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Recent advances in hybrid solar cells based on metal oxide nanostructures

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ABSTRACT

Hybrid solar cells are novel photovoltaic devices combining the advantages from organic and inorganic components. This paper mainly reviews our recent research advances in hybrid polymer-based solar cells (HPSCs) that have organic conjugated polymers as main electron donor and nanostructures of metal oxides (ZnO and TiO_2) as main electron acceptor in photoactive layer, with emphasis on the theoretical models for studying charge carrier transport dynamics by intensity modulated photocurrent spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy (IMVS), the preparation of nanomaterials for efficient devices, and the device performance related to nanostructural characteristics; a few examples of other hybrid solar cells that have a similar architecture but a different photovoltaic principle in respect to HPSCs are also included. Finally, main challenges in basic researches and practical applications of these solar cells are discussed.

1. Introduction

The conversion of solar energy into electricity has become a significantly widespread approach in the global use of renewable energy. Solar cells are of a crucial importance for solar photon harvesting and photon-to-current conversion in photovoltaic power generation system. The power conversion efficiency (η) of the solar cells based on crystalline silicon, chalcogenides and III – V semiconductors has surpassed 20% [1], but they are suffering from the use of high purity semiconductor materials, the high energy consumption, the limited supply of raw materials, and thereby the high cost in fabricating devices. To explore low-cost photon-to-current conversion materials and efficient solar cells and to understand the photovoltaic mechanism underlying are the major challenges in the research field of solar cells. The development of nanoscience and nanotechnology creates the good opportunities for low-cost and efficient solar cells [2]. For examples, dye-sensitized solar cells based on the inorganic TiO_2 mesoporous films sensitized by organic dye molecules have reached the efficiency of $\eta = 11 - 12\%$ [3–5], and the solar cells consisting of hybrid perovskite and mesoporous/nanostructured TiO_2 film have achieved the efficiency over 20% [6–9]. While these photovoltaic devices have shown a great potential in practical application [5,10], the long-term stability of them is still a major challenge. On the other hand, the polymer-based solar cells (PSCs) consisting of conjugated polymer as electron donor (D) and nanocrystals as electron acceptor (A) are the novel solid-state photovoltaic devices with many particular advantages such as solution-processibility on a large scale, light-weight and flexibility, which provide an important guarantee for a large-scale production, convenient transportation and broad application.

PSCs have generally two families according to the types of acceptor materials. The first one is organic polymer-based solar cells (OPSCs), which have a C_{60} or C_{70} derivative ($PC_{61}BM$, $PC_{71}BM$) as electron acceptor and an organic conjugated polymer as electron donor in photoactive layer. In the past years, OPSCs have been extensively and intensively investigated, with great advances in device materials, condensed structures in photoactive layer, and structure-related device performances [11–16], as well as large-scale production technology [17]. While the efficiency of OPSCs up to $\eta = 10\%$ has been achieved [1,18], the long-term stability in the condensed structure of photoactive layer, which correlates with the serious aggregation of acceptor particles upon exposure to elevated temperature and is crucial to maintain the stable device

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performance, is still the major difficulty encountered in the practical application of OPSCs. Another kind of PSCs is referred to as hybrid polymer-based solar cells (HPSCs) that have inorganic nanostructures as electron acceptors in photoactive layer. In 2002, Huynh et al. [19] reported the solar cells with a photoactive layer consisting of poly(3-hexylthiophene) (P3HT) and CdSe nanorods and obtained an efficiency of $\eta = 1.70\%$. In 2009, Mor et al. [20] fabricated the solar cells ($\eta = 3.80\%$) based on TiO_2 nanotube array and P3HT. In 2010, Dayal et al. [21] prepared the solar cells by using low band gap semiconductors poly(2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)) (PCPDTBT) and CdSe nanosized terapods and obtained the efficiency exceeding 3.13%. During 2010 – 2012, Seok et al. [22–24] achieved the efficiencies of 5.13%, 6.18% and 6.30% in the devices based on Sb_2S_3-sensitized mesoporous-TiO_2 films in combination with P3HT, PCPDTBT and PCPDTBT/$PC_{61}BM$ blend, respectively. Recently, on the basis of the synergistic effects of multicomponents with complementary properties, we achieved the efficiency of $\eta = 5.01\%$ in the HPSCs based on poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinyl- ene) (MEH-PPV) and ZnO nanorod array (ZnO-NA) as main electron acceptor and transporter [25]. Although the working principle and device architecture of HPSCs are similar to those of OPSCs, more efforts are still needed to enhance the efficiency of HPSCs and to understand the fundamental issues therein. In comparison to OPSCs, HPSCs have some unique advantages. First, the size and shape, the crystallographic structure, and the optoelectronic property of semiconductor nanocrystals can be tailored individually during synthesis for a tunable device performance; in particular, the controlled growth of nanostructures can facilitate the access to the thermally stable nanomorphology in photoactive layer. Second, the nanostructures can be easily assembled at low cost. Furthermore, HPSCs integrate together the electrical, optical and mechanical properties of inorganic and organic materials. A variety of semiconductor (e.g., ZnO, TiO_2, PbS, PbSe, CdSe and $CuInS_2$) nanostructures have been explored as effective acceptors for HPSCs. As for the acceptor and donor materials used in HPSCs, one may refer to the reviews published elsewhere [6,26–33]. Since nanostructures are often prepared by using some organic insulating ligands as capping agents to prevent them from aggregation, the HPSCs based on the nanostructures normally encounter the deficiencies related to the ligands that can deteriorate device performance by impeding the charge transfers between nanostructures and at polymer/nanostructure interfaces despite the compatibility between organic and inorganic components can be improved by the organic ligands [26,27,32,33]. Note, the advantage and disadvantage related to the device architecture in HPSCs are discussed in later sections.

Up to now, studies of HPSCs have been focusing on the exploration of materials and device structures. If a breakthrough in the efficiency of HPSCs is achieved after the reasonable design and optimization of materials and device structures, HPSCs will be of a great application potential. The nanostructures of ZnO and TiO_2 are promising acceptor materials for HPSCs, because they are environment-friendly, transparent in visible spectrum and easily available. This review provides an overview on our recent investigations on the materials and structure-related device performance in the HPSCs with ZnO and TiO_2 nanostructures as main electron acceptors. We start with a brief introduction to the basic knowledge of HPSCs, including working principle, device architecture and characterization. Then, we focus on our recent research advances in the theoretical models for studying the charge carrier transport dynamics by intensity modulated photocurrent spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy (IMVS) techniques, the efficient materials and devices, and the nanostructure-related device performance; we also extend hybrid solar cells to those with organic conjugated polymer mainly as an auxiliary material (e.g., buffer layer) rather than a photoactive component, and therefore other hybrid solar cells that have a similar architecture to HPSCs but work differently in photovoltaic principle are also covered in this review. Finally, the main conclusion remarks from our results and the perspectives for efficient hybrid solar cells are provided. Noticeably, we have published a review in Chinese summarizing our recent researches on HPSCs [34], and the present review is a majorly revised version with addition of latest results.

2. Basic knowledge of HPSCs

2.1. Working principle

HPSCs are a kind of excitonic devices, of which the photon-to-current conversion generally involves that polymer absorbs photons to generate excitons (bound electron–hole pairs) and the photogenerated excitons diffuse to D/A interface for dissociation into free charge carriers [electrons (e) and holes (h)] that are sequentially transported within A and D components to their respective collection electrodes for photocurrent generation (Fig. 1). The exciton binding energy (E_b) in conjugated polymers is estimated to be 0.4 – 0.5 eV, much higher than the thermal energy at ambient temperature ($k_BT \sim 26$ meV, where k_B is the Boltzmann constant and T is the temperature) [12,13], and thereby only about 10% of photogenerated excitons can directly separate into free charge carriers in the conjugated polymers [35]. Furthermore, the internal built-in electric field (E_{bi}) provided by the work function (W_f) difference of electrodes is usually not strong enough to cause the dissociation of the excitons generated in conjugated polymers [36,37]. Hence, photoexcitation generally cannot produce free charge carriers in conjugated polymers, and the excitons generated by the polymer absorption in HPSCs need to diffuse to D/A interface for dissociation into free charge carriers with electrons injected into acceptor material and holes remaining in the polymer.

The electron injection from donor into acceptor occurs on a time scale of picoseconds [14,15]. In order to generate photocurrent, the charge carriers must be collected by electrodes. Since the hole mobility in conjugated polymers is normally quite low ($10^{-1} – 10^{-7}$ $cm^2 V^{-1} s^{-1}$) [11], the photocurrent in HPSCs mainly results from the contribution of photogenerated electrons with a negligible contribution of photogenerated holes [38]. The electrons are transported toward electrode by diffusion process. Our results [39] revealed that E_{bi} imposes an ignorable effect on electron diffusion process, but it can help the photogenerated electrons to diffuse toward correct electrode. The nanostructures normally contain many intraband surface states (SS) with an

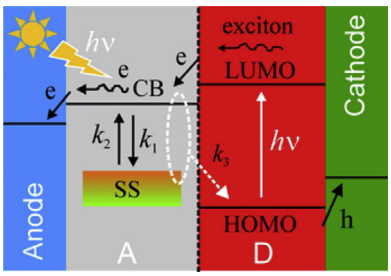

Fig. 1. Charge transfer processes in HPSC devices, where the SS states influence the electron transport by trapping (k_1) and detrapping (k_2) processes. The parameters k_1, k_2 and k_3 are the rate constants for trapping, detrapping and recombination processes of photogenerated electrons, respectively.