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Photocurrent enhancement in hybrid cadmium sulfide/conjugated polyaniline nanofiber composites by introducing iodine

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ABSTRACT

In this paper, the effect of iodine on the photocurrent of conjugated polymer/inorganic semiconductor nanocomposites is investigated. Via a redox process, iodine nanoparticles are coated on the surface of highly active nanofiber of conjugated polyaniline (PANI), forming an electron donor (i.e., I_2@PANI). After subsequent incorporation of CdS nanoparticles (serving as electron acceptors), the photocurrent of the I_2@PANI–CdS system is greatly enhanced as compared to that of the PANI–CdS hybrid. This obvious enhancement is due to the fact that the existence of I_2 causes significant improvement in the charge transfer, which has favorable penetration ability into the porous semiconductor film, fast charge transfer and relatively slow recombination with injected photoelectrons. As a result, the total concentration of charge carriers in the CdS nanoparticles may increase as compared to that in bulk CdS. As a result, the photocurrent of CdS in I_2@PANI–CdS nanocomposites is remarkably enhanced.

1. Introduction

Solar cells assembled from blending polymers with inorganic materials have the potential efficiency gap for clean energy of sun. However, the solar power conversion efficiency (PCE) of polymer solar-cell devices is ∼2.5%, not attaining the efficiencies of conventional solar cells which are typically above 10% [1]. As we know, because of the presence of ubiquitous electron traps, the electron mobilities are extremely low (typically below 10^{-4} cm^2 V^{-1} s^{-1}) for many conjugated polymers [2,3]. As a result, the inefficient charge transport due to the low carrier motilities limits the performance of polymeric devices. To overcome these limitations, inorganic semiconductors as another material are introduced to couple with the conjugated polymers for improving electron transport taking advantage of their high intrinsic carrier mobilities. Moreover, the nanostructured interpenetrating network in this solar cell device is constructed by electron donor (polymer) and electron acceptor materials (inorganic materials), enhancing the donor/acceptor interfacial area available for photogenerated exciton dissociated into charge carriers and enabling holes and electrons to be transported and collected, thus reduces the distance for the exciton that needs to travel before reaching an interface [4–8]. Charge photogeneration is therefore increased in this case [9–11]. However, the efficiency of these devices is still limited by the recombination of photogenerated hole–electron pairs at particle grain boundaries during charge transport across semiconductor particles [12–14]. The advent of methods to well improve the charge transfer rates and reduce the recombination of photogenerated hole–electron pairs can be achieved by designing inorganic semiconductors on the nanometer scale, with control of the morphology of composites and tuning of the interface states between conjugated polymers and inorganic semiconductors [15–21]. A series of effective methods to control the morphology of active layers were investigated, such as post annealing or solvent treatment, interfacial buffer layer, solvent additives and applied electric field on active layer during forming films [22]. Among them, doping active additives is a simple and convenient method to improve the performance of polymer solar cells (PSCs), which is suitable for large-scale manufacture and compatible with flexible substrates. Therefore, in this article, the iodine (I_2) was chose as the active additive to doping into CdS semiconductor/conjugated polyaniline (PANI) nanocomposites system, and the photoresponse of as-prepared active sample was studied.

Polyaniline (PANI) is an air stable conducting polymer and has attracted considerable attention for both fundamental research and industrial development because of its high electrical

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conductivity. Recent researches have shown that PANI can act as the excellent matrix for forming polymer–nanomaterial composites [23,24], such as the nanosized ZnO or CdS/PANI structures for luminescence [25,26]. These inorganic semiconductors can act as scaffolds in splitting and transferring a flow of photoinduced charge carriers in organic/inorganic hybrid structure, showing promising prospects in photoelectronic applications. Here we introduce nanocrystalline CdS as electron acceptors in hybrid conjugated polymer/inorganic semiconductor composites, not only because it is cheap and environmentally friendly, but also due to its tunable reactivity in high purity and crystallinity at low temperature [27,28]. The iodine nanoparticles are firstly coated onto the surface of polyaniline (PANI) nanofibers to increase the conductivity of PANI, serving as an electron donor (i.e., I_2@PANI). After subsequent incorporation of CdS nanoparticles, the photocurrent response of the system (I_2@PANI–CdS) is significantly enhanced.

2. Experimental

2.1. Electrochemical synthesis of PANI nanofibers

All reagents were supplied by Aladdin Chemistry Co., Ltd. and used as received without further purification. The PANI nanofibers were grown on indium tin oxide (ITO) electrodes in 0.093 g aniline and 0.98 g sulphuric acid electrolyte for 15 min at a working potential of 3.00 V at room temperature (Fig. 1a). The dark green products were washed with distilled water and ethanol for three times, and then dried in vacuum.

2.2. Preparation of I_2@PANI nanoparticles and I_2@PANI–CdS colloidal suspensions

I_2@PANI nanoparticles were prepared as follows: 1.0 g PANI, 0.01 g iodine and 0.01 mol/L KI were added into 50 mL 0.01 mol/L H_2SO_4 aqueous solutions, and then mixed by 25 mL ethanol at room temperature for one week. After that, the products were washed with distilled water for many times until pH 7, and dried in a vacuum oven. I_2@PANI nanocomposites with various mass percentages of I_2 were synthesized by adjusting the content of I_2 under the same condition (including 0.001 g, 0.005 g, 0.01 g, 0.015 g, 0.02 g, 0.025 g, 0.03 g, the mass percentages of I_2 in I_2@PANI are calculated to be 0.1%, 1%, 1.5%, 2%, 2.5%, 3% versus 1.0 g PANI). Then, I_2@PANI nanocomposites (0.5 g) were dispersed in cadmium acetate methanol solution (0.067 g mL^{-1}). And thioacetamide methanol solution (0.018 g mL^{-1}) was subsequently added under N_2 atmosphere, allowing the reaction for 12 h at room temperature to produce I_2@PANI–CdS methanol colloidal suspensions [29].

2.3. Preparation of I_2@PANI–CdS nanocluster layer

ITO (0.6 ± 0.04 cm^2) served as a conductive electrode after cleaning by distilled water, aether and methanol by sequence. Then the CdS, PANI–CdS and I_2@PANI–CdS methanol colloidal suspensions was drop coated on the surface of ITO, respectively. To form well-dispersed colloidal suspensions, a little N,N-dimethylformamide was added into the as-prepared suspensions before drop coating. Thickness of the as-prepared active hybrid ITO electrodes

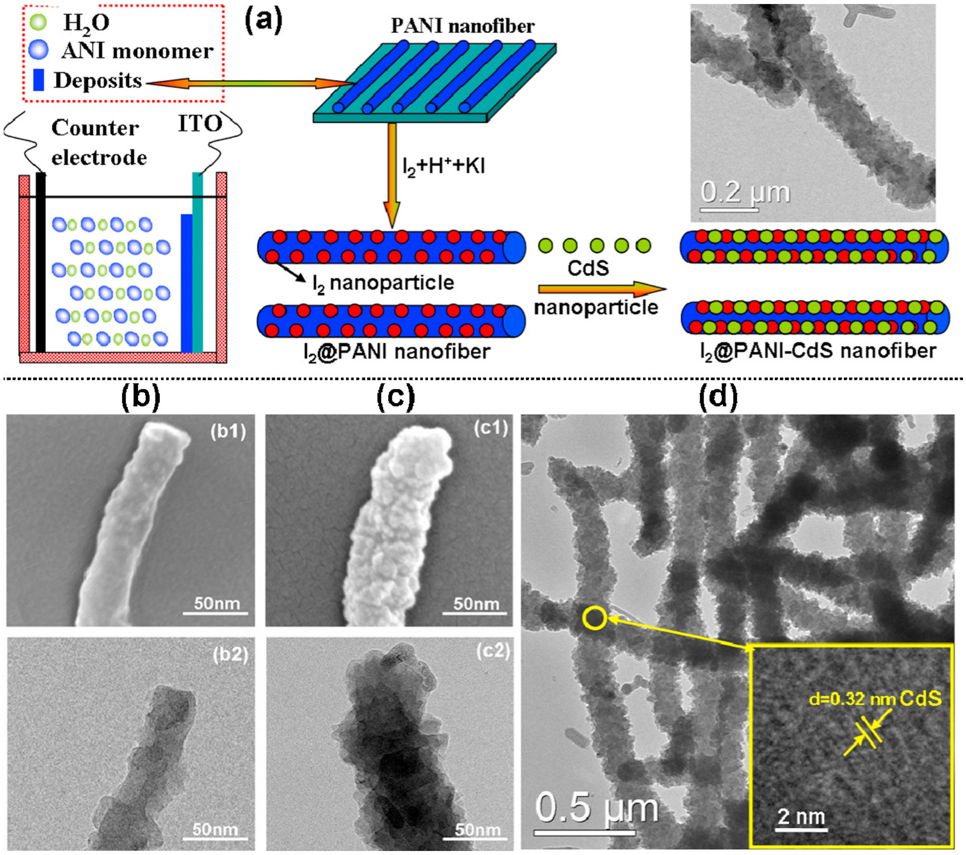

Fig. 1. (a) The assumed growth mechanism of the designed materials. Electron microscopic images of (b) PANI nanofiber, (c) I_2@PANI and (d) I_2@PANI–CdS (content of I_2: 1.5 wt%). (b1) and (c1) SEM. (b2), (c2) and (d) TEM. The inset of (d) is HRTEM of CdS nanoparticles.

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