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CERAMICS INTERNATIONAL

Ceramics International 39 (2013) 8097-8101

www.elsevier.com/locate/ceramint

Improved efficiency of dye-sensitized solar cells through fluorine-doped TiO₂ blocking layer

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> Received 21 March 2013; received in revised form 25 March 2013; accepted 25 March 2013 Available online 6 April 2013

Abstract

We report on improvement in the performance of dye-sensitized solar cells (DSSCs) through a fluorine (F)-doped TiO₂ dense layer for use as a blocking layer. The F-doped TiO₂ layer was deposited on commercial F-doped SnO₂ (FTO) substrate by the hydrolysis of a TiCl₄ aqueous solution with NH₄F. Their structural, morphological, and optical properties were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and UV–vis spectroscopy examinations. The photocurrent density–voltage characteristics show that DSSCs fabricated with the F-doped TiO₂ layer exhibits higher conversion efficiency (~5.24%) than ones with the undoped TiO₂ layer (~4.76%), and the bare FTO substrate (~3.88%). This improvement is attributed to the combined effects of reduced interfacial resistance and effective blocking behavior by the F-doped TiO₂ dense layer. © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

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Keywords: Dye-sensitized solar cell; F-doped TiO2; Interfacial resistance; Blocking layer

1. Introduction

Dye-sensitized solar cells (DSSCs) have been regarded as a good alternative to silicon solar cells because of their advantages, such as low manufacturing cost, less toxic production environment, and various industrial applications [1,2]. Generally, DSSCs usually consist of a nanoporous TiO₂ layer deposited onto F-doped SnO₂ (FTO) glass (working electrode), photo-energy absorbing dye molecules, Γ/I_3 electrolyte, and a Pt-coated FTO glass (counter electrode) [3]. For the conventional DSSCs, the nanoporous TiO₂ layer provides not only large surface areas for dye loading, but also recombination sites, such as the TiO2/electrolyte and FTO/electrolyte interfaces in the working electrode [4]. This could cause backelectron transfer from the conduction band of the TiO2 to the redox level of Γ/I_3 electrolyte and the HOMO level of Ru-dye. In particular, retarding the recombination at the interface between the FTO glass surface and the electrolyte have received great attention for the high-efficiency DSSCs [5]. Thus, in an attempt to prevent the back electron transfer, a dense TiO2 layer was employed between the FTO glass and nanoporous TiO₂ layers [6-8]. However, the inserted dense TiO₂ layer showed non-ohmic behavior between the nanoporous TiO₂ layer and the FTO glass [9]. Although considerable efforts were made to develop highquality blocking layers for use in DSSCs, works on the fabrication of efficient blocking layers having low interfacial resistance have not been extensively done so far. For example, Lee et al. deposited an Nb-doped TiO2 dense layer on the FTO glass by pulsed laser deposition so as to form ohmic contacts [10]. However, the Nbdoped TiO₂ layer yielded high conductivity only when deposited on the SrTiO₃ substrate [11]. Moreover, non-metallic element-doped TiO₂ layers have advantages, such as thermal stability and low cost (lower than Nb) [12]. Thus, in this work, F-doped TiO₂ dense layers were introduced between FTO glass and nanoporous TiO₂ electrode by a hydrolysis method to form a blocking layer having low interfacial resistance. In other words, we investigated the effect of an F-doped TiO₂ blocking layer on the performance of DSSCs.

2. Experimental procedure

2.1. Sample preparation

The FTO glass (8 Ω/\Box , Pilkington) substrates for depositing undoped and F-doped TiO₂ dense layers were sequentially

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cleaned with acetone, methanol, and DI water. The FTO substrate was then immersed into a 40 mM TiCl₄ (Titanium (IV) chloride, Aldrich) solution at 80 °C for 30 min to deposit a undoped TiO₂ layer. The F-doped TiO₂ layer was deposited on the FTO substrate from the hydrolysis of TiCl₄ with 10 at% of NH₄F (Ammonium fluoride, Aldrich). The samples were rinsed with ethanol and then annealed at 450 °C for 30 min. The layer thicknesses were measured to be 70 ± 5 nm by an Alpha step profiler (Nanomap-LS).

To form TiO₂ paste, TiO₂ nanoparticles (Degussa, P25) (16.2 wt%) were dispersed into DI water (67.5 wt%) with HPC (Aldrich) (11.9 wt%) and Acetyl acetone (Aldrich) (4.4 wt%), and then ground using Al₂O₃ mortar for 4 h. The TiO₂ paste was then coated onto the F-doped TiO₂ and undoped TiO₂ dense layers (0.25 cm² in size) on the FTO glass substrates by squeeze printing, followed by sintering at 500 °C for 1 h. For dye adsorption, the sintered samples were immersed into a 0.5 mM Ru(dcbpy)₂(NCS)₂ (N719, Solaronix) solution for 24 h in a dark room and washed with ethanol. The Pt electrode was prepared by a drop coating method onto the FTO glass using a 5 mM H₂PtCl₆ · 6H₂O (Aldrich) solution in isopropa-

nol and then sintered at 450 °C for 30 min. An iodine electrolyte based on 0.3 M BMII was used [13].

2.2. Characterization

The morphologies of the samples were assessed by fieldemission scanning electron microscopy (FESEM, Hitachi SU70) and atomic force microscopy (AFM, XE-100). The structural properties were characterized by X-ray diffraction (XRD, Bruker D8-Advance with Cu K_{α} radiation) and X-ray photoelectron spectroscopy (XPS, Axis-His-corrected by the reference C 1*s* peak with 284.5 eV). The optical properties were examined by UV–vis spectrophotometer (Shimadzu, UV-1800). The photocurrent–voltage curves of DSSCs were investigated under standard irradiance (AM 1.5 simulated sunlight) using a 150 W xenon lamp (LAB 50).

3. Results and discussion

Fig. 1 shows SEM images obtained from bare and TiO_2 -coated FTO glass substrates. Unlike the bare FTO glass



Fig. 1. SEM images obtained from (a) bare FTO glass, (b) undoped TiO_2 layer and (c) F-doped TiO_2 layer.



Fig. 2. AFM images of (a) undoped TiO₂ layer and (b) F-doped TiO₂ layer.



Fig. 3. XRD plots for bare FTO glass, undoped $\rm TiO_2$ layer and F-doped $\rm TiO_2$ layer.



Fig. 4. XPS Ti 2p core level spectra from undoped and F-doped TiO₂ layers.

(Fig. 1(a)), the TiO₂-coated FTO substrates consist of small grains. For the undoped TiO₂ dense layer, the grains vary from ~17 to 75 nm in size (Fig. 1(b)), while the F-doped TiO₂ dense layer contains grains in the range ~5–30 nm (Fig. 1(c)). Furthermore, the F-doped TiO₂ layer shows a somewhat rougher surface than the undoped TiO₂ layer. The AFM results (Fig. 2) showed that the root-mean square (RMS) roughness is 33.8 and 76.1 nm for the undoped and F-doped samples, respectively. It is noted that the F-doping causes a roughening of the surface of the TiO₂ layers.

Fig. 3 exhibits XRD plots for the bare and TiO₂-coated FTO glass substrates. In addition to the diffraction peaks from the FTO glass, the undoped TiO₂ sample reveals peaks at 27.4°, 36.0° , and 41.2° , corresponding to the (110), (101), and (111) planes of rutile TiO₂ (JCPDS no. 21-1276). The F-doped TiO₂ sample exhibits the same peaks. It means that the phase transition has not occurred by F-doping. Thus, the different performance of DSSCs is not attributed to the changes of phase.

Fig. 4 shows the XPS Ti 2p core level spectra from the TiO₂ dense layers with and without F-doping. The Ti $2p_{3/2}$ core level peak is observed at ~458.14 eV and ~458.36 eV for the undoped and F-doped samples, respectively. Notably, the Ti 2p core level for the F-doped TiO₂ sample shifts toward the higher binding-energy side by 0.22 eV compared to that of the undoped sample. This could be due to the fact that F atom has lower electronegativity than oxygen atom [14].

Fig. 5(a) shows the transmittance of the bare and TiO₂coated FTO glass substrates. At an effective region for photoenergy conversion (namely, at 550 nm), the F-doped TiO₂ layer exhibits a transmittance of 70.8%, whereas the undoped TiO₂ layer shows only 66.5%. Fig. 5(b) exhibits the absorption coefficients of the TiO₂ samples, which were obtained from Fig. 5(a). The transmittance is given as

$$I = I_o e^{-\alpha t} \tag{1}$$

where *I* and *I*_o is the intensity of transmitted and incident light, respectively, α is the absorption coefficient, and *t* is the thickness (70 nm). Since the transmittance in an indirect semiconductor is described as *I*/*I*_o, the relation between α and optical energy bandgap (*E*_g) is given as

$$\alpha = (h\nu - E_g)^2 \tag{2}$$

where *h* is the Planck constant, and ν is the frequency of incident photon. Then, the optical bandgap (E_g) is determined by an extrapolation method, namely, a value at which $\alpha^{1/2}$ is zero [15]. The extrapolation showed that the optical bandgap was ~3.56 and ~3.81 eV for the undoped and F-doped TiO₂ layers, respectively. A comparison shows that the F-doping causes a shift of the surface Fermi level toward the higher-energy side, being indicative of degenerated F-doped TiO₂. This is consistent with the high-energy side shift of the Ti 2p



Fig. 5. (a) Transmittance of bare FTO glass, undoped TiO_2 layer and F-doped TiO_2 layer. (b) The absorption coefficients of undoped and F-doped TiO_2 samples as a function of photon energy.



Fig. 6. Photocurrent density–voltage characteristics of DSSCs fabricated with bare and TiO_2 -coated FTO glass substrates.

Table 1 Photovoltaic properties of DSSCs fabricated with bare and TiO_2 -coated FTO glass substrates.

Samples	$J_{sc} \text{ [mA/cm}^2\text{]}$	V_{oc} [V]	ſſ	η [%]
Bare FTO glass	10.60	0.65	0.56	3.88
Undoped TiO ₂	12.44	0.66	0.58	4.76
F-doped TiO ₂	13.89	0.67	0.57	5.24

core level for the F-doped TiO₂ (Fig. 4). The work functions of the bare and TiO₂-coated FTO glass substrates were examined by a surface analyzer (AC-2, RIKEN). The work function was measured to be ~5.69, ~4.84, and ~4.48 eV for the FTO glass, undoped TiO₂ and F-doped TiO₂ layers, respectively, being consistent with the optical bandgap data. The degenerated n-type TiO₂ layer between the FTO glass substrate and the nanoporous TiO₂ layer is expected to form an ohmic contact [10], leading to the improved performance of DSSCs by reducing interfacial resistance.

Fig. 6 shows the photocurrent density-voltage characteristics of DSSCs fabricated with the bare and TiO₂-coated FTO glass substrates. Associated photovoltaic parameters are summarized in

Table 1. The DSSCs with the undoped TiO₂ dense layer show ~17.4% higher current density, leading to ~22.6% better conversion efficiency than the cells with the bare FTO glass. This implies that the undoped TiO₂ dense layer effectively serves as a blocking layer. In case of the DSSCs with the F-doped TiO₂ dense layer, they show $\sim 11.7\%$ higher current density than the cells with the undoped TiO₂ dense layer, leading to ~10.1% enhanced conversion efficiency. This implies that the F-doped TiO₂ dense layer effectively serves as a blocking layer with reduced interfacial resistance through controlling band structure. In other words, the F-doped TiO₂ dense layer reduces the interfacial resistance by forming ohmic contact, causing efficient flow of electrons. Furthermore, the F-doped TiO2 dense layer serves as an efficient blocking layer. These results imply that the F-doped TiO₂ dense layer could serve as a promising blocking layer for fabricating high-performance DSSCs.

4. Summary

F-doped TiO₂ dense layers were deposited onto FTO glass substrates by the hydrolysis of of TiCl₄ with 10 at% of NH₄F for use as a blocking layer. DSSCs fabricated with the F–TiO₂ dense layer exhibited higher photo-conversion efficiency than conventional DSSCs with an undoped TiO₂ dense layer. The improved performance was ascribed to the fact that the F-doped TiO₂ layer served as a blocking layer to prevent the back electron transfer and resulted in the reduced interfacial resistance.

Acknowledgments

This work was supported by the World Class University Program through the National Research Foundation of Korea funded by MEST (R33-2008-000–10025-0).

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