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Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

The origin of efficiency enhancement of inorganic/organic Hybrid solar Cells by robust samarium phosphate nanophosphors



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ARTICLE INFO

Article history:

Received 13 May 2014

Received in revised form

16 July 2014

Accepted 17 July 2014

Keywords:

Hybrid solar cell
Samarium phosphate
Electron/hole transport
Rare-earth compounds
Titanium dioxide

ABSTRACT

An effective energy level regulation of acceptor by doping samarium phosphate nanophosphors (SmPO₄ NPs) was reported for inorganic/organic hybrid solar cell applications. SmPO₄ NPs doped TiO₂/P3HT bulk heterojunction (BHJ) solar cell shows an enhanced power conversion efficiency of approaching 3% as compared with that of its counterpart without SmPO₄ NPs (1.98%). The underlying photophysical mechanism was probed by applying femtosecond transient absorption spectroscopy and the results show that the efficiency enhancement was ascribed to the improved hot electron, less energetic electron, hole transports at the interface of BHJ apart from down-conversion photoluminescence of SmPO₄ NPs. It has been evidenced that the hot electron transfer life time was shortened by more than 40% (i.e., from $\tau_{\text{hot-e}} = 30.2$ to 17.9 ps) than pure TiO₂ acceptor while the hole transfer lifetime was boosted by almost 20% (i.e., from 6.92 to 5.58 ns). Such charge carrier improvements stem from the efficient energy level regulations by SmPO₄ NPs. In detail, the conduction band (CB) edge of TiO₂ has been elevated by 0.57 eV while the valence band (VB) edge has been elevated by 0.32 eV, thus not only narrowing down the energy offset between CB energy levels of acceptor TiO₂ and donor P3HT, but also meanwhile enlarging the band gap of TiO₂ itself that permits to inhibit electron-hole recombination within TiO₂. This work demonstrates that samarium ions can efficiently facilitate exciton generation, dissociation and charge transport and have an important role in enhancing photovoltaic performance.

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1. Introduction

Rare-earth ions, which can broaden the absorption domain and improve the charge transfer by the doping effects [1–3], have attracted significant attention due to their intrinsic and unique conversion properties [4–7]. Especially, samarium ions have demonstrated excellent performances in enhancing exciton generation, ultraviolet light harvest via a down-conversion luminescence process in dye-sensitized solar cells (DSSCs) [7–9], or organic photovoltaic cells (OPV) [10]. Bearing such merits of samarium ions in mind, it is envisioned that samarium ions should also be critical to the new concept of hybrid solar cells (HSCs). So far, although silicon solar cell [11], DSSCs [12] or various kinds of hybrid solar cells (HSCs) such as hybrid Si-organic solar cells [13] and hybrid-DSSC devices [14] have attained a solar-to-electric power conversion efficiency (PCE) of more than 10% milestone, nevertheless all of them suffer

from either the expensive raw materials and fine processing [15] or the challenging long-term stability [16–18].

Inorganic/organic HSCs, with a bulk-heterojunction (BHJ) architecture generally consisting of an organic conjugated polymer as the hole transport material and inorganic semiconductor as electron transport material in a photoactive layer, have attracted increasing attention and aroused great interests to the researchers [19–23]. The concept of inorganic/organic HSCs can exploit the advantageous properties of two systems, such as utilizing the inexpensive raw materials and facile solution-processed manufacturing of polymer to enable potentially low-cost solar cells [24–26]. Despite the advantages of inorganic/organic HSCs, as a relatively newly emerging hotspot, to attain a desirable efficiency of solar cells based on inorganic nanoparticles and a well-known conducting polymer poly(3-hexylthiophene) (P3HT) BHJ remains challenging and still in their infancy. Over the last five years, the PCE of HSCs is typically low [13,22,27–29]. In particular, most of the reported PCE of hybrid inorganic/organic solar cells based on P3HT is around 2%, ranging from 1.7–3.0%, depending on the type of inorganic nanocrystals (except quantum dots, which are more related to colloidal quantum dot solar cells [30]), their morphologies and others [15]. Because

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of the outstanding physicochemical properties of titanium dioxide (TiO₂), such as photostability, non-toxicity, inexpensiveness and appropriate electronic band structure, it is widely recognized as the most promising and versatile photocatalyst. Therefore TiO₂-P3HT system hold shows great promise in pursuing efficient and low-cost HSCs. However, the solution-processed light-harvesting films prepared by the hydrothermal techniques are typically amorphous or probably polycrystalline [31,32] and suffer from poor charge carrier transport. One promising approach to overcome this demerit is the doping of samarium ions. However, little research has been done to elucidate the origins of doping effect by the samarium ions thus far. Herein, the role of SmPO₄ NPs acting as widening absorption range of donor P3HT and tailoring energy band positions of acceptor TiO₂ was studied by photoluminescence (PL) spectrum and cyclic voltammetry (CV) characteristics. Through pump-probe spectroscopy and femtosecond transient absorption spectroscopy, both the electron and hole transport dynamics were successfully monitored and concrete evidences have been provided that both the electron and hole transfers at the interface from donor to acceptor have been boosted.

2. Experimental

2.1. Materials

All analytical purity chemical reagents including tetrabutyl titanate, polyethylene glycol (PEG, molecular weight of 20000), nitric acid, phosphoric acid, P25 (Degussa), OP emulsifying agent (Triton X-100), diammonium hydrogen phosphate, acetonitrile, isopropanol, samarium nitrate hexahydrate, ammonium phosphate dibasic, P3HT and poly(3,4-ethylenedioxyethenethiophene)-polystyrene sulfonic acid (PEDOT:PSS) were purchased from Sigma-Aldrich, Hongkong, China except where otherwise indicated. The weight average molecular weight M_w of P3HT was 10237 with the polydispersity index (PDI) = $M_w/M_n = 1.19$, where $M_w = 10237$ and the numerical molecular weight $M_n = 8582$. Fluorine-doped tin oxide glass (FTO, sheet resistance $8 \Omega \text{ cm}^{-2}$) was purchased from Hartford Glass Co., USA.

2.2. Preparation of SmPO₄ nanophosphors

SmPO₄ NPs were prepared by a modification of the hydrothermal method as reported before [33]. Firstly, SmN₃O₉·6H₂O (0.843 mmol) was thoroughly dissolved in de-ionized water (10 mL), then was quickly transferred into a Teflon-lined stainless-steel autoclave, followed by adding 0.862 mmol of (NH₄)₂HPO₄ into the autoclave under stirring. Afterwards, an appropriate amount of de-ionized water was added until the filled degree reached 80% of the total container volume. Then, the pH value of the mixed solution was adjusted to 4 using phosphoric acid. The obtained solution was hydrothermally treated at 200 °C for 12 h. After being naturally cooled to room temperature, the obtained product was centrifuged, washed until the pH value of the system reached 7, and then dried in air at ambient temperature, followed by sintering in air at 850 °C for 30 min.

2.3. Synthesis of SmPO₄ NPs:TiO₂ acceptor colloid

The acceptor colloid was prepared by the following procedure in a similar way as reported before [16,34]. Tetrabutyl titanate (10 mL) was added to distilled water (100 mL) under stirring, then a white precipitate was formed immediately. The precipitate was filtered, washed with distilled water, and then transferred to 150 mL of a mixed solution containing nitric acid (1 mL) and acetic acid (10 mL) at 80 °C. Under vigorous stirring, a light blue TiO₂ precursor was formed, followed by an ultrasonic stirring for

30 min. Finally, the mixture was hydrothermally treated in an autoclave at 200 °C for 24 h to form a colloid of TiO₂. Subsequently, the P25 (0.75 g, 10 wt%) and SmPO₄ NPs (0.375 g, 5 wt%) were dispersed into the TiO₂ colloid by ultrasonically vibrating for 90 min and hydrothermally treating at 200 °C for 12 h to form an acceptor colloid containing TiO₂ and SmPO₄. At last, the resultant slurry was concentrated to 1/5 of its original volume by a thermal evaporation, and PEG-20000 (0.5 g) and a few drops of the Triton X-100 emulsification reagent were added, finally an even and stable TiO₂ colloid was produced.

2.4. Fabrication of HSC devices

A layer of nanocrystalline SmPO₄ NPs:TiO₂ acceptor film with a thickness of 200 nm was prepared by coating the acceptor colloid on FTO glass using a doctor blade technique, followed by sintering in air at 450 °C for 30 min. Then, the acceptor film was dipped and completely immersed into 20 mL of 25 mg mL⁻¹ P3HT methylbenzene solution using a ground weighting bottle for 12 h to uptake P3HT molecules; After 12 h, the acceptor film was pulled out, washed several times using methylbenzene, and finally dried in nitrogen atmosphere. Next, the PEDOT:PSS layer was spin-coated onto the BHJ. Finally, about 50 nm thickness of Pt electrode was deposited on the top of the PEDOT: PSS layer by thermal evaporation under vacuum.

2.5. Characterizations

The phases were identified by an X-ray diffractometer (XRD, MiniFlex II, Rigaku Ltd., Japan) using Cu K α radiation ($\lambda = 0.154 \text{ nm}$) at a power of 30 kV and 40 mA. The XRD data were collected in a scan mode at a scanning speed of $5^\circ \cdot \text{min}^{-1}$ in the 2θ range between 10 and 80°. The microstructure of the SmPO₄ NPs was characterized by using a transmission electron microscope (TEM, JEM-2010, JEOL Ltd., Japan) working at 200 kV, and high-resolution TEM (HR-TEM) and selected area electron diffraction (SAED) were also carried out. Samples for TEM and HR-TEM were prepared by ultrasonically dispersing the samples in the absolute ethanol, followed by placing a small volume of this suspension on carbon-enhanced copper grids, and drying in air. The number average molecular weight (M_n) and weight average molecular weight (M_w) of P3HT were determined by gel permeation chromatography (GPC, WATERS515) by diluting P3HT in tetrahydrofuran (THF) with the concentration of 2 g L^{-1} by dissolving 1 mg P3HT into 0.5 mL THF, which was applied as mobile phase and delivered at a rate of 1.0 mL min^{-1} , then the polydispersity index (PDI) is calculated by $\text{PDI} = M_w/M_n = 1.19$, where $M_w = 10237$ and $M_n = 8582$. The morphologies of the BHJ and the cross-section of the BHJ were characterized by using a field emission scanning electron microscope (FE-SEM, S4800, Hitachi Ltd., Japan). Energy dispersive X-ray spectroscopy (EDS) spectrum was recorded by using an FE-SEM equipped with an EDS detector (OXFORD 7021). The cyclic voltammetry (CV) characteristics were obtained using a BAS 100B instrument (BASi Inc., USA) at room temperature and a scan rate of 50 mV s^{-1} with tetrabutylammoniumhexafluorophosphate (TBAPF₆, 0.1 M) in acetonitrile as the supporting electrolyte, a platinumized platinum (0.5 cm^2) as the counter electrodes, Ag/Ag⁺ electrode as the reference electrode (versus F_c/F_c⁺). The TiO₂, SmPO₄ NPs:TiO₂ and SmPO₄ films were used as work electrodes, respectively. The photocurrent-voltage (J - V) characteristics of the assembled HSCs were recorded on an Electrochemical Workstation (Xe Lamp Oriol Sol₃A™ Class AAA Solar Simulators 94023 A, USA) under irradiation of a simulated solar light from a 100 W xenon arc lamp in ambient atmosphere.

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