Sci. Bull. (2016) 61(3):245–251
DOI 10.1007/s11434-016-0999-9

www.scibull.com
www.springer.com/scp

Article

Materials Science

Size dependence of photovoltaic properties and surface states modulation in ZnO nanowire/poly(3-hexylthiophene) hybrid nanostructures

Yuqian Huang · Ke Cheng · Jingjing Liu · Ming Xue · Zhongcheng Kuang · Zuliang Du

Received: 14 October 2015 / Revised: 21 November 2015 / Accepted: 14 December 2015 / Published online: 25 January 2016

Abstract An appropriate diameter and wire-to-wire distance is critical for optimizing the performance of hybrid inorganic/organic photovoltaic devices. For a deep understanding of their influences on such hybrid structures, the well-ordered ZnO nanowires with different diameters are fabricated by the versatile hydrothermal growth. The dependence of the photovoltaic performance on the surface states, wire diameter and wire-to-wire distance is investigated. We demonstrate that the pristine thick ZnO nanowires film possess a higher surface photovoltage (SPV) response than the thin one. This is mainly due to the influence of surface states on the thin ZnO nanowires, which can capture the photo-generated carriers. When the two kinds of ZnO nanowires are fabricated into a hybrid inorganic/organic structure, the thin ZnO nanowires/poly(3-hexylthiophene) hybrid film has a higher SPV response than the thick one, which is contrary to the pristine ZnO nanowires. This is benefited from the smaller diameter and wire-to-wire distance of the thin ZnO nanowires owned. The crystallinity, wire diameter and wire-to-wire distance have the crucial influence on the final photovoltaic performance. The results shown here give us insights toward designing efficient hybrid photovoltaic devices.

Keywords ZnO nanowires · Crystallinity · Wire diameter · Surface states · Hybrid heterojunction solar cells

Y. Huang · K. Cheng · J. Liu · M. Xue · Z. Kuang · Z. Du (✉)
Key Laboratory for Special Functional Materials of Ministry of Education, Collaborative Innovation Center of Nano Functional Materials and Applications, Henan University, Kaifeng 475004, China
e-mail: zld@henu.edu.cn

1 Introduction

Organic photovoltaic devices based on conducting polymers offer low cost, light weight and flexibliity comparing with their inorganic counterparts [1, 2]. However, charge carrier mobilities in organic semiconductors are generally much lower than those of inorganic semiconductor [1, 3]. This disadvantage is partly resolved by introducing an inorganic semiconductor with a high absorption coefficients and long-lived charge carriers. The most common strategy is so-called bulk heterojunction, in which the donor and acceptor materials are intimately blended through the bulk [4–6]. In this way, excitons do not need to travel long distance to reach the donor/acceptor interface, and charge separation can take place throughout the whole depth of the photo-active layer. The most popular electron acceptors are C60 derivatives and inorganic nanocrystal. Power conversion efficiency of ~5 % has been reported for the poly(3-hexylthiophene) (P3HT)/phenyl-C61-butryic acid methyl ester (PCBM) solar cells [7]. However, the carriers transport to the collection electrode through a “hopping” manner in the traditional inorganic nanocrystal based hybrid system. The hopping transport process increases the recombination probabilities when the electrons pass through the inorganic/organic interface [8, 9].

In an ideal structure, both the conjugated polymer and the inorganic electron acceptor should have straight pathways to the corresponding electrodes in order to minimize the carrier transport time and reduce the probability of recombination [3]. One-dimensional (1D) nanostructures, such as nanowires and nanotubes, have been extensively investigated for this goal [10–13]. Among them, the array of zinc oxide (ZnO) nanowires is considered as one of the most promising candidates for such applications as they can easily grow normal to the substrate using low-temperature hydrothermal growth [14–16]. In other aspects, ZnO offers a large direct band gap of 3.37 eV, which has electron mobility as high as 155 $cm^2/(V\ s)$ and is suitable for improving the performance of the bulk heterojunction polymer solar cells. Olson et al. [17] demonstrated that hybrid photovoltaic devices could be fabricated using the combination of a semiconducting polymer and a ZnO nanorod array prepared by a solution process for the first time. Abdulalnohsin and Cui [13] reported a P3HT/ZnO nanorod cell exhibiting an efficiency of 0.53 %. Generally, the poor performance in such hybrid polymer photovoltaic devices is mainly caused by the lower charge separation and collection efficiency. Several groups [12, 13] have devoted their efforts to study the influences of the solvent selection and subsequent annealing process on the polymer. As we know, the solvent selection and annealing process have a close correlation to the final blend morphology, which can strongly affect the final performance of the solar cells [18]. However, few reports illustrate the dependence of the photovoltaic performance on the crystallinity, the wire diameter and the wire-to-wire distance of the inorganic counterpart.

This work adopted a two-step chemical process to produce vertical aligned ZnO nanowires with different wire diameters on the indium tin oxide (ITO) substrate. We studied the photovoltaic properties of P3HT/ZnO nanowires hybrid structure using the surface photovoltage spectrum, which is a powerful tool to investigate the photogenerated carriers and electronic structures of the semiconductors. The influence of the wire diameter and wire-to-wire distance on the photovoltaic performance was also investigated systematically. It was demonstrated that the photovoltaic performance could be improved by shorting the wire diameter and the wire-to-wire distance. And the influence of surface states on the ZnO nanowire surface was also discussed. We concluded that better crystallinity could eliminate the surface states effectively, which was crucial for a smooth electron transport in the ZnO nanowires. The results could give us insights toward designing efficient hybrid photovoltaic devices.

2 Experimental

2.1 The fabrication of ZnO nanowires array

ZnO nanowires array was fabricated in a two-step aqueous chemical process. The typical procedure for the thin ZnO nanowire arrays was as follows: Firstly, 4-nm-diameter ZnO nanocrystal was synthesized according to the method of Pacholski et al. [19]. A NaOH solution in methanol (0.03 mol/L) was added slowly to the solution of zinc acetate dehydrate (0.01 mol/L) in methanol at 60 °C and stirred for 2 h. Then the ITO substrate was coated uniformly with the ZnO nanocrystals using a dip-coating method. This ZnO nanocrystal-coated ITO substrate was heated in air at 350 °C for 2 h before growing nanowires. Secondly, the as-prepared ZnO seeds film was suspended upside-down in an aqueous solution including zinc nitrate hydrate (0.016 mol/L) and methenamine (0.025 mol/L) at 95 °C for 3 h without any stirring. Because nanowires growth slowed down after this period, substrate was repeatedly introduced to fresh solution in order to obtain longer wire arrays (total reaction times up to 12 h). The substrate was then rinsed with distilled water and baked in air at 350 °C for 2 h to remove any residual organics. The larger diameter ZnO nanowire arrays were prepared almost the same as the small one expected a 30 r/min stirring during the growth procedure.

2.2 The fabrication of hybrid ZnO nanowire/P3HT

P3HT was used as purchased commercially. The P3HT was spin-coated (800 r/min, 10 s) on the top of the ZnO nanowire arrays film from chloroform solution with a concentration of 2 g/L. The sample was then heated at 150 °C under vacuum for 20 min to facilitate the infiltration of the P3HT. The sample was allowed to cool naturally for about 2 h to help the recrystallization of P3HT.

2.3 Characterization

A JSM-5600 was used for scanning electron microscopy (SEM) imaging. The crystallinity of the ZnO nanowire arrays were characterized by X-ray diffraction (XRD) with X'pert MRD-Philips diffractometer equipment with Cu Kα radiation. The photoluminescence (PL, SPEX F212, SPEX Co.) spectra were measured to obtain the surface information and optical properties of the samples. UV-Vis absorption spectra were measured using a HEIλOSα spectrometer. The surface photovoltage (SPV) measurement system based on the lock-in amplifier is constituted by the source of light, a lock-in amplifier (SR830-DSP) with a light chopper. The construction of the photovoltaic cell is a sandwich-like structure as shown in Fig. 1.

3 Results and discussion

Figure 2 presented the SEM images of the ZnO nanowires. The entire ITO substrate was coated with a highly uniform and densely packed array of ZnO nanowires from the top-view images shown in Fig. 2a, c. Cross-sectional SEM images shown in Fig. 2b, d suggested that the ZnO nanowires had a tendency to grow perpendicular to the substrate