Journal of Power Sources 260 (2014) 233–242

Contents lists available at ScienceDirect

Journal of Power Sources

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

Rice-like brookite titania as an efficient scattering layer for nanosized anatase titania film-based dye-sensitized solar cells

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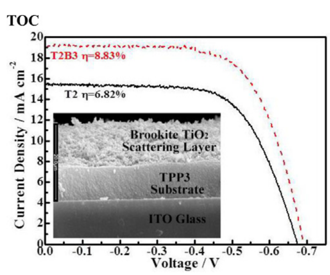
HIGHLIGHTS

- Rice-like brookite TiO_2 with high purity were prepared via hydrothermal method.
- The brookite particles were used as overlayer of nanosized anatase TiO_2 photoanode.
- Bilayer TiO_2 film-based DSSCs were fabricated by using the above photoanode.
- Brookite overlayer enhances V_{OC} of DSSCs fabricated with anatase TiO_2 photoanode.
- Bilayer DSSC's efficiency is improved by 29% as compared to the anatase-based one.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 December 2013
Received in revised form
7 February 2014
Accepted 23 February 2014
Available online 19 March 2014

Keywords:
Rice-like brookite titania
Scattering layer
Dye-sensitized solar cell
Conversion efficiency

ABSTRACT

Rice-like brookite TiO_2 particles with high phase purity and ~600 nm particle diameter were synthesized through a hydrothermal method, and then bilayer TiO_2 film-based dye-sensitized solar cells (DSSCs) were fabricated by using photoanode consisting of nanosized anatase TiO_2 film as underlayer and the above brookite TiO_2 submicrometer particle film as overlayer. The effects of the brookite overlayer on the light scattering and photoelectrochemical performances of the anatase TiO_2 film-based DSSCs were investigated by using UV–vis diffused reflectance absorption spectra (DRS), open-circuit voltage decay (OCVD) curves and electrochemical impedance spectra (EIS) measurements. It is found that the bilayer film-based DSSCs have much better light harvesting capability, higher open-circuit voltage and longer electron lifetimes than the single anatase TiO_2 film-based one. After optimizing the thicknesses of underlayer and overlayer, the corresponding bilayer TiO_2 film-based DSSC gives conversion efficiency up to 8.83%, with a 29% improvement in the efficiency as compared to that (6.82%) of the single film-based one under AM 1.5G one sun irradiation. The present results represent a clear advance towards efficient light scattering materials for the nanosized TiO_2 film-based solar cells with low-cost and high efficiency.

1. Introduction

Since O'Regan and Grätzel published their pioneering work on the promising applications of TiO_2 nanocrystal porous film electrodes in dye-sensitized solar cells (DSSCs) with a 7% conversion efficiency in 1991 [1], DSSCs as unconventional solar cell have been attracting increasing interests due to its relatively high performance and low-cost production [2–6]. For many years, TiO_2 nanomaterials such as nanoparticles, nanotubes and nanowires and the ruthenium-bipyridyl dye families such as N719, N3 and C101 are the most efficient materials for the photoanodes, and have

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http://dx.doi.org/10.1016/j.jpowsour.2014.02.092
0378-7753/

dominated the highly efficient solar cells [3–6]. Nevertheless, the maximum conversion efficiency plateaued over the following years with a current record of 10% [2–6]. The main issues restricting the efficiency are the charge recombination and the light utilization efficiency of the solar cells. Recently, Grätzel's group reported that porphyrin-sensitized TiO_2-based solar cells with cobalt (II/III)-based redox electrolyte exceeded 12% efficiency [7]. This report provides an important clue for improving the conversion efficiency of the solar cells by enhancing its spectral response range and light utilization capability.

It is well-known that lots of surface traps on the TiO_2 nanoparticles usually result in serious charge recombination during the electron transfer between TiO_2 nanoparticles or from TiO_2 film to the conductive substrate, which slows the electron transport rate and limits the performance improvement of the solar cells. Moreover, TiO_2 nanoparticle film with higher surface area can increase the dye adsorption amount, but such higher surface area is usually fabricated by using smaller particle sizes, which would result in quite a good transparency but a poor light scattering of the film electrode [8]. Therefore, extending the retention period of the incident light in a solar cell by fabricating scattering layer or centers in the photoelectrode is one of promising approaches to enhance the light harvesting. Following this strategy, submicrometer/micrometer-scale TiO_2 particles with diameter of 200–400 nm were used as scattering materials because the optical absorption capability can be enhanced to a large extent when nanosized TiO_2 film was combined with the above large particles [8–15], and several investigations have verified that the inclusion of such scattering centers or layers can increase the short-circuit current density and the conversion efficiency of the DSSCs [12–15].

Among the three main TiO_2 crystallographic forms (anatase, rutile and brookite), anatase, rutile or their mixture occupied a larger proportion in the photoanode materials of DSSCs [16–22], since it is difficult to obtain pure form of brookite TiO_2 [23–28]. Recently, crack-free TiO_2 film made of pure brookite nanoparticles was used as n-type semiconductor layer in an all-solid-state dye-sensitized hybrid solar cells by using polythiophene polymers as hole-transporting materials, and an optimum conversion efficiency (0.48%) was reached for the as-prepared 14 nm-sized brookite colloid at standard AM 1.5 irradiation [23]. Further investigation about the energy band structures of TiO_2 polymorphs reveals that the bandgaps of three crystallographic forms are in the order of $E_{g\ \mathrm{brookite}} > E_{g\ \mathrm{anatase}} > E_{g\ \mathrm{rutile}}$ [26]. The same elementary composition implies these crystallographic forms should have similar valence band (VB) level, and therefore the higher E_g of brookite can result in higher conduction band (CB) level, indicating the brookite TiO_2 would exhibit a higher open-circuit voltage (V_{OC}) of DSSCs as compared to anatase or rutile [26]. Therefore, it can be conjectured that pure brookite should be promising in the application of DSSCs although high-quality brookite TiO_2 has seldom been reported up till now [24–28].

Herein, rice-like brookite TiO_2 particles with high phase purity and ~600 nm diameter were synthesized through a simple hydrothermal method by using $Ti(SO_4)_2$ as titanium source. This rice-like brookite TiO_2 submicrometer particles and commercial nanosized anatase TiO_2 paste (TPP3) were used to fabricate the bilayer TiO_2 film-based solar cells, in which the photoanode consists of the nanosized anatase TiO_2 film as underlayer and the rice-like brookite TiO_2 particles as overlayer. After optimizing the thicknesses of the rice-like brookite TiO_2 overlayer and the nanosized anatase TiO_2 underlayer, the device efficiency is significantly improved from 6.82% to 8.83% with enhanced light harvesting capability and open-circuit voltage. Furthermore, the effects of the brookite TiO_2 overlayer on the light scattering and photoelectrochemical performances of the nanosized TiO_2 film-based solar cell were investigated by using UV–vis diffused reflectance absorption spectra (DRS), open-circuit voltage decay (OCVD) curves and electrochemical impedance spectra (EIS) measurements.

2. Experimental section

2.1. Synthesis of rice-like brookite

All reagents are of analytical grade and used as received without further purification. TPP3 paste containing anatase TiO_2 nanoparticles (20 nm) was obtained from commercial source (Heptachroma Co, Ltd). A typical preparation process of brookite TiO_2 particles as follows: A fixed amount of $Ti(SO_4)_2$ was dispersed in 40 mL distilled water as the source of titanium. After fully dispersed, the sample was adjusted by saturated NaOH solution to give a suspension of pH12.50. The solution was sealed in a Teflon-lined stainless steel autoclave (100 mL) and heated at 240 °C for 24 h. After the hydrothermal reaction, the reactor was cooled to room temperature naturally. The white precipitate formed was separated from the solution by centrifugation (4000 rpm), and was then washed several times with distilled water and absolute ethanol, and then dried at 70 °C in air. Finally, the dried powder was further calcined at 500 °C for 3 h with a heating rate of 2 °C min^{-1} to obtain crystallized brookite particles.

2.2. Preparation of photoanodes

Nanosized anatase TiO_2 film photoanode was prepared by spreading the above TPP3 paste on a clean FTO glass (15 $\Omega\ sq^{-1}$) by using a doctor blading technique. The thickness of the nanosized TiO_2 films was controlled by adhesive tape (Scotch, 50 μm) serving as spacers. After drying in atmosphere, the film was sintered at 500 °C for 30 min to obtain the nanosized anatase TiO_2 film.

Brookite TiO_2 paste was prepared by mixing 1.0 g of the above brookite particles with 5.0 mL of ethanol, 0.2 mL of acetic acid, 3.0 g of terpinol and 0.5 g of ethyl cellulose through ball-milling for 10 h. The obtained rice-like brookite paste was then spread on the above anatase TiO_2 film, and then sintered at 500 °C for 30 min again to remove the binders in the paste. Afterward, the bilayer TiO_2 film electrode was further treated in $TiCl_4$ aqueous solution to improve its photoelectrochemical performances.

For comparison and optimizing the film thickness of both the anatase TiO_2 and the brookite TiO_2 particle films, series of single and double layer films with different thicknesses of anatase TiO_2 and brookite TiO_2 films were prepared by adjusting the numbers of adhesive tape during the corresponding film preparation process with the doctor blading technique. For example, T*n* represent the anatase TiO_2 film prepared with *n* layers of the adhesive tape; and T*n*B*x* represent the bilayer TiO_2 film prepared by spreading the rice-like brookite paste on the calcined T*n* film by using *x* layers adhesive tapes as spacer.

2.3. Fabrication of DSSCs

Dye sensitization was achieved by soaking the film electrode into a 0.3 mM N719 dye (Solaronix) in ethanol solution for 20 h, followed by rinsing in ethanol and drying in air. The dye-sensitized film electrode was assembled in a typical sandwich-type cell. A Pt-coated FTO counter electrode was placed over the dye-sensitized electrode. The electrolyte which consists of 0.5 M LiI, 0.05 M I_2 and 0.1 M 4-*tert*-butylpyridine in 1:1 acetonitrile–propylene carbonate was injected into the interspace between the photoanode and the counter electrode. In order to reduce the scattered light from the edge of the glass electrodes of the dyed TiO_2 layer, a light-