An efficient and low-cost TiO₂ compact layer for performance improvement of dye-sensitized solar cells

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Abstract

A TiO₂ organic sol was synthesised for the preparation of a compact TiO₂ layer on fluorine-doped tin oxide (FTO) glass by a dip-coating technique. The resultant thin film was used for the fabrication of dye-sensitized solar cells (DSSCs). The compact layer typically has a thickness of ca. 110nm as indicated by its SEM, and consists of anatase as confirmed by the XRD pattern. Compared with the traditional DSSCs without this compact layer, the solar energy-to-electricity conversion efficiency, short circuit current and open circuit potential of the DSSCs with the compact layer were improved by 33.3%, 20.3%, and 10.2%, respectively. This can be attributed to the merits brought by the compact layer. It can effectively improve adherence of TiO₂ to FTO surface, provide a larger TiO₂/FTO contact area, and reduce the electron recombination by blocking the direct contact between the redox electrolyte and the conductive FTO surface.

Key words: TiO₂ organic sol, compact film, blocking layer, DSSCs

1 Introduction

Dye-sensitized solar cell (DSSC) consists of a dye-adsorbed porous TiO₂ layer on fluorine-doped tin oxide (FTO) glass as a working electrode, a Pt thin film counter electrode and an electrolyte normally containing I⁻/I₃⁻ redox couple [1-4]. Under the illumination of solar light, dye molecules are excited and electrons are produced. To generate meaningful electrical power from DSSC, the electrons need to pass 4 important interfaces of DSSC: dye/TiO₂, TiO₂/FTO, electrolyte/counter electrode, and dye/electrolyte. The nanoporous nature of the TiO₂ layer provides high surface area that is of great importance to the efficient photon-to-electricity conversion because it enhances dye loading and solar light absorption [5]. However, it also provides abundant TiO₂ surface sites (direct route) and bare FTO conducting sites (indirect route), where the photo-injected electrons may recombine with I₃⁻ species in the redox electrolyte ($2e^- + I_3^- \rightarrow 3I^-$) [6-8]. The recombination will cause the loss of the photocurrent. So the photovoltaic performance of DSSC is seriously decreased [9].

The introduction of a compact layer between the interface of the FTO/porous TiO₂ (see Figure 1) has been proven theoretically and practically effective to block the electron recombination via the indirect route [10-14]. This compact layer is much denser than the TiO₂ layer; therefore, it can reduce the contact surface area for bare FTO sites and the redox electrolyte (so called blocking effect). Semiconductors, such as TiO₂ [15-17], Nb₂O₅ [18], ZnO [19] and some insulating materials, such as CaCO₃ [20] and BaCO₃ [21], have been used as a blocking layer for the fabrication of DSSCs. Among them, the compact TiO₂ layer is the most suitable candidate as the blocking layer and has been investigated most frequently. Besides the blocking effect, higher density of the compact layer, together with larger contact area and improved adherence between the TiO₂ layer and FTO surface provides more electron pathways

from TiO_2 to FTO for photo-generated electrons, which facilitates electron transfer and subsequently improves the electron transfer efficiency.

The modification layer can be coated directly on the conductive substrate by dip-coating [22], spray pyrolysis method [23], chemical vapour deposition [24] and sputtering methods [9, 25]. However, the overall cost for the resulting DSSCs can be dramatically augmented if the coating process involves complicated fabrication procedures or equipment.

In this work, a TiO_2 organic sol is synthesized under very mild reaction conditions. TiO_2 compact layer was introduced from the TiO_2 organic sol with a dip-coating method, which is simple and low cost. Compared with the porous structure derived from a commercially available TiO_2 paste, the resulting TiO_2 compact layer possesses a dense structure that was found to be beneficial to the performance improvement of the DSSCs. It is to note that, to our knowledge, this is the first time for such a TiO_2 organic sol to be used for the modification of the DSSC photoanode. The organic sol synthesis and coating processes do not require high temperature and high pressure reaction environment (i.e., hydrothermal reaction [26]), or sophisticated and costly equipment (such as spray pyrolysis method [23], chemical vapour deposition [24] and sputtering methods [9, 25]); therefore, this preparation method for the compact TiO_2 film is a low cost process.

The improvement of the DSSC performance, in terms of open circuit voltage (V_{oc}), short-circuit current density (J_{sc}) and solar energy-to-electricity conversion efficiency (η), was observed. The mechanism for the increased efficiency of the DSSCs is proposed based on the physiochemical characteristics of the compact films. The photovoltaic investigations of the DSSCs also include dark-current measurement,

IPCE, open-circuit voltage decay (OCVD) and the dependence of J_{sc} on incident irradiation power (P_{in}).

2 Experimental

2.1 Materials

Titanium butoxide (97%), diethanolamine (99%), anhydrous acetonitrile (99.8%), 1-butanol (99.9%) and chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, $\geq 37.5\%$ as Pt) were purchased from Sigma-Aldrich. Ethanol (99.5%) and isopropanol (99.7%) were supplied by Ajax Finechem and Merck respectively. Milli-Q water was used for the sol preparation. TiO_2 paste (DSL 18NR-T), dye (B2) and liquid electrolyte (EL141) containing Li/LiI redox couple were from Dyesol Co. The dye was N-179 dye ($(RuL_2(NCS)_2(TBA)_2 \cdot (H_2O)_4)$, L=2,2'-bipyridyl-4,4'-dicarboxylic acid, TBA = tetrabutylammonium). Fluorine-doped tin oxide (FTO) glass ($\leq 14 \Omega/square$) was from Pilkington.

2.2 TiO_2 organic sol preparation and compact TiO_2 film formation

A TiO_2 organic sol for TiO_2 compact layer was prepared at room temperature by a method illustrated in our previous work [27]. Briefly, 68 mL of Tetrabutyl titanate and 16.5 mL of diethanolamine were dissolved in 210 mL absolute ethanol, and then the mixture was stirred vigorously for 1 hour at room temperature (Solution A). A mixture of 3.6 mL H_2O and 100 mL ethanol (Solution B) was added dropwise into the Solution A under stirring. The resulting solution was aged for 24 hours at room temperature resulting in the TiO_2 organic sol. The resultant sol was then used for the coating of a compact TiO_2 film (namely, C film) on the FTO surface by dip-coating with a withdrawing speed of 2 mm/s followed by a sintering process in a furnace at 450 °C for 2 h.

Both the FTO substrates with and without the C film were subject to the coating of a porous film by a screen-printing technique with a commercial TiO_2 paste [28]. The resultant films were dried in an oven at 85°C for 10 min and the coating process was repeated until a thickness of 12-15 μm was obtained. Subsequently the films were sintered in a furnace at 450°C for 30 min. The resultant porous TiO_2 films with and without the C film were designated as compact-porous film (namely, CP film) and porous film (namely, P film), and the corresponding electrodes were CP and P electrode, respectively.

2.3 Characterization of TiO_2 films

The surface morphologies of the C, P and CP films were characterized by scanning electron microscopy (SEM, JSM 890). The crystalline phase of the TiO_2 thin films were determined by XRD (X-ray diffraction) using a diffractometer (Philips PW3020) with $\text{Cu K}\alpha$ radiation.

2.4 Counter electrode preparation, dye adsorption and dye loading measurement

Counter electrodes were fabricated by depositing a transparent platinum thin film on FTO substrate from H_2PtCl_6 isopropanol solution with a spin-coating and pyrolyzing method [29].

The P and CP films were immersed into a dye solution (3×10^{-4} M in butanol and acetonitrile, 1:1, v/v) for 24 h. The dye-anchored films were washed with anhydrous acetonitrile after the dye adsorption process, and then dried in N_2 flow before measurements. In order to analyse the dye loading, dye was desorbed completely from the dye-adsorbed films into NaOH ethanolic solution (10^{-4} M) [30]. A spectrophotometer (Varian, Cary 4500) was used to measure the desorbed dye concentration in this solution.

2.5 Cells assembly and characterizations

The electrolyte solution was applied onto the dye-anchored TiO₂ films using a micropipet. Then the electrolyte/dye/TiO₂ glass plates were fixed together with the counter-electrode. A mask with a window area of 0.15 cm² was used to define the active illumination area of the DSSCs.

The photocurrent-photovoltage curves (*J-V* curves), dark current and OCVD of solar cells were recorded by a Princeton Applied Research (PAR) Scanning Potentiostat (Model 362) using a 500W Xe lamp (Changtuo, Beijing) coupled with an AM 1.5G filter (Sciencetech, Canada). The incident light intensity was measured by a broadband probe (Newport, 70268) and a radiant power meter (Newport, 70260).

The IPCE as a function of wavelength was measured with a Newport 66902 150 Watt Xe-lamp in combination with an Oriel Cornerstone 130 monochromator and a Keithley 236 source measure unit controlled by LabVIEW software. The number of incident photons on the device was calculated for each wavelength by using a calibrated Si-diode as a reference. The reported data were the average values of four. The solar energy-to-electricity conversion efficiency (η) of DSSC was calculated by equation (1):

$$\eta = \frac{J_{sc} V_{oc} FF}{P_{in}} \times 100\% \quad (1)$$

where J_{sc} is the short-circuit photocurrent density, V_{oc} is the open-circuit voltage, P_{in} is the light power per unit area and FF is the fill factor which is calculated by equation (2):

$$FF = \frac{P_{max}}{J_{sc} V_{oc}} = \frac{I_{max} V_{max}}{J_{sc} V_{oc}} \quad (2)$$

Where I_{max} and V_{max} are the current and potential at the maximum power point respectively in J - V curves of the solar cells. The J - V characterization was conducted under P_{in} of $85\text{mW}\cdot\text{cm}^{-2}$ for the η calculation.

The dependence of P_{in} on the J_{sc} and V_{oc} was also investigated. The incident photon-to-current conversion efficiency (IPCE) of DSSC, a measure of the external quantum efficiency, is defined as:

$$IPCE = \frac{\text{number of collected electrons}}{\text{number of incident photons}} = \frac{hcJ_{sc}}{e\lambda P_{in}} \quad (3)$$

Where λ , e , h and c are the incident wavelength, elementary charge, Planck constant and speed of light, respectively.

OCVD experiment is conducted by monitoring the subsequent decay of V_{oc} after stopping the illumination on DSSC under open-circuit conditions [31].

From the OCVD experiment, the electron lifetime (τ_n) is determined by the reciprocal of the derivative of the decay curves normalized by the thermal voltage, using Equation 4 [31]:

$$\tau_n = -\frac{k_B T}{e} \left(\frac{dV_{oc}}{dt} \right)^{-1} \quad (4)$$

where k_B is Boltzmann constant, T is absolute temperature, e is the positive elementary charge, and dV_{oc}/dt is the derivative of the transient open-circuit voltage.

3 Results and discussions

3.1 Characterization of the TiO_2 films

SEM analysis showed both P and C films have a crack-free and uniform structure. P film has a typical porous structure with an average particle size of 30-50 nm. In a sharp contrast with the P film, the C film has a dense and flat surface, as well as a

compact internal structure with an average particle size of 10-20 nm. Figure 2 shows the SEM cross-section image of a CP film, where the layered structure of the CP film is clearly indicated. The thickness of the C film is normally ca. 110 nm. The TiO₂ film from the organic sol dip-coating process (i.e., C film) is much more compact than that from aqueous TiO₂ sol-gel dip-coating method [15]. The C film has a very similar compact structure to that from the conventional spraying pyrolysis deposition (SPD) method [23], which may be due to the fact that both methods used organic precursor rather than aqueous TiO₂ colloid. Comparing with the SPD compact film, the C film has a more uniform and flat surface (with no lumps that are caused by the aggregation of mist from the spraying). The porous structure of the P film enlarges the surface area greatly, up to a factor of 1000 as compared to a flat surface, which facilitates the dye adsorption loading and also enables light harvesting due to its reflective nature [23].

The X-ray diffraction patterns of the C film, P film and CP film are shown in Figure 3. Anatase and rutile phase peaks were marked as “A” and “R”, respectively. The C film consists of pure anatase phase TiO₂, showing only diffraction peaks corresponding to the anatase phase. In contrast, P film and CP film have both anatase and rutile phases. The XRD patterns and relative intensity of the P film and CP film were almost identical. In fact, the content of anatase phase of TiO₂ for the P film and CP film are 92.3% and 92.5%, respectively. This implies that, compared with the P film, the compact layer of the CP film will have little influence on the surface behaviour, such as dye adsorption and mass transport of I/I₃⁻ between the porous TiO₂ layer and the counter electrode.

3.2 Dark current measurement

Controlling the back electron transfer in DSSC is vital to enhance the solar energy-to-electricity conversion efficiency. Dark current measurement in DSSC cannot be related directly to the back electron transfer process, since the electrolyte concentration in the films and the potential distribution across the nanoporous electrode in dark are different than those under illumination [32]. However a comparison of dark current between the investigated cells can provide useful information regarding the back electron transfer process. So dark current measurement of DSSC has been considered as a qualitative technique to describe the extent of the back electron transfer [25]. The origination of the dark current stems from the existence of naked FTO sites due to the porous nature of the TiO_2 structure. The porous structure provides pathways for the commonly used liquid redox electrolyte (e.g., I_3^- species) to penetrate through the P film and contact the bare conductive FTO surface. At these bare sites, the potential is thermodynamically favourable for the reduction of the oxidative species, mainly I_3^- . This causes electron recombination and results in the loss of photocurrent. A comparison between the dark currents obtained from DSSCs with and without the compact layer can provide a qualitative measure for the current leakage due to the back electron transfer [15, 25, 33]. Preventing the recapture of injected electrons by I_3^- at the photoanode is critical to reduce the current leakage in DSSC.

Figure 4 shows the dark current-voltage characteristics of the DSSCs of the P film and CP film with the applied bias from 0 to +0.75 V. The onset of the dark current for the P film occurs at a bias about +0.40 V, with a subsequent dramatic increase of dark current with the increase of potential. In contrast, for the DSSC with the CP film, the onset potential shifted to +0.60V; furthermore, the dark current of the CP film increased much slower than that of P film when potential was greater than +0.60V. In

other words, under the same potential bias, when the potential was $>+0.4\text{V}$, the dark current for the CP film was noticeably smaller than that for the P film. The increase of the onset potential and the reduction of the dark current demonstrated that the CP successfully reduced the reaction sites for the reduction of I_3^- , i.e., the leakage of electrons from the bare FTO was blocked by the compact layer.

3.3 Incident photon-to-current conversion efficiency (IPCE)

The IPCE is defined as the ratio of the number of electrons in the external circuit produced by an incident photon at a given wavelength. Using equation (2), the IPCE values of the DSSCs with the P and CP electrode as a function of the illumination wavelength are shown in Figure 5. As expected, the DSSC with the CP film showed higher conversion efficiency in the wavelength range of 400~700 nm than that with P electrode. For example, the porous TiO_2 film shows a maximum IPCE of 64% at a wavelength of 540 nm, while the compact CP film illustrates an IPCE of 82%. The IPCE can be rationalized using the following equation [34]:

$$IPCE(\lambda) = A \varphi_{inj} \eta_{coll} \quad (5)$$

where A is the absorptivity referring to the fraction of the incident light absorbed by the dye molecules. φ_{inj} is the injection efficiency, that is, the probability that the excitation of an adsorbed dye molecule leads to electron injection into the TiO_2 conduction band, and η_{coll} is the collection efficiency.

The parameters A and φ_{inj} , are directly related to the dye loading on the TiO_2 surface of the CP and P film sample. In order to identify the mechanism of the IPCE enhancement using the compact layer, the dye loadings on the TiO_2 surface of the both electrodes were investigated. The adsorbed dye on TiO_2 surface in both samples was firstly eluted completely in the NaOH ethanolic solution, and then subject to the quantitative analysis using a UV-vis spectroscopy. Using an absorptivity of

$\varepsilon=13900\text{M}^{-1}\cdot\text{cm}^{-1}$ at 540nm, the number of dye molecules absorbed on the surface of the P and the CP films were 1.005×10^{17} and 1.006×10^{17} respectively. The dye loading of the both samples were similar; therefore, parameters A and φ_{in} , of both samples can be considered the same. It could be assumed that the parameters A and φ_{inj} played a minor role on the IPCE and dominating factor for the IPCE enhancement logically should be the increased electron collection efficiency η_{coll} consistent with literature [35]. The increased η_{coll} is due to the use of the compact layer with the mechanism behind this potentially due to the increased number of electron pathways of the compact layer and the blocking effect for the back electron transfer to the electrolyte. The former originates directly from the dense structure of the compact layer as demonstrated in SEM images in Figure 2. Under a given solar light intensity and for a given amount of dye photo reaction sites, the number of photo-generated electrons is constant. The electron collection efficiency and the electron recombination ratio will determine the IPCE. An increased contact area of compact TiO_2 with the FTO surface is obviously in favour of the decrease of the electron transfer resistance and the increase of the electron collection efficiency. At the same time, the compact layer also significantly reduced the naked FTO reaction sites, where the back electron transfer reaction was dramatically suppressed. These two factors worked synergistically together and lead to the increase of the η_{coll} , and ultimately, enhancement of IPCE.

3.4 Photocurrent density-photovoltage (J - V) curves

J - V curves of the DSSCs with and without the blocking layer are shown in Figure 6 and the photovoltaic characteristics of these DSSCs were summarised in Table 1. Compared with the traditional DSSC without the compact layer, the performance of the DSSC with the compact layer, in terms of solar energy-to-electricity conversion efficiency, short circuit current density and open circuit potential, was significantly

improved by 33.3%, 20.3%, and 10.2%, respectively. The dye adsorption and light scattering properties of the CP film showed negligible difference to the P film. Therefore, the improvement of the overall performance of the solar cell was logically due to the introduction of the C film.

The short-circuit current of DSSC is mainly influenced by two factors: dye loading and the charge recombination at photoanode [36-38]. In our experiment, the calculated dye loading amounts for the P and CP films were found to be 1.98×10^{-4} g/cm² and 1.99×10^{-4} g/cm² respectively, suggesting that the dye loading amount has little influence on the J_{sc} . Hence, the main factor influencing the J_{sc} of the DSSC's studied should be the charge recombination at FTO/electrolyte interfaces. With the application of the compact film, the recombination sites (bare FTO sites) are reduced and the charge recombination in the DSSC is effectively suppressed as demonstrated in the dark current measurement in Figure 4. At the same time, comparing with the porous structure of the P film, the TiO₂/FTO contact area was increased also due to the introduction of the C film (see SEM image in Figure 2). Furthermore, the density of the C layer is higher than that of the porous structure of the P film. As a result, more effective electron pathways are generated via this compact layer to facilitate electron transfer. Consequently, more electrons can be collected at the conduction band of the photoanodes and transferred to external circuit, resulting in the improvement in J_{sc} of the DSSC.

At a given sun illumination, the flux of injected electrons should be the same for the DSSCs with the P film and CP film. The improvement of V_{oc} may be explained due to the improved adherence and the increased number of electron pathways and therefore less resistance to electron transfer to the FTO interface. The compact layer also

favours the accumulation of electrons at the interface of FTO resulting in a more negative Fermi level and thus a larger V_{oc} [39].

It is interesting to note that the IPCE of the DSSC cell with the compact layer had only a small improvement, (i.e., range from 0% to 8% depending on the wavelength of the incident light), comparing with the DSSC without the compact layer (see Figure 5). In contrast, the photocurrent of the DSSC cell dramatically increased (ca. 20%) when the blocking layer was applied between the FTO and porous layer (see Figure 6). This non-consistency was attributed to the different experimental conditions (i.e., different light intensity) used in these two measurement. The light intensities ($<0.108\text{mW/cm}^2$) of the monochromatic light applied in the IPCE measurement were much lower than the light intensity (85mW/cm^2) used in photocurrent measurement. It was suggested that the spectral measurement of the IPCE of DSSC can not be used to predict the IPCE under white light, solar light or even very high intensities of monochromatic light [35]. In other words, IPCE is also light intensity dependent. Therefore, the spectral measurements of the IPCE should be compared under the same light intensity to provide quantitative information of the blocking effect of the compact layer.

3.5 Open-circuit voltage decay (OCVD) measurement

OCVD technique has been employed as a powerful tool to study the electron lifetime in DSSC and can provide some quantitative information on the electron recombination velocity in DSSC [40, 41]. In order to conduct the OCVD measurement, the simulated solar light is illuminated at DSSC and a steady-state voltage was obtained. This indicated that equilibrium between electron injection and electron recombination is attained at the FTO surface. A potentiostat then monitors the decay of photovoltage, (V_{oc}), after interrupting the illumination. The decay of the

photovoltage reflects the decrease of the electron concentration at the FTO surface, which is mainly caused by the charge recombination. In other words, the recombination velocity of photoelectron is proportional to the response of the OCVD. Figure 7a shows the OCVD decay curves of the DSSCs with and without the blocking layer, i.e., the CP film and P film. It was observed that the OCVD response of the DSSC with the blocking layer (CP film sample) was much slower than that without the blocking layer (i.e., P film sample), especially in the shorter time domain (within 15 seconds).

Electron lifetime (τ_n) was proposed to quantify the extent of electron recombination with the redox electrolyte and has been proven effective. τ_n was calculated with the OCVD results in Figure 7a according to Equation 4. Figure 7b compares the results of the dependence of τ_n on the open circuit voltage for DSSC with and without the compact layer. It clearly demonstrates that, at any given open-circuit potential, the electron lifetime of the CP film cell was longer than that of the P film. Because the dye adsorption and light scattering due to the introduction of the C film are negligible as illustrated in previous sections, the difference in OCVDs was mainly due to the blocking effect of the compact layer. This suggests that the electrons injected from excited dye can survive longer and hence can facilitate electron transport without undergoing losses at the bare FTO surface. In conclusion, the OCVD measurements in Figure 7 demonstrated that the compact layer was able to reduce the photoelectron recombination speed effectively and prolong the lifetime of the photoelectrons.

3.6 Variation of J_{sc} with P_{in}

Because the amount of the photo-generated electrons is directly proportional to the P_{in} , the variation of P_{in} can be used to adjust the amount of photo-generated electrons in the study of the electron transfer process. The investigation of the dependence of J_{sc}

on P_{in} may provide useful information on the electron transfer kinetics due to the introduction of the compact layer. Figure 8 shows that J_{sc} of the DSSCs with the P and CP electrodes were in direct proportion with P_{in} within the maximum illumination level studied (100 mW/cm^2). This indicates that the current density for both P and CP solar cells were limited by the P_{in} , rather than other electron transfer processes, such as mass transport of I_3^- or electron transfer at the counter electrode under the investigated power range [42]. More importantly, the slope for the CP electrode (i.e., 0.161), was 15.8% higher than that for the P electrode (i.e., 0.139), which indicates that 15.8% more electrons were collected from the same amount of photo-generated electrons (under the same P_{in}) at the FTO surface. This again confirms that the use of the compact layer facilitates the electron transfer at the porous TiO_2/FTO interface as explained in the previous sections.

4 Conclusions

The effect of the compact layer on the performance of the DSSCs was investigated. The compact TiO_2 film can not only improve adherence of TiO_2 to FTO and provide a larger TiO_2/FTO contact area, but also effectively reduce the electron recombination by minimising the direct contact between the redox electrolyte and the conductive FTO surface. Compared with the traditional DSSCs without the compact layer, the solar energy-to-electricity conversion efficiency, short circuit current and open circuit potential of the DSSCs with the compact layer were improved by 33.3%, 20.3%, and 10.2%, respectively.

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Figure captions:

Fig.1 Schematic diagram of the DSSC with a compact TiO_2 layer.

Fig.2 SEM cross-section image of the CP film.

Fig.3 XRD spectra of the C, P, CP films.

Fig.4 Dark current of the DSSCs with the P and CP electrodes

Fig.5 Photocurrent action spectra of the DSSCs with the P and CP electrodes

Fig.6 J - V curves of the DSSCs with the P and CP electrodes

Fig.7 (a) Open-circuit voltage decay curves of the DSSCs with the P and CP films ;

(b) Comparison of electron lifetime as a function of open-circuit voltage of DSSCs with the P and CP films.

Fig.8 The variation of J_{sc} with P_{in} for the DSSCs with the P and CP electrodes.

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6

(a)

(b)

Fig.7

Fig.8

Table 1 Photovoltaic characteristics of the DSSCs with the P and CP electrode

Electrodes	$J_{sc}(mA\ cm^{-2})$	$V_{oc}(mV)$	$FF(\%)$	$\eta\ (\%)$
P electrode	11.62	626	66.3	5.7
CP electrode	13.98	690	66.7	7.6