Influence of TiO₂ Film/Substrate Contact on Photovoltaic Performance and Improved Efficiency in Dye-Sensitized Solar Cells

Hai-Long Yao, Guan-Jun Yang∗, Cheng-Xin Li, and Chang-Jiu Li∗

State Key Laboratory for Mechanical Behavior of Materials, School of Materials Science and Engineering, Xi’an Jiaotong University, Xi’an, 710049, China

The influence of the nano-porous TiO₂ film/FTO substrate contact on the photovoltaic performance of dye-sensitized solar cells is investigated by controlling film/FTO substrate contact through the use of insulating Al₂O₃ clusters and TiO₂ underlayer at the interface. The electrochemical properties of the DSCs are examined to correlate the photovoltaic performance and the film/FTO substrate contact condition. Results show that the short-circuit current density and thereby the photo-to-electric energy conversion efficiency of the DSCs are significantly decreased by increasing Al₂O₃ clusters coverage ratio. A modified equivalent circuit model is proposed to understand the relationship between the electric contact resistance and short-circuit current density. Although the increased electric contact resistance itself presents no significant effect on the photovoltaic performance, the decreased performance is mainly attributed to the decreased electron collection in the cell due to the presence of Al₂O₃ clusters at the film/FTO substrate interface. The result reveals that the film/substrate contact should not be negligible, even though the electric contact resistance of this interface can be neglected. The mechanism by which the film/FTO substrate contact affects cells performance reveals that the porous film cannot be considered as independent column structure but as a network structure being able to transfer electron both perpendicularly and laterally. A spray-deposited TiO₂ underlayer was applied to improve the film/FTO substrate interface contact resulting in an increased J_sc and thereby a higher energy conversion efficiency.

Keywords: Film/Substrate Interface, Alumina, Photovoltaic Performance, Underlayer, Dye-Sensitized Solar Cells.

1. INTRODUCTION

Dye-sensitized solar cells (DSCs) have attracted great interest as an alternative to conventional Si-based solar cells due to their merits, such as high efficiency, low cost, easy fabrication and flexibility.1,2 The highest solar energy conversion efficiency for liquid DSCs is 13%, which was achieved by Gratzel.2 The dye-sensitized solar cell consists of photoanode, which includes dye molecules adsorbed on the surface of a nano-porous TiO₂ film composed of nano-TiO₂ particles on a conductive substrate, electrolyte solution (or solid) and a platinum counter-electrode.1,2 Dye molecules excited by light irradiation to produce excitations inject electrons into the conduction band of the film. The electrons transport in the film cross the film/substrate interface and then are collected by the transparent conductive substrate. The film/substrate contact is the essential routine for the electron collection,3–5 and the cell performance is believed to be increased with the improvement of film/substrate contact.6–8 However, the effect of the film/substrate interface on the cell performance is not clear yet. To interpret the transport processes of electrons crossing the film/substrate interface, several theoretical models have been proposed. The film/substrate contact (usually that between semiconductor film and conductive substrate) is a complex hetero-junction9,10 and is considered as a metal/semiconductor contact due to the high conductivity of the transparent conductive substrate.11 Using kinetic model, the electron transport kinetic constants are examined at different processes in the DSCs.12,13

∗Authors to whom correspondence should be addressed.
The electrostatic potential distribution is not usually discussed, whether in the dark or under irradiation.\textsuperscript{14} The junction model is based on an electrostatic approach and agrees with the kinetic model that no electric field is present in the TiO\textsubscript{2} film.\textsuperscript{14} However, there is lack of experimental evidence for this.\textsuperscript{15,16} The thermionic emission model, which takes the thermionic emission at the TiO\textsubscript{2} film/substrate interface into account, reveals that a built-in field does not necessarily limit the open-circuit voltage.\textsuperscript{17,18} Based on the tunnel-junction model, it has been considered that the DSCs can operate without built-in field, if electron tunneling is considered at the film/substrate interface.\textsuperscript{19} However, it is still quite difficult to directly explain the effect of the film/substrate interface in the DSCs by using those reported models.

An equivalent circuit model is often applied to interpret the electron transport process in the DSCs, including the particle/particle interface and the film/substrate interface. In the typical equivalent circuit model, it has been assumed that the TiO\textsubscript{2} film consists of independent columns, each perpendicular to the FTO substrate surface and in an ideal contact with it.\textsuperscript{20–24} The electron transport properties are interpreted by using a classical model for a porous or mixed-phase electrode\textsuperscript{25} and the model for the impedance of porous electrodes is commonly pictured as a distributed circuit (transmission line).\textsuperscript{20, 25–27} In the model, the distributed elements can be modeled by using simple resistances, which is based on the physical assumption that the dc behavior of the charge transport processes can be extrapolated at all frequencies in both the liquid and solid phase.\textsuperscript{28, 29} Based on electrochemical impedance spectra (EIS), this typical equivalent circuit model can reflect the electron transport property in the film and film/substrate interface in the DSCs.\textsuperscript{30–32} It is considered that the high frequency arc in the spectra contains the film/substrate electric contact resistance and the charge transfer resistance on the counter-electrode.\textsuperscript{2, 33} In fact, it is difficult to directly examine the film/substrate electric contact resistance from the typical electrochemical impedance spectra except by using special approaches.\textsuperscript{9} From EIS results, most investigators have considered that the influence of film/substrate interface contact on cell performance was lower than the electron transport resistance in the film and even can be negligible in the DSCs with a high-temperature sintered film.\textsuperscript{9, 34, 35}

In fact, the above-mentioned theoretical assumption of independent columns with ideal contact with FTO substrate is far distant from the reality that particle connections in the film are random. The porous film is an inner-connected network composed of nano-sized TiO\textsubscript{2} particles, and the electrons present a random walk in the whole film.\textsuperscript{36–38} However, the film/substrate contact is considered to only influence its corresponding and independent column in film according to this theoretical assumption.\textsuperscript{20–24} Although the typical equivalent circuit model seems to explain the electron transferring through the high-temperature sintered film/substrate interface,\textsuperscript{6–8} the influence of the film/substrate contact has yet to be completely illuminated.

In this study, the influence of film/substrate contact on the photovoltaic performance of DSCs was examined by controlling film/substrate contact through the introduction of insulating Al\textsubscript{2}O\textsubscript{3} particles on the substrate before depositing the porous photoanode TiO\textsubscript{2} film, which is generally considered to block the direct transfer of electrons for current collection. The affecting mechanism of film/substrate contact on the electron photovoltaic performance of the solar cells was discussed. Enhanced film/FTO substrate contact was achieved by depositing TiO\textsubscript{2} underlayer between the nano-porous TiO\textsubscript{2} film and FTO conductive substrate through using ultrafine TiO\textsubscript{2} nano-particle.

2. EXPERIMENTAL PROCEDURE

2.1. Fabrication and Characterization of the Al\textsubscript{2}O\textsubscript{3}-Coated FTO Substrate

The commercially available Al\textsubscript{2}O\textsubscript{3} nano-powder (JA25, Jingrui New Material, Xuancheng, China) of 25 nm in diameter was used to control the film/substrate interface. 10 mg of nano-particles were mixed with 100 ml distilled water to make a suspension, and then the suspension was ultrasonically dispersed for 30 min. The atomized suspension was accelerated and deposited onto a fluorine-doped SnO\textsubscript{2}-glass substrate (FTO) (TEC-15, LOF, Nippon Sheet Glass, Tokyo, Japan) by using a spray deposition system.\textsuperscript{39} During the spray deposition, the substrate temperature was maintained at 120 °C. Nitrogen was used as the accelerating gas at a flow rate of 2500 L·h\textsuperscript{−1}. The standoff distance from the nozzle exit to the FTO substrate surface was 200 mm. The relative traverse speed of the nozzle over the substrate was 100 mm·s\textsuperscript{−1}. The amount of insulating Al\textsubscript{2}O\textsubscript{3} particles on substrate was controlled by spray passes through an automatic robot (Robot M-6i, ABB, Switzerland).

The morphology of the deposited Al\textsubscript{2}O\textsubscript{3} particles on the FTO substrate was characterized by a field emission scanning electron microscope (FESEM, QUANTA 600F, FEI Co., USA). The size distribution of the Al\textsubscript{2}O\textsubscript{3} particles on the substrate was examined by using FESEM images. The optical transmittance of the coated-substrate was examined in the wavelength range from 350 nm to 800 nm by a Perkin–Elmer Lambda 900 spectrophotometer (Model Lambda 35, Perkin Elmer, USA) equipped with an integrating sphere. A plate of barium sulphate was used as the reference for the reflectance measurements.

2.2. Fabrication of TiO\textsubscript{2} Underlayer

A TiO\textsubscript{2} underlayer of optimal thickness was prepared as our previous work.\textsuperscript{40} The commercial ultrafine TiO\textsubscript{2} nano-particle (JR05, Jingrui New Material, Xuancheng, China)
of 5–10 nm diameter was used to deposit TiO₂ underlayer. 0.1 g ultrafine TiO₂ nano-particle was mixed with the solvent composed of 90 mL distilled water and 10 mL ethanol, and finally was ultrasonically dispersed for 1 hour. The atomized suspension was accelerated and deposited onto FTO conductive substrate by using a spray deposition system. The parameters of spray deposition was same as that described in Section 2.1. The TiO₂ underlayer with an optimal thickness of 178 nm on FTO substrate surface was achieved by controlling the spray passes through an automatic robot (Robot M-6i, ABB, Switzerland).

2.3. Fabrication and Characterization of TiO₂ Film

The fabrication of TiO₂ film was reported elsewhere. The commercially available TiO₂ nano-powder of 25 nm in diameter (P25, Degussa, Germany) was used as a feedstock for the preparation of porous TiO₂ film for the photoanode. TiO₂ film was deposited on the substrate coated with Al₂O₃ powder or TiO₂ underlayer by a lab developed vacuum cold spray system. The system consists of a vacuum chamber, a powder feeder, an accelerating gas feeding unit, a particle-accelerating nozzle, a two-dimensional worktable, and a control unit. During the vacuum cold spraying, dry nano-TiO₂ particles are accelerated to high velocity and impact on FTO substrate surface to form a porous TiO₂ film. To compare with the effect of insulating Al₂O₃ particle coverage, a photoanode TiO₂ film was also deposited on the bare FTO substrate without Al₂O₃ particle deposition. Helium was used as the accelerating gas at a flow rate of 7.5 L min⁻¹. The chamber pressure was lower than 1000 Pa during spray, and standoff distance from the nozzle exit to the FTO substrate surface was 15 mm. The relative traverse speed of the nozzle over the substrate was 20 mm s⁻¹. TiO₂ thickness was examined by a surface profiler (AMBIOS, XP-2, USA).

2.4. Fabrication and Characterization of DSCs

The fabrication and characterization of the DSCs has been reported elsewhere. Photoanodes were prepared by immersing the TiO₂ films in an absolute ethanol solution of 0.3 mM N719 ruthenium complex dye (Solaronix, Aubonne, Switzerland) for 24 hours at room temperature. To eliminate the physically adsorbed organics and water in the film, the TiO₂ films were heat to 450 °C for 30 min. A platinized FTO used as the counter-electrode was prepared using a magnetron sputtering system (Explorer 14, Denton Vacuum, 7 min) at room temperature. Then the photoanode and counter electrode were sealed using a hot-melt film with a thickness of 60 μm (Dupont, 1702). The space between the photoanode and counter electrode with an active area of 0.4 cm² was filled in with an electrolyte composed of 0.6 M DMPII (Institute of Plasma Physics, China), 0.05 M I₂ (Aldrich), 0.1 M LiI (Aldrich), and 0.5 M 4-tert-butylpyridine (Acros) in dehydrated acetonitrile (Aldrich).

The photovoltaic performance of the DSCs was measured under one sun irradiation using a solar simulator (100 mW·cm⁻², Oriel 3A, Newport, calibrated with standard crystalline silicon solar cell) equipped with a Keithley 2400 digital source meter. The incident photon-to-current conversion efficiency (IPCE) spectra for the cells were measured on an IPCE measuring system (PV measurements). Current of cells was measured in the dark by a potentiostat (Solartron 1287). The electron transport properties at the film/FTO interface was investigated in the dark by the electrochemical impedance spectroscopy (EIS) using a potentiostat (Solartron 1287) equipped with a frequency response analyzer (Solartron 1260) in the dark with bias potentials and 10 mV amplitude over a frequency range of 10⁻¹ to 10⁶ Hz. The impedance parameters were determined by fitting the impedance spectra by Z-view software with the equivalent circuit reported in the literature. All the parameters were obtained from at least three cells.

3. RESULTS AND DISCUSSION

3.1. Microstructure of the Insulating Al₂O₃ Powder on FTO Substrate Surface

Figure 1 shows the surface morphology of the Al₂O₃ particles deposited on the FTO substrate surface and the size distribution with different numbers of spray passes. Figures 1(a)–(c) clearly show that the Al₂O₃ particles were deposited on the FTO substrate surface (as shown as arrows). The Al₂O₃ coverage ratio was determined by the SEM images. Results show that the Al₂O₃ coverage ratio on the FTO substrate surface was increased from 2.1% to 6.7% with the increase of number of spray passes. Figure 1(d) shows that the size distribution of the Al₂O₃ powder on substrate is in a range from 50 nm to 400 nm with the maximum size at ~200 nm, which is much smaller than the TiO₂ film thickness (∼150 nm). Figure 2 shows the effect of Al₂O₃ coverage on the optical transmittance. The optical transmittance of the coated-substrate was similar with the bare substrate in the wavelength range from 350 nm to 800 nm, indicating that the Al₂O₃ particle coverage did not significantly decrease the light transmittance of the substrate. This fact indicates that the substrate optical properties with Al₂O₃ particles should have no effect on the performance of the dye-sensitized solar cells from the viewpoint of light penetration.

3.2. Effect of Al₂O₃ Coverage on Photovoltaic Performance of the DSCs

Figure 3 shows the photovoltaic performance for the DSCs assembled on the FTO substrate without and with Al₂O₃ particle coverage. Table 1 shows the photovoltaic parameters for all the cells. It can be found that the short circuit current density (Jsc) was significantly decreased with the increase of Al₂O₃ coverage and was the lowest for the cells with 6.7% Al₂O₃ coverage. The open
circuit voltage and fill factor of the solar cells did not change. Due to the significant decrease of $J_{sc}$, the photo-to-electric energy conversion efficiency was also significantly decreased. Figure 3(b) shows the relative performance of the cells with different coverage ratios of insulating Al$_2$O$_3$ particles by the parameters $J_{sc}$, $V_{oc}$, $FF$ and efficiency. Clearly, the $J_{sc}$ was significantly decreased by a maximum of 15.3% for Al$_2$O$_3$ coverage ratio up to 6.7%, resulting in a significant decrease by 15.1% in conversion efficiency.

These results were consistent with the change of incident photon-to-electron conversion efficiency (IPCE) shown in Figure 4, which was decreased with the increase of the Al$_2$O$_3$ coverage ratio. It has been reported that the IPCE was determined by the light harvesting efficiency, the quantum yield of the charge injection, the efficiency for dye regeneration and the efficiency of collecting the injected charge at the back contact. In this study, the photoanode were prepared by using the same process in spite of the Al$_2$O$_3$ particle on the FTO substrate surface. Therefore, the decrease of the cell performance can be mainly attributed to the efficiency of collecting the injected charge at the back contact determined by the film/substrate interface.

3.3. Effect of Film/Substrate Interface on the Electrochemical Properties of DSCs

To interpret the effect of the film/substrate contact, the electrochemical impedance spectra of the cells were measured to examine the electrochemical properties of the DSCs in the dark. Figure 5(a) shows the typical Nyquist plots of the cells measured at the $-0.8$ V in the dark. The impedance spectra of different potentials were fitted and summarized using the typical equivalent circuit model.
proposed in literature.\(^4\)\(^{44}\)\(^{46}\) Figure 5(c) shows that the sum of the charge transfer resistance at the counter-electrode and film/substrate electric contact resistance (\(R_{Pt+co}\)) was significantly increased with the \(Al_2O_3\) coverage ratio up to \(-6.7\%\). Since the identical platinized FTO was applied to the counter-electrode, the increase of \(R_{Pt+co}\) was mainly attributed to the increase of the electric contact resistance (\(R_{co}\)).\(^{32}\)\(^{33}\) Since the insulating \(Al_2O_3\) particles hinder the electron direct transportation from substrate to \(TiO_2\) film during measuring impedance at a bias voltage in the dark, the recombination reaction between electron and electrolyte in the \(TiO_2\) film was decreased by reducing the electron concentration. Therefore, the charge transfer resistance (\(R_{ct}\)) for the solar cells was increased with the increase of \(Al_2O_3\) coverage ratio as shown in Figure 5(d).
Figure 5. Electrochemical property of DSCs with FTO substrate covered by Al₂O₃ particle at different coverage ratios measured at bias voltages in the dark. (a) Nyquist plots for cells at −0.8 V. (b) Transmission lines for DSCs. (c) Charge transfer resistance at counter-electrode and electric contact resistance (R_{Pt+}) of the cells at different bias voltage in the dark. (d) Charge transfer resistance (R_{cb}) at the TiO₂/electrolyte interface of cells at different bias voltage in the dark.

Figure 6. Relative equivalent circuit of DSCs. (a) the equivalent circuit of the DSCs under illumination, (b), (c) the simplified equivalent circuit model of the DSCs. (R_{co} is the electric contact resistance at the TiO₂ film/substrate interface, R_{t} is the electron transport resistance in the TiO₂ film, R_{ct} is the charge transfer resistance at the TiO₂/electrolyte interface, R_{s} is the total resistance of R_{cb}, R_{Pt} and the resistance of ion diffusion, R_{TCO} is the resistance of electron on FTO recombining with electrolyte, red arrows refer to the current direction, I_{ph} refers to the photocurrent in the film, I refers to the current on the FTO substrate, red circle refers to the excited dye molecules).

Effect of the film/substrate contact resistance. However, the cell performance was significantly decreased by the insulating Al₂O₃ particle at the film/substrate interface, which cannot be explained by the equivalent circuit model. It can be found that the porous film is an inner-connected network composed of nano-sized TiO₂ particles, and the electrons present a random walk in the whole film. The difference between the experimental and theoretical result should be attributed to the assumption of neglecting the real film structure. Therefore, the reason of the decreased J_{sc} should not be independently considered from the view of equivalent circuit model.

To illuminate electron transportation pathway whether or not be hindered by Al₂O₃ clusters at the film/substrate interface, current of cells was measured in the dark condition. In this case, the current measured in the dark reflects electrons from the FTO substrate recombining with the electrolyte at the FTO substrate/electrolyte interface and at the TiO₂/electrolyte interface. Figure 7 shows...
the current density of cells with different Al₂O₃ coverage ratios. It can be found that the current density of the cells with Al₂O₃ of 6.7% was lower than that of the cell without Al₂O₃. This fact indicates a decrease of electron transferring from the FTO substrate to the TiO₂ film during measuring in the dark condition. At the point of −0.5 V, the difference of the current density between the cells was 13.8%, which was comparable to the decreased $J_{sc}$ of 15.3%. This implies that the Al₂O₃ coverage ratio. For the cell under bias in the dark, the electrons transport from the substrate to the TiO₂ film crossing the film/substrate interface.50–52 According to the typical equivalent circuit model, which simplified the film as the independent columns with electron transferring perpendicularly (electron transferring laterally is not allowed),20–24 the decrease of the current measured in the dark should be proportional to the Al₂O₃ coverage ratio shown in Figure 8(a). In reality, the film is a network structure and electrons transport randomly in the whole film according to the random walk model with electron transferring both perpendicularly and laterally.36–38 This implies that although there is no electron directly transporting into columns separated by the Al₂O₃ clusters, there is electron transportation from its surrounding film shown in Figure 8(b). As a result, it reduces the electron concentration in the film, especially in the region near to the Al₂O₃ particles. This process in-turn decreases the electron transport property in the film, which further restrains the electrons crossing the film/substrate interface from the substrate to film. Therefore, the decrease of the current measured in the dark is larger than the Al₂O₃ coverage ratio.

There is a similar process of electron transportation for the cells under illumination to the process of cell under bias in the dark. Under illumination, the photogenerated electrons transport in the film, across the film/substrate interface and finally are collected by the conductive substrate.4 If the photoanode is considered as independent columns, the electron concentration increases in the TiO₂ particles of the column just above Al₂O₃ particles. However, the porous film is actually an inner-connected network with charge transportability.36–38 The high concentration electrons can diffuse into the TiO₂ particles around the Al₂O₃ particles as shown in Figure 8(c). Effective electron transportation pathways are completely cut by the Al₂O₃ particles at film/substrate interface, which consequently cut the electron collection of cells through this Al₂O₃ particle area.

Figure 7. Current measured in the dark of the cell without and with Al₂O₃ at different coverage ratios.

Figure 8. Schematic diagram of electron process in photoanode with Al₂O₃ at the film/substrate interface. (a) Photoanode considered as independent columns, (b) photoanode considered as a network structure at bias voltage in the dark, (c) photoanode considered as a network structure under illumination. (Arrow refers to electron transportation direction; Hollow circles refer to TiO₂ particle; Solid circles refer to Al₂O₃ particle.)
at film/substrate interface. It can be inferred that the electron concentration in the TiO₂ particles around the Al₂O₃ particles is higher than that without Al₂O₃ particles, increasing electrical potential of the surrounding film of Al₂O₃ particles. As a result, the cell regions surrounding the Al₂O₃ particles would work at a condition deviating from the short-circuit, although the cells are at the apparent short-circuit condition. This process could further decrease effective electron collection of the cells through the film/substrate interface. This result demonstrates that, regarding to the effect of the film/substrate interface, the film must be considered as having a network-structure film, rather than one with an independent column structure.

3.5. Improvement of Film/Substrate Interface Contact by Using TiO₂ Underlayer

To enhance the film/substrate interface contact, a TiO₂ underlayer was deposited between FTO conductive substrate and porous TiO₂ film by using ultra-fine TiO₂ nano-particle. In this case, the TiO₂ underlayer with an optimal thickness of 178 nm was achieved by controlling the spray passes as described in literature. As discussed in literature, this spray-deposited TiO₂ underlayer not only decreased the electron recombination at FTO/electrolyte interface as a result of protection effect against ionic penetration of electrolyte through the substrate, but also enhanced the connection between the porous TiO₂ film and the conductive layer on the substrate. By assembling DSCs, it can be found that the J_sc of solar cell with underlayer was increased to 14.3 mA cm⁻² and thereby increasing energy conversion efficiency from 5.38 to 6.32%, as shown in Figure 9. Therefore, the cell performance was improved by enhancing the film/substrate interface contact through using a spray-deposited TiO₂ underlayer. This result further confirmed that the film/substrate interface contact significantly influenced the cell performance and also proposed an approach for improving this interface contact.

4. CONCLUSIONS

The influence of film/FTO substrate contact on the photovoltaic performance of the cells has been investigated by depositing insulating Al₂O₃ particle and TiO₂ underlayer on the FTO substrate. The size of the isolated Al₂O₃ clusters on the FTO substrate around 200 nm was much smaller than the TiO₂ film thickness. The optical transmittance of the Al₂O₃-covered substrates remained nearly constant regardless of the Al₂O₃ particle coverage ratio to ∼6.7%. The short-circuit current density and thereby conversion efficiency was decreased with the increase of Al₂O₃ particle quantity on the FTO substrate surface. Although the film/substrate electrical contact resistance was increased, R_ox itself had little effect on cell performance based on the conventional theory. The main reason for the decreased performance was attributed to the decreased electron collection in the cells, which indicated the film/substrate contact had a significant effect on the cell performance. These results demonstrate that the porous film cannot be regarded as independent columns, but a network structure being able to transfer electrons both perpendicularly and laterally. A spray-deposited TiO₂ underlayer was applied to improve the film/substrate interface contact resulting in an improvement of J_sc and thereby energy conversion efficiency.

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References and Notes


Figure 9. Photovoltaic performance of DSCs without and with TiO₂ underlayer.
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