

Surface modification of TiO₂ electrode by various over-layer coatings and O₂ plasma treatment for dye sensitized solar cells

Jun Tak Kim, Sang Ho Kim*

Department of Materials Engineering, Korea University of Technology and Education, 307 Gajeon-ri, Byungcheon-myun, Cheonan-city, Chungnam 330-708, South Korea

ARTICLE INFO

Article history:

Received 3 November 2009

Received in revised form

22 February 2010

Accepted 14 April 2010

Available online 6 May 2010

Keywords:

DSSC

TiO₂ over-layer

O₂ plasma

ABSTRACT

The anti-recombination property and the surface area of TiO₂ influence the efficiency of dye-sensitized solar cells (DSSCs). The effects of various over-layers and O₂ plasma treatment on TiO₂ electrodes have been investigated. Over-layers were coated by dip coating in a solution of saturated Ba(NO₃)₂, Mg(NO₃)₂ and N₂O₆Sr, which reduced the recombination of electrons from the photo excited state of Ru dye. O₂ plasma treatment was applied to improve both the contact ability with the dye and the electron takeover capability by reducing oxygen vacancies on both the TiO₂ and the over-layer surface. The photo conversion efficiency of DSSC was improved by both over-layer coating and O₂ plasma treatment. In particular, dipping in saturated Ba(NO₃)₂ solution and O₂ plasma treatment (BP), the photo conversion efficiency was greatly improved from 5.27% to 6.76%. The reason was that the over-layers and O₂ plasma treatment decreased electron recombination. The energy barrier of the modified over-layers blocks the electron transfer from TiO₂ to the electrolyte, and consequently increases electron density by extending the electron lifetime. O₂ plasma treatment also increased the Ru dye absorption.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Dye-sensitized solar cells (DSSCs) consist of TCO, a thin film of porous TiO₂ electrode, dye, and a counter electrode, containing I⁻ and I₃⁻ as electron donor and electrolyte, respectively [1–3]. The TiO₂ electrode in a DSSC has a large surface area and provides sufficient anchoring sites for the dye sensitizers to provide effective light harvesting and electron injection [4]. However, electron transfer from Ru dye does not work perfectly, because many electrons recombine with the holes at the interface between TiO₂ and the electrolyte. To reduce this recombination, many over-layer coatings on TiO₂ electrode, such as BaTiO₃ [5], MgTiO₃ [4], Al₂O₃ [6,7], ZnO [8], have been investigated.

In DSSCs, oxygen vacancies, acting as electron trap sites, facilitate the recombination of injected conduction band electrons with the I₃⁻ ions in the electrolyte [6]. Recently, it was reported that an O₂ plasma treatment of TiO₂ can reduce the oxygen vacancies, increase the dye absorption, and improve the performance of DSSCs [6,9]. Therefore, in the present study, we examined the effects of various over-layer coatings as well as O₂ plasma treatment on the photo conversion efficiency of a DSSC.

2. Experimental

In this study, we prepared eight DSSC samples, as indicated in Table 1. Two samples had bare TiO₂ electrodes and the other six samples consisted of a specific over-layer (Ba(NO₃)₂, Mg(NO₃)₂, or N₂O₆Sr) coated onto TiO₂ electrodes. One of each type of sample received an additional surface treatment with O₂ plasma. Optically transparent FTO (F-doped SnO₂, 15 Ω/cm²) coated glass was used as a substrate for spreading the TiO₂ electrodes (Ti-nanoxide HT/SP, Solaronix SA) by a screen printing method. The area and thickness of the TiO₂ electrodes were 0.25 cm² and approximately 5 μm, respectively. The spread electrodes were calcined at 450 °C for 30 min in air. The over-layer was then prepared on the calcined substrate using saturated Ba(NO₃)₂, Mg(NO₃)₂, or N₂O₆Sr solution. First, each of the calcined TiO₂ electrodes was dipped into one of the aqueous solutions for 2 min. Second, after washing with D.I water, these dipped electrodes were sintered at 550 °C for 30 min in air [5]. One of each of the duplicate samples was then treated with O₂ plasma. The plasma process was carried out at a base pressure of 10 mTorr and RF power of 50 W for 2 min in pure O₂ [9]. The fabricated TiO₂ electrodes were then immersed into 0.4 mM of Ru dye (N719 dye, Solaronix Co.) solution in absolute ethanol for 24 h. The counter electrodes were fabricated by applying a drop of 0.2 mM H₂PtCl₆·6H₂O onto FTO glass at 450 °C for 30 min in air. The counter electrode was then sealed with surlyn (DuPont, 60 μm) and liquid electrolyte. The dye-absorbed TiO₂ electrode and counter electrode were assembled in a sandwich, and then

* Corresponding author. Tel.: +82 41 560 1325; fax: +82 41 560 1360.
E-mail address: shkim@kut.ac.kr (S. Ho Kim).

liquid electrolyte was injected. The liquid electrolyte was prepared by blending tetrapropylammonium iodide (TPAI), iodine, and 4-tert-butylpyridine in a solution of ethylene carbonate mixed with α -butyrolactone and acetonitrile.

The crystal structure of the TiO_2 electrodes was investigated by X-ray diffraction (XRD, Rigaku Co.) with $\text{Cu K}\alpha$ radiation over the 2θ range of 20 – 45° . UV–vis absorption spectra of the TiO_2 electrodes were measured using a spectrophotometer (Cary Co.). Photocurrent–voltage characteristics of the DSSCs were measured in AM 1.5 G solar illumination using a Xe lamp at 100 mW/cm^2 and a multimeter (K101, Polaonix., Korea). DSSC circuit impedance was measured in the dark using electrochemical impedance spectroscopy (EIS). The frequency range was 0.01 – 10^6 Hz, and the magnitude of the modulation signal was 10 mV .

3. Results and discussion

Fig. 1(a) and (b) shows the X-ray diffraction pattern of the TiO_2 electrode, with and without over-layers. Fig. 1(a) displays the wide-scan TiO_2 peaks observed, and Fig. 1(b) is the narrow scanned (1 0 1) TiO_2 peaks. As can be seen from Fig. 1(b), the diffraction peaks of the crystal plane (1 0 1) of TiO_2 shift to a higher 2θ angle as the over-layers are coated. These shifts were probably induced by an epitaxial growth between the parallel planes in the square facet of the tetragonal unit cell of TiO_2 and

the cubic unit cells of the over-layers. The reason for this is not clear at this point; the unit cells have a crystal structure of perovskite in BaTiO_3 [5] and SrTiO_3 , and of rhombohedral in MgTiO_3 [4]. The lattice parameter of each over-layer has some mismatch with that of the tetragonal unit cell of TiO_2 [5]; specifically, the lattice parameters a and c of the tetragonal unit cell of TiO_2 are 3.785 and 9.513 \AA , while the lattice parameter a of BaTiO_3 , SrTiO_3 , and MgTiO_3 is 5.724 , 3.905 , and 5.054 \AA , respectively. The lattice parameter of the crystal plane (1 0 1) of TiO_2 is calculated as 10.238 \AA using the Pythagorean theorem. Therefore, we assumed that when the crystal plane (1 0 1) of TiO_2 combines with the crystal plane of these over-layers, a contractive force is applied on the crystal plane (1 0 1) of TiO_2 . Because of this force, the diffraction peaks of TiO_2 planes shift to a higher 2θ angle [5]. This is an indirect evidence of the presence of over-layer coatings.

Fig. 2 shows the UV–vis absorption spectra of dye anchored to the TiO_2 electrodes with and without over-layers and O_2 plasma treatment. With over-layers, the absorption was increased. This means that dye-anchoring could be increased further by

Table 1

Sample list in this study. (T: uncoated TiO_2 electrode; B: $\text{Ba}(\text{NO}_3)_2$; S: $\text{N}_2\text{O}_6\text{Sr}$; M: $\text{Mg}(\text{NO}_3)_2$; N: no plasma treatment; P: plasma treated).

Sample	Dipping solution			Treated O_2 plasma	Remarks
	$\text{Ba}(\text{NO}_3)_2$	$\text{Mg}(\text{NO}_3)_2$	$\text{N}_2\text{O}_6\text{Sr}$		
TN	–	–	–	–	Reference
TP	–	–	–	O	Reference
BN	O	–	–	–	
BP	O	–	–	O	
MN	–	O	–	–	
MP	–	O	–	O	
SN	–	–	O	–	
SP	–	–	O	O	

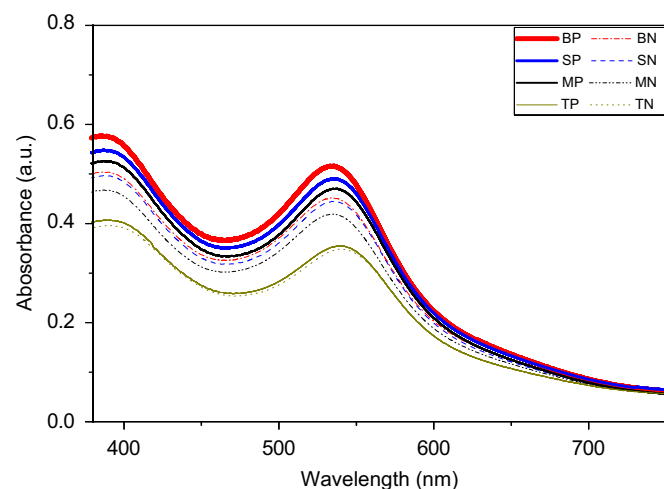


Fig. 2. UV–vis absorption spectra of dye-anchoring of the TiO_2 electrode with and without over-layers and O_2 plasma treatment.

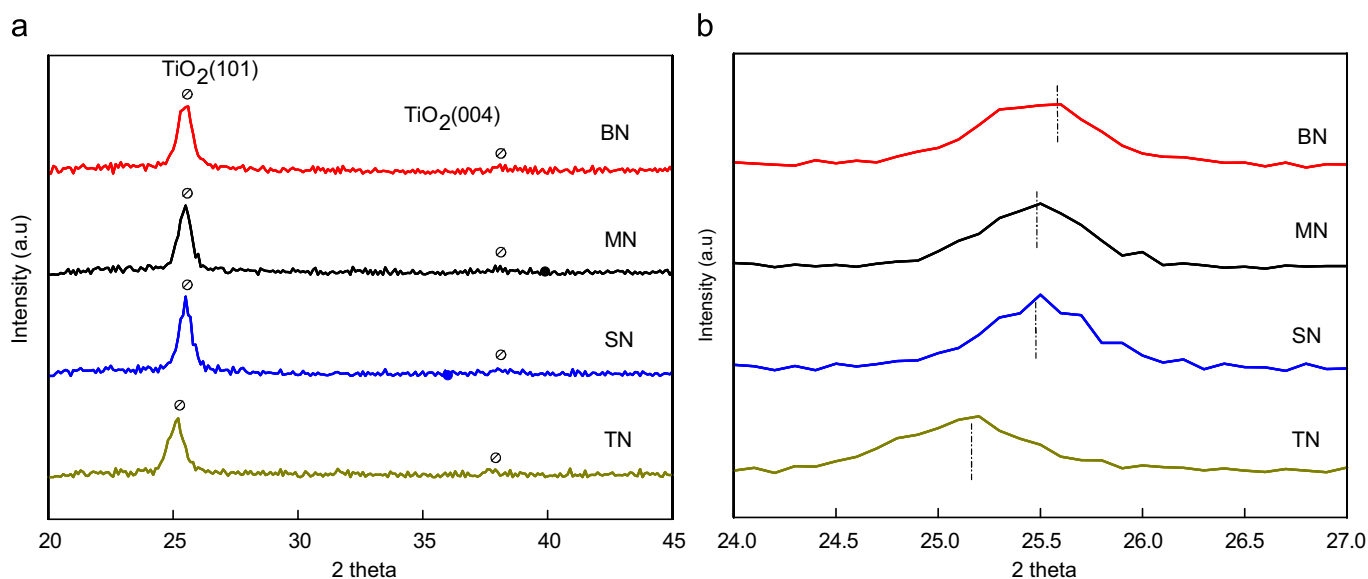


Fig. 1. Wide-scan XRD patterns of the TiO_2 electrode with and without over-layer coatings (a) and narrow-scanned TiO_2 (1 0 1) peaks (b).

Download English Version:

<https://daneshyari.com/en/article/79182>

Download Persian Version:

<https://daneshyari.com/article/79182>

[Daneshyari.com](https://daneshyari.com)