**Alumina Coatings on Fluorine-Doped Tin Oxide@Titanium Dioxide as Photoanode for
Dye-Sensitized Solar Cells**

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Figures

Figure 1. X-ray diffraction patterns of the FTO nanoparticles, F-T and F-T-*x*A films.

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Figure 2. Typical TEM images of the synthesized FTO nanoparticles, F-T nanoparticles and F-T- x A nanoparticles gained from corresponding films. (a) FTO nanoparticle with a diameter of about 20 nm. (b) F-T nanoparticles. (c) F-T-A nanoparticles. (d) F-T-2A nanoparticles. (e) F-T-3A nanoparticles.

Figure 3. Typical J - V curves of DSCs based on FTO NPs, F-T films and F-T- x A films (a) under illumination of AM 1.5 G and (b) under dark, The area of all devices is 0.36 cm^2 .

Figure 4. Nyquist plots of representative EIS datas at 800 mV forward bias under illumination for F-T and F-T- x A based DSCs. Inset: equivalent circuit corresponding to different interface in dye sensitized solar cells.

Figure 5. IPCE for the DSCs based on F-T and F-T- x A.

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Tables

Table 1. Photovoltaic Parameters of DSCs for F-T and F-T-*x*A with same thickness.

Electrodes	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	η (%)	Absorbed dye ($\times 10^{-8}$ mol/cm ²)
F-T	14.61	0.613	52	4.66	9.93
F-T-A	16.47	0.629	49	5.11	8.33
F-T-2A	17.73	0.614	48	5.24	8.44
F-T-3A	15.20	0.586	48	4.27	9.47

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Abstract Titanium dioxide coated fluorine doped tin oxide film (F-T film) is synthesized and applied as photoanode in dye-sensitized solar cells (DSCs). Efforts to improve the photovoltaic performance are made by coating an Al₂O₃ barrier layer to serve as the charge recombination barrier. Due to the less electron recombination with oxidized dye or I₃⁻ after two times of Al₂O₃ coating combined with an efficient electron extraction of F-T film, F-T-2A DSCs exhibits a maximal efficiency of 5.24% improved by 12.4% for F-T DSCs without surface modification. However the cell performance fades due to decreased photoelectron injection from dye molecules into TiO₂ conduction band when the barrier became thicker. The thickness of Al₂O₃ by deposition cycle is well controlled and studied. Electrochemical impedance spectra are applied to disclose the low electron transfer resistance of F-T-2A DSCs for the better cell performance.

Keywords Fluorine doped tin oxide@titanium dioxide film; alumina barrier layer; dye-sensitized solar cell; electron recombination

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29 1 Introduction

30 Conventional dye-sensitized solar cells (DSCs) are typically fabricated with mesoporous
 31 nanocrystalline TiO_2 films as photoanodes. Improvements in the photovoltaic performance
 32 have been limited because of slow electron transport and charge recombination in TiO_2 films
 33 [1]. One way to solve this problem is to use TiO_2 coated FTO nanoparticle film (F-T film) as
 34 photoanode in DSCs [2,3]. We have recently demonstrated a higher efficiency compared to
 35 that received from mere P25 photoanode with one tenth dye loading using titanium coated
 36 FTO nanoparticles as photoanodes [4]. Unlike simply providing a direct electron transport
 37 channel using one-dimensional (1D) nanowires/nanotubes in DSCs which would dramatically
 38 decrease the dye absorption and then lead to an uncompetitive efficiency [5] or utilizing
 39 semiconductor with higher electron mobility like ZnO which is unstable in acid or SnO_2
 40 having weak bonding with dye molecules [6], F-T film can shrink the transport distance of
 41 electron via FTO's conductivity, maintain a relative high dye loading level by TiO_2 shell, and
 42 keep the stable nature of traditional photoanodes. It can also decouple the contradictory
 43 demand in bare TiO_2 film between fast charge transport which desires heavy doping and less
 44 electron recombination which desires light doping [2], because the light-injected electrons
 45 from the TiO_2 -dye interface in F-T DSCs only need to traverse a ultra thin layer of TiO_2 prior
 46 to being extracted by the highly conductive FTO core via a drift-assisted transport [7] instead
 47 of diffusive transport [8] in bare TiO_2 DSCs (a slow mechanism with electron escape times of
 48 1-10 ms for $\sim 10\text{-}\mu\text{m}$ -thick TiO_2 films) [9]. At the same time, due to the difference of Fermi
 49 levels between FTO (approximately -4.8 eV vs E_{vac}) and TiO_2 (approximately -4.4 eV vs E_{vac})
 50 [2,10], electrons flowing from TiO_2 to FTO layer in F-T photoanode results in band bending
 51 [11,12] of TiO_2 . Under illumination, the conduction band of TiO_2 inclines to FTO, and the
 52 electrons can favorably drift downhill from TiO_2 to FTO [13,14,15]. Thus enhanced electron
 53 extraction in F-T DSCs with no harm on dye absorption can be observed.

54 In DSCs made from F-T films, there exist several interfacial electron-transfer dynamics
 55 which are fundamental to the performance of the solar cells, especially the

TiO₂/dye/electrolyte interfaces where the adsorption of photosensitizer, and the injection, transport, and the recombination of photoelectrons occur [16]. Because of the configuration of dye molecules, there exist some vacancies without the absorption of dye molecules [17] on the surface of F-T film leading to the recombination of injected electrons with oxidized dye molecules or the electrolytic ions, and the limited efficiency for DSCs as a result. So modifying the TiO₂/dye/electrolyte interfaces to minimize the possible recombination pathways via various methods is a focused research topic to improve the photovoltaic performance and stability of the DSCs. One important approach is to coat the surface of F-T film with large band gap semiconductor thin layers at the aim of increasing the physical separation of injected electrons with the oxidized dyes or redox couples. Studies to date have demonstrated improvements in DSCs device performance for films fabricated from TiO₂ films coated with barrier layers like Nb₂O₅ [18], MgO [19,20], Al₂O₃ [21,22,23], ZrO₂ [24,25], SiO₂ [26]. Among them, Al₂O₃ has a matching band structure with the valence band situated well below the TiO₂ valence band, and the conduction band is several electron volts above (at more negative potential) both the TiO₂ conduction band edge and dye excited state oxidation potential indicating Al₂O₃ would function as physical barrier layers for both electron injection and charge recombination reactions [21]. Generally, a thicker Al₂O₃ barrier layer may result in a slower charge recombination rate but may reduce the forward charge injection at the same time. Therefore, an optimal thickness of the barrier layer should be pursued for harvesting the best performance of F-T solar cells.

In this work, F-T **film** was used instead of TiO₂ as the photoanode. Redox-inactive Al₂O₃ was examined as a blocking layer on F-T for elimination of electron shunting. Surface sol-gel process conducted under mild experimental conditions was further used to deposit a conformal ultrathin layer of Al₂O₃ on F-T photoanodes, with the aim to modulate interfacial electron transfer dynamics and thereby improve the performance of DSCs combined with enhanced electron extraction of F-T film. A power conversion efficiency of 5.24% is obtained, improving by 12.4% of the solar cell based on bare F-T electrodes. The demonstrated results indicate that the surface property of the electrode is crucial to solar cell performance and this

study on F-T DSCs offers a strategy toward optimizing the energy conversion efficiency of solar cells based on integrated effects of F-T film's enhanced electron extraction and Al_2O_3 film's suppression of electrons recombination.

2 Experimental

2.1 Fabrication of FTO nanoparticle film

All chemicals used in this paper were analytical grade without further purification. The synthesis of FTO was based on a modified method according to the previous report [27]. 4.513 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.3ml 40% HF were dissolved in 200 mL deionized water. A solution of 8 mL acetylacetone in 30 mL methanol was slowly added to the above mixed solution for 1 h with rapid stirring. 2 h later, aqueous ammonia solution was dropped into the mixed solutions until the PH reached 9.5 to get gel formation. The resulting gel product was filtered and washed several times with deionized water till removal of the entire Cl^- which could be checked by 0.1 M AgNO_3 solution before being transferred to the oven for further drying at 50 °C. Dried material was ground homogeneously with a given mass of PEG 10000 and deionized water at a ratio of m:m (PEG):m (H_2O) = 1:1:1 in a ball grinding mill for 7 h and nanopowder of FTO were obtained by calcinating in furnace for 2 h at 600 °C. After cooling down, a paste was achieved by grinding FTO nanopowder with PVDF and N-Methylpyrrolidinone at a mass ratio of m (FTO):m (PVDF):m (N-Methylpyrrolidinone) = 7:1:14. The FTO nanoparticulate film was prepared by doctor blading of a thin layer FTO nanoparticle paste on the FTO substrate and sintered at 450 °C for 30 minutes.

2.2 Surface modification

To coat a TiO_2 shell, the FTO nanoparticulate electrodes were processed with TiCl_4 treatment by immersing the FTO anodes in 45 mM TiCl_4 aqueous solution in a sealed watch glass and kept at 80 °C for 30 minutes, later rinsing with water and placing the electrodes in an oven at 50 °C until being completely dried. This process should be repeated twice according to our previous report [4]. To prepare co-surface treatment samples, after TiO_2 coating, the electrodes should be hydroxylated by dropping 10 μl deionized water until they

dried, then dipping the electrodes in a solution of suitable precursor as 0.05 M solution of aluminum isopropoxide in dry ethanol followed by rinsing with ethanol and sintering at 550 °C for 30 min, The thickness of the barrier layer was controlled precisely by the deposition cycle 1, 2 and 3 represented as F-T-xA ($x = 1, 2, 3$).

2.3 Solar cell fabrication

After surface treatment, the electrodes were sensitized overnight in 0.5 mM (Bu₄N)₂-[Ru(4,4-(COOH)-2,2'-bipyridine)₂(NCS)₂] (N719) in ethanol solution. A 50 μm hot melt sealing foil (Surlyn) was sandwiched between the electrode and a platinized FTO with two open pores. The electrolyte, consisting of 0.3 M DMPII, 0.5 M LiI, 0.05 M I₂, and 0.4 M 4-TBP in methoxypropionitrile, was injected from the side of the electrodes.

2.4 Materials characterization

X-ray diffraction (XRD) measurements were carried out using a D/Max-3c X-ray diffractometer with Cu Kα ($\lambda = 0.154$ nm), scanning from 5° to 80° and using an operation voltage and current of 40 kV and 30 mA, respectively. Scanning electron microscopy (SEM) images and EDS data were taken on a JEOL JSM-6700 FSEM. Transmission electron microscope (TEM) images were collected by using a JEM-2100 microscope. Specimens for TEM observation were prepared by dispersing the material powder into alcohol by an ultrasonic treatment.

2.5 Electrochemical measurements

A 350 W xenon light source (ShangHai) was used to provide the *J-V* curves under an incident irradiance of AM 1.5G (100 mW/cm²) for solar cells. EIS analyses were conducted with the bias voltage set at an applied voltage of 0.8 V and the frequency set from 0.1 Hz to 100 kHz with oscillation amplitude of 5 mV at AM 1.5G (100 mW/cm²). The IPCE was measured as a function of wavelength from 300 to 800 nm by using CROWNTECH Q-test station 500TI. The N719 dye absorbed on the TiO₂ films was obtained by using the UV-VIS-NIR spectrophotometer (TU-1901, Beijing). The specific operation is: the dye was desorbed from photoanodes in 0.1 M NaOH solution which is 25 ml water/ethanol (V/V = 1:1), then

the UV-vis spectrophotometer was employed to measure the absorbance of the desorbed-dye solution at 500 nm. According to the Lambert-Beer's law, the concentration of desorbed-dye solution was achieved by measuring the absorbance of a dye solution at known concentration.

3 Results and discussion

The XRD patterns of FTO, F-T and F-T-xA are shown in Fig. 1. The diffraction patterns of FTO, F-T and F-T-xA are well matched with cassiterite SnO_2 . The major peaks centered at 2θ of 26.6° , 33.8° , 37.9° , 51.8° and 65.9° can be indexed to the (110), (101), (200), (211), and (301) facets of tetragonal cassiterite (JCPDS 41-1445). However the peaks associated with dopant F, TiO_2 and Al_2O_3 can't be directly identified by XRD.

The presence of F doping, TiO_2 and Al_2O_3 was instead verified by EDS (Fig. S1). The atomic ratio of F/Sn is calculated to be about 1:7. After TiCl_4 treatment, the amount of Ti atoms account for 12.02%. For one, two and three cycles of Al_2O_3 coating, the ratio of Al atoms increases from 1.41% to 5.40% immediately, suggesting a growing thickness of the Al_2O_3 layer along with the Al_2O_3 coating cycles.

(Fig. 1)

The morphologies, particle sizes and structures of FTO, F-T and F-T-xA are characterized by the TEM. Fig. 2a is the image of the portion of the connected FTO nanoparticles. The average diameter of the FTO nanocrystalline is about 20 nm with irregular morphologies. Fig. 2b, c, d and e show the results from TEM investigation of the F-T, F-T-A, F-T-2A and F-T-3A. The core-shell structure can be clearly observed in TEM images. After TiCl_4 treatment, a shell of TiO_2 composed of nano-sized particles covers on the surface of FTO core particles which increases the active layer and leads to enhanced dye loading and light absorption [28]. Meanwhile a drift-assisted transport of photoinduced electrons formed at the FTO/ TiO_2 interface to get an enhanced electron extraction [7]. To retard electron shunting, Al_2O_3 is deposited conformally on the surface of F-T film with thickness of about 1.5 nm after one time of sol-gel treatment, 2 nm for two times and 2.5 nm for three times.

(Fig. 2)

The photovoltaic performance of DSCs based on F-T and F-T-*x*A with a film thickness of 8 μm (Fig. S2) were characterized under the simulated AM 1.5G illumination (100 mW/cm^2). Typical *J-V* curves of these DSCs are shown in Fig. 3a. The photovoltaic parameters from the *J-V* measurements are summarized in Tab. 1, including open circuit voltage (V_{oc}), short-circuit current (J_{sc}), energy conversion coefficient (η), fill factor (*FF*) and the amount of absorbed dye. With similar amount of absorbed dye for different photoanodes (Fig. S3), the measured photocurrent of F-T DSCs is 14.61 mA/cm^2 and a conversion efficiency of 4.66% is obtained. One time of Al_2O_3 coating causes the photocurrent and conversion efficiency to be improved to 16.47 mA/cm^2 and 5.11%, because of the less recombination and small influence of the electron injection. After two times of Al_2O_3 coating, the conversion efficiency reaches 5.24 % which is improved by 12.4% compared to F-T DSCs with a much higher photocurrent 17.73 mA/cm^2 . In above two situations, “kinetic redundancy” occurs in which the desirable charge-transfer step is much faster than the competing undesirable step, such as in the case of electron injection into TiO_2 conduction band, which occurs at a much faster rate than the competing undesirable decay of the excited electron recombination [29]. While three times later, both values decrease due to the stronger interference with electron injection than with electron recombination caused by the thick Al_2O_3 layer. The lower *FF* found in our F-T-*x*A DSCs than F-T DSCs corresponds to the uneven thickness of Al_2O_3 layer. The result has shown that two times of Al_2O_3 coating on F-T film makes the electron recombination and injection reach a perfect balance which leads to the highest conversion efficiency 5.24%.

Previous investigations on the Al_2O_3 barrier layer were only on TiO_2 nanocrystalline electrodes or FTO electrodes. For instance, Palomares et al. showed a 2-2.5 nm Al_2O_3 barrier layer coated on TiO_2 film resulted in a ~ 4 fold retardation of the electron recombination with dye cations, and an efficiency of 5% was reached [30]. Another study by Liu *et al.* prepared a thin Al_2O_3 -sheathed 3-dimensional (3-D) fluorinated tin oxide (FTO) as photoanodes of DSCs, at the aid of drift transport at the FTO/ Al_2O_3 interfaces, an efficiency of 1.536% was obtained [7]. In addition, Gao *et al.* received improved photovoltaic performance made by using Al_2O_3

193 barrier layer coating on TiO₂ nanotubes in conjunction with TiCl₄ surface modification [31].

194 We have demonstrated FTO@TiO₂ anode for DSCs with high efficiency at low dye loading
195 levels [4]. Coating of Al₂O₃ barrier layer on F-T films is conducted to further increase the
196 PCE by retarding the recombination processes. An efficiency of 5.24% is obtained.

(Fig. 3)

198 The retardation of the electron recombination is reflected in the dark current
199 characterizations. *J-V* curves of F-T to F-T-*x*A DSCs were traced in the dark (Fig. 3b). The
200 thicker Al₂O₃ layer leads to a more efficient barrier layer for recombination and a higher
201 recombination resistance [32]. So an enhanced suppression of the dark current with increasing
202 barrier thickness of Al₂O₃ layer is received. In the figure, we can clearly indicate that cells
203 with F-T-3A show the lowest dark current. The dark current increases from F-T-2A to F-T-A,
204 then to uncoated F-T cells. The consequence of dark current density can well explain *J_{sc}* under
205 AM 1.5G illumination for cells with F-T, F-T-A, and F-T-2A due to the retardation of electron
206 recombination. However, *J_{sc}* of F-T-3A is the lowest among the samples except for its lowest
207 dark current density. The situation may be ascribed to the coating Al₂O₃ film above the
208 optimal thickness, which hampers electron injection although it also retards electron
209 recombination [21].

(Tab. 1)

(Fig. 4)

213 To uncover the competition between electron recombination and injection at the
214 interfaces of different photoanodes, the EIS of F-T and F-T-*x*A under illumination are shown
215 in Fig. 4 at an applied bias of 0.8 V and a frequency range from 0.1 Hz to 1 MHz, with AC
216 amplitude of 5 mV. Since DSCs can be viewed as an equivalent circuit combining a series
217 resistor with some parallel connected resistor and capacitor [33] as illustrated in the inset of
218 Fig. 4. The equivalent circuit can be simplified to a connection of a shunt resistor *R_s*, to two

sets of parallel connected resistors and capacitors, which is denoted as R_1 , CPE_1 and R_2 , CPE_2 , respectively [34]. R_s represents the series resistance reflecting the resistance of FTO substrate, while R_1 and R_2 represent charge transport resistance at the counter electrode (first semicircle in Nyquist plot) and charge transfer resistance at the photo working electrode/electrolyte (second semicircle in Nyquist plot), respectively. Due to the lagging of current versus alternating voltage when it is applied on a capacitor, two semicircles can be well seen in a typical Nyquist diagram (Fig. 4). The charge transfer resistance R_2 of F-T, F-T-A, F-T-2A and F-T-3A is 23.05 Ω , 18.86 Ω , 17.88 Ω and 20.66 Ω respectively, as extracted from the Nyquist plots. The resistance R_2 of F-T- x A is small compared with 22.3 Ω for a similar photoanode structure constructed by TiO_2 nanotubes modified with $TiCl_4$ treatment in conjunction with an Al_2O_3 barrier layer [31]. It illustrates that a more efficient transport is achieved in F-T than in TiO_2 nanotube film, namely a drift transport. Two times of Al_2O_3 coatings result in minimum resistance that explains the maximal J_{sc} and thus the improved performance. This is a result of acquiring a perfect balance between electron recombination and injection. Furthermore, the resistance of F-T and F-T- x A achieve a little value which indirectly proves the enhanced electrons extraction of the F-T structure.

(Fig. 5)

Fig. 5 shows the incident photo-to-current conversion efficiency (IPCE) of the solar cells based on F-T and F-T- x A. The IPCE reached the maximum values at 522 nm which is the absorption peak of the N719 in visible region. As can be seen, the IPCE peak value increases significantly from 52.5% to 79.6% after one time of Al_2O_3 coating. The sequence of integral area is in good agreement with J_{sc} received from J - V characterizations. Two times of Al_2O_3 coating make the IPCE value reaches the maximal value of 80.4%. This can be ascribed to two times of Al_2O_3 coating causing less photoinduced electrons recombination with excited dye and I_3^- in the electrolyte combined with a fast electron extraction of F-T structure. The slightly higher IPCE at low wavelength results in a higher J_{sc} , which is in good agreement with that received from J - V characterizations.

4. Conclusion F-T based electrodes were modified with an Al₂O₃ barrier layer for enhanced photovoltaic performance. The Al₂O₃ barrier layer suppresses the recombination between the injected electron and electrolyte or dye cations, but it suffers from the drawback of inhibiting photoelectron injections from the dye molecules to the F-T electrodes. This problem can be controlled by adjusting the thickness of Al₂O₃ barrier layer. In our experiments, F-T-2A presents superior properties with an accumulated recombination suppression effect and enhanced electron extraction deduced from EIS. The performance of the solar cells was improved significantly when compared with F-T DSCs. A high power conversion efficiency of 5.24% is finally obtained. This work identified that surface treatment is extremely important to optimize the DSC efficiency.

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