor (FF) was calculated using

$$\mathrm{FF} = \frac{(JV)_{\max}}{J_{\mathrm{sc}}} \times V_{\mathrm{oc}} \tag{1}$$

where $(JV)_{\max}$ is the maximum product of J and V that can be calculated from the *J–V* curve, J_{sc} is the short circuit current density and the V_{oc} is the open circuit voltage. Defined as the ratio of the electric power output of the cell at the maximum power to the incident optical power (P_{light}), the energy conversion efficiency (η) can be calculated using the following equation:

$$\eta = \frac{\mathrm{FF} \times J_{\mathrm{sc}} \times V_{\mathrm{oc}}}{P_{\mathrm{light}}} \tag{2}$$

Series resistance (R_{s}) and shunt resistance (R_{sh}) were obtained from the *J–V* curves by using

$$R_s = \left(\frac{dV}{dI}\right)_{I=0} \tag{3}$$

and

$$R_{sh} = \left(\frac{dV}{dI}\right)_{V=0}, \tag{4}$$

respectively.

3. Results and discussion

3.1. Characterization of the Bi_2S_3 nanorods

Fig. 2(a) and (b) are the TEM and HRTEM images of the Bi_2S_3 nanorods, respectively. From the images, crystalline Bi_2S_3 nanorods with the diameter about 10 nm and the length about 100 nm are clearly observed, which is similar to the result reported by Sigman and Korgel [10]. To confirm the existence of the oxide layer on the nanorods treated in the KOH solution, the treated sample