Reducing the excess energy offset in organic/inorganic hybrid solar cells: Toward faster electron transfer

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ABSTRACT

The photoexcited electron transfer rate represents one of the most important properties required for photovoltaic devices. However, the fabrication of solar cells with a faster electron transfer remains a technological challenge. Regulating the energy level alignment of acceptor-donor system by the incorporation of foreign ions is one of the most promising strategies to achieve this aim. Herein we demonstrate that the incorporation of silver ions into TiO_2 nanocrystals results in a remarkable reduction of energy offset between the conduction band edge of acceptor and the lowest unoccupied molecular orbital of donor. In particular, the electron transfer life time was shortened from 30.2 to 18.3 ps, i.e., almost 40% faster than pure TiO_2 acceptor, thus leading to a notable enhancement of power conversion efficiency by almost 38% in organic/inorganic hybrid solar cells. The reduction of the 'excess' energy offset accelerates the electron transfer, which is expected to have an important role in applications of solar energy conversion and photon detectors.

1. Introduction

Organic/inorganic hybrid solar cells (HSCs) are one of the promising candidates to provide clean energy owing to their low cost, simple architecture and flexible solar modules[1]. These HSCs are capable of exploiting the unique advantageous properties of both types of materials such as low-temperature solution-processing of organic semiconductors and high electron mobility of inorganic semiconductors [2]. As one of the newly emerging hotspots, HSCs based on the well-known conducting polymer poly(3-hexylthiophene) (P3HT) have attracted much attention [1,3–7] thus far. Despite recent advances, the fabrication of low-cost and high power conversion efficiency (PCE) HSCs remains a technological challenge. Over the past five years, most of the P3HT-based organic/inorganic HSCs have demonstrated a PCE ranging from 1% to 3%, depending on the type of the inorganic nanocrystals, their morphologies, shapes, and others [3,8–10]. Many attempts have been made to enhance the performances of HSCs by controlling the size, shape and morphologies of the semiconductors, utilizing low

band gap organic materials, or introducing buffer layers [11–14], etc. Among them, one facile and efficient approach is to introduce foreign metal ions (such as Ag, Ni, Mo, Cr, Co, etc.) into inorganic semiconductors [15–20]. Ag-doped titanium dioxide (TiO_2), being considered as a promising photocatalytic material [21–23], has drawn considerable attention in solar cells [24–26]. On one hand, Ag–TiO_2 nanocomposites have exhibited intriguing properties thus far, including the increased scattering, the enhanced solar light harvest by broadening the photo response of TiO_2 from the ultra-violet (UV) to visible light, the improved anatase crystallinity and the boosted conductivity of the TiO_2 electrodes and also the inhibited recombination of the photoexcited carriers, etc. These merits of Ag–TiO_2 nanocomposites have been widely documented in literatures [24,26–28]. On the other hand, the silver ion does not damp out the plasmon mode as strongly as other metals because its d–s band gap falls within the ultraviolet visible (UV–vis) region [29]. Therefore, Ag-decorated TiO_2 photocatalyst holds great promise in the applications of solar energy.

Although Ag-doped TiO_2 nanocrystals have exhibited excellent characteristics, nonetheless the origin of the intrinsic driving force behind the excellent performances remains unknown. What is more, the inefficient charge separation and the strong geminate recombination [30] within the bulk heterojunction (BHJ) remain

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the bottlenecks for the ultimate device performance [9]. These open questions and existing problems motivate us to promote the dissociation of photogenerated electron–hole pairs and to accelerate the charge transport rate. Because the charge transfer rate of photoexcited electron/hole at the interface of BHJ during the charge photogeneration is one of the key factors influencing the device performance [31]. Herein, an effective strategy to overcome these obstacles is to incorporate the silver ions into the inorganic semiconductors. However, the crucial role of energy level regulation induced by Ag-modified TiO_2 and the complicate photoexcited electron transport dynamics at the interface of donor and acceptor have not yet been clarified. Therefore, silver-doped TiO_2 nanocrystals were first synthesized using the hydrothermal method in this work and then employed to control the energy level of acceptor. Finally, the effects of Ag doping on the energy level regulation, photoexcited charge carrier transfer and the photovoltaic device performances were examined by cyclic voltammetry (CV), steady-state photoluminescence (PL) and transient PL spectroscopies, etc.

2. Experimental

2.1. Materials

All analytical purity chemical reagents including tetra-butyl titanate, silver nitrate ($AgNO_3$), polyethylene glycol (PEG, molecular weight of 20,000), acetonitrile, nitric acid, acetic acid, P25 (Degussa), isopropanol, tetrabutyl-ammonium hexafluorophosphate ($TBAPF_6$), OP emulsifying agent (Triton X-100), methylbenzene, conjugated polymer P3HT and poly(3,4-ethylenedioxylenethiophene)-polystylene sulfonic acid (PEDOT:PSS) were purchased from Sigma–Aldrich Ltd., Hongkong, China except where otherwise indicated. Fluorine-doped tin oxide glass (FTO, $8\,\Omega\,cm^{-2}$) was purchased from Hartford Glass Co., USA.

2.2. Synthesis of Ag-doped TiO_2 colloid

The Ag-doped TiO_2 colloid was prepared by a minor modification of the hydrothermal method [32,33]. Tetrabutyl titanate (10 mL) was added to distilled water (100 mL) under stirring, followed by a white precipitate immediately. Then, 5 mL of 1 M $AgNO_3$ water solution was added into the tetrabutyl titanate solution. After that, the precipitate was filtered, washed with distilled water, and then transferred to a mixed solution (150 mL) containing nitric acid (1 mL) and acetic acid (10 mL) at 80 °C. Under vigorous stirring, a light blue Ag-doped TiO_2 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 Ag-doped TiO_2. Subsequently, the P25 (0.075 g) and OP emulsifying agent (1 mL) were dispersed into the colloid by ultrasonically vibrating for 90 min and hydrothermally treating at 200 °C for 12 h to form a white colloid. 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 Ag-doped TiO_2 colloid was produced.

2.3. Fabrication of HSC

A layer of Ag-doped TiO_2 acceptor film with a thickness of 200 nm was prepared by coating the Ag-doped TiO_2 colloid on FTO glass using spin-coating technique, followed by sintering in air at 450 °C for 30 min. Then the acceptor film was soaked in a 0.15 M P3HT methylbenzene solution for 12 h to uptake P3HT for the fabrication of BHJ. Next, the PEDOT:PSS layer was spin-coated onto the

BHJ. Finally, Pt electrode was deposited on the top of the PEDOT:PSS layer by thermal evaporation under vacuum.

2.4. Characterizations

The morphology of acceptor layers were characterized by using a field emission scanning electron microscope (FE-SEM, Hitachi S4800, Japan). The cross-section samples for SEM characterization were prepared by breaking a HSC anode in half. Elemental analysis was conducted using Genesis energy dispersive spectrum (EDS) software. The CV and electrochemical impedance spectroscopy (EIS) results were obtained using a BAS 100B instrument (BASi Inc., USA) at room temperature and at a scan rate of $50\,mV\,s^{-1}$ with 0.1 M $TBAPF_6$ in acetonitrile as the supporting electrolyte, a platinized platinum ($1.0\,cm^2$) as the counter electrodes, and Ag/Ag^+ electrode as the reference electrode. The crystalline structures of the samples were characterized by X-ray diffraction (XRD) patterns on a X-ray diffractometer (MiniFlex II, Rigaku Ltd., Japan) using Cu Kα radiation (λ = 0.154 nm) at 50 kV and 250 mA at room temperature. X-ray photoelectron spectrum (XPS) measurements were performed using an Al Kα X-ray source on a multifunctional imaging electron spectrometer (Thermo ESCALAB 250XI, USA). The residual concentration of silver ions was monitored by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Leeman Co., USA, PROFILE SPEC). The PL spectrum was measured by using a spectrophotometer (FLS920, Edinburgh, UK), in which a xenon lamp and a photomultiplier tube (R955, Hamamatsu, Japan) were used as excitation source and fluorescence detector, respectively. The photocurrent–voltage (J–V) curves of the assembled HSCs were recorded on an Electrochemical Workstation (Xe Lamp Oriel Sol3A^{TM} Class AAA Solar Simulators 94023A, USA) under irradiation of a simulated solar light from a 100 W xenon arc lamp in ambient atmosphere, which was calibrated using a Newport-certified single crystal silicon solar cell.

Charge Photogeneration Dynamics: Transient PL measurements were carried out on a spectrometer (250IS/SM, Bruker Optics, Germany) with intensified charge coupled device detector (IStar740, Andor, UK). The samples were excited by 120 fs laser pulses at 400 nm with a repetition rate of 10 Hz. The time resolution of this experiment was determined to be ~60 ps. Transient absorption spectrum (TAS) measurements of the BHJs were performed by the mode-locked Ti:sapphire laser (Mira 900, Coherent Inc., USA) in combination with a regenerative amplifier (Legend-F, Coherent Inc., USA). The ultrafast light source with a temporal resolution of ~120 fs was generated by a mode-locked titanium-sapphire laser operating at 800 nm. Each data was obtained by averaging 100 individual measurements to improve the signal-to-noise ratio (SNR), and the typical detection sensitivity of the difference absorption ($\triangle$OD) was better than 10^{-4}.

3. Results and discussion

3.1. Characterizations of acceptors

The XRD patterns of Ag-doped TiO_2 and bare TiO_2 nanocrystals calcined at 450 °C are shown in Fig. 1A. Both of the samples exhibit the identical diffraction peaks at 25.48°, 37.75° and 48.01°, corresponding to the distance spacings of 3.51, 2.37 and 1.89 Å, respectively, which can be indexed as the anatase phase of TiO_2 (JCD 01-084-1286). In addition, a typical but weak peak at 27.443° was also observed for both of the samples, implying the presence of the rutile phase (JCD 00-001-1292) with the corresponding d-space of d = 3.25 Å. In short summary, it was revealed from the XRD patterns that the prepared nanocrystals are predominantly anatase phase TiO_2 with only a small amount of rutile phase TiO_2.