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Sputtered Nb₂O₅ as a Novel Blocking Layer at Conducting Glass/TiO₂ Interfaces in Dye-Sensitized Ionic Liquid Solar Cells

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The preparation of a novel Nb₂O₅ blocking layer deposited between fluorine-doped tin oxide (FTO) and nanocrystalline TiO₂ layer and its application for dye-sensitized ionic liquid solar cell have been studied. The Nb₂O₅ blocking layer prepared by the sputtering method on FTO has been characterized by scanning electron microscopy (SEM), cyclic voltammetry (CV), and X-ray photoelectron spectroscopy. Thin Nb₂O₅ films work as a potential blocking layer between FTO and TiO₂ nanocrystalline film in ionic liquid electrolyte cells, improving V_{oc} and finally giving a better conversion efficiency of dye-sensitized TiO₂ solar cells. The remarkable improvements of V_{oc} and the fill factor for the dye-sensitized solar cells suggest that such a thin Nb₂O₅ layer is an effective blocking layer at FTO and TiO₂ interface, contributing to the suppression of recombination processes between unidirectional transporting electron and redox electrolytes in the process of TiO₂ photoelectron conversion systems. SEM and CV reveal that the Nb₂O₅ blocking layer is electronic blocking rather than morphological blocking at the FTO/nanoTiO₂ interface, which may give another direction on the suppression of charge recombination during photoelectron conversion process.

1. Introduction

Since the first successful introduced nanocrystalline dye-sensitized solar cell (DSC) appeared in 1991,¹ great progress has been made in this domain, not only in promising sensitizers, novel kinds of electrolytes, but also in multilayered or modified electrodes. However, from the point of practical application, organic liquid electrolytes may not be a good choice because of their shortcomings such as sealing, evaporation, and high-temperature instability. Therefore, many attempts to form quasi-solid-state electrolytes by using gelators,^{2–3} organic-capped nanoparticles,^{4–5} or polymers⁶ and application of low molecular oligomers⁷ as polymer electrolytes have been investigated with interesting progress. Recently, much attention^{8–11} has been paid to improve the performance of the ionic liquid DSCs because of their promising features such as high ionic conductivity, nonvolatility, improved electrochemical stability, and non-flammability.^{12–14}

According to the unidirectional electron transporting principle of DSCs, there are four important interfaces in the devices as shown in Figure 1. These are, the interfaces of FTO/TiO₂, TiO₂/dye, dye/electrolyte (or hole-transporting materials), and electrolyte/counterelectrode (usually Platinized FTO electrode). These interfaces not only play an important role in the parameters of the DSCs but also are hot topics in light-emitting diodes (LEDs),¹⁵ silicon solar cells,¹⁶ and other photovoltaic devices.¹⁷

In the last several years, there is great progress in electrode surface modification of TiO₂ including some mechanism study through introducing Nb₂O₅,¹⁸ SrTiO₃,^{19–20} Al₂O₃,²¹ and so on,^{22–23} which mainly focus on the decrease of the charge recombination at the interface of TiO₂/dye. On the other hand, other investigations on the interface of dye/electrolyte (or hole transporting materials) have been carried out through so-called

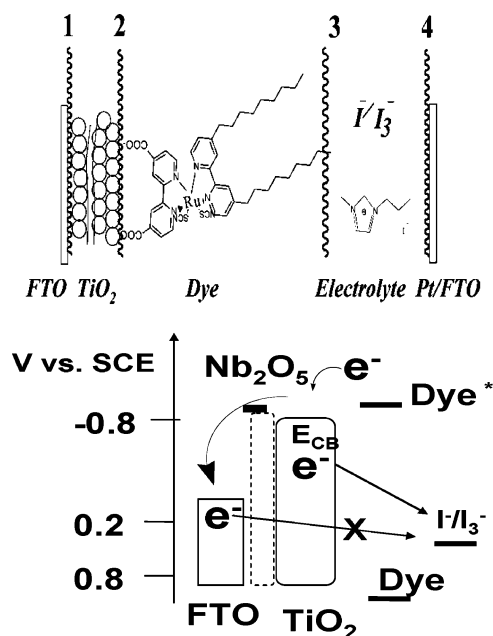


Figure 1. Schematic views of interfaces in the DSC device and the electron transfer of the new structured electrode.

intersurface engineering in solid-state DSCs with self-assembly method.²⁴ Although some groups have studied the interface of FTO/TiO₂ mainly to establish some models^{25–30} of DSCs or just only to characterize^{31–32} and investigate its effectiveness^{33–35} by employing a compact TiO₂ layer, there is no intense investigation on such important interface in DSCs.

Meanwhile, some research^{36–37} has suggested that charge recombination at the nanocrystalline/redox electrolyte interface is expected to play a significant role in lowering the photovoltage. There are two recombination pathways occurring at this interface. The injected conduction-band electrons may recombine with oxidized dye or tri-iodide and polyiodide redox species

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in the electrolyte. Usually the formal reaction is ignored because of the rapid rate of reduction of oxide dye molecules by I⁻ ions. Many attempts have been done to suppress such back electron-transfer reactions taken place at the surface of TiO₂ in the last several years using surface treatment of TiO₂ electrode.^{18–23} On the other hand, the porous interfaces between FTO substrate and TiO₂ layers can also be electron recombination sites, i.e., electron leakage sites exist especially when solid or highly viscous redox species such as ionic liquid iodides once infiltrate into the interfaces. It should be pointed out those electrons caught to the oxidized dye molecules occur in case of the penetration (infiltration) of redox electrolytes. Therefore, it is vital to attach importance to the interface of FTO/TiO₂, which is emphasized by Prof. L. M. Peter in his very recent articles.^{38–40}

In our previous work,⁴¹ we first developed Nb₂O₅ by spray pyrolysis method and sputtering method⁴² as blocking layer at FTO/TiO₂ interface with excellent results (improvement of V_{oc} and fill factor (FF) and conversion efficiency). And we find that sputtering method might be the best way to prepare blocking layer compared with spray pyrolysis method, for the latter method gives lower J_{sc} with the same improvement of V_{oc} and FF. Moreover, the former method has the merits of good reproducibility, of homogeneous coverage and suitability for the large scale production. The improvement should come from the Nb₂O₅ forming potential barrier between FTO and TiO₂, which can suppress back electron transfer from FTO to electrolytes without lowering conductivity between them as shown in Figure 1.

In this article, we report here on details of the characterizations of Nb₂O₅ blocking layer, the optimization methods and further discussion of the role of Nb₂O₅ blocking layer in the photoelectron conversion process.

2. Experimental Section

I₂ was purchased from Aldrich. LiI and other organic solvents were purchased from Wako Chemical Co. 1-Ethyl-3-methylimidazolium dicyanamide (EMIm-DCA) and 1-propyl-3-methylimidazolium iodide (PMImI) were purchased from Sanku Chemical Co. and Shikoku Chemical Co., respectively.

Nb₂O₅-modified FTO substrates were prepared by depositing Nb₂O₅ particles onto FTO (Nippon Sheet Glass, SnO₂: F, 10Ω/□) by using radio frequency magnetron sputtering equipment (SPW-025S, ULVAC, Japan). The sputtering target was Nb₂O₅ (99.99%, High Pure Chemicals, Japan) disk with the diameter of 100 mm. Different thicknesses of Nb₂O₅ were deposited onto FTO at direct current power of 150 W under a working pressure of 0.5 Pa of mixture of O₂ and Ar (volume ratio is 1 to 4). According to the relationship between the thickness of Nb₂O₅ blocking layer and sputtering time (~150 nm per hour), we estimate the thicknesses of Nb₂O₅ for different sputtering time. 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 I₂ in PMImI and EMIm-DCA ([PMImI]:[EMIm-DCA] = 2:1) are employed for ionic liquid DSCs.

Nanoporous TiO₂ electrodes were prepared on a transparent conductive substrate (Nippon Sheet Glass, SnO₂:F, 10Ω/□) or FTO/Nb₂O₅ blocking substrate from the colloidal Nanoxide-T paste (Solaronix) by doctor-blade techniques. The films were annealed at 450 °C for 30 min in air. The resulting TiO₂ films (thickness was around 5.5 μm, measured by a profiler, Sloan Technology, Dektak3) were cut into pieces and heated again at 110 °C for 15 min. Then the electrodes were immersed into 3.0 × 10⁻⁴ M *cis*-bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicar-

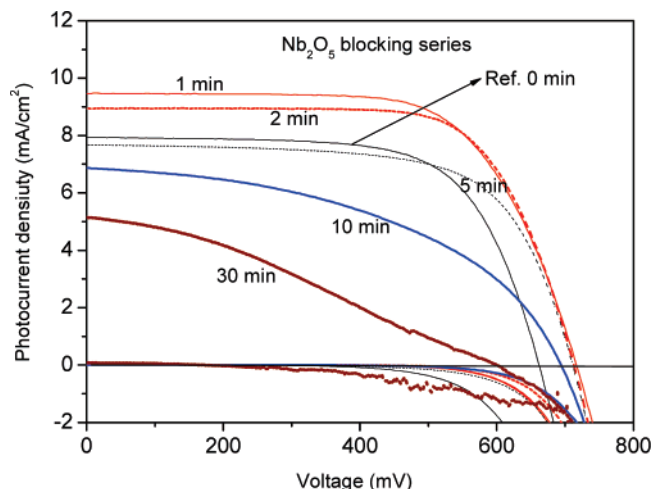


Figure 2. J – V curves of the cells employing Z-907 sensitized FTO/nanoTiO₂ and FTO/Nb₂O₅/nanoTiO₂ electrodes under AM 1.5 irradiation. (Electrolyte: PMImI:EMIm-DCA = 2:1, 0.2 M I₂, 0.5 M TBP, and 0.1 M LiI; 5.5 μm of nanoTiO₂ was employed).

boxylato)(2,2'-bipyridyl-4,4'-di-nonyl) ruthenium(II) (known as Z-907, Solaronix) in acetonitrile/*tert*-butyl alcohol (1:1) for 18 h. After being washed with acetonitrile, the sensitized electrode was covered with platinized conducting glass as a counterelectrode. Typical areas of the electrodes were around 0.2 cm². The photoelectrochemical properties of the DSCs were studied by recording the current–voltage (I – V) characteristics of the unsealed type cells under illumination of AM1.5 (1 Sun; 100 mW/cm²) using a solar simulator (Yamashita Denso, YSS-80). The morphologies of the electrodes were observed by scanning electron microscopy (SEM, S-4700, Hitachi). For the three-electrode measurements in 0.1 M LiClO₄ and 1 mM ferrocene in acetonitrile, a 1 cm² area of the bare FTO or Nb₂O₅ sputtered FTO glass served as working electrode, a platinum foil counter electrode and Ag/AgCl reference electrode (BAS 100B/W electrochemical system). The optical transmittance and absorption spectra measurements were performed with a JASCO (V-570) UV–vis–near-IR spectrophotometer at wavelength 300 from 1200 nm. V_{oc} dependence on log J_{sc} was measured by changing the irradiation intensity of 100 mW/cm² (AM 1.5) light source with ND filters. The X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Kratos AXIS 165 (Shimadzu) using a Mg Kα monochromatized X-ray source. Etching processes were carried out using a 4-keV Ar⁺ ion beam with an etching rate around 2 nm/min.

3. Results and Discussion

3.1. Comparison of J – V Curves with the Nb₂O₅ Blocking Layer. Figure 2 presents the J – V curves of the solar cells with and without Nb₂O₅-blocking layers with ~5.5 μm nanoTiO₂ layer at AM 1.5 irradiation of 100 mW/cm². All parameters are listed in Table 1. After introducing Nb₂O₅ layer at the interface of FTO and nanoTiO₂, most devices give higher V_{oc} values and better FF. Especially in the case of Nb₂O₅ 2 min (the number represents the sputtering time), this device gives a great improvement of V_{oc} about 50 mV with drastic increment of J_{sc} . Its photoelectron conversion efficiency is 4.5%, which is 20% higher than that of the reference electrode.

As suggested in our previous letter,⁴¹ our newly structured FTO/Nb₂O₅/nanoTiO₂ electrode that should form 100-mV⁴³ potential barriers can effectively prohibit the recombination of injected electron in FTO with the redox couple in electrolyte, which means it can enhance the efficiency of electron collection

TABLE 1: Comparison of J – V Characteristics of the Devices with and without a Nb_2O_5 -Blocking Layer

thickness of blocking layer	electrodes	V_{oc}/mV	$J_{sc}/\text{mA cm}^{-2}$	FF	η (%)
	bare FTO	663 ± 5	7.91 ± 0.2	0.66 ± 0.01	3.5 ± 0.1
2–3 nm	Nb_2O_5 1 min	711 ± 3	9.22 ± 0.3	0.68 ± 0.01	4.4 ± 0.1
5 nm	Nb_2O_5 2 min	710 ± 4	9.32 ± 0.4	0.68 ± 0.02	4.5 ± 0.1
13 nm	Nb_2O_5 5 min	710 ± 7	7.58 ± 0.3	0.66 ± 0	3.6 ± 0.1
26 nm	Nb_2O_5 10 min	694 ± 10	7.31 ± 0.4	0.47 ± 0.02	2.4 ± 0.1
80 nm	Nb_2O_5 30 min	589 ± 20	5.13 ± 0.3	0.32 ± 0.01	1.0 ± 0.1

at FTO, giving an improvement on shunt resistance and V_{oc} for the accumulation of injected electrons. On the other hand, the accumulated electrons lead to the increase of conduction band electrons, as reflected by the J_{sc} increment.

However, along with an increase in the thickness of Nb_2O_5 , the devices give poor J_{sc} , V_{oc} , and poorer FF values. Compared with the pyrolysis method as reported earlier,⁴¹ Nb_2O_5 deposited by sputtering method might be more homogeneous coverage rather than island shape on FTO surface. The poor performance based on thicker Nb_2O_5 indicates that excessively thick blocking layers beyond tunneling distance would play a negative role in the photoelectron conversion process. On the basis of these results, the cells' performance is so sensitive that we need to control appropriate thickness of the Nb_2O_5 blocking layer in DSCs. And more detailed electrochemical analysis is carried out to understand the properties of effective blocking layer in Nb_2O_5 system.

3.2. Surface Morphology of the FTO/ Nb_2O_5 Substrate.

Figure 3 shows the SEM surface morphology of a bare FTO glass and Nb_2O_5 blocking FTO. The bare FTO surface shows characteristic morphology of tin oxide crystals (Figure 3 a), which particles size is around 200–300 nm. For the first 2 or 5 min of sputtering (parts b and c of Figure 3), it is difficult to find other particles except SnO_2 on FTO. This might be due to the diffusion of Nb_2O_5 species to boundary of FTO. In the case of Nb_2O_5 1 h, there are some 10–15-nm-sized Nb_2O_5 particles homogeneously distributed on FTO surface, as shown in Figure 3 d.

3.3. Optical Properties of FTO/ Nb_2O_5 Substrate. Since the cells were illuminated from FTO substrate side when the cells are in working condition, we need to think about its optical properties when the blocking layer was introduced. As shown in Figure 4, the absorption and transmission spectra do not change almost when the sputtering time less than 10 min, i.e., the thickness of Nb_2O_5 layer is less than 25 nm. However, Nb_2O_5 5 min and Nb_2O_5 10 min systems (Table 1) give poor J_{sc} and V_{oc} , which means that the drastic drop of J_{sc} is not due to the loss of harvest of light. We attribute this to the thicker Nb_2O_5 beyond tunneling distance preventing unidirectional electron transport in the system. Therefore, appropriate thickness of Nb_2O_5 blocking layer can favor keeping high J_{sc} and V_{oc} followed by high conversion efficiency.

3.4. XPS Analysis of the FTO/ Nb_2O_5 Substrate. XPS measurements were employed to examine the valence of Nb species and its interaction with FTO. The best FTO/ Nb_2O_5 2 min substrate was examined in the experiments. Figure 5 presents the change of XPS spectrums of Nb 3d and Sn 3d of the Nb_2O_5 -modified FTO at different etching time. As shown in Figure 5a, compared with the spectra before etching (etching 0 min), after etching 3 min, the intensity of the peaks of Nb 3d is still quite strong except for a 0.4-eV shift of the peak to lower binding energy. However, along with etching 20 min, the signal of Nb species is too low to be observed because of the elimination of the Nb_2O_5 deposited on FTO. Interestingly, in the profile of Sn 3d, a new component at lower binding energy

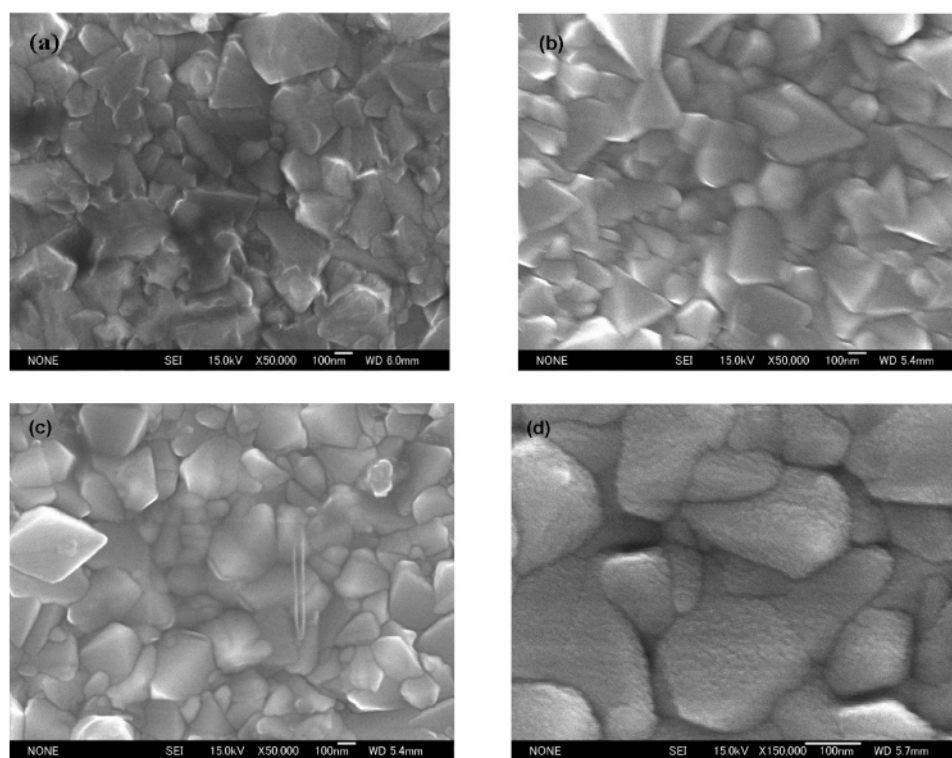


Figure 3. SEM micrographs of bare FTO and FTO/ Nb_2O_5 substrates (a) bare FTO substrate and (b–d) sputtering Nb_2O_5 for 2 min, 5 min, 1 h.

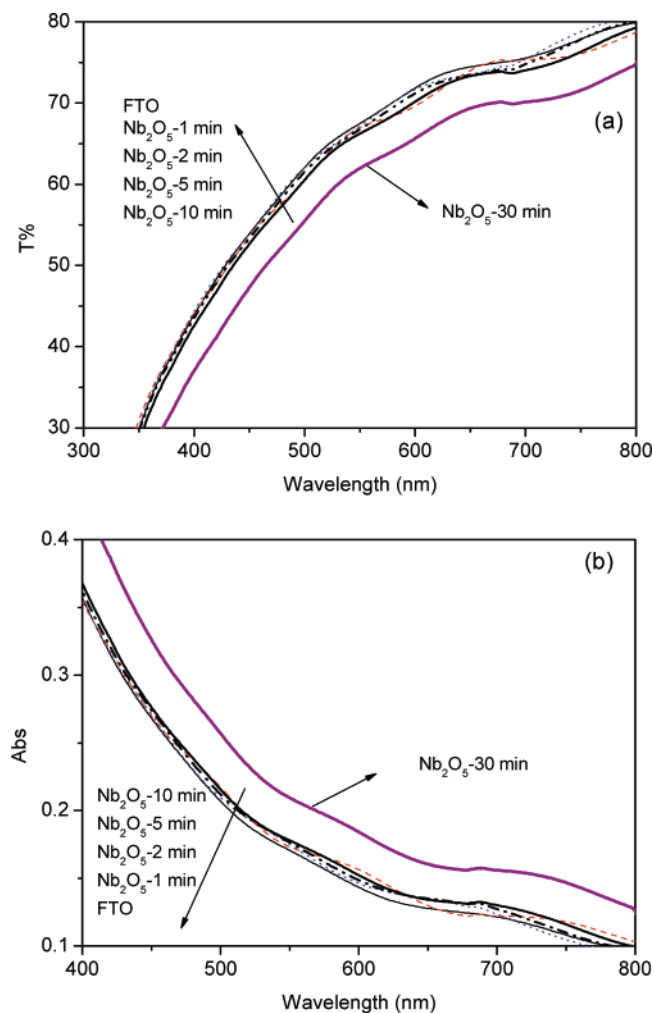


Figure 4. Optical properties of bare FTO and FTO/Nb₂O₅ substrates (a) transmittance spectra and (b) absorption spectra.

(484.7 eV) characteristic of Sn⁰ observed. However, this peak disappeared after etching 20 min for the detection into deep of FTO layer.

The resulting Nb 3d spectrums and fitted analysis before etching and after etching 3 min are shown in parts c and d of Figure 5. Before etching of the FTO/Nb₂O₅ substrate, there are two main peaks are observed, which are attributed to the 3d_{3/2} and 3d_{5/2} peaks of Nb⁵⁺ (207.7 and 210.5 eV). However, some small amount of Nb⁴⁺ exists. We also observe the surface of the Nb₂O₅ target changes from yellow to dark blue, indicating the Nb₂O₅ has been reduced⁴⁴ by electron beam.

Along with the etching time to 3 min, the signal of Nb⁴⁺ is still observable. The existence of lower valence of Sn⁰ and Nb⁴⁺ is attributed to the reductive high-speed electron beam during the sputtering process. Moreover, Nb⁴⁺ is detected with XPS spectrum after calcinations at 450 °C (data not shown here). In addition, this phenomenon is consist with our previous results that Nb⁵⁺ and Nb⁴⁺ exist in the preparation of Nb₂O₅ blocking layer by spray pyrolysis of Nb(OEt)₅. All these evidence indicate that at 400–500 °C, Nb⁴⁺ is present as a minority in Nb₂O₅ blocking layers.

3.5. Electrochemical Characterization. Figure 6a shows cyclic voltammetric curves of ferrocene (Fc)/(Fc⁺) redox reaction at various electrodes. The redox current of bare FTO is the highest with around 120 μA compared with those Nb₂O₅-modified FTO substrates. And along with sputtering time, the surface of FTO can be well covered with a few μA level of

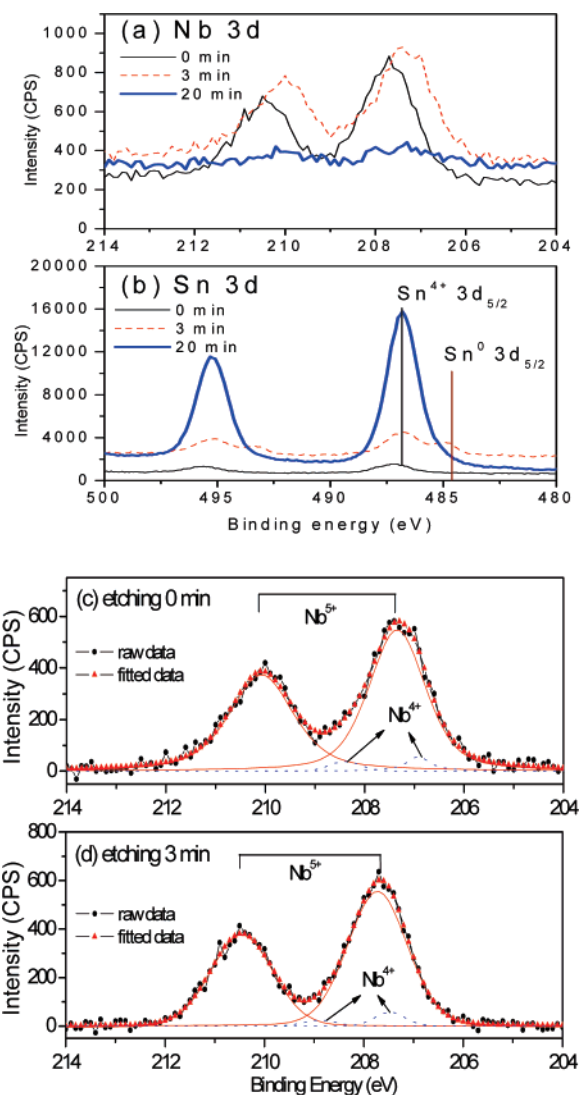


Figure 5. The XPS of Nb 3d and Sn 3d peaks of the FTO/Nb₂O₅ substrate after different etching times. The etching times are 0, 3, and 20 min for (a) Nb 3d, (b) Sn 3d and the spectra of Nb 3d peaks are fitted before etching (etching time 0 min) (c) and after etching for 3 min (d).

current, which is lower 1–2 order than that of the bare FTO. Interestingly, in the case of Nb₂O₅ 2 min substrate, it shows moderate reduction peaks with 70 μA of maximum current while there is almost no oxidation peak was detectable. And this phenomenon is well consistent with the TiO₂ blocking layer,³⁸ where the redox of I[−]/I₃[−] was used.

Combined with *J*–*V* performance fabricated with these electrodes, shown in Table 1 and Figure 2, it is clear that the more compact of Nb₂O₅/FTO, the poorer performance the cell shows. That is, the Nb₂O₅ 2 min gives the best conversion efficiency while it slightly suppresses electron transfer in the ferrocene redox system.

After annealing at 450 °C, the Nb₂O₅ 2 min shows the same level of reduction current compared with that of the bare FTO, and FTO/Nb₂O₅/nanoTiO₂ electrode shows similar phenomenon. Meanwhile, the oxidation currents of the heat-treated substrates increase to some extent compared with the non-heat-treated substrate. This is because some of Nb₂O₅ blocking layer may diffuse into FTO layer or nanoTiO₂ layers after calcination at 450 °C.

Taking into consideration that the TiO₂ blocking layer (also called compact TiO₂ layer by others) usually employed in solid

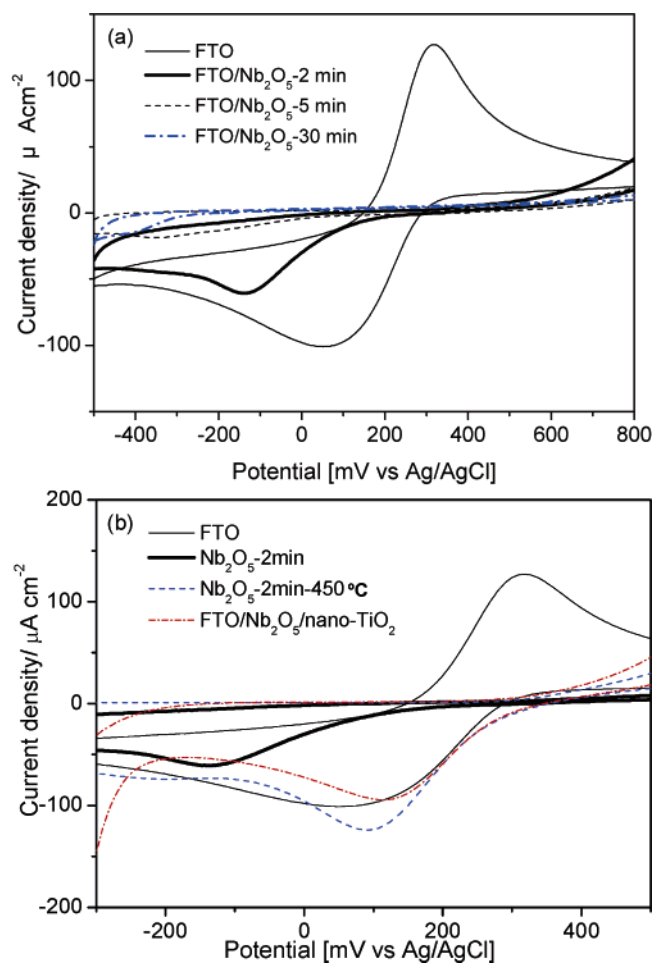


Figure 6. Cyclic voltammogram of bare FTO and FTO/Nb₂O₅ substrates (electrodes) at scan rate of 100 mV/s: (a) FTO and FTO/Nb₂O₅ substrates sputtering at 2, 5, and 10 min; (b) Nb₂O₅/FTO and with nanoTiO₂ layer after 450 °C annealing.

DSCs should be more compact to suppress the electron leakage from FTO. Nb₂O₅ blocking system demonstrates a different way to suppress electron leakage through so-called electronically suppress electron leakage because the conduction band potential of Nb₂O₅ is 100 mV more negative than that of TiO₂.⁴³

Earlier theoretical analysis predicts that the potential in the first layer of TiO₂ particles in contact with FTO substrate.^{45–47} In our system, trace amounts of Nb species should change the potential distribution in the FTO/Nb₂O₅/nanoTiO₂ interface for favorable electron transport direction. Other experiments and simulation analyses need to be done to investigate this system. At this moment, it is beyond the scope of this paper.

3.6. V_{oc} Dependence on Temperature and $\log J_{sc}$. Plots of V_{oc} vs T have been proposed to be useful measurements of activation barriers for carrier recombination at semiconductor/liquid interface.^{48–49} The V_{oc} dependences on the temperature of none-blocked electrode and Nb₂O₅-blocking electrodes are shown in Figure 7. In both two systems, V_{oc} shows a linear dependence on temperature. The same tendencies were observed in the literature.^{50–52} Extrapolation of V_{oc} to $T = 0$ K in Figure 7 implies the position of the conduct band (CB) of the semiconductor relative to the redox potential of the electrolyte.^{53–54}

As shown in Figure 7, the slopes of nonblocked reference electrode and Nb₂O₅ BL electrode are -1.76 and -2.04 mV/K, respectively. However, y intercepts of nonblocked reference electrode and Nb₂O₅-blocking electrode are 1.20 and 1.32 V,

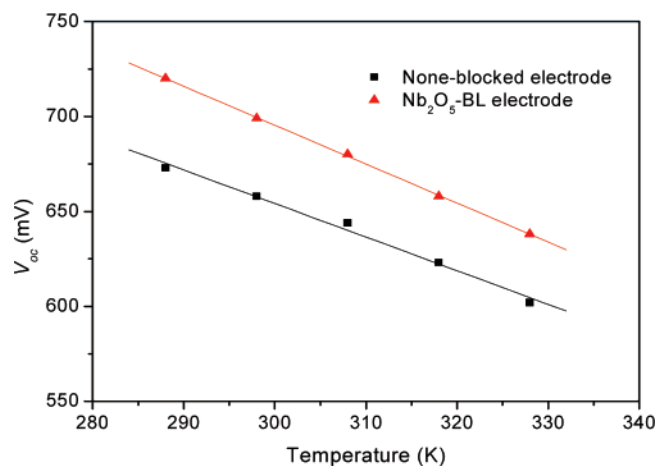


Figure 7. V_{oc} dependence of the DSCs fabricated from nonblocked electrode and Nb₂O₅-blocking electrode as a function of the temperature.

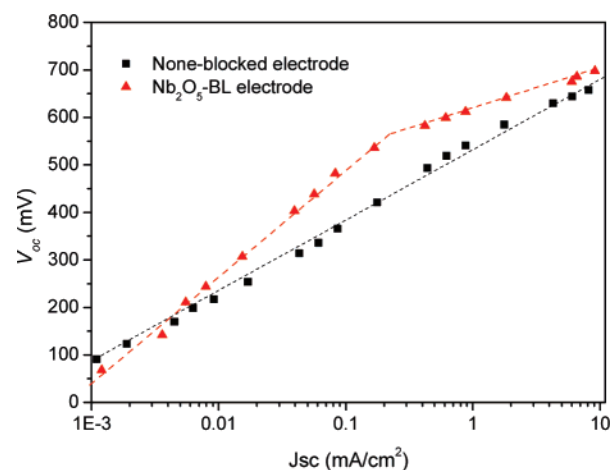


Figure 8. Relationships between V_{oc} and $\log J_{sc}$. The electrodes were nonblocked electrode and Nb₂O₅ blocking electrode. The thickness of the nanoTiO₂ films was 5.5 μ m.

respectively. Therefore, a trace amount of Nb₂O₅ can change the band potential of FTO/nanoTiO₂ to some extent. In addition, Kim et al.⁵⁵ found that the application of IZO (indium zinc oxide) substrates can change V_{fb} of TiO₂. Usually, the improvement of V_{oc} is related with the shift of TiO₂ conduction band and the decrease recombination of the back electron transfer. In our Nb₂O₅-blocking system, the latter mechanism might be more reasonable although a trace amount of diffused Nb₂O₅ can change TiO₂ band potential to some extent. Anyway, a very small amount of Nb⁵⁺ at the interface of FTO/nanoTiO₂ can improve electron injection efficiency, leading to unidirectional electron flow, which is a very important point when we design or fabricate DSC.

The V_{oc} dependence on $\log J_{sc}$ is shown in Figure 8. The slope of the V_{oc} dependence vs $\log J_{sc}$ shows 148 mV/decade for the nonblocked electrode. This value is higher than that obtained from organic liquid electrolyte³⁵ and even under the lower intensity it still shows the linearly tendency. However, in the case of the Nb₂O₅ BL electrode, the slope of the V_{oc} dependence vs $\log J_{sc}$ shows 83 mV/decade in the region of V_{oc} larger than 500 mV while gives 217 mV/decade in the region of $V_{oc} < 500$ mV. The different slopes in the whole range may suggest that there may exist different recombination mechanism,³⁶ which we attribute to the change of chemical capacitance⁵⁰ or shift of CB of TiO₂ of the Nb₂O₅ BL electrode compared with nonblocked electrode.

4. Conclusions

In summary, we have demonstrated that Nb₂O₅ can form an effective blocking layer at FTO/nanoTiO₂ interfaces and greatly improve the V_{oc} and FF, proving the importance of blocking layer at FTO and TiO₂ interfaces in ionic liquid DSCs. So far, compared with spray pyrolysis method, the sputtering method might be one of the best ways in preparation of Nb₂O₅ blocking layer on FTO. The cyclic voltammetric behaviors reveal that in the case of effective Nb₂O₅-blocking system, Nb₂O₅ species works as an electronic barrier blocking rather than morphological blocking, which means that the introduction of very small amount of Nb₂O₅ might change the dipolar phase between FTO and nanoTiO₂. In addition, this kind of structure is quite different from that of TiO₂ compact layer as blocking layer employed in DSCs.

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