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Highly efficient triarylene conjugated dyes for dye-sensitized Zn_2SnO_4 solar cells

Jie Dou [a,b], Yafeng Li [a,b,*], Fengyan Xie [a,b], Tahsin J. Chow [c], Mingdeng Wei [a,b,*]

[a] State Key Laboratory of Photocatalysis on Energy and Environment, Fuzhou University, Fuzhou, Fujian 350002, China
[b] Institute of Advanced Energy Materials, Fuzhou University, Fuzhou, Fujian 350002, China
[c] Institute of Chemistry, Academia Sinica, No. 128, Sec. 2, Academia Rd., Nangang Dist., Taipei 11529, Taiwan

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ABSTRACT

Zinc stannate (ZTO) is a class of ternary oxides that are known for their stable properties and high electron mobility. Also, its chemical compositions and band structures are easy to be controlled, and which is thus ideal for applications in dye-sensitized solar cells (DSCs). However, the structures of most dyes are optimized for the widely used TiO_2. Therefore, the efficient dyes that are especially suitable for ZTO are highly desired. In this study, the dyes containing phenylene-thiophenylene-phenylene bridge (PSP) were found to match well with the band structures of ZTO and could be used as efficient sensitizers for ZTO-based solar cells. Moreover, the pre-calcination temperatures have great influence on the band structures of ZTO. When ZTO nanoparticles were pre-sintered, although the adsorption amount of dyes was decreased, the charge collection efficiency was confirmed to be enhanced greatly. A cell sensitized by optimized PSP dyes exhibited a power conversion efficiency of 4.68%, which was much higher than that of widely used N719 and D131.

1. Introduction

Dye-sensitized solar cells (DSCs) have attracted widespread attention due to the low cost, simple technology and the relatively high photoelectric conversion efficiency. During the past decades, considerable research focuses on the development of photoanodes with various nanostructures, the dyes with broad absorption spectra, the electrolytes with different redox composites and the counter electrodes with low-cost and high catalytic activity. As well known, photoanode is one of the critical factors that influence the efficiency of the DSCs. Thus far, the great proportion of scientific research has been devoted to the photoanodes based on binary metal oxides, such as TiO_2 (Hwang et al., 2015; Wu et al., 2014) and ZnO (Kunzmann et al., 2016). Compared with binary metal oxides, the chemical compositions and band structures of the complex ternary oxides are easier to be controlled. Therefore, the ternary oxides provide great potential for ideal materials used in DSCs. Among ternary oxides, Zn_2SnO_4 is a n-type semiconductor with a band gap of 3.6 eV, which is known for its stable properties under extreme conditions and relatively high electron mobility of 10–15 $cm^2 V^{-1} s^{-1}$. More recently, Hong and his co-works reported a facile hydrothermal synthesis of fine and uniform Zn_2SnO_4 nanoparticles with an average size of 8 nm, which exhibited a good photovoltaic performance (Kim et al., 2012). However, the power conversion efficiency of Zn_2SnO_4 based DSCs is still much lower than TiO_2 due to the unfavorable band structure of Zn_2SnO_4 (Zhao et al., 2016; Wang et al., 2013).

As for DSCs, some approaches were reported to be effective in enhancing the performance of solar cells. For example, the severe charge recombination is disadvantageous for the further improvement of efficiency. Below the conduction band (CB) edge, the electronic states which situated at the surface of photoanode nanocrystal, could serve as recombination traps and centers to decrease speed of electron transport (Barnes et al., 2009; Peter et al., 2006). For this reason, the reduced density of surface centers and traps (Bisquert et al., 2004), in together with the energy barrier for restraining electron transfer to the electrolyte (Palomares et al., 2003) could improve the performance by reducing the charge recombination. Moreover, the surface treatment that changes flat-band position and shifts energy of the semiconductor relative to the redox potential by interfacial dipole (Rühle et al., 2005) and HNO_3 treatment (Shin et al., 2013) have been reported to enhance the efficiency of DSCs (Chen et al., 2014; Park et al., 2009). At the same time, the sample treatment in ternary metal oxide has not be widely intensively and not much examples have been demonstrated. The influence of pre-calcination on the perfor-

* Corresponding authors at: State Key Laboratory of Photocatalysis on Energy and Environment, Fuzhou University, Fuzhou, Fujian 350002, China.
E-mail addresses: liyf@fzu.edu.cn (Y. Li), wei-mingdeng@fzu.edu.cn (M. Wei).

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mance of DSCs based on ternary oxides has never been studied in previous reports, which deserves a detailed investigation. In our previous studies, the surface treatment on the surface of photoanodes with Al^{3+} ions or chemical-bath deposition method had great influence on enhancing this power conversion efficiency (Li et al., 2011).

In addition to changing the band structure of complex oxides, more attention should be paid to the development of dyes which match better with ternary oxides. At current stage, the structures of the most dyes are optimized for TiO_2. However, the dyes especially suitable for ternary oxides are seldom designed. Therefore, the new type organic dyes with proper orbital energy level and wide absorption spectra will be in great demand for ZTO-based DSCs. By optimizing the structure of these dyes, the energy level between the dyes and ZTO will match better, which makes the excited electrons inject into the CB of electrode materials quicker and improve the photoelectric conversion efficiency of DSCs. Recently, Kim group reported that Zn_2SnO_4-based DSCs with an organic dye (SJ-E1 and SJ-ET1) demonstrated outstanding enhanced efficiency compared to the DSCs sensitized by N719 (Hwang et al., 2014). However, the organic dyes are still in great demand for the development of highly efficient dye-sensitized ZTO solar cells.

In the present paper, we fabricated high-efficiency DSCs using ZTO nanoparticles and organic sensitizers. Two different organic sensitizers (Npsp and CBpsp), which have a donor-π-conjugated-accepter (D-π-A) structure, were synthesized and first used for the DSCs based on the ternary oxide. Moreover, the ZTO nanoparticles were calcined prior to the preparation of the paste to explore the influences of this factor on the performance. The optimized DSCs with Npsp exhibited a power conversion efficiency of 4.68%, which was much higher than that of conventional ruthenium complex dye (N719) and organic dye (D131).

2. Experimental section

2.1. The synthesis and characterization of the samples

The preparation of ZTO nano crystals with the size of 20 nm and the long procedure of preparing ZTO paste can be received on our previous paper (Huang et al., 2010; Annamalai et al., 2010). In a synthesis of the common method, 0.5843 g of tin chloride pentahydrate and 0.4543 g of zinc chloride were dissolved in 54 mL mixture solvent of ethanol and distilled water. The volume ratio of deionized water to ethanol was 1:1. Then, 13 mL of 1.0 M Na_2CO_3 aqueous solution was dripped to the above mixture solution. After stirring for 15 min, the suspension was transferred to the 90 mL sealed Teflon autoclave and held at 200 °C for 24 h. The fabricated samples were washed by distilled water and ethanol and then heated to 300 °C, 450 °C and 600 °C at a speed of 3 °C min^{-1} and kept at different temperatures for 3 h in air. After cooled to room temperature, the white powder ZTO was collected.

The fabricated samples were characterized by scanning electron microscope (S-4800 instrument), transmission electron microscope (TEM, FEI F20 S-TWIN instrument), X-ray diffraction (Rigaku Ultima IV, Cu Kα, λ = 1.5418 Å) and Surface Area Analyzer (ASAP 2010, Micromeritics Instrument).

2.2. DSCS fabrication and measurements

The manufacture of the DSCs was executed by screen printing method on FTO (14 Ω/sq^2, Nippon Sheet Glass) using the ZTO powder with ethyl cellulose (20 wt%, Wako Co.) and the mixture solution compose of ethanol and α-terpineol (Aladdin Co.), then heated at 525 °C for 2 h. For the ZTO photoanode with thickness of ~20 μm, the working electrode with the photoactive area of 0.25 cm^2 was immersed into a solution including 0.3 mM different dyes in mixture solvent of acetonitrile and isopropyl alcohol (v/v = 1:1) for 18 h. As a counter electrode, the Pt-coated FTO glass was prepared by dropwise adding the H_2PtCl_6 (5 mM) solution on the FTO glass. Then those Pt-coated FTO glass were kept at 400 °C for 15 min in air. To prevent the DSCs from short-circuiting, the polyethylene spacer was placed between the photoanode and the counter electrode. The electrolyte composition is 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide, 0.5 M 4-tertbutylpyridine, 0.1 M LiI and 0.05 M I_2 in acetonitrile.

The film thickness was evaluated by Surfcom 130A (Tokyo Seimitsu). The photovoltaic performance of the solar cells was measured with a source meter (Keithley 2400). An AM1.5 solar simulator PEC-L11 (Peccell Technology Co. Ltd., with a 1000 W Xe lamp and an AM1.5 filter) was used as the light source (100 mW cm^{-2}). The spectra of IPCE were acquired from the PEC-S20 (Peccell, Technology Co. Ltd.). IMVS and IMPS were investigated using the electrochemical work station (IM6, Zahner). Under a modulated blue light emitting diodes (457 nm), the frequency response analyzer was driven by a Zahner (PP211) source supply. The EIS experiments were also measured on the electrochemical work station (IM6, Zahner). The frequency range of EIS experiments was from 65 mHz to 65 kHz with a bias direct voltage of −700 mV and the alternating potential modulation signal was 10 mV in the dark. The data were fitted and analyzed by the Zview software. The UV–vis spectra were determined with the Lambda-950 (Perkin-Elmer). To compare the loading amount of dyes, the sensitized photoanode was immersed in the 0.1 M NaOH solution with deionized water and ethanol (v/v = 1/1) as solvents. The dyes could be desorbed from the ZTO photoanode completely after immersion for about 24 h in the dark.

3. Results and discussion

A typical XRD pattern of ZTO calcined at 450 °C is shown in Fig. 1a. The diffraction reflections can be indexed to a cubic structural Zn_2SnO_4 (JSPDS24-1470), in which the diffraction peaks at 34.29, 55.12 and 60.41 degree can be indexed to (311), (511) and (440) crystal planes of Zn_2SnO_4, respectively. The TEM image shown in Fig. 1b confirms that the size of ZTO nanoparticles calcined at 450 °C was found to be about 15–20 nm. The lattice fringes of 0.306 and 0.261 nm can be observed from the HRTEM image of a single ZTO particle in inset of Fig. 1b, which corresponds to (220) and (311) faces of ZTO. The N_2 adsorption-desorption isotherms were performed to investigate the pore structures of ZTO and the result was illustrated in Fig. S1. In the case of the ZTO sample calcined at 450 °C, the specific surface area is 53.5 m^2 g^{-1}. The pore size distribution suggests that the obtained ZTO has a mean pore size value of about 18 nm.

In order to investigate the organic dyes that are more suitable for the cells composed of complex ternary oxides, the dyes Npsp and CBpsp containing phenylene-thiophenylene-phenylene bridge (PSP) were fabricated according to the previous reports (J. Chang et al., 2012; Chang et al., 2012). The structures of PSP dyes are shown in Fig. 2. These organic dyes are composed of 4-*tert*-butylphenylamine donor (D), a phenylene-thiophene-phenylene spacer (PSP) and a cyanoacrylic acid acceptor (A), forming a D-π-A system.

The photocurrent density (J)-voltage (V) curves of the DSCs based on ZTO nanoparticles sensitized by Npsp are revealed in Fig. 3a and the detailed electrochemical parameters are listed in Table 1. Herein, the photoanode containing the plain ZTO nanoparticles was labeled as Cell 1. With the purpose of studying the influence of pre-calcination on the performance of the photovoltaic