Thin Solid Films 520 (2012) 3510–3514

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

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

Titanium dioxide thin films prepared by electrolysis from aqueous solution of titanium–lactic acid complex for dye-sensitized solar cells

Masaya Chigane *, Tsutomu Shinagawa

Electronic Materials Research Division, Osaka Municipal Technical Research Institute, 1-6-50, Morinomiya, Joto-ku, Osaka 536-8553, Japan

ARTICLE INFO

Article history:
Received 24 May 2011
Received in revised form 25 December 2011
Accepted 29 December 2011
Available online 8 January 2012

Keywords:
Titanium dioxide
Electrolysis
Titanium–lactic acid complex
Dye-sensitized solar cells

ABSTRACT

Titanium oxide (TiO_x) thin films were prepared on transparent conducting substrate (fluorine-doped tin oxide) by cathodic electrolysis of a solution containing a titanium bis(ammonium lactato)dihydroxide and an ammonium nitrate at 323 K. Post-deposition treatment: calcination at 723 K or hot-water treatment at > 363 K promoted the growth of an anatase type crystalline phase in the TiO_2 thin film, as evidenced by X-ray diffraction and X-ray photoelectron spectroscopy. The calcined films were used as electrodes of a dye-sensitized solar cells and the cells' energy conversion efficiency was comparable to that obtained with commercially available TiO_2 nanoparticle electrodes.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Titanium dioxide (TiO_2) thin films are often used as photoanodes for dye-sensitized solar cells (DSSCs) because these films possess an appreciable affinity for organic dye molecules [1,2]. Because of their low manufacturing cost and amenability to constructing flexible cell architectures, DSSCs have attracted attention as an alternative or a supplement to traditional silicon-type solar cells and they can contribute the progress of dissemination of solar cells. TiO_2 electrodes in DSSCs are usually fabricated by calcination of nano-colloidal TiO_2 paste coated on transparent conductive substrates. However the preparation and storage of colloidal TiO_2 are not trivial and the coating process is wasteful because it requires the use of excess paste. Alternatively, electrodeposition from aqueous solutions of titanium species is a low-cost and low-resource-consuming fabrication technique since the deposition reaction occurs only on the substrate. Although only a few authors have reported the electrolytic preparation of TiO_2 for DSSC anode [3,4], we have previously demonstrated that the electrolysis of an aqueous $(NH_4)_2TiF_6$ solution results in smooth deposition of titanium oxide thin films [5]. Using this method, we achieved a DSSC conversion efficiency of 0.63% for a hollow TiO_2 particles film prepared by electrodeposition and subsequent calcination of TiO_2 on a transparent conductive substrate preadsorbed with polystyrene particles. The $(NH_4)_2TiF_6$ solution is stable for long periods (more than 6 months), thus allowing a single prepared solution to be used for repeated electrolyses. However this solution also suffers from drawbacks that preclude its commercial use, including the liberation of F^-during electrochemical deposition under high acidity (pH 3.5) condition leading to bad working environment and requiring effluent treatment remained.

As a possible alternative to $(NH_4)_2TiF_6$, the water-soluble and environmentally benign compound titanium bis(ammonium lactato) dihydroxide (TALH) has received attention. TALH has been used to produce thin films [6–8] and spherical particles [9,10] by means of simple layer-by-layer self-assembly, in which substrates are alternatively immersed in TALH solution and in a solution of polycations (*e.g.* poly(diallyldimethyl ammonium) chloride). In the present study we first used TALH as a non-toxic titanium resource for the electrodeposition of titanium oxide films and assayed DSSC performance of the calcined films. Others have previously reported the growth of an anatase TiO_2 phase resulting from hot-water treatment of films prepared from a polyethylene oxide (PEO)–TiO_2 hybrid system via a sol–gel process and have also examined these films' photocatalytic activity [11,12]. In light of it we also investigated the formation of the TiO_2 anatase phase in our films by means of hot-water treatment.

2. Experimental details

Electrolyses were performed using a potentiostat/galvanostat with a function generator and a coulombmeter (Hokuto Denko HAL3001, HB305 and HF202-D, respectively). A glass plate coated with conductive fluorine-doped tin oxide (FTO, $10\,\Omega\,\text{square}^{-1}$, Asahi Glass Co., Ltd, A11DU80) was used as working electrode (substrate), and a platinum sheet was used as the counter electrode. A mask was placed on the substrate to fix the deposition area of titanium oxide (TiO_x) films 0.25 cm^2. Deionized water ($>12\text{ M}\Omega\text{ cm}$;

---

* Corresponding author.
E-mail address: chigane@omtri.or.jp (M. Chigane).

0040-6090/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2011.12.072

Millipore Corporation Elix Advantage 5) was used to prepare and rinse the film samples. In advance of the electrolysis, the substrate was degreased by anodic polarization (5 mA cm^{-2} for 30 s) in 1 mol dm^{-3} NaOH. An aqueous solution containing a 0.05 mol dm^{-3} TALH (Aldrich; reagent grade) and a 0.1 mol dm^{-3} NH_4NO_3 was used to electrodeposit the TiO_x films. The TiO_x films were prepared at 323 K by galvanostatic electrolysis at −3 mA cm^{-2} until a charge density of 20 C cm^{-2} was achieved. The as-prepared films were calcined at 723 K for 1 h after raising the temperature from room temperature to 723 K over a period of 2 h. Alternatively, some as-deposited films were immersed in boiling water at 363–368 K for 1 h.

X-ray photoelectron (XP) spectra of the films were acquired with Kratos AXIS-Ultra DLD. The photoelectrons emitted by a monochromated Al Kα (1486.6 eV; 150 W) radiation were collected with a pass energy of 40 eV through a hemispherical analyzer. The pressure in the analysis chamber was lower than 1×10^{-6} Pa during measurements. The charge-up effects on the binding energies of Ti 2p and O 1s photoelectron peaks were corrected by referencing the C 1s signal of adventitious contamination hydrocarbon to 284.8 eV.

Surface and cross-sectional morphological observations of the films were carried out with field emission scanning electron microscopy (FE-SEM; JEOL JSM-6700F) with the acceleration voltage of 3 kV.

X-ray diffraction (XRD) patterns of the films were recorded on a RIGAKU RINT 2500 diffractometer (Cu Kα; $\lambda=0.1541$ nm; 40 kV; 100 mA), with an incident angle (θ) fixed at 0.5°. The film deposition area was fixed 3 cm^2 (15 mm × 20 mm) especially for XRD measurements so as to obtain sufficient diffraction signal. The diffraction angle (2θ) was scanned in 0.05° increments with a counting time of 10 s.

For DSSC measurements, the calcined films (0.25 cm^2 area) on FTO substrates were immersed in an ethanolic solution of 0.3 mmol dm^{-3} ruthenium dye (bis-tetrabutylammonium *cis*-di(thiocyanato)-bis-2,2′-bipyridine-4-carboxylic acid, 4′-carboxylate ruthenium(II); Solaronix N719) for 16 h at room temperature. The DSSC electrolyte solution was composed of 0.1 mol dm^{-3} LiI, 0.05 mol dm^{-3} I_2, 0.6 mol dm^{-3} 1,2-dimethyl-3-propylimidazolium iodine (DMPII, Solaronix) and 0.5 mol dm^{-3} 4-*tert*-butylpyridine in acetonitrile. A platinum-coated glass substrate was used for a counter electrode. The electrolyte and a separation polymer sheet (25 μm of thickness; Solaronix SX-1170) were sandwiched between the dye-stained TiO_2 electrode and the counter electrode. Photovoltaic current density (*J*)–voltage (*V*) curves were obtained with a solar simulator (Bunkoh-Keiki Co., Ltd; K0208) equipped with a Keithley 2400 sourcemeter. Photoirradiation was achieved by a 150 W xenon lamp operating an intensity of 100 mW cm^{-2} under 1.5 air mass solar irradiance. A reference DSSC containing a TiO_2 nanoparticle electrode prepared by a squeegee method from TiO_2 colloidal solution (Solaronix Ti-Nanoxide D) [13] and subsequently calcined in the same way as the electrodeposited films also was subjected to DSSC measurements. The amount of Ru complex dye adsorbed on the films was determined photometrically by measuring the absorbance at 500 nm of the solution of dye extracted from TiO_2 films by 0.08 mol dm^{-3} NaOH [14,15]. A linear calibration curve was plotted to calculate an absorption coefficient of 10710 L mol^{-1} cm^{-1} at 500 nm. After dye elution the TiO_2 films were dissolved in 4 mL dm^{-3} H_2SO_4, 0.4 g dm^{-3} $(NH_4)_2SO_4$ and 0.2 mL dm^{-3} H_2O_2 aqueous solution (30%; Santoku Chemical Industries, Co., Ltd.) and then a Ti-peroxo complex solution was prepared. The amount of deposited TiO_2 per unit area (mg cm^{-2}) of FTO substrate was determined photometrically by measuring the absorbance of the complex solution at 408 nm.

3. Results and discussion

To investigate the effect of NO_3^- on the TiO_2 electrodeposition process, we compared the XP spectrum of a film obtained from NH_4NO_3 deposition solution with spectra of films obtained from deposition solutions using different anions (SO_4^{2-} and Cl^-), as representatively shown in Fig. 1. In all cases titanium was detected on the surface of samples due to some electrodeposited titanium compounds. The presence and absence of Sn peaks corresponding to FTO substrates for the samples from $(NH_4)_2SO_4$ (Fig. 1(b)) or NH_4Cl (Fig. 1(c)) solution and NH_4NO_3 solution (Fig. 1(a)), respectively, suggest that titanium compounds film can sufficiently cover the substrate by using NO_3^-. Moreover by the electrolyses in $(NH_4)_2SO_4$ and NH_4Cl solutions the FTO substrate became blackish brown because of considerable deterioration of FTO by the reduction of SnO_2 by the applied cathodic current (−3 mA cm^{-2}). In contrast the appearance of the substrate was not changed with NH_4NO_3 solution, indicating availability of only NH_4NO_3 electrolyte. In all cases some cathodic reactions for the deposition of titanium compounds film occurred, and therewith in case of NH_4NO_3 an additional reaction caused effective film covarage onto the substrate. In view of the previous report on the electrodeposition of TiO_x films via reduction of NO_3^- to NO_2^- [5], we propose the following series of reactions for the electrodeposition of TiO_x from a Ti–lactic acid complex anion:

$$(NH_4)_2Ti(OH)_2(C_3H_4O_3)_2 \rightarrow Ti(OH)_2(C_3H_4O_3)_2{}^{2-} + 2NH_4{}^{+} \quad (1)$$

$$NO_3{}^{-} + H_2O + 2e^{-} \rightarrow NO_2{}^{-} + 2OH^{-} \quad (2)$$

$$Ti(OH)_2(C_3H_4O_3)_2{}^{2-} + 2OH^{-} \rightarrow Ti(OH)_4 + 2C_3H_4O_3{}^{2-} \quad (3)$$

$$Ti(OH)_4 \rightarrow TiO_2 + 2H_2O. \quad (4)$$

Fig. 2 shows the morphology of the TiO_x films with and without calcination. Both films were prepared at −3 mA cm^{-2} for

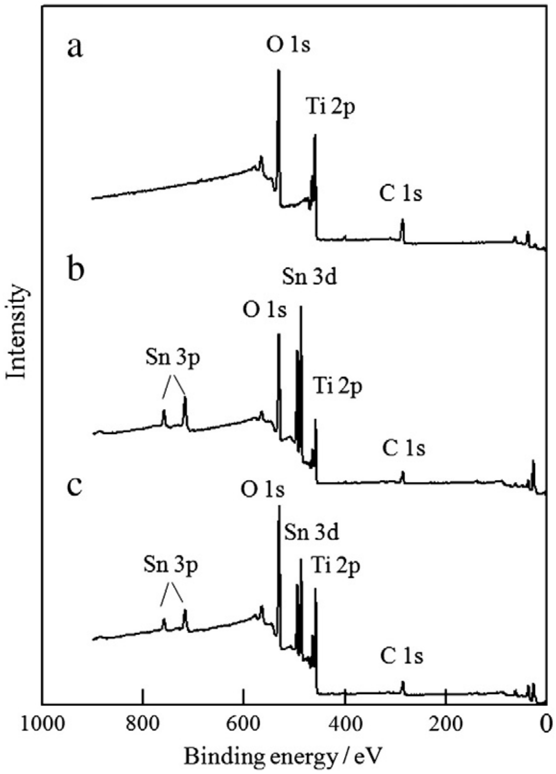

Fig. 1. XP spectra obtained in the wide binding energy region of the FTO substrates after galvanostatic electrolyses at −3 mA cm^{-2} for 20 C cm^{-2} of charge density in the electrolyte solutions containing 0.05 mol dm^{-3} TALH and (a) 0.1 mol dm^{-3} NH_4NO_3, (b) 0.1 mol dm^{-3} $(NH_4)_2SO_4$ and (c) 0.1 mol dm^{-3} NH_4Cl. Representative photoelectron peaks are identified.

Download English Version:

https://daneshyari.com/en/article/10670267

Download Persian Version:

https://daneshyari.com/article/10670267

Daneshyari.com