Sputtered Nb$_2$O$_5$ as an effective blocking layer at conducting glass and TiO$_2$ interfaces in ionic liquid-based dye-sensitized solar cells

Jiangbin Xia, Naruhiko Masaki, Kejian Jiang and Shozo Yanagida*

The thin Nb$_2$O$_5$ layer works as a remakable blocking layer when deposited by the rf magnetron sputtering method between fluorine-doped tin oxide and a mesoporous TiO$_2$ layer, improving open-circuit photovoltage (V_{oc}) and fill factor (FF) with power conversion efficiency over 5.5% at 1 sun irradiation of the dye-sensitized TiO$_2$ solar cells using ionic liquid electrolytes.

In dye-sensitized TiO$_2$ solar cells (DSCs) that composed of a dye-adsorbed mesoporous TiO$_2$ layer on fluorine-doped tin oxide (FTO) glass as a window electrode, redox electrolytes as charge carrier and the counter electrode, unidirectional charge flow with no electron leakage at the interfaces is essential for the high energy conversion efficiency. The electrolytes, usually containing an I$^-$/I$_3^-$ redox couple in organic solvents are sealed between two electrodes. For the application requirement, organic liquid electrolytes cause a serious problem of low durability due to electrolyte evaporation. Recently, much attention[1–3] has been paid to improve the performance of the ionic liquid-based DSCs because of the features of ionic liquid such as high ionic conductivity, non-volatility, electrochemical stability and non-flammability.[4–6]

According to the unidirectional electron transporting principle of DSCs, there are four important interfaces in the devices as shown in Fig. 1 when hydrophobic sensitizing dye Z-907 (*cis*-bis(isothiocyanato)(2,2′-bipyridyl-4,4′-dicarboxylato)(2,2′-bipyridyl-4,4′-di-nonyl) ruthenium(II)) is employed. These are, the interfaces of FTO/TiO$_2$, TiO$_2$/dye, dye/electrolyte, and electrolyte/counter electrode (usually platinized FTO electrode). Recently, many researchers have paid much attention to the interface of TiO$_2$/dye especially through constructing core-shell structured electrodes by introducing Nb$_2$O$_5$,[7] SrTiO$_3$,[8,9] Al$_2$O$_3$[10] and so on[11] for TiO$_2$ electrode surface modification. On the other hand, a few groups have investigated the effect of the interface of FTO/TiO$_2$, revealing its effectiveness of employing a blocking TiO$_2$ layer,[12b,15,16] which is called compact TiO$_2$.[12–15]

In our previous work,[17] we first succeeded in introducing a nano-thick Nb$_2$O$_5$ layer by the spray pyrolysis method as a blocking layer at the FTO/TiO$_2$ interface, obtaining some promising results (improvement of V_{oc} and FF). However, the J–V curve of DSC gives some lower J_{sc} and less than 4% conversion efficiency as far as ionic liquid electrolytes are employed. In this communication, we report the preparation of

Center for Advanced Science and Innovation, Osaka University, Suita, Osaka 565-0871, Japan. E-mail: yanagida@mls.eng.osaka-u.ac.jp; Fax: +81-6-6879-7351; Tel: +81-6-6879-7351

a Nb$_2$O$_5$ blocking layer employing the sputtering method achieving over 5.5% energy conversion efficiency for ionic liquid-based DSCs. Since the surface modification of mesoporous TiO$_2$ layers (electrode) is a well-known strategy to improve cell performance, the comparison between these two methods is undertaken to verify the effects on suppression of charge recombination at these two interfaces (FTO/nano-TiO$_2$ and nano-TiO$_2$/dye as motioned above) in ionic liquid DSCs. Through this study, we can get a comprehensive understanding of the importance of the controlling unidirectional charge flow at both interfaces in DSCs.

The improvement should come from the Nb$_2$O$_5$ blocking layer that create potential barrier between FTO and TiO$_2$ layers, which can suppress back electron transfer from FTO to I$^-$/I$_3^-$ redox electrolytes in the vicinity of FTO/TiO$_2$ interfaces without lowering electron injection between TiO$_2$ and FTO as shown in Fig. 1.

The sputtering method was applied to form the thin Nb$_2$O$_5$ layer on FTO during the fabrication of the structure of FTO/Nb$_2$O$_5$/porous TiO$_2$ (Nanoxide-T, Solaronix, 5.5 μm) electrodes. The general procedure was as follows:. The Nb$_2$O$_5$ modified FTO substrates were fabricated through depositing Nb$_2$O$_5$ onto FTO (Nippon Sheet Glass, SnO$_2$: F, 10 ohm sq^{-1}) with a radio frequency magnetron sputtering equipment (SPW-025S, ULVAC, Japan). The sputtering target was Nb$_2$O$_5$ (High Pure Chemicals,
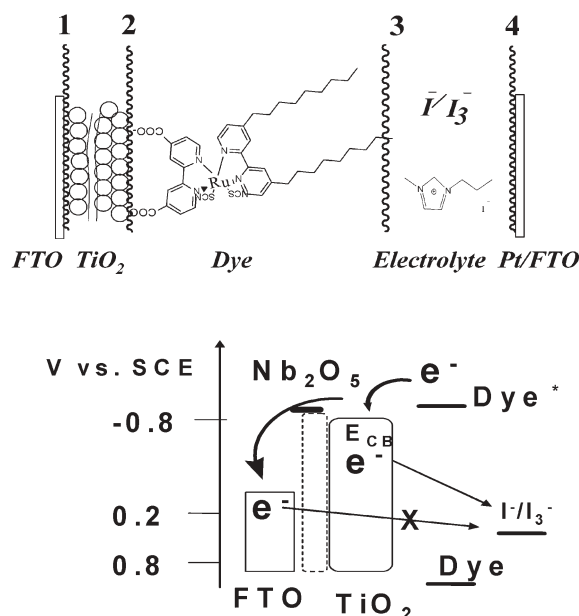

Fig. 1 Schematic views of interfaces in the DSC device and the electron transfer of the new structured electrode.

Japan) disk of 99.99% purity with the diameter of 100 mm. Different thicknesses of Nb_2O_5 layers were deposited onto FTO at dc power of 150 W under a working pressure of 0.5 Pa of a mixture of O_2 and Ar (volume ratio was 1 to 4). The Ru dye, Z-907 (Ru-520 DN, Solaronix) and the ionic liquid electrolyte composed of 0.5 M *tert*-4-butylpyridine, 0.1 M LiI and 0.2 M I_2 in PMImI (1-propyl-3-methylimidazolium iodide) and EMIm-DCA (1-ethyl-3-methyl-imidazolium dicyanamide) ([PMImI] : [EMIm-DCA] = 2 : 1) were employed for ionic liquid-based DSCs. Here ruthenium dye Z-907 with the long alkyl chain was employed because of its thermal stability of absorbed states.[18] As far as the conversion efficiency is concerned, other ruthenium dyes such as N3 and N-719 give similar results during the examination of the Nb_2O_5 blocking layer effect. The ethanol solution of 0.005 M $NbCl_5$ was prepared and used as a precursor for surface modification by the dipping method.[7] The 4 μm thickness of 400 nm TiO_2 (Catalysis & Chemicals Ind. Co. Ltd.) is used as a scattering layer of DSCs.

As shown in Table 1, when compared to the non-blocked electrode ⟨nano-TiO_2/dye⟩, the Nb_2O_5 blocking electrode ⟨Nb_2O_5-BL/nano-TiO_2/dye⟩ (obtained by sputtering for 2 min at 150 W being estimated around 5 nm) improves V_{oc} about 50 mV with even higher J_{sc}, leading to an energy conversion efficiency of 4.5% without decreasing the fill factor, which is 20% higher than that of the non-blocked electrode. Fig. 2 presents the J-V curve of the interface-optimized DSC and that of the non-blocked DSC for reference under AM 1.5 irradiation of 100 mW cm^{-2}. As similar to the nano-TiO_2 electrodes with compact TiO_2 layer as blocking layer, the novel electrode with the Nb_2O_5 blocking layer can decrease the dark current greatly. The dye Z-907 absorption on both the blocking Nb_2O_5 and the nano-TiO_2 layers may block dark current, improving the unidirectional electron flow at FTO/Nb_2O_5 layer/nano-TiO_2/dye/electrolyte interfaces.[12b]

It has recently been suggested[19,20] that the charge recombination sites leading to a decrease of V_{oc} should be mainly at nanocrystalline TiO_2/redox electrolyte interfaces. The injected conduction-band electrons may recombine with oxidized dye molecules on the interfaces or with tri-iodide and poly-iodide redox species in the electrolyte. And generally, the former recombination is negligible because of the quick reduction of the oxidized dye molecules by I^- ions in the electrolytes. Many attempts have been done to suppress such back electron transfer reaction that may take place at the interface between TiO_2 and dye or redox electrolytes in the last several years using surface treatment[7–11] of TiO_2 electrode as mentioned in the introduction. On the other hand, the porous interfaces between FTO substrate and nano-TiO_2 can also act as electron recombination sites, *i.e.*, electron leakage sites exist especially when solid or quasi-solid state electrolytes like ionic liquid electrolytes once infiltrate into the interfaces. Therefore, the
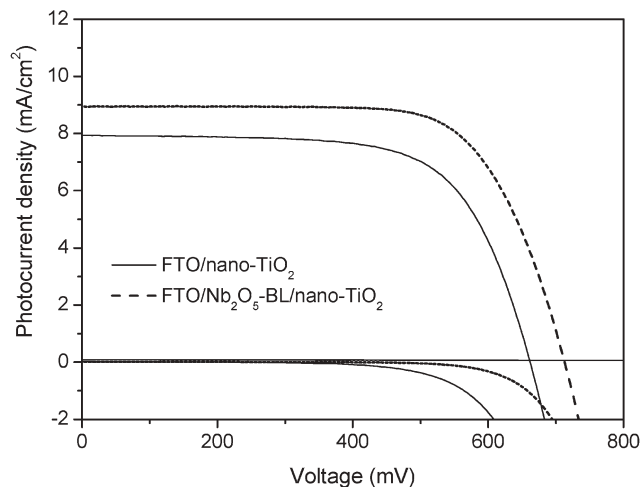

Fig. 2 J-V curves of cells employing Z-907 sensitized FTO/nano-TiO_2 (line) and FTO/Nb_2O_5-BL/nano-TiO_2 electrodes (dash line) under AM 1.5 irradiation (100 mW cm^{-2}, electrolyte: PMImI : EMImI-DCA = 2 : 1, 0.2 M I_2, 0.5 M TBP and 0.1 M LiI. 5.5 μm nano-TiO_2 employed).

suppression of electron leakage at FTO/TiO_2 interface is very crucial because photoelectron density at FTO/TiO_2 is very high.

Our successful structured FTO/Nb_2O_5/TiO_2 electrode should form 100 mV^{21} potential barrier between Nb_2O_5 and TiO_2 particles, prohibiting effectively the recombination of injected electron in FTO with the redox couple in electrolytes, which means enhancement of the electron collection at FTO, giving an improvement of shunt resistance and V_{oc} because of the minimized leakage of injected electrons at the interfaces. Meanwhile, the accumulated electrons lead to the increment of conduction band electrons as reflected by the J_{sc} increase.

On the other hand, the improved fill factor may be ascribed to the improved series resistance.[22] Interestingly, the radius of Nb^{5+} (0.69Å) is almost the same as that of Sn^{4+} which is favourable for the Nb species to diffuse into the FTO layer, contributing to the decrease of resistance as verified in recent paper.[23]

It is interesting to note that the treatment of $NbCl_5$ solution on mesoporous TiO_2 electrodes will improve V_{oc} and J_{sc} in liquid electrolyte DSCs, which was explained as due to core-shell structured mesoporous TiO_2 electrode.[7] The Nb_2O_5 layer was proposed to form potential barrier on mesoporous TiO_2 electrode, contributing to suppress back electron transfer at interface between TiO_2 and dye molecules. Considering the Nb_2O_5 blocking effects, FTO/TiO_2 and TiO_2/dye interfaces, the surface modification with $NbCl_5$ was extended to ionic liquid-based DSC electrodes.

Table 1 shows the effects between the blocking method and nano-TiO_2 surface modification. In the case of $NbCl_5$ surface

Table 1 Comparison of the parameters of the ionic liquid DSCs fabricated by mesoporous TiO_2 electrodes with or without Nb_2O_5 blocking layers (BL) on FTO before and after optimization with the $NbCl_5$ surface treatment

Electrodes	V_{oc}/mV	J_{sc}/mA cm^{-2}	FF	η (%)
nano-TiO_2/dye (non-blocked electrode)	663 ± 5	7.91 ± 0.2	0.66 ± 0	3.5 ± 0.1
Nb_2O_5-BL(5 nm)/nano-TiO_2/dye	710 ± 5	9.32 ± 0.4	0.68 ± 0.02	4.5 ± 0.1
nano-TiO_2/treated with $NbCl_5$/dye	675 ± 2	9.12 ± 0.2	0.67 ± 0.01	4.2 ± 0.1
Nb_2O_5-BL/nano-TiO_2/treated with $NbCl_5$/dye	720 ± 5	9.73 ± 0.2	0.68 ± 0.01	4.8 ± 0.1
nano-TiO_2/scattering layer/dye	682 ± 5	11.2 ± 0.2	0.66 ± 0.01	5.0 ± 0.2
Nb_2O_5-BL/nano-TiO_2/scattering layer/dye	719 ± 5	11.4 ± 0.3	0.67 ± 0.01	5.5 ± 0.1

modification, it can improve J_{sc} greatly followed by more than a 10 mV increment of V_{oc}. While the treatment was applied to the Nb$_2$O$_5$ blocked electrodes, both V_{oc} and J_{sc} were improved drastically, leading to the respectable conversion efficiency in ionic liquid-based DSCs. In addition, the introduction of 4 μm of 400 nm-sized TiO$_2$ as a scattering layer employed in ionic liquid-based DSCs, the cell gives 11.4 mA cm^{-2} of J_{sc}, 719 mV of V_{oc} and 0.67 of FF, leading to a conversion efficiency of 5.5%.

In summary, we have demonstrated that the sputtering of Nb$_2$O$_5$ on FTO can form a nm-thick film, giving effective blocking layer at interstitial FTO and mesoporous TiO$_2$ interfaces. The resulting mesoporous TiO$_2$ anodes greatly improve V_{oc} whilst keeping good fill factor, proving the importance of the blocking layer at FTO and TiO$_2$ interfaces in ionic liquid-based DSCs. Compared to the previous spray pyrolysis method[17] for making Nb$_2$O$_5$ blocking films, the present sputtering method will be the best way for introduction of the blocking layer on FTO. Through the combination with the surface modification of mesoporous TiO$_2$ layer method, we verified that unidirectional charge transfer at the interfaces of FTO/nano-TiO$_2$ and nano-TiO$_2$/dye are very important for higher conversion efficiency in ionic liquid-based DSCs. Further investigations need to be done to study the interaction of Nb$_2$O$_5$ blocking layer with FTO and nano-TiO$_2$ layers. Other facile methods for construction of the effective blocking layer and their comparisions are currently being undertaken.

Notes and references

1 P. Wang, B. Wenger, R. Humphry-Baker, J.-E. Moser, J. Teuscher, W. Kantlehner, J. Mezger, E. V. Stoyanov, S. M. Zakeeruddin and M. Grätzel, *J. Am. Chem. Soc.*, 2005, **127**, 6850.
2 H. Matsumoto, T. Matsuda, T. Tsuda, R. Hagiwara, Y. Ito and Y. Miyazaki, *Chem. Lett.*, 2001, **29**, 26.
3 N. Yamanaka, R. Kawano, W. Kubo, T. Kitamura, Y. Wada, M. Watanabe and S. Yanagida, *Chem. Commun.*, 2005, 740.
4 R. Hagiwara and Y. Ito, *J. Fluorine Chem.*, 2000, **105**, 221.
5 T. Welton, *Chem. Rev.*, 1999, **99**, 2071.
6 A. B. McEwen, H. L. Ngo, K. LeCompte and J. L. Goldman, *J. Electrochem. Soc.*, 1999, **146**, 1687.
7 A. Zaban, S. G. Chen, S. Chappel and B. A. Gregg, *Chem. Commun.*, 2000, 2231.
8 S. M. Yang, Y. Y. Huang, C. H. Huang and X. S. Zhao, *Chem. Mater.*, 2002, **14**, 1500.
9 Y. Diamant, S. G. Chen, O. Melamed and A. Zaban, *J. Phys. Chem. B*, 2003, **107**, 1977.
10 T. Taguchi, X. T. Zhang, I. Sutanto, K. Tokuhiro, T. N. Rao, H. Watanabe, T. Nakamori, M. Uragami and A. Fujishima, *Chem. Commun.*, 2003, 2480.
11 E. Palomares, J. N. Clifford, S. A. Haque, T. Lutz and J. R. Durrant, *J. Am. Chem. Soc.*, 2003, **125**, 475.
12 (a) L. Kavan and M. Grätzel, *Electrochim. Acta*, 1995, **40**, 643; (b) S. Ito, P. Liska, P. Comte, R. Charvet, P. Péchy, U. Bach, L. Schmidt-Mende, S. M. Zakeeruddin, A. Kay, M. K. Nazeeruddin and M. Grätzel, *Chem. Commun.*, 2005, 4351; (c) J. N. Hart, D. Menzies, Y. B. Cheng, G. P. Simon and L. Spiccia, *C. R. Chimie*, 2006, **9**, 622; (d) T. S. Kang, S. H. Moon and K. J. Kim, *J. Electrochem. Soc.*, 2002, **149**, E155; (e) H. W. Han, X. Z. Zhao and J. Liu, *J. Electrochem. Soc.*, 2005, **152**, A164.
13 B. A. Gregg, F. Pichot, S. Ferrere and C. L. Fields, *J. Phys. Chem. B*, 2001, **105**, 1422.
14 (a) P. J. Cameron and L. M. Peter, *J. Phys. Chem. B*, 2003, **107**, 14397; (b) P. J. Cameron and L. M. Peter, *J. Phys. Chem. B*, 2005, **109**, 7392.
15 B. Peng, G. Jungmann, C. Jäger, D. Haarer, H. W. Schmidt and M. Thelakkat, *Coord. Chem. Rev.*, 2004, **248**, 1479.
16 S. Hore and R. Kern, *Appl. Phys. Lett.*, 2005, **87**, 263504.
17 J. B. Xia, N. Masaki, K. J. Jiang, Y. Wada and S. Yanagida, *Chem. Lett.*, 2006, **35**, 252.
18 P. Wang, S. M. Zakeeruddin, J.-E. Moser, M. K. Nazeeruddin, T. Sekiguchi and M. Grätzel, *Nat. Mater.*, 2003, **2**, 402.
19 S. Y. Huang, G. Schlichthörl, A. J. Nozik, M. Grätzel and A. J. Frank, *J. Phys. Chem. B*, 1997, **101**, 2567.
20 M. Grätzel, *Prog. Photovoltaics*, 2000, **8**, 171.
21 K. Sayama, H. Sugihara and H. Arakawa, *Chem. Mater.*, 1998, **10**, 3825.
22 G. Kron, U. Rau and J. H. Werner, *J. Phys. Chem. B*, 2003, **107**, 13259.
23 J. B. Xia, N. Masaki, K. J. Jiang and S. Yanagida, *J. Photochem. Photobiol. A*, submitted.