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Extremely enhanced photovoltaic properties of dye-sensitized solar cells by sintering mesoporous TiO_2 photoanodes with crystalline titania chelated by acetic acid

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HIGHLIGHTS

- Incorporating the crystalline titania chelated by acetic acid into photoanodes.
- The incorporation lead to the decrease of charge transfer resistance.
- Power conversion efficiency of dye-sensitized solar cells reaches to 10.49%.
- The enhancement results from the remarkable increase of photocurrent.

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ABSTRACT

The study presents a significant improvement on the performance of dye-sensitized solar cells (DSSCs) through incorporating the crystalline titania chelated by acetic acid (TAc) into the mesoporous TiO_2 photoanodes. The effects of TAc on the blocking layer, mesoporous TiO_2 layer, and post-treatment have been investigated. The TAc blocking layer displays compact construction, revealing superior response time and resistance to suppress dark current compared to the blocking layer made from titanium(IV) isopropoxide (TTIP). The power conversion efficiency of DSSCs with the TAc treatment can reach as high as 10.49%, which is much higher than that of pristine DSSCs (5.67%) and that of DSSCs treated by TTIP (7.86%). We find that the TAc incorporation can lead to the decrease of charge transfer resistance and the increase of dye adsorption. The result may be attributed to the fact that the TAc possesses high crystallinity, exposed (101) planes, and acid groups chelated on surface, which are favorable for dye attachment and strong bonding at the FTO/TiO_2 and the TiO_2/TiO_2 interfaces, These improvements result in the remarkable increase of photocurrent and thereby that of power conversion efficiency.

1. Introduction

Due to the simple process and low threshold, dye-sensitized solar cells (DSSCs) have received great attentions since they are introduced in 1991 [1]. DSSCs mainly consist of several components: a transparent conductive photoanode, a mesoporous oxide layer (typically, TiO_2), photo-excitable dye, an electrolyte, a catalyst (typically, Pt), and a conductive photocathode (typically, transparent). In the past three decades, each component of DSSCs has been widely investigated; many new potential materials or new structures have been proposed as replacements for DSSCs to enhance the power conversion efficiency (PCE), increase the applicability, or reduce the manufacturing cost (usually, replacements of Pt) [2–5].

Among these studies to improve DSSCs, the mesoporous oxide layer is one of the most studied components due to its versatile nature and ease to carry out [6–8]. The main efforts are to enhance light absorption, suppress charge recombination, and reduce charge transport resistance. The light absorption can be enhanced through the excitation of localized surface plasmon resonance (LSPR) of metal nanoparticles (usually, Ag or Au) incorporated into the TiO_2 mesoporous layer, which amplifies the local electric field near the dye to alter the absorbed intensity [9–12]. However, the metal surfaces are also known to quench the excitation of dyes due

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to the nonradiative energy transfer [13,14]. The optimal enhancement only occurs at an appropriate distance because the quenching is weakened with distance, which is much faster than the LSPR enhancement, and the LSPR enhancement decreases gradually at longer distance [15]. The feature discounts the LSPR effect on the light absorption of dye. Besides the LSPR effect, the metal nanowires can also reduce the recombination of the excited electrons with the holes/tri-iodide ions through fast electron transfer along axial direction and thereby enhance the PCE [16,17]. Regardless of metal nanoparticles or nanowires, however, they are corroded by I^-/I_3^- electrolyte. Even though the metal nanoparticles/nanowires can be coated with metal oxides to avoid direct contact with the I^-/I_3^- electrolyte [16–19], I^-/I_3^- ions may penetrate the thin coating shell within a very short time [20]. A simpler method to improve the PCE is to pre- or post-treat the TiO_2 photoanodes with titanium precursors [21–26]. The blocking layer (pre-treatment) is effective to suppress back electron transfer and reduces charge recombination of excited electrons with I_3^- ions at the transparent-conductive-layer/electrolyte interface. However, the surface of the blocking layer may be insufficient for adherence with the mesoporous TiO_2 layer, which harms the DSSC performance [27]. The post-treatment can enhance the bonding strength among TiO_2 particles and improve the electron transport properties, which are similar to the results of high-order nanostructural TiO_2 particles [28–30]. Unfortunately, even sintering at 450 °C, the titanium precursors may become amorphous titania connecting with TiO_2 particles [31].

As aforementioned, most of the improvement methods feature shortcomings. The problem leads to the question: is there other more effective method, which can overcome the drawbacks, to improve DSSCs? In this study, anatase TiO_2 chelated with acetic acid (TAc), which was synthesized in acidic solution at low temperature, was used as a sintering agent instead of titanium precursors (e.g., titanium alkoxide, titanium tetrachloride). Crystalline TiO_2 particles featuring the (101) planes mainly exposed on their surface are known to be favorable for dye attachment [32]. Due to the high crystallinity, numerous (101) planes, and reactive surface, the TAc incorporating mesoporous TiO_2 photoanodes reveals strong connection among TiO_2 particles, high electron transport, and much dye adsorption, resulting in PCE of 10.49% and 85% enhancement compared to the PCE of the pristine DSSCs, which further exceed most of improvement reported in the literature.

2. Experimental

2.1. Preparation of TAc solution

TAc was synthesized using a sol-gel method, as reported previously [33], with some of the parameters slightly modified to obtain more stable suspension. Briefly, titanium(IV) isopropoxide (TTIP, 12 g) was mixed with acetic acid (2.4 g). Then, the mixture was added into DI water (200 g). The aqueous solution became turbid immediately. After stirring at room temperature for 12 h, nitric acid (2 g) was added to the aqueous solution, which was then heated at 80 °C for 90 min, resulting in a stable light-blue titania sol chelated with acetic acid (TAc solution, 1.948%, w/w).

2.2. Assembly of DSSCs

Firstly, FTO glass was rinsed with acetone, ethanol, and deionized water. A 12.5-wt% TiO_2 slurry consists of P25, ethyl cellulose, terpineol, and ethanol in a weight ratio of 2.5:1:7.5:9. Various amount of the TAc solution (0, 2, 4, 5, 6, 13 g) was added into the TiO_2 slurry. The mixture was screen-printed on the washed FTO glass and then annealed at 100 °C for 30 min. After repeating the above-mentioned process by six times, a S400 (400–500-nm TiO_2, QF-Ti-1125G, Yong-Zhen Technomaterial) slurry, which composition was the same as the TiO_2 slurry except the P25 was replaced by S400, was coated on the mesoporous TiO_2 electrodes as a scattering layer. The thickness of the 7-layer coating after thermal annealing at 500 °C for 30 min was ~24 μm. The annealed TiO_2 electrodes were immersed in a N719 solution (0.3 mM) at 50 °C for 3 h, rinsed with acetonitrile, and then dried at room temperature. The Pt counter electrodes were prepared by coating H_2PtCl_6 (0.01 *M*) on FTO glass and then annealing it at 450 °C for 30 min. The dyed TiO_2 electrodes were assembled with Pt counter electrodes into DSSCs, using a 60 μm thick Surlyn film as a spacer and then pressed at 40 psi and 125 °C for 20 s. The electrolyte solution (0.6 *M* 1-butyl-methylimidazolium iodide, 0.5 *M* *tert*-butanol, 0.1 *M* guanidinium thiocyanate, 0.2 *M* LiI, 0.05 *M* I_2 in acetonitrile) was filled into the cells through the pre-drilled holes in the Pt counter electrodes.

2.3. Pre- and post-treatments

The pre-treatment and post-treatment were carried out by immersing the FTO glass into TAc solution and dropping TAc (0.0445 g) on the mesoporous TiO_2 electrodes, respectively, and then annealing at 100 °C for 30 min. To evaluate the effect of TAc on the pre- and post-treatments, the TTIP isopropanol solution (0.3 *M*) was also used for the treatments with the same process, serving as a control group.

2.4. Characterization

The particle size distribution of the TAc was determined using a dynamic light scattering analyzer (NanoPlus, Micromeritics). The crystalline phase of the TAc was characterized through X-ray diffraction (XRD) using an X-ray diffractometer (Miniflex II, Rigaku) and Cu Kα radiation. The morphology of the mesoporous TiO_2 photoanodes was examined using an optical microscope (M835, M&T Optics) and a field-emission scanning electron microscope (JSM-6700F, JEOL). The BET surface areas of the mesoporous TiO_2 layer were measured by N_2 adsorption-desorption isotherms at 77 K using a surface area analyzer (ASAP 2020, Micromeritics). The amount of dye adsorption was determined by desorbing the dye with 0.1 *M* NaOH and then evaluating the absorbance using an UV–Vis spectrophotometer (Lambda 850, PerkinElmer). The photocurrent density-voltage (J-V) characteristics were measured under irradiation of 100 mW cm^{-2} using a solar simulator (MFS-PV, Hong-Ming Technology) equipped with a source meter (Keithley 2400, Keithley Instruments). Electrochemical impedance spectra (EIS) were measured over the frequency range of 50 mHz–100 kHz with a potential perturbation of 10 mV using an electrochemical workstation (Zennium, Zahner).

3. Results and discussion

The as-prepared TAc features the particle size distribution over 11–28 nm, with an average diameter of 16.3 nm, and reveals anatase phase (Fig. S1a and b). The acetic acid chelates the surface of TAc through the formation of chemical bonds between the carboxylic groups of the acetic acid and the Bronsted acid sites of titania [33]. Fig. 1 displays the photocurrent density-voltage curves of the DSSCs incorporating various TAc amounts into mesoporous TiO_2 layer. The corresponding optoelectronic characteristics are listed in Table 1. The PCE increased upon increasing the TAc content to a maximum but then decreased upon increasing the TAc content furthermore. To realize the cause of the enhancement, we desorbed the N719 from the mesoporous TiO_2 working electrodes by 0.1 *M* NaOH solution. With increasing TAc content, Table 2 and Fig. S2 shows that the dye-loaded amount increases from 1.78 to