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Post-modification using aluminum isopropoxide after dye-sensitization for improved performance and stability of quasi-solid-state solar cells

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Abstract

In this study, dye-sensitized TiO_2 electrodes were immersed into a solution of aluminum isopropoxide and after hydrolysis quasi-solid-state solar cells were fabricated. The interaction between the dye and the resulting Al_2O_3 overlayer was investigated by ultraviolet–visible (UV–vis) spectrum, Fourier transform infrared (FTIR) spectrum and X-ray photoelectron spectrum (XPS). The current density–voltage (I–V) characteristics showed that the overlayer increased the photovoltage and decreased the photocurrent under low intensity irradiation, and increased both the photovoltage and photocurrent under AM 1.5 irradiation. The Al_2O_3 overlayer at the dye/electrolyte interface resulted in a 28% improvement in overall photo-to-electrical conversion efficiency from 2.60 to 3.32%. Dark current measurements showed that Al_2O_3 acted as an insulator barrier to retard recombination between the TiO_2 and dye/quasi-solid-state electrolyte interface. Without encapsulation, dye-sensitized solar cells with Al_2O_3 coating after sensitization also exhibited improved stability compared to cells without coating.

Keywords: Dye-sensitized solar cell; Post-modification; Recombination; Stability

1. Introduction

As an alternative energy source to traditional silicon solar cells, dye-sensitized solar cells (DSSCs, Grätzel cells) have attracted much attention since 1991 because of their high efficiency, low cost, and potential flexibility [1]. A record conversion efficiency of 11% was achieved in cells using *cis*-$(SCN)_2$bis(2,2′-bipyridyl-4,4′-dicarboxylate) ruthenium (N3) dye with guanidinium thiocyanate added to the electrolyte [2]. Investigations have focused on both the efficiency [3,4] and stability [5,6] of the cells for their future practical service. In order to achieve high power efficiencies under solar irradiation, it is essential to retard the recombination [7], which consists of two interfacial recombination pathways: the injected electrons in the conduction band of TiO_2 may recombine either with the oxidized dye or with the oxidized redox couple in the electrolyte. The latter has been confirmed to be the dominant loss mechanism due to the fast regeneration of the oxidized dye for standard devices [8]. Methods for coating the electrodes with other metal oxides [9,10] or quantum dots [11] have been developed to minimize the recombination reactions by forming energy barriers, shifting the conduction-band potential, or decreasing surface traps. Semiconductors with higher band gaps such as Al_2O_3 [12,13], MgO [14], Nb_2O_5 [15], SiO_2 [10], ZnO [16] or ZrO_2 [17] have been used to form insulating barriers at the TiO_2/dye interface, increasing the physical separation of injected electrons from the oxidized dye/redox couple in the electrolyte.

Although much work has been done to research the TiO_2/dye interface, little attention has been paid to the dye/electrolyte or TiO_2/electrolyte interface. Previous studies have shown that dye coverage on the TiO_2 surface has not achieved a close-packed monolayer, even at saturation [18,19]. This results in a multiple TiO_2, dye/electrolyte interface where the electrolyte can either regenerate the oxidized dye or recombine with the injected electrons in the TiO_2. A better coverage of TiO_2 surfaces with dye molecules can retard electron transfers from the TiO_2 layers to iodine in electrolytes [20]. Increasing the coverage ratio of the TiO_2 surface to separate the electrolytes can be achieved by adsorbing more dye or applying coatings before or after dye-sensitization. However, thicker overlayers between the TiO_2 and dye will also result in retardation of the electron injec-

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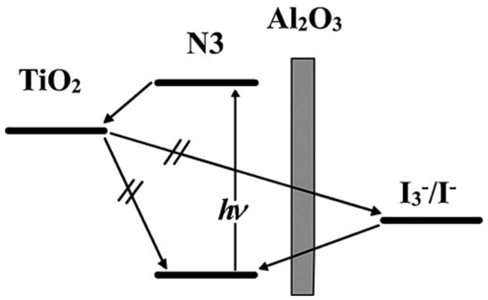
tion dynamics so they no longer compete successfully with dye excited-state decay [10]. Therefore, using barriers to modify the TiO_2, dye/electrolyte interface might be a good choice. Kroeze et al. [21] used a series of amphiphilic ruthenium dyes with varied hydrocarbon chain lengths acting as an insulating barrier for electron–hole recombination, and they found that increasing the dye alkyl chain length resulted in slower charge recombination. Nonetheless, it also reduced rates for both electron injection and dye regeneration. Clifford et al. [22] employed the deposition of a secondary Al_2O_3 layer to absorb a secondary dye for co-sensitization. Sugihara [23] exchanged protons in N3 molecules with alkali-metal cations in situ on N3-loaded TiO_2 film.

There has been much research carried out on the instability of DSSCs [24,25]. TiO_2 has a potential intrinsic problem due to its efficient photocatalyzation property. UV light can induce excitation of TiO_2, resulting in oxidation of the dye or the electrolyte. The solid-state cells showed fast degradation under full-spectrum sunlight illumination due to the fact that TiO_2 could oxidize the hole-transporting material CuI in the presence of UV light [26] and the decomposition of the electron transfer-bridge between the sensitizer and CuI [27]. Improved stability was achieved by controlling the pore filling of the porous dyed TiO_2 layer with molten salt-capped CuI crystals acting as a protective coating [28], or using a composite electrolyte containing nano-sized SiO_2 particles as an insulator layer [29]. In liquid or quasi-solid-state dye-sensitized solar cells, I_3^- might be oxidized by TiO_2 under UV irradiation.

We expected that Al_2O_3 coating in quasi-solid-state DSSCs could also improve the stability as the insulating layers did in solid-state DSSCs. If we can use thin semiconductor insulating barrier layers to modify the dye-sensitized films to space TiO_2 and the electrolyte, maybe we can retard the recombination, and also improve the stability of the dye and electrolyte.

In this study, we coated the dye-sensitized TiO_2 film with/without (blank sample) an Al_2O_3 overlayer (Scheme 1) and then fabricated quasi-solid-state dye-sensitized solar cells. The Al_2O_3-modified N3-sensitized TiO_2 films were characterized by ultraviolet–visible (UV–vis) spectroscopy, Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). The *I–V* characteristics showed improved open-circuit voltages (V_{OC}) and decreased short-circuit current densities (J_{SC}) under low light intensity illumination. Both V_{OC} and J_{SC} improved when the light intensity was increased, with a 28% improvement in photo-to-electron conversion efficiencies (η) compared to the blank cells under AM 1.5. Without encapsulation, the blank cell's performance declined quickly, while the cell with Al_2O_3 coating exhibited better stability.



Scheme 1. Illustration of the interfacial charge transfer processes occurring at the TiO_2/dye/electrolyte interface of a DSSC. Also shown is the Al_2O_3 overlayer as developed in this study.

2. Experimental

Aluminum triisopropoxide (99.99+%) and dihydrogen hexachloroplatinate(IV)hexahydrate (99.9%) were purchased from Alfa Aesar. The dye known as "N3" was purchased from STI under the name B4 dye. Lithium iodide (99%) was purchased from Acros. 4-*tert*-Butylpyridine was purchased from Fluka. TiO_2 particles were purchased from Degussa under the name P25, which is a mixture of ca. 25% rutile and 75% anatase, with a BET surface area of $50 \pm 10\,m^2/g$ and a mean particle size of 21 nm. The following chemicals were analytical reagent grade. Iodine, isopropanol, ethanol, petroleum ether, acetonitrile and Triton X-100 were purchased from Beijing Chemical Co. Polyethylene glycol (PEG, $M_w = 20{,}000$) and poly(ethylene oxide) (PEO, $M_w = 2{,}000{,}000$) were purchased from Tianjin Tiantai Chemical Reagents. Acetylacetone was purchased from Shanghai Chemical Reagent Co. Ltd.

TiO_2 emulsion was prepared by adding 17 ml deionized water to 3 g of P25 in a conical flask. 0.27 ml of acetylacetone was added to prevent reaggregation of the TiO_2 particles followed by a 15-min sonication. A surfactant (Triton X-100, 0.13 ml) was added to facilitate the spread of the colloid on the substrate. After that, 0.75 g of PEG and 0.15 g of PEO were added to increase the porosity of the film.

A thin compact TiO_2 layer was deposited onto the fluoride-doped tin oxide (FTO) conducting glass with the area of 2 cm × 2 cm. The layer was prepared by dip coating the glass into a petroleum ether solution of $Ti[OCH(CH_3)_3]$ followed by hydrolyzation in the air [30]. The compact layer functions in two ways: on one hand, it improves the ohmic contact and adhesion between the porous TiO_2 layer and the FTO substrate; on the other hand, it can avoid short circuit between the penetrating electrolyte and the FTO substrate. Then the substrate was covered with two parallel adhesive tapes 1 cm apart to control the thickness of the TiO_2 film. Porous TiO_2 film with an average area of 1.6 cm × 1.2 cm was obtained by spreading the semiconductor emulsion between the tapes over the substrate with a glass rod. After air drying, the film was sintered at 450 °C for 30 min. The average thickness of the film was 8 μm. The photoelectrodes were sensitized by dipping in 0.5 mM ethanol solution of N3 overnight.

A 15 mM isopropanol solution of $Al[OCH(CH_3)_2]_3$ was employed as precursor for dip coating to form an Al_2O_3 layer, following the method used for multilayer dye co-sensitization [22]. After sensitization, the electrodes were rinsed with ethanol, dried and immersed in a 15 mM aluminum isopropoxide solution in isopropanol at room temperature for various periods of time: 30 s, 2 min, 5 min or 15 min. All the films with different post-modification time were characterized using IR spectra, but only the *I–V* data of the sample of 30 s were given out because it exhibited the best results. The samples for UV–vis adsorption spectrum, dark current measurements, the photovoltage transient measurements and the stability test were fabricated with the immersion time 30 s. For XPS measurement, the sample was immersed for 5 min, considering the sensitivity of the method. To achieve the hydrolysis of the aluminum isopropoxide, the film was exposed to ambient air for 1 h. No dye desorption was observed during this treatment. A quasi-solid-state polymer electrolyte was added between the modified N3-TiO_2 films and the platinum counter electrodes, as reported before [16]. The quasi-solid-state polymer electrolyte containing 0.0383 g of P25 TiO_2 powder, 0.1 g of LiI, 0.019 g of I_2, 0.264 g of PEO and 44 μl of 4-*tert*-butylpyridine in 1:1 acetone–propylene carbonate was spread on the dye-sensitized TiO_2 films with and without post-modification by spin coating to form a hole-conducting layer; then, a platinum-coated conducting glass counter electrode was laminated. To prepare the platinum counter electrode, H_2PtCl_6 (7.5 mM) solution in 2-propanol was deposited onto the transparent conducting oxide glass and the electrode was then sintered at 380 °C for 15 min.

The UV–vis reflectance absorption spectra were measured with a Hitachi U-3010 spectroscope. The FTIR spectrum was measured with a PerkinElmer Spectrum GX FTIR spectrometer. A PHI-5300 ESCA X-Ray Photoelectron Spectrometer using

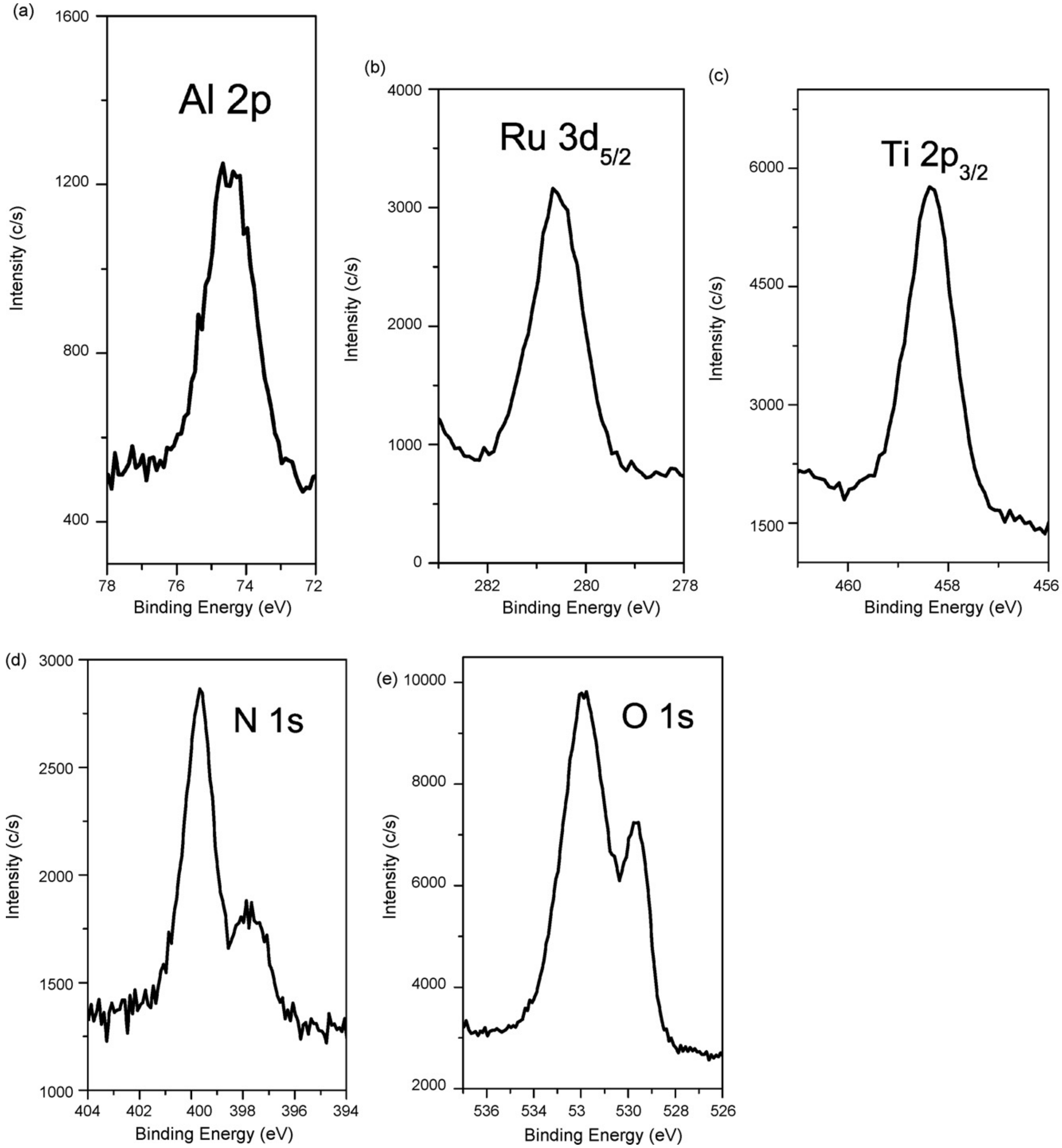


Fig. 1. XPS spectra of Al_2O_3 post-modified N3 dye-sensitized TiO_2 film. (a) Al 2p spectra, (b) Ru 3d spectra, (c) Ti 2p spectra, (d) N 1s spectra, and (e) O 1s spectra.

an Al Kα source was employed to analyze the composition and the electronic energy states of the post-modified N3-sensitized TiO_2 films. Photocurrent–voltage (*I*–*V*) and dark current measurements were performed using a Keithley Model 4200-SCS semiconductor characterization system with real-time plotting and analysis with an active area of 0.25 cm^2. The light intensities employed were 30 and 100 mW/cm^2, AM1.5. The transient photovoltages of DSSCs were studied by probing the cells with a weak laser pulse at 532 nm, which was generated by a frequency-doubled Nd:YAG laser (pulse duration of 15 ns). The transient photovoltage signal was tested under the open-circuit condition and recorded using a TDS220 oscilloscope (Tektronix).

3. Results and discussion

3.1. Characterization of the dye-sensitized films with post-modification

The formation of Al_2O_3 coating on the dye-sensitized TiO_2 film was verified by XPS measurement. Fig. 1 shows the XPS spectra for the post-modified N3-sensitized TiO_2 film. The peak detected at 74.4 eV in Fig. 1a agreed with the binding energy of Al 2p, indicating the existence of Al^{3+}. The Ti $2p_{3/2}$ peak was observed at 458.4 eV in Fig. 1c. Fig. 1b and d presented evidences of N3 dye with the peaks of Ru $3d_{5/2}$ and N 1s. The N 1s spectrum showed two peaks at 399.7 and 397.8 eV in Fig. 1d, respectively, which agreed with the nitrogen in bipyridyl and SCN groups in N3 dye, respectively [31]. The O 1s spectrum contained two contributions. The shoulder peak at 529.7 eV was attributed to characteristic oxygen in TiO_2, while the main peak at 531.9 eV was assigned to the oxygen in Al_2O_3 [32]. A relative increase in intensity of the higher binding energy peak compared to pre-modification [32] is consistent with Al_2O_3 post-modification.

The UV–vis adsorption spectrums of the dye-sensitized TiO_2 films with/without Al_2O_3 coating are shown in Fig. 2. The maximum absorbance did not change too much, which was consistent with the observation of no dye desorption. There was a blue shift of 10 nm of the maximum absorption peak from 542 to 532 nm after coating, implying that Al_2O_3 coating deprotonated N3 on the TiO_2 film [23]. With the point of zero charge (P_{ZC}) of 9.2, Al_2O_3 is more basic than TiO_2 ($P_{ZC} = 5.5$) and it can react with the carboxylic groups on N3, which are not bound to TiO_2.

The in situ deprotonation of N3 on the dye-sensitized TiO_2 film was also characterized by the FTIR measurement (Fig. 3). The 2114 cm^{-1} peak assigned to the –SCN group, was observed in all films without change since the dye was not detached from the TiO_2 film during the coating. Four peaks located at 1540, 1440, 1233 and 1022 cm^{-1}, attributed to the bipyridyl ring [23], appeared the same in all cases. The 1720 cm^{-1} peak was assigned to the –C=O group in COOH; it was strong for the N3-TiO_2 film without coating, and got weaker as the coating time was increased. The 1600 and 1380 cm^{-1} peaks were attributed to the asymmetric and symmetric stretching vibrations of –COO^- group [33], and their intensity increased with coating time. Both UV–vis and IR data support the finding that the carboxylic acid in N3-TiO_2 partly changed to a carboxylate in situ after Al_2O_3 coating. The presence of –COOH in N3 can induce aggregation of the dye molecules through hydrogen bonding and lead to recombination of the injected electrons. So after Al_2O_3 coating, the change from –COOH to –COO^- can be beneficial to reduce the charge recombination.

3.2. Performance and stability of quasi-solid-state solar cells

We compared the current–voltage characteristics of two cells with and without Al_2O_3 coating (30 s) under different intensities of simulated sunlight (Figs. 4 and 5).

An increase of 50 mV in the V_{OC} was clearly observed in the cell with coating compared to the conventional cell. Under 30 mW/cm^2 light irradiation, both cells showed a similar J_{SC}, while the cell with coating had a slightly reduced J_{SC}. The efficiency was 5.70% for the blank cell and 5.82% for the cell with coating. However, the cell with Al_2O_3 coating showed a 24%

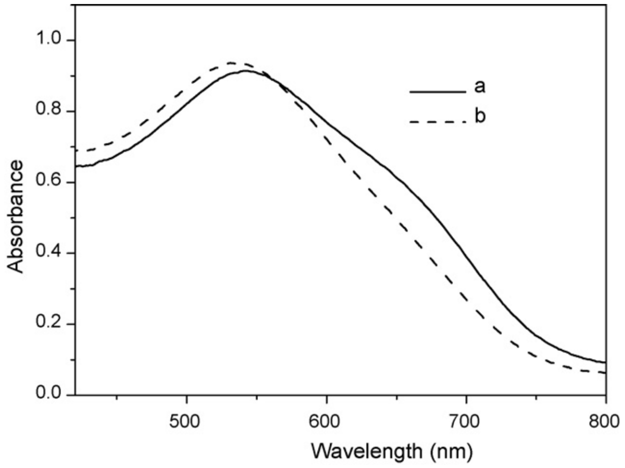


Fig. 2. UV–vis absorption spectra of N3-TiO_2 films (a) without and (b) with Al_2O_3 coating.

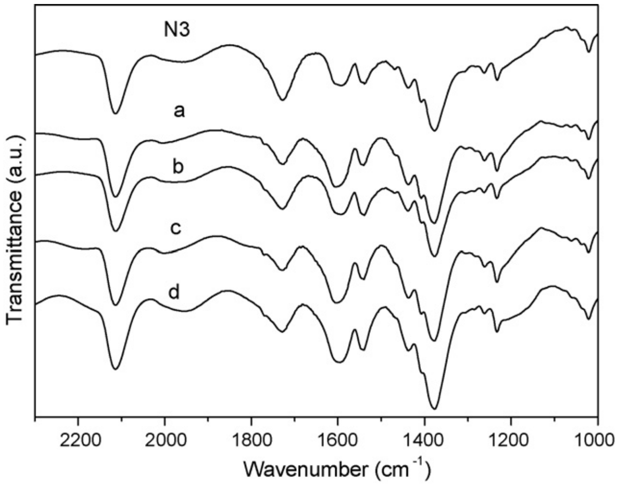


Fig. 3. IR spectra for N3-TiO_2 film (N3), N3-TiO_2 films with different immersion times in aluminum isopropoxide solution: (a) 30 s, (b) 2 min, (c) 5 min, and (d) 15 min.

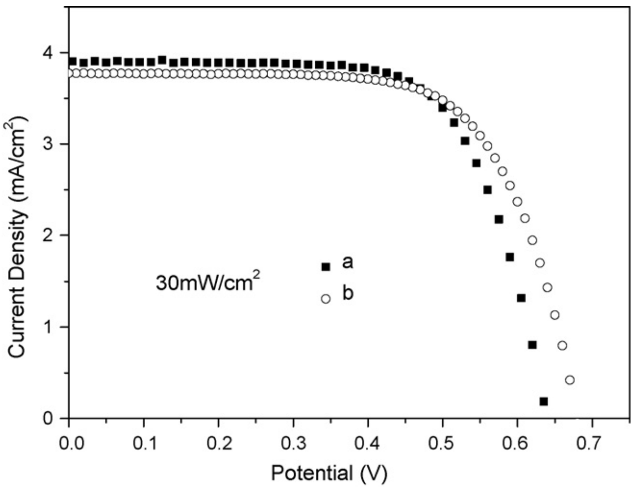


Fig. 4. *I–V* curves of the cells (a) without and (b) with Al_2O_3 coating under 30 mW/cm^2 light illumination.

higher J_{SC} than the cell without Al_2O_3 under 100 mW/cm^2 light irradiation, and the overall efficiency increased from 2.60 to 3.32%, which constituted a significant enhancement, by 28%. Similar phenomena have been reported before by Fujishima et al. [34] when they coated TiO_2 with Al_2O_3 in solid-state dye-sensitized solar cells. When the light intensity of the irradiation was raised, the probability of interfacial charge recombination increased. Under this condition Al_2O_3 coating could have played such an important role in retarding interfacial recombination that J_{SC} was increased too.

The dark current curves in Fig. 6 show that the dark current onset was shifted to a larger potential, and the dark current value at the same potential was decreased. This observation indicated that the Al_2O_3 coating at the TiO_2, dye/electrolyte interface retarded the charge recombination either by prohibiting N3 dye aggregation or by spacing TiO_2 and the electrolyte. Therefore, the photovoltage was enhanced and the dark current was reduced.

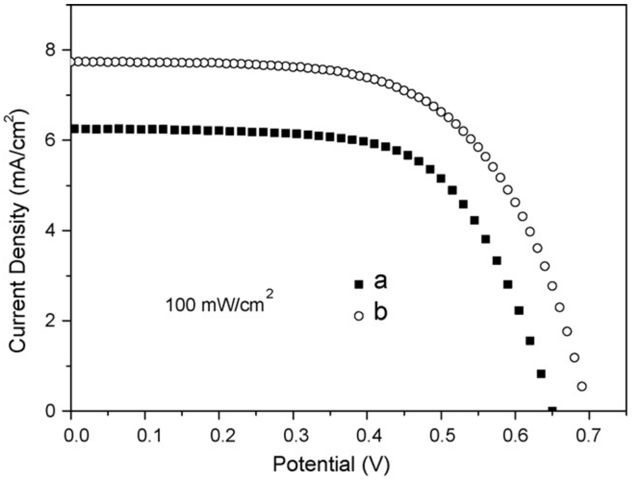


Fig. 5. *I–V* characteristics of the cells (a) without and (b) with Al_2O_3 coating under 100 mW/cm^2 light illumination.

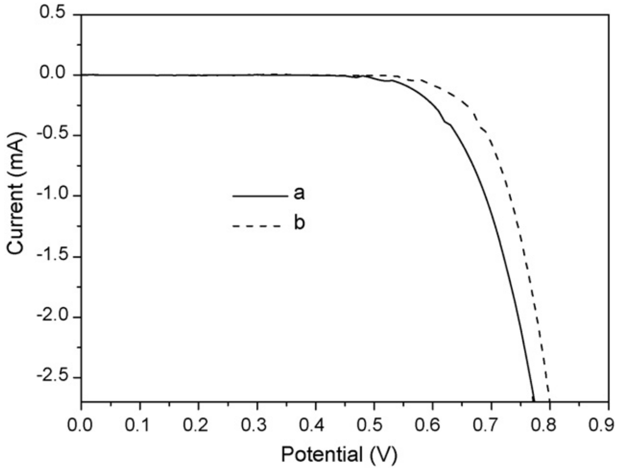


Fig. 6. Dark currents of cells (a) without and (b) with Al_2O_3 coating.

The photovoltage transient measurements carried out under the open-circuit condition denoted the recombination rate of the injected electrons and the electrolytes. Fig. 7 shows the normalized transient photovoltage curves of the dye-sensitized solar cells with and without Al_2O_3 coating under the open-circuit condition. As seen in the figure, the decay was slower in cells with Al_2O_3 coating, which is consistent with the dark current measurements and indicates that the Al_2O_3 coating depressed the recombination between the injected electrons and the electrolytes. The Al_2O_3 coating between the dye-sensitized TiO_2 film and the electrolyte served as an insulating barrier layer, as reported for the insertion of Al_2O_3 barrier layers between the TiO_2 film and a sensitizer dye.

We tested the cells over a 3-day period to check the stability without encapsulation under ambient conditions with a temperature of 20° and 38% humidity.

Table 1 gives the data of the photo-to-electric conversion efficiencies, short-circuit currents and open-circuit voltages of the cells. The cell with Al_2O_3 coating showed better stability under both low and high illumination; especially in the stability of its photovoltage. Considering that the photovoltage represents

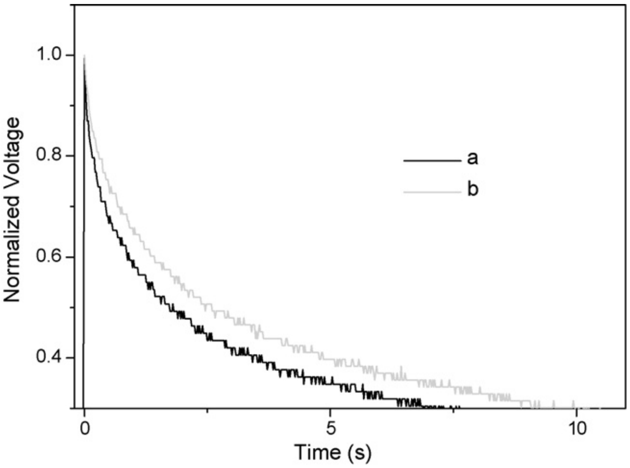


Fig. 7. Normalized transient photovoltage spectra for cells (a) without and (b) with Al_2O_3 coating.

Table 1
Performance of the sample cells (a) without and (b) with Al_2O_3 coating during 3 days testing

		Intensity of illumination			
		30 mW/cm^2		100 mW/cm^2	
		a	b	a	b
η (%)	0 h	5.70	5.82	2.60	3.32
	24 h	1.43	5.52	0.36	3.20
	48 h	0.37	4.46	0.18	1.98
J_{SC} (mA/cm^2)	0 h	3.92	3.76	6.24	7.72
	24 h	1.12	3.68	1	7.88
	48 h	0.33	2.88	0.52	4.28
V_{OC} (V)	0 h	0.64	0.68	0.65	0.70
	24 h	0.565	0.655	0.565	0.685
	48 h	0.54	0.66	0.56	0.69

the gap between the Fermi level of the TiO_2 semiconductor and the Nernst potential of the redox couple in the electrolyte, the stable photovoltage with Al_2O_3 coating implies good stability of the I_3^-/I^- redox couple in the quasi-solid-state electrolyte. The Al_2O_3 coating may reduce the risk to organic materials (electrolyte solvents, etc.) in the direct vicinity of the efficient photocatalyst TiO_2 under illumination (especially with UV light included) by separating TiO_2 away from the electrolyte solvent and I_3^-/I^- redox couple, thus preventing the degradation of the organic materials and enhancing the stability of the electrolyte. The coating may also depress desorption of the dye from the TiO_2 to the solvent of the electrolyte, which leads to maintenance of the photocurrent.

4. Conclusion

We coated a dye-sensitized TiO_2 film with an Al_2O_3 overlayer using a "wet-chemical" method and then fabricated quasi-solid-state dye-sensitized solar cells. The Al_2O_3 coating in situ deprotonated N3 on TiO_2 films, prohibited N3 dye aggregation, spaced TiO_2 and the electrolyte, and therefore retarded the charge recombination between the injected electrons and the electrolyte. To compare with the previously reported pre-modification, the post-modification shows similar improvement in photovoltaic performance of devices. However, it exhibits enhancement in device stability which was not shown in the early research. The cells with Al_2O_3 coating showed lower back current and better performance: under low light intensity illumination, the V_{OC} increased by ~50 mV, the J_{SC} decreased a little, and the overall efficiency was improved slightly; under 100 mW/cm^2 AM 1.5, both the V_{OC} and J_{SC} increased, resulting in a significant 28% improvement in overall efficiency. The Al_2O_3 coating also resulted in better stability of solar cells without encapsulation due to depression of the dye desorption and electrolyte degradation. Further attempts to achieve multiple dye co-sensitization are ongoing.

Acknowledgments

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