Materials Letters 124 (2014) 302–305

Contents lists available at ScienceDirect

Materials Letters

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

Orderly interconnected nanosheets for dye-sensitized solar cells

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ARTICLE INFO

Article history:
Received 9 December 2013
Accepted 19 March 2014
Available online 26 March 2014

Keywords:
Nanocrystalline materials
Solar energy materials
Electron transport
Electron recombination

ABSTRACT

We report on the microstructure and dynamics of electron transport and recombination in dye-sensitized solar cells incorporating orderly interconnected nanosheets, which provide a large surface area for the adsorption of light-harvesting molecules. The nanosheet anode has significantly higher charge-collection efficiency than its nanoparticle counterparts.

1. Introduction

Dye-sensitized TiO_2 solar cells (DSSCs) have received considerable attention as a potential, cost-effective alternative to silicon solar cells [1–4]. The photoanodes of dye-sensitized solar cells are typically fabricated using films of TiO_2 nanoparticles that are deposited as a paste and sintered to produce electrical continuity [5]. A very important feature of DSSCs is the anode, which includes mesoporous wide-band-gap oxide semiconductor anode films with an enormous internal surface area, typically a thousand times larger than that of bulk films [6,7]. To date, the high conversion efficiency in dye-sensitized solar cells has been achieved with anode films that consist of TiO_2 nanocrystallites sensitized by ruthenium-based dyes [8–10]. The electron-collecting layer in a DSSC is typically a nanoparticulate anode film, with a three-dimensional network of nanoparticles [11]. The structural disorder at the contact between two nanoparticles leads to enhanced scattering of free electrons, thus reducing electron mobility [12–14]. One possible solution is to use one-dimensional nanoarchitectures that are able to give a direct pathway for the rapid collection of photogenerated electrons and, therefore, reduce the degree of charge recombination [13]. However, such one-dimensional nanostructures have low internal surface areas, which limit their conversion efficiencies at a relatively low level compared with that of nanoparticle anode film. In this paper, we examine the morphology and electron dynamics in TiO_2 orderly interconnected nanosheets. A very important aspect to the orderly interconnected nanosheet anode film is that it provides a surface area as large as that of nanoparticle anode film for the adsorption of Z907Na molecules leading to high light-harvesting efficiency. In addition, electron transport in orderly interconnected nanosheet anode is faster than percolation through a random walk in randomly packed TiO_2 nanoparticle anode.

2. Experimental

The solution for the CBD (chemical bath deposition) process was prepared by dissolving $Ti(OC_2H_5)_4$ in ethanol, glycerol and water at room temperature. The weight ratio of ethanol/glycerol/water was 10:5:1. The titanium concentration in the solution was 0.1 mol dm^{-3}. Borosilicate glass slide substrate was used as a substrate for the deposition. The substrate was put into bottles filled with Ti/glycerol solution and sealed, and then were kept at 160 °C for 7 days in a drying oven. After the deposition, the film obtained was rinsed with ethanol and dried at room temperature. The film was then transformed into TiO_2 powders by heating at 450 °C for 30 min in air. The FTO substrate (Asahi Glass, 10 Ω/sq., 0.8×1.2 cm^2) was first cleaned thoroughly by acetone/propanetriol sonication and then coated with a thin film of the above titania powders. Orderly interconnected nanosheets were grown by immersing in ethanol solutions containing 2 mM $Ti(OC_2H_5)_4$, 3 mM tetrabutylammonium fluoride and 2 mM polyethylenimine at 180 °C for 5 days in a Teflon-lined autoclave. The samples were annealed at 450 °C in oxygen for 3 h with heating and cooling rates of 1 °C to induce crystallinity again. The assembling DSSCs and the setup for determining the solar cell characteristics are detailed elsewhere [6–9].

3. Results and discussion

Scanning electron microscopy (SEM) images of the TiO_2 film with prepared orderly interconnected nanosheets are shown in

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http://dx.doi.org/10.1016/j.matlet.2014.03.111
0167-577X/

Fig. 1. Fig. 1a shows scanning electron microscope top-surface images indicating that the film is well stacked with submicrometer-sized TiO_2 sheets. In order to see it clearly, Fig. 1b presents a magnified SEM image of the orderly interconnected nanosheets with typical wall thicknesses of 10 – 25 nm and nanosheet spacings of 5 – 20 nm. Each thick sheet is divided into two thin sheets. The thin sheet is divided into two thiner sheets again. We used the nitrogen adsorption to measure the surface areas of orderly interconnected nanosheets by a Micromeritics ASAP2010 nitrogen adsorption apparatus. The test showed that orderly interconnected nanosheet film has a high BET surface area of 79 m^2/g, which is comparable to the BET surface area (74 m^2/g) of nanoparticles used in our experiment.

The transport of photoinjected electrons competing with recombination in DSSCs is a main bottleneck for developing higher conversion efficiency, study of these in interconnected nanosheet anode is important for further advances in nanosheet technology. Transport and recombination properties were measured in our work using intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS) as described previously, respectively. The thicknesses of the orderly interconnected nanosheet and nanoparticle anode films (6.3 and 6.2 μm, respectively) in the cells were about the same. Fig. 2a compares transport for interconnected nanosheet and nanoparticle anodes as a function of the incident photon flux I_0. The electron transport of the nanoparticulate anode film is slower than that of orderly interconnected nanosheet anode film, presumably due to the fact that transport is limited by the residence time of electrons in traps with both the particle network (e.g., distribution of the number of inter-particle connections) and the interparticle contact area, while the orderly interconnected nanosheets are good electrical conductors along the direction of the sheet axes.

To collect photogenerated electrons, electrons must travel a certain distance in the anode film to reach the transparent conductive oxide layer, while photogenerated electrons have a chance of reacting with electrolyte oxidized species giving rise to a recombination process which constitutes a major loss factor of the dye-sensitized solar cell. Fig. 2b shows that the recombination time constant τ_r for the orderly interconnected nanosheet anode film is several orders of magnitude larger than that of the nanoparticle anode film over the light-intensity range investigated. The slower recombination could indicate that fewer potential surface recombination sites exist in orderly interconnected nanosheet film than in nanoparticle anode film. Therefore, orderly interconnected nanosheet anode film can be made thicker than its nanoparticle counterparts for a given recombination loss, which would allow for a higher light-harvesting efficiency, especially at the long-wavelength end of the visible and in the near-infrared region.

Fig. 3 shows the short-circuit photocurrent density I_{sc} dependences of the interconnected nanosheet and nanoparticle anodes on film thickness at 610 nm illumination. The photocurrent densities are seen to increase with the thickness of both orderly interconnected nanosheet and nanoparticle films. However, the rate of increase of J_{sc} with thickness is larger for the ordered nanosheet anode film than the nanoparticle anode film. Orderly interconnected nanosheet and nanoparticle films have comparable Z907Na molecules coverage and are exposed to the same redox electrolyte; the increase rate of I_{sc} vs film thickness is primarily determined by the charge-collection efficiency η_{cc}. η_{cc} for orderly interconnected nanosheet anode film is described by the relation $\eta_{cc}=1-(\tau_c/\tau_r)$ [15]. Calculation of η_{cc} at the highest light intensity (8.34×10^{16} cm^{-2} s^{-1}) in Fig. 2 for the orderly interconnected nanosheet anode film is 25% larger than that of the nanoparticle anode film. η_{cc} at the lowest light intensity (1.25×10^{15} cm^{-2} s^{-1}) for the orderly interconnected nanosheet anode film is 22% larger than that of the nanoparticle anode film.

Fig. 4 compares the incident photon to electron conversion efficiency (IPCE). Incident monochromatic IPCE spectra show a maximum of 82.3% for Z907Na molecules on the orderly interconnected nanosheet TiO_2 anode. A very important aspect of the high IPCE value of orderly interconnected nanosheet anode film is that it provides a surface area as large as that of a nanoparticle anode film for the adsorption of Z907Na molecules leading to high light-harvesting efficiency, while the maxima of IPCE in the visible region contributed by the dye absorption are located at approximately 545 nm with values of 67.1% for nanoparticle anode. It is clear that, for nanocrystallite anode and interconnected nanosheet anode, the dissimilarity in the transport and recombination process arising from the various structures of the interconnected nanosheet and nanoparticle anodes is taken into account, and the great improvement in the IPCE value results predominantly from charge collection efficiency η_{cc} value of adsorbed Z907Na molecules on the orderly interconnected nanosheet TiO_2 anode.

Fig. 5 compares the photocurrent density–voltage (I–V) properties of orderly interconnected nanosheet and nanoparticle anodes under simulated AM1.5 light. The cell containing the orderly interconnected TiO_2 nanosheet anode with thickness of 6.9 μm exhibited an open circuit potential (U_{OCP}) of 0.787 V, a fill factor (FF) of 0.774, and a short circuit current (I_{sc}) of 14.246 mA/cm^2, yielding a conversion efficiency of 8.68%. The Z907Na-sensitized nanoparticle solar cell exhibited FF=0.753, I_{sc}=11.632 mA/cm^2,

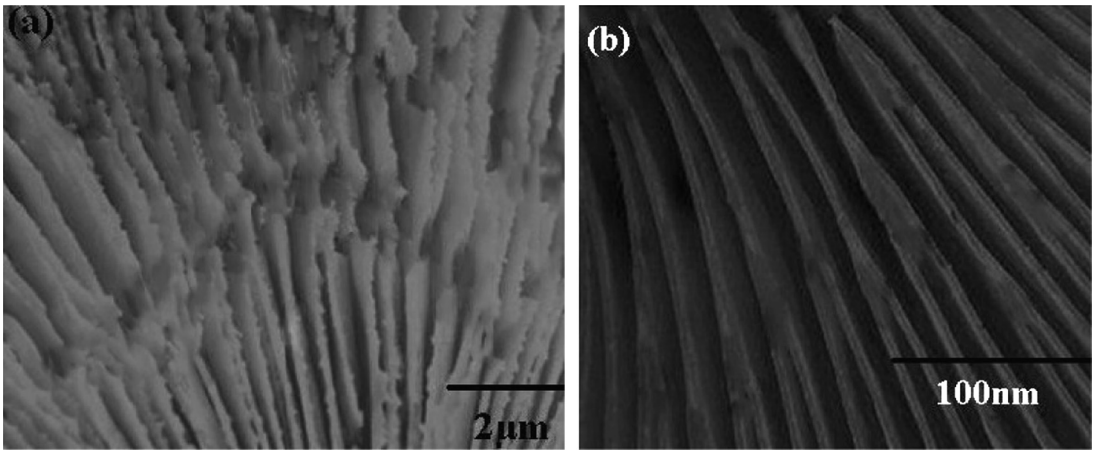

Fig. 1. Morphology of the TiO_2 orderly interconnected nanosheet film. (a) SEM image of the top view of the TiO_2 orderly interconnected nanosheet film. (b) A magnified SEM image of the TiO_2 orderly interconnected nanosheets.