



Effect of cerium ion modifications on the photoelectrochemical properties of TiO₂-based dye-sensitized solar cells



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ARTICLE INFO

Article history:

Received 28 August 2017

Received in revised form

2 October 2017

Accepted 3 October 2017

Keywords:

Cerium

TiO₂

Photoelectrodes

DSSCs

ABSTRACT

Several different quantities of Ce/TiO₂ materials were synthesized in the same condition by a wet method. Dye-sensitized solar cells (DSSCs) were fabricated by using porous Ce/TiO₂ film electrodes derived from P25 nanoparticles. Various techniques such as X-ray diffraction, Scanning electron microscope and Brunauer-Emmett-Teller are used to characterize the products. The short-circuit current density and photo-electric conversion efficiency reach optimum values: 13.87 mA cm⁻² and 7.00% respectively when the amount of Ce(NO₃)₃·6H₂O is 0.050 g/1 g P25, which may be attributed to better transportation of electrons and more adsorption of dyes and sunlight.

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1. Introduction

Compared with conventional solar cells, dye-sensitized solar cells (DSSCs) have become an attractive alternative due to their low cost and high energy conversion efficiency [1,2]. While, it is necessary to further improve the energy-conversion efficiency in order to commercialize DSSCs successfully. Currently, research efforts are focusing on the improvement of the sensitized photoanodes, dyes [3], electrolytes [4], cathodes, their interfaces and the fabrication technologies [5]. As a vital part of DSSCs, the photoanode plays a key role in the aspect of transferring electrons and adsorbing dyes. Therefore, the methods of improving conversion efficiency of solar cells have been attributed to two main factors: the first one is modifying the structure of photoanode to utilize a wider range of wavelength of sunlight [6,7], the other one is improving the amount of adsorbed dyes on the photoanode to increase the short circuit current [8]. So far, the most appropriate material of fabricating photoanode is nano titanium dioxide (nano-TiO₂), as a result of its large specific surface areas, photochemical

stability and so forth. However, TiO₂ has a defect of large band gap (3.2 eV), which makes TiO₂ merely utilize the ultra violet light which owns higher energy to excite electrons. Thus, how to modify the nano titanium to make it use a wider range of wavelength of sunlight has become a novel research hot issues [9,10].

According to previous literatures [11,12], doping nano-TiO₂ with some other elements, especially the rare-earth elements, can solve the problem effectively. That is because rare-earth elements can not only ameliorate the internal structure of semi-conductors but also provide energy conversion properties to improve the photo-electric conversion efficiency [11–13].

In 2010, Wu et al. doped rare-earth oxide europium-doped yttria (Y₂O₃:Eu³⁺), a luminescence medium and P-type dopant, into the DSSCs to improve photocurrent, photovoltage and conversion efficiency [14]. Photoanodes of hybrid TiO₂/La₂O₃ prepared by modification of TiO₂ films via doping or coating in the isopropanolic La³⁺ solution have been studied by Yu et al. [15]. Doping the TiO₂ photoelectrodes with Eu³⁺ and Sm³⁺ ions, also brings a considerable increase in the cell parameters [16]. Doping with Al will introduce oxygen vacancies which can act as carriers for electron conduction, hence the conductivity is increased [17–19]. Moreover, doping titania electrode with lanthanide ions provides complexation centers on the TiO₂ surface, thus its dye adsorption is enhanced [20]. Asemi et al. made an attempt to introduce the same amount of

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Ce³⁺ into TiO₂ nanorods with different reaction time, demonstrating doping with Ce³⁺ can improve the conversion efficiency of photoanode [21]. Overall, rare earth oxides are found to have multiple physical and chemical properties, strong adsorption selectivity and ideal thermal stability, due to their f electron and multi-electron configuration.

In the past, our research team has investigated the modification of doping photoanode with two rare-earth elements: La³⁺ [22] and Sm³⁺ [23] and has drawn corresponding conclusions: compared with unmodified photoanode's, the modified photoanode's conversion efficiency improves by 20%–30%, which may be attributed to the photo-electric characteristic of rare-earth elements. Considering about the properties of Ce³⁺ and no previous reports on doping nano-TiO₂ with different amounts of Ce³⁺, we further investigated the nano-TiO₂ photoanode doped with the optimum amount of Ce³⁺ at the peak of conversion efficiency and obtained some conclusions.

2. Experimental

2.1. Materials

TiO₂ nanopowder was purchased from Degussa AG, Germany. Ce(NO₃)₃·6H₂O was purchased from Aladdin, China. Anhydrous lithium iodide(LiI), iodine(I₂), 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 4-*tert*-butylpyridine (TBP) and guanidine isothiocyanate(GuSCN) were purchased from HeptaChroma, China. Acetonitrile, valeronitrile and ethyl cellulose(EC) were purchased from J&K. Fluorine-doped SnO₂ conducting glass(FTO, sheet resistivity = 15Ω square⁻¹), *cis*-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) bis(tetrabutylammonium) (N719) was purchased from Solaronix, Switzerland.

2.2. Synthesis of Ce/TiO₂ nano-crystalline particles

Different Ce-TiO₂ particles were fabricated by a wet method as follows: 1 g P25 was dissolved in an amount of 0.1 M nitrite acid solution under vigorous stirring at 80 °C. After 3 h, a light blue translucent solution was obtained. A certain amount of Ce(NO₃)₃·6H₂O (0.030 g, 0.040 g, 0.050 g, 0.075 g, 0.100 g) was added into the stirred solution for 1 h at 80 °C. Then the as-prepared sample was transferred to an 80 mL Teflon autoclave and kept at 200 °C for 12 h. After cooling down to 25 °C, the white precipitate was centrifuged, washed with absolute ethanol and distilled water for 3 times respectively, and dried at 60 °C. Then the powder was calcined at 500 °C for 4 h(5 °C min⁻¹). The obtained samples were then denoted as Ce/TiO₂.

2.3. Fabrication of TiO₂ photoanode and DSSCs assembly

FTO-coated glasses were cleaned by sonication in water with detergent, deionized water and ethanol. Next, the TiO₂ thick films were prepared on fluorine-doped tin oxide (FTO) conductive glasses via a knife-coated method. The Ce-doped or original TiO₂ films were calcined at 500 °C for 15 min for removing organics. Prior to dye adsorption, the as-prepared sample was placed in 120 mL of 40 mM TiCl₄ solution which was prepared with mixture of TiCl₄ and ice, in a beaker covered with para film at 70 °C for 45 min. The resultant films were calcined at 500 °C for 30 min at a heating rate of 5 °C min⁻¹. After cooling down to 110 °C, the P25 and Ce-TiO₂ films were sensitized in a dye solution of N719 for 22 h. Then the films were rinsed with absolute ethanol to eliminate excess unadsorbed dyes and dried in air. Then the photoelectrode was assembled with Pt counter-electrode and an electrolyte to form a sandwich-type cell. The electrolyte was composed of 0.6 M DMPII,

0.03 M I₂, 0.5 M 4-TBP and 0.1 M GuSCN in a mixed solvent of acetonitrile and valeronitrile by 85:15 vol ratio.

2.4. Characterizations

Morphologies of the samples were observed by a Scanning Electron Microscope (SEM, S-4800, Japan Hitachi Ltd). X-Ray Diffraction (XRD) analysis of crystal phases and crystal sizes was conducted by an X-ray diffractometer(D/MAX-2500, Japan, Rigaku) with Cu Kα radiation in the condition of a 40 kV working voltage, 40 mA working ampere and a 2θ range from 10° to 80°. Nitrogen adsorption-desorption isotherms of Ce/TiO₂ materials were measured on a domestic N₂ adsorption apparatus at -196 °C. Prior to analysis, the samples were degassed at 150 °C for 2 h on a vacuum line. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area. Photocurrent-photovoltage(*J*-*V*) was measured by a source measuring unit (model 2400, Keithley) under simulated AM 1.5 one-sun condition(solar AAA simulator, oriel China, calibrated by a standard crystalline silicon solar cell). The electrochemical impedance measurement (EIS) of the photoanodes was obtained by an electrochemical workstation (CHI-660D, Shanghai Brilliance Co., Ltd). The amount of dye adsorbed was measured by UV-vis spectroscopy. In order to measure the surface concentration of the dye in the TiO₂ electrode, the dye was desorbed into a 0.1 M NaOH solution in ethanol and water (60:60, v/v) and absorption spectra of the desorbed-dye solution was measured via a UV-vis spectrophotometer.

3. Results and discussion

X-ray diffraction (XRD) patterns of P25 and the TiO₂ doped with different amounts of Ce show that the anatase structure of TiO₂ prevails in the case of the mixed oxides. All peaks of the prepared samples can be the anatase and rutile phases, indicating that the anatase and rutile crystal structures are still retained after being doped. According to the XRD profiles, the anatase crystal structures and the particle sizes were not easily influenced by Ce with the different amounts. Ce/TiO₂ particles have smaller power than pure P25 based on characteristic diffraction peaks of the rutile phase, which is ascribed to the fact that ionic radii of Ce⁴⁺ and Ce³⁺ are 0.093 nm and 0.103 nm, respectively. Meanwhile, ionic radii of Ce⁴⁺ and Ce³⁺ are larger than 0.068 nm which is ionic radius of Ti⁴⁺. Therefore, it is difficult to allow doped cerium ions enter into the TiO₂ lattice. Doped cerium ions only exist as the so-called second phase on the surface of TiO₂, which inhibits the crystallite growth of rutile phase. So the phase transformation of TiO₂ is suppressed [24]. No crystalline Ce₂O₃ and Ti-Ce phase can be observed from XRD patterns as a result of the tiny amount of dopant. In addition, there are no obvious shifts in the peak, which indicates that there is no distortion in the TiO₂ and illustrates that Ce ion did not enter into the bulk lattice of TiO₂ [25]. From the full width at half-maximum of the strongest anatase diffraction, the crystallite sizes are calculated to be 27 nm for both original and Ce-doped TiO₂ samples, which are consistent with the SEM analysis. In Fig. 2, P25 sample was compared with that of 0.030 g-Ce/TiO₂, 0.040 g-Ce/TiO₂, 0.050 g-Ce/TiO₂, 0.075 g-Ce/TiO₂ and 0.100 g-Ce/TiO₂ mesoporous film in the same SEM micrographs. Regardless of the substituent, the film is composed of nanoparticles whose diameters are about 30 nm. Meanwhile, in the surface of nanoparticles, there are mesopores ranging from 20 to 30 nm in diameter. This structure is particularly suitable to guarantee more dye to be loaded and transport electrons through the pores [26]. These mesopores can even make a contribution to providing more surface and leading to more dye adsorption, which is also an important reason for the improvement

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