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Slow interfacial charge recombination in solid-state dye-sensitized solar cell using Al_2O_3-coated nanoporous TiO_2 films

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Abstract

Al_2O_3-coated TiO_2 porous films were used to fabricate solid-state dye-sensitized solar cells using CuI as hole conductor. Investigation with transient photovoltage measurements showed that the Al_2O_3 interlayer slowed down the interfacial recombination of electrons in TiO_2 with holes in CuI by forming a potential barrier at the TiO_2/CuI interface. As a consequence, the cell made from Al_2O_3-coated TiO_2 film showed superior cell performance than the cell made from TiO_2 film only, especially under relative high intensity of simulated sunlight.

Keywords: Solid-state dye-sensitized solar cell; Interfacial charge recombination; TiO_2; CuI; Al_2O_3

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1. Introduction

Solid-state dye-sensitized solar cells (DSSCs) are an offshoot technology of dye-sensitized liquid junction cells [1–14]. One of the popular configurations of solid state DSSCs is comprised of two interpenetrating networks of n-type TiO_2 and p-type CuI, with a monolayer of ruthenium bipyridyl dye molecules placed at the interface [5–7]. Ruthenium dye molecules anchor on the surface of TiO_2 porous film by the

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carboxlate groups on bipyridyl ligands with two thiocyanate groups pointing to CuI. Charge carriers are generated in an interfacial way in very high efficiency when the dye molecules are excited by light since the HOMO of the ruthenium dye molecule mainly consists of atomic orbitals of NCS group [15] that interact strongly with CuI; [5] while the LUMO is mainly comprised of the π^* orbitals of bipyridyl groups that overlap with the conduction bond of TiO_2 [15]. In the subsequent process of charge transportation, electrons flow to the conductive glass electrode through TiO_2 network, while holes flow to the counter-electrode such as gold through CuI network. The charge collection by these two electrodes should also have high efficiency since only majority carriers are involved in the transportation process. However, the reported values of solar energy conversion efficiency of solid-state DSSCs were below 4%, [6,7] which were much lower than the value of 10–11% of dye-sensitized liquid junction cells.

One of the possible reasons for the low conversion efficiency is the serious interfacial charge recombination in solid-state DSSCs, [5] which consists of either reduction of the oxidized dye by an electron from TiO_2 before hole injection into CuI regenerates the dye (process 3 in Fig. 1) or recombination of an electron from the TiO_2 with a hole in the CuI (process 5 in Fig. 1). Considering the fast regeneration of dye cations by CuI, process 5 should be the dominant recombination in a solid-state DSSC. Due to mesostructured nature of the two interpenetrating networks of TiO_2 and CuI, it is difficult to form substantial potential barrier at the TiO_2/CuI interface to suppress the interfacial recombination through process 5. Any direct contact of CuI with TiO_2 will act as recombination center [5].

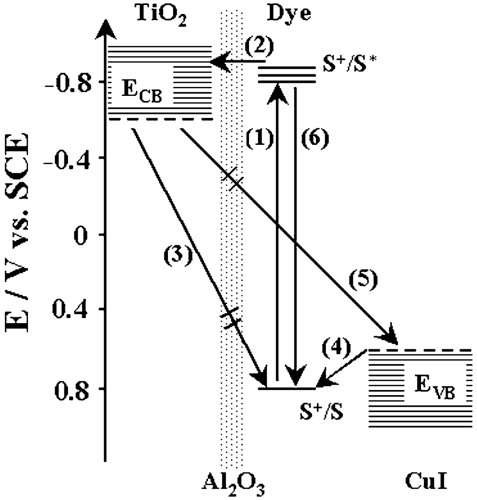

Fig. 1. Illustration of the interfacial charge-transfer processes occurring in the TiO_2/dye/CuI solid-state DSSC. Also shown is the blocking function of Al_2O_3 interlayer on interfacial recombination as described in this paper.

It was reported that interfacial charge recombination in dye-sensitized liquid junction cells could be suppressed by an insulator layer inserted between porous electrodes and dye monolayer [16–20]. While these reports dealt with liquid junction cell, it is interesting to check the influence of such insulating interfacial layer on the performance of solid-state DSSC since the insulator layer might act as a potential barrier at TiO_2/CuI interface (shown in Fig. 1). We reported in elsewhere that solid-state DSSC fabricated from Al_2O_3-coated TiO_2 electrodes performed better than that fabricated from TiO_2 electrode only [21]. In the present report, we compare the photovoltage transients of the cells with and without Al_2O_3 interlayer and find direct evidence that the Al_2O_3 layer improves the cell performance through slowing down the interfacial recombination.

2. Experimental

The working electrodes ($2 \times 2.5\,cm^2$) were comprised of conducting glasses (fluorine-doped SnO_2, Asahi, sheet resistance $\approx 10\,\Omega$/square) onto which a compact TiO_2 layer was deposited by spray pyrolysis [22]. This layer (about 50 nm in thickness) avoids direct contact between the p-CuI and the doped SnO_2 layer, which would short-circuit the cell. Porous TiO_2 film ($\sim 10\,\mu m$) was prepared onto this dense layer by the method reported in elsewhere, using a suspension of hydrolyzed titanium isopropoxide (Wako chemicals) mixed with Degussa P-25 (Nihon Nerisol) TiO_2 particles [21]. Al_2O_3 ultrathin layer was coated onto the TiO_2 porous film by the surface sol-gel method [21,23]. A 0.1 mol/l solution of aluminum tri-sec-buthoxide (Kanto Chemicals) in anhydrous isopropanol (Wako chemicals) was used as precursor for coating. After preheated at 110°C to remove the water condensed inside porous film, TiO_2 porous films were dipped into the coating solution at 60°C for 30 min. Then, the films were rinsed with anhydrous isopropanol and sintered at 450°C for another 20 min. Aluminum tributhoxide was chemisorbed uniformly onto the surface of TiO_2 film by reacting with the hydroxyl group and residual water in the dipping process, and converted into Al_2O_3 overlayer after sintering. XPS measurement (Perkin-Elmer 5600, Mg target) showed the existence of Al_2O_3 on TiO_2 porous film. And the average thickness of Al_2O_3 layer was calculated as 0.19 nm [21]. The Al_2O_3-coated TiO_2 film electrodes or TiO_2 reference electrodes were then immersed into ethanol containing 0.5 mM $RuL_2(SCN)_2$ (N535 dye, Solaronix) for 12 h at room temperature.

The coating of CuI onto dyed electrodes was performed in N_2 atmosphere inside a glove box. A solution of CuI (Wako chemicals) in anhydrous acetonitrile was used as the coating solution into which a small amount of 1-methyl-3-ethylimidazolium thiocyanate (IMSCN) was added by the molar ratio of 5% to CuI as a crystal growth inhibitor [6]. The dyed electrode was placed on a hotplate preheated to 115°C. CuI was deposited by drop coating to a constant thickness of 4 μm above the surface of TiO_2 film. After depositing, the film was heated for another 10 min to evaporate residual solvent inside film. Then, the electrode was covered with gold plate, sealed with epoxy resin.

Photocurrent-voltage characteristics of solar cells were measured by a Keithley model 2400 digital source meter using an Oriel solar simulator installed with AM 1.5 filters. A Nd:YAG pulse laser (Surelite OPO, 8 ns pulse width) was used for transient photovoltage measurements. The laser irradiated the cell from the side of TiO_2 porous film. Then photovoltage transients were recorded by connecting the cell directly to an oscilloscope (Tektronix, TDS5032).

3. Results and discussion

We investigated the effect of Al_2O_3 layer on the interfacial recombination by means of transient photovoltage measurement. Since all the charges generated in the cell by the laser pulse will recombine through the interface under open circuit conditions, this measurement provides a direct investigation on the effect of Al_2O_3 on interfacial recombination in solid-state DSSC. The wavelength of laser was selected as 532 nm because the dye molecules have maximum absorption around this wavelength. The average energy of each laser pulse was about 100 μJ with a standard deviation of 20 μJ. Fig. 2 compares the photovoltage transients of two cells fabricated from TiO_2 and Al_2O_3-coated TiO_2 porous film, respectively. Comparison on the absolute value of photovoltage in the transients of the two cells was not critical for the investigation on interfacial recombination. We thus normalized the two curves and only compared the uprising time and the decay lifetime of the photovoltage transients. As shown in Fig. 2, the photovoltage transients of both cells showed fast uprising and then decayed in a single exponential way. The uprising time was 0.15 ms for the cell made from TiO_2 film, while 0.34 ms for the cell made from

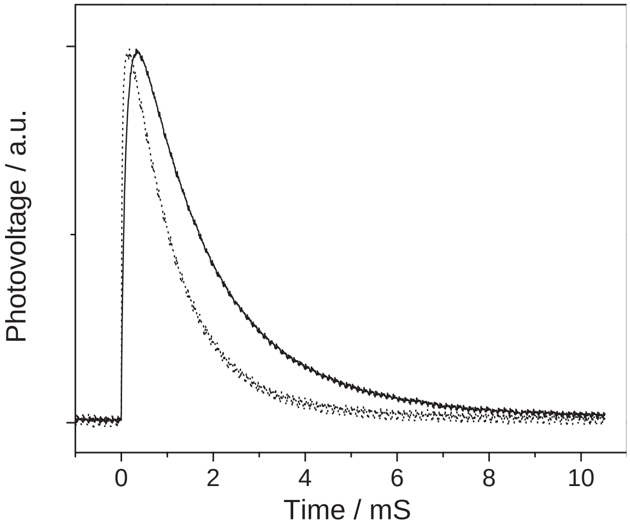

Fig. 2. Photovoltage transients of the solid-state DSSCs based on TiO_2 (dotted line) and Al_2O_3-coated TiO_2 (straight line) films.

Al_2O_3-coated film. An increase in excess of 100% in the uprising time indicates that the cell made from Al_2O_3-coated TiO_2 film has better charge collection efficiency, i.e. photo-injected electrons can move longer distance in a cell containing Al_2O_3 interlayer. It is reasonable considering the blocking function of this insulator interlayer on interfacial recombination. The subsequent decay of both photovoltage transients could be well fitted by single exponential functions. The lifetimes for the decay were calculated as 1.19 ms for the conventional cell, but 1.78 ms for the cell containing Al_2O_3 interlayer. The increase in excess of 50% in the lifetime shows another direct evidence that Al_2O_3 interlayer could slow down the interfacial recombination in a solid-state DSSC.

We compare the current–voltage characteristics of two cells with and without Al_2O_3 interlayer under different intensity of simulated sunlight (shown in Fig. 3). The cell parameters measured are list in Table 1. An ultrathin Al_2O_3 interlayer was found to improve the solar energy conversion efficiency of the solid-state DSSC. An increase in V_{oc} was clearly observed in the cell containing Al_2O_3 interlayer compared to the cell made from TiO_2 film only. Similar phenomena have been reported on liquid junction cell due to the slowing down of interfacial recombination by insulator layers [16–20]. In 5 mW/cm^2 illumination, both cells showed J_{scs} of 0.4 mA/cm^2. However, the cell containing Al_2O_3 layer showed larger J_{sc} than the cell without this layer as increasing the light intensity. In 89 mW/cm^2-simulated sunlight, J_{scs} as measured were 9.10 and 9.46 mA/cm^2, respectively. This phenomenon also indicates the charge collection of cell is improved by the blocking function of Al_2O_3 layer on interfacial recombination. Further investigation showed that the J_{scs} of both cells increased linearly to irradiation power in the range of 4.1–31.4 mW/cm^2, yet both

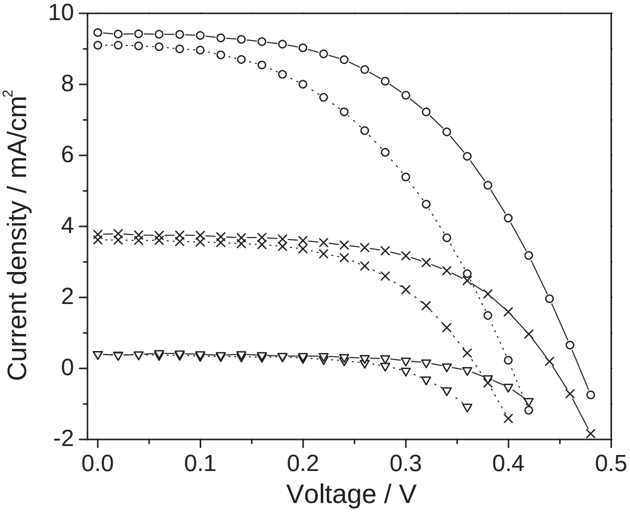

Fig. 3. Photocurrent-voltage curves of solid-state DSSCs with (straight line) and without (dotted line) the incorporation of Al_2O_3 interlayer under 4.1 mW/cm^2 (triangle), 31.4 mW/cm^2 (crosses), 89 mW/cm^2 (open circle) AM 1.5 simulated sunlight.

Table 1
Comparison of the performance parameters of the solid-state DSSCs based on TiO_2 and Al_2O_3-coated TiO_2 film under different intensity of simulated sunlight

	Light intensity $(mW/cm)^2$	V_{oc} (V)	J_{sc} $(mA/cm)^2$	FF	Efficiency (%)
TiO_2	4.10	0.29	0.40	0.51	1.45
	17.6	0.35	1.97	0.58	2.27
	31.4	0.37	3.62	0.56	2.38
	89.0	0.40	9.10	0.48	1.94
TiO_2-Al_2O_3	4.10	0.35	0.40	0.56	1.92
	17.6	0.42	2.08	0.57	2.86
	31.4	0.45	3.77	0.57	3.03
	89.0	0.47	9.46	0.52	2.59

deviated from the linear function under higher light intensity. It indicates that the interfacial recombination is a serious problem in solid-state DSSC even in the case that an insulator interlayer was inserted. Increasing irradiation power enhances the probability of interfacial charge recombination. The cell containing Al_2O_3 layer showed an increase of ~27% in conversion efficiency compared to the cell without this layer under 31 mW/cm^2 simulated sunlight, yet showed more increase (~34%) in conversion efficiency under 89 mW/cm^2 simulated sunlight due to the slowing effect of Al_2O_3 layer on interfacial recombination.

The solid-state DSSC works as a kind of dye-sensitized heterojunction consists of two interpenetrating network of n- and p-type semiconductors. This special structure lets it difficult to form substantial potential barrier at interface by itself. The wide band gap of Al_2O_3 ensures the formation of large enough potential barrier on the surface of TiO_2 [20]. Therefore, an ideal Al_2O_3 layer could passiviate the surface of TiO_2 and confine the movement of injected electrons in TiO_2 phase. A ca. 0.19 nm-thick Al_2O_3 layer slowed down the interfacial recombination as indicated by the transient photovoltage measurements. Slowing down interfacial recombination improves the charge collection efficiency. It also enlarges the difference of electron quasi-Fermi level (QFL) in TiO_2 and hole QFL in CuI under illumination. This is the reason that Al_2O_3 interlayer improved the V_{oc} of a solid-state solar cell.

4. Conclusion

In summary, a ca. 0.19 nm-thick Al_2O_3 layer was found to slow down the interfacial charge recombination in the solid-state DSSC by forming a potential barrier at the TiO_2/CuI interface. Photovoltage transient of the cell containing Al_2O_3 layer showed a doubled uprising time and 1.5 time decay lifetime compared to that of the cell without this layer. The Al_2O_3 layer improves the conversion efficiency in a factor of 1.27 under 31.4 mW/cm^2 simulated sunlight, while 1.34 under simulated sunlight of 89 mW/cm^2. We point out herein the importance of suppressing interfacial recombination for improving the conversion efficiency of solid-state

DSSC. Yet a ca. 0.19 nm thick Al_2O_3 layer was shown not good enough to block the interfacial recombination completely. However, thicker Al_2O_3 layer will reduce the efficiency of electron injection from dye monolayer to TiO_2 and as a consequence leads to lower cell efficiency [21]. In this viewpoint, modifying the TiO_2/CuI interface from the side of CuI might be a good choice.

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