

Enhanced photovoltaic properties of overlayer-coated nanocrystalline TiO₂ dye-sensitized solar cells (DSSCs)

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Received: 21 May 2007 / Accepted: 18 March 2008 / Published online: 8 April 2008
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Abstract TiO₂ dye-sensitized solar cells (DSSCs) coated with various oxide layers were fabricated via a screen printing method and the effects of the oxide layers on the photovoltaic properties were systematically investigated. The open circuit voltage (V_{oc}) was closely dependent to the conduction band (CB) edge position and the band gap energy (E_g) of the oxide layers, while the short circuit current density (J_{sc}) was related to the iso-electric point (IEP). V_{oc} showed an increasing behavior with the CB edge position of the oxide layers, which could be explained by the blocking effect of the insulating layers. Although J_{sc} was basically proportional to the IEP and the resulting dye adsorption, there were other factors like the resistance of oxide layers. The cell efficiency could be enhanced by 60% when the cells were coated with the oxide layers of high E_g and IEP.

Keywords TiO₂ · Dye-sensitized solar cell (DSSC) · Oxide coating layer · Band gap energy (E_g) · Iso-electric point (IEP)

1 Introduction

Dye-sensitized solar cells (DSSCs) based on oxide-semiconductor nanocrystals such as TiO₂ are of great interest as alternatives to the conventional solar cells due to their high performance and low-cost production [1, 2]. The cell performance is influenced by the parameters such as morphology and optical properties of nanocrystalline oxide films [3–6], electrochemical characteristics of redox electrolytes [7, 8], and photochemical properties of molecular sensitizers [9–14]. Oxide layers coated on the TiO₂ nanocrystals have received much attention [15] because the cell efficiency can be enhanced through the modification. For instance, in case that the oxide layers such as ZnO [16], CaCO₃ [17], Nb₂O₃ [18], and SrTiO₃ [19] were coated on the TiO₂ electrodes, the overall cell efficiency was improved due to the enhanced short circuit currents and/or open current voltages. The improvement in cell efficiency has been ascribed to following two factors. First, the insulating layers with wide band gap and high conduction band edge can retard the back transfer of electrons from TiO₂ to the electrolytes or dye molecules [20]. Second, the enhanced dye adsorption by the oxide layers can improve the cell performance [15]. Because the oxides layers are more basic than TiO₂, carboxyl groups in the dye molecules can be adsorbed more easily. In this study, effects of various oxide layers on the performance of TiO₂ DSSCs are investigated more systematically.

2 Experimental procedures

2.1 TiO₂ electrode preparation

Porous TiO₂ thick films (~20 μm) were prepared on conducting glasses (indium tin oxide, Samsung SDI) via a

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screen printing method. Dense TiO_2 thin films ($\sim 30\text{nm}$) were deposited between the porous film and conducting glass in order to avoid direct contacting between electrolytes and the conducting glass. To make the paste, Degussa P25 TiO_2 powders were mixed with some organics by a three-roll mill. As-prepared films were dried at 200°C for 1h to remove the solvent. Then, various oxide layers were coated onto the porous TiO_2 layer by a spin coating method at 5,000rpm for 30s followed by annealing at 450°C for 1h for the complete removal of organics. Starting materials and the solvent for coating solutions were Zn-acetate-tetrahydrate, Ti-isopropoxide, Sn(IV)-acetate, Zr-butoxide, Mg-methoxide, Al-butoxide and 2-methoxyethanol, respectively. To make the Zn-solution, diethanolamine was added as a chelating agent. All chemicals were purchased from Aldrich and used as-received. The thickness of oxide layers was controlled to be approximately 20nm by adjusting the concentration of coating solutions.

2.2 Cell fabrication and characterization

For the fabrication of solar cells, the electrodes formed were immersed in a solution of ruthenium dye (ruthenium (2,2'-bipyridyl-4,4'-dicarboxylate) $_2$ (NCS) $_2$ (Solaronix), dissolved in ethanol) for 2h at 50°C . The resulting electrode with dye-adsorbed film was assembled with a Pt-sputtered glass electrode to form a sandwich-type dye cell. A drop of an electrolyte solution (Solaronix) was infiltrated into the dye cell. Photocurrent–voltage characteristics of each film were measured with a potentiostat (CHI 608A, CH Instruments) under the illumination of AM 1.5 (intensity = $100\text{mW}/\text{cm}^2$). To characterize the dye adsorption, dye molecules were desorbed from the photoelectrodes by soaking in alkaline alcoholic solutions. UV-Vis Spectrophotometer (LAMBDA 650, Perkin-Elmer) was used to determine the amounts of dye molecules in the solution. High resolution-transmission electron microscopy (HR-TEM; JEM 3000F, JEOL) was used to investigate the thickness and uniformity of the oxide layers coated on nanocrystalline TiO_2 . The transient photocurrent was measured using an oscilloscope (TDS 420A, Tektronix) and the Nd:YAG laser (NL 303H, EKSPLA, 355nm, $0.2\text{J}/\text{cm}^2$, 10Hz, 4.5ns pulse duration).

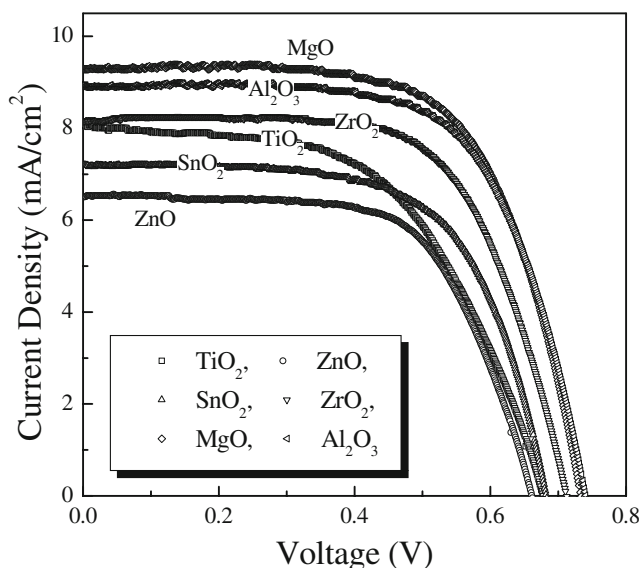


Fig. 1 Current–voltage characteristics for DSSCs coated with various oxide layers

3 Results and discussions

Current–voltage characteristics of DSSCs coated with various oxide layers are compared in Fig. 1. As can be seen in Fig. 1, photovoltaic properties of TiO_2 DSSCs are directly influenced by the oxide layers, since the major solar cell parameters such as the open circuit voltage (V_{oc}) and the short circuit current density (J_{sc}) show remarkable changes with the oxide layers. Measured solar cell parameters and the important information on the coating layers are listed in Table 1. According to the Table 1, the cell efficiency is also dependent on the species of the oxide layers (i.e. on the conduction band (CB) edge position, band gap energy (E_g) and the iso-electric point (IEP) of oxide layers). In order to investigate the effects of oxide layers on the cell efficiency, it is desirable to consider their effects on V_{oc} and J_{sc} separately. Although the fill factor (FF) is also an important cell parameter, it was excluded since it does not show any remarkable changes with the oxide layers.

At first, we investigated the effects of oxide layers on the V_{oc} . As can be seen in Fig. 2, which shows the V_{oc} as a

Table 1 Solar cell parameters for cells coated with various oxide layers

Oxide layer	E_g (eV)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	Efficiency (%)	IEP (pH)
ZnO	3.0	0.662	6.51	53	2.30	9.5
TiO_2	3.2	0.678	8.06	46	2.53	5.5
SnO_2	3.8	0.682	7.20	54	2.66	4.0
ZrO_2	5.0	0.711	8.16	57	3.32	5.1
MgO	7.8	0.734	9.29	58	3.98	12.5
Al_2O_3	8.8	0.740	8.91	58	3.84	9.2

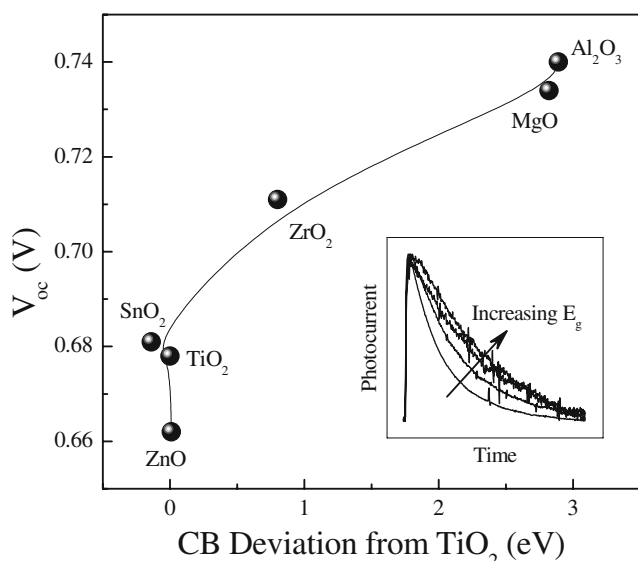


Fig. 2 V_{oc} for DSSCs coated with various oxide layers as a function of conduction band (CB) deviation from TiO₂. Inset shows the photocurrent transient for DSSCs coated with high-CB oxide layers (TiO₂<ZrO₂<MgO<Al₂O₃)

function of the CB deviation from TiO₂, V_{oc} is almost proportional to the CB deviation especially for high CB oxide layers. They exhibited the similar behavior when plotted as a function of E_g , but CB edge position is selected as an independent parameter since it is a more direct factor to affect the V_{oc} . Two possible mechanisms for the increased V_{oc} can be suggested; blocking effects and surface dipole effects. In the case of the DSSCs coated with oxide layers of higher conduction edges (usually higher E_g), the coating layers act as blocking barriers for the recombination of the injected electrons either with the oxidized dye molecules or with the oxidized redox couple.

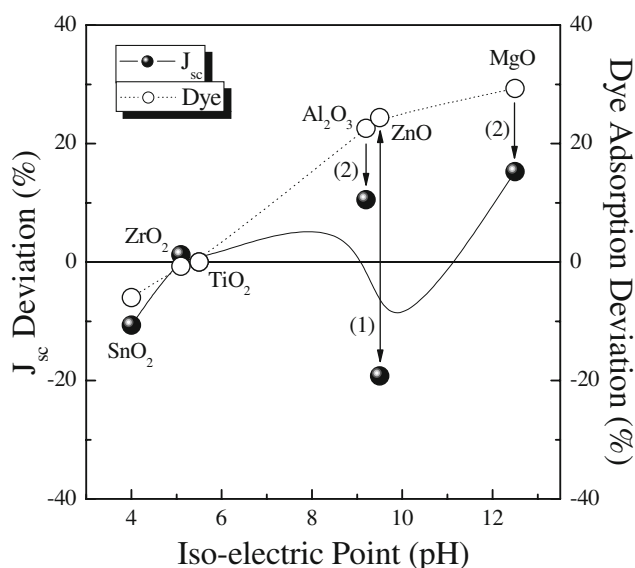


Fig. 3 Deviation in J_{sc} and dye-adsorption of DSSCs coated with various oxide layers compared to the DSSC coated with TiO₂ layer

The photocurrent transient seen in the inset of Fig. 2 confirms that the charge recombination has been retarded by the oxide layers with high CB edge and E_g since the characteristic time increases. If the recombination of the injected electrons is retarded, the electron population and the resulting quasi Fermi level of TiO₂ nanocrystals near the coating layer will increase. As a result, V_{oc} will increase due to the increased offset between the quasi Fermi level of TiO₂ nanocrystals and the red/ox level of electrolytes. This is the “blocking effect” of the insulation layer. The other possible mechanism is “surface dipole effect” which is not related directly to the charge recombination. If the coating layers induce the positive charges near the surface of the coating layers, an electrostatic field will be generated, which can increase the offset of conduction edges. Then, the V_{oc} will also increase. The oxide layers with high IEP such as MgO and Al₂O₃ can introduce the electrostatic field, since they attract more dye molecules which can deprotonate the TiO₂ nanocrystals.

Effects of oxide layers on the J_{sc} were also investigated. It is readily understood that J_{sc} will be influenced by the amounts of adsorbed dye molecules, since they can produce electrons by absorbing the light. J_{sc} and the amounts of dye-adsorption are presented as a function of IEP in Fig. 3. To compare them clearly, deviations from the TiO₂ layer are plotted. J_{sc} is expected to increase with increasing IEP since the dye adsorption increases monotonically as seen in Fig. 3. However, there are two exceptions in the increasing trend. In the case of ZnO layer [denoted as (1) in Fig. 3], J_{sc} is smaller than TiO₂ by 19%, while dye adsorption is larger by 24%. Much smaller J_{sc} relative to the dye adsorption can be ascribed to the defective nature of ZnO. Many defects

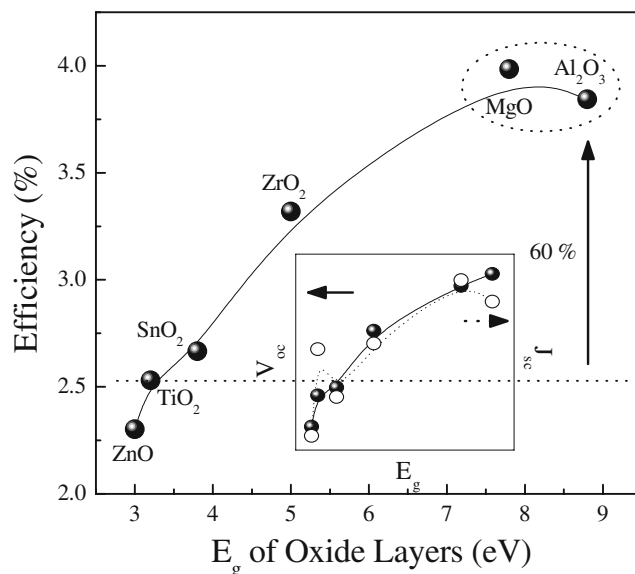


Fig. 4 Cell efficiency of DSSCs coated with various oxide layers as a function of E_g of the oxide layers. Inset shows V_{oc} and J_{sc} as a function of E_g of the oxide layers

and states of ZnO layer may trap the electrons, which can lower the current density. Corrosion of ZnO in the electrolytes can be another reason. In cases of MgO and Al₂O₃ [denoted as (2) in Fig. 3], increment in J_{sc} is smaller than dye adsorption by 12% and 14% for Al₂O₃ and MgO, respectively. This result can originate from the highly insulating nature of MgO and Al₂O₃. While J_{sc} is enhanced by the high electron population due to the large dye-adsorption, the increment may be lessened since the injection of electrons through the insulating layers is difficult.

The cell efficiencies of the DSSCs coated with various oxide layers are presented in Fig. 4. The cell efficiency can be calculated as the following equation.

$$\text{Efficiency (\%)} = \frac{V_{oc} \times J_{sc} \times FF}{P_{input}} \times 100 \quad (1)$$

The cell efficiency shows an increasing manner with the increasing E_g . This result can be readily understood since V_{oc} and J_{sc} shows a similar manner to the efficiency as can be seen in the inset of Fig. 4.

4 Conclusions

TiO₂ DSSCs coated with various oxide layers were fabricated and the effects of the oxide layers on the V_{oc} , J_{sc} and the resulting cell efficiency were investigated. V_{oc} increased with the increasing conduction band (CB) edge position of the oxide layers, which could be explained by the “blocking effect” of oxide layers with high CB edges. Although J_{sc} was basically proportional to the iso-electric point (IEP) and resulting dye-adsorption, defects and insulation of oxide layers made some exceptions. The cell efficiency, which can be determined by V_{oc} , J_{sc} and the fill factor, showed an increasing manner with the increasing E_g , since both of V_{oc} and J_{sc} showed an increasing behavior. In cases of MgO and Al₂O₃ layers, the cell efficiency was near 4%, which was enhanced by approximately 60% compared to TiO₂ layer.

Acknowledgements This work was supported by the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea government (MOST) (R01-2007-000-11075-0) (RIAM).

References

1. B. O'regan, M. Grätzel, *Nature* **353**, 737 (1991)
2. M.K. Nazeeruddin, K. Kay, I. Rodicio, B.R. Humphry, E. Mueller, N. Vlachopolous, M. Grätzel, *J. Am. Chem. Soc.* **115**, 6382 (1993)
3. L. Kavan, M. Grätzel, J. Rathousky, A. Zukal, *J. Electrochem. Soc.* **143**, 394 (1996)
4. H.K. Jheong, Y.J. Kim, J.H. Pan, T.-Y. Won, W.I. Lee, *J. Electroceram.* **17**, 929 (2006)
5. B.-K. Koo, D.-Y. Lee, H.-J. Kim, W.-J. Lee, J.-S. Song, H.-J. Kim, *J. Electroceram.* **17**, 79 (2006)
6. N.-G. Park, J. van de Lagemaat, A.J. Frank, *J. Phys. Chem. B* **104**, 8989 (2000)
7. H. Nusbaumer, J.-E. Moser, S.M. Zakeeruddin, M.K. Nazeeruddin, M. Grätzel, *J. Phys. Chem. B* **105**, 10461 (2001)
8. I. Montanari, R. Monkhhouse, J. Nelson, J.R. Durrant, *J. Phys. Chem. B* **105**, 7517 (2001)
9. A. Fillinge, B.A. Parkinson, *J. Electrochem. Soc.* **146**, 4559 (1999)
10. A. Laschewsky, O. Quari, P. van Cleuvenbergen, *Chem. Mater.* **13**, 3888 (2001)
11. A. Kay, M. Grätzel, *J. Phys. Chem.* **97**, 6272 (1993)
12. J. He, J. Zhao, T. Shen, H. Hidaka, N.J. Serpone, *J. Phys. Chem. B* **101**, 9027 (1997)
13. T.A. Heimer, S.T. D'Arcangelis, F. Frazad, J.M. Stipkala, G.J. Meyer, *Inorg. Chem.* **35**, 5319 (1996)
14. K. Hara, T. Horiguchi, T. Kinoshita, K. Sayama, H. Sugihara, H. Arakawa, *Sol. Energy Mater. Sol. Cells* **64**, 115 (2000)
15. H.S. Jung, J.K. Lee, M. Nastasi, S. Lee, J.Y. Kim, J.S. Park, K.S. Hong, H. Shin, *Langmuir* **21**, 10332 (2005)
16. Z.-S. Wang, C.-H. Huang, Y.-Y. Huang, Y.-J. Hou, P.-H. Xie, B.-W. Zhang, H.-M. Cheng, *Chem. Mater.* **13**, 678 (2001)
17. S. Lee, J.Y. Kim, K.S. Hong, H.S. Jung, J.K. Lee, H. Shin, *Sol. Energy Mater. Sol. Cells* **90**, 2405 (2006)
18. S.G. Chen, S. Chappel, Y. Diamant, A. Zaban, *Chem. Mater.* **13**, 4629 (2001)
19. Y. Diamant, S.G. Chen, O. Melamed, A. Zaban, *J. Phys. Chem. B* **107**, 1977 (2003)
20. E. Palomares, J.N. Clifford, S.A. Haque, T. Lutz, J.R. Durrant, *J. Am. Chem. Soc.* **125**, 475 (2003)