Photoelectrochemical quantification of electron transport resistance of TiO₂ photoanodes for dye-sensitized solar cells

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Abstract

A simple photoelectrochemical method is developed to measure the intrinsic electron transport resistance (R_0) of TiO_2 photoanodes. R_0 is considered as the sum of electron transport resistance at the TiO_2/FTO interface and among TiO_2 nanoparticulates during electron transport process, which is independent of the manner of electron injection, its physical and chemical environments. Because TiO_2 photoanodes are the common electron transport pathways for dye sensitized solar cells (DSSCs) process and the photoelectrocatalytic oxidation process, R_0 can be also considered as a quantitative measure of the electron transport resistance of the photoanodes in the DSSC process. The proposed method will provide a simple and rapid alternative to quantitatively evaluate the quality of the TiO_2 photoanodes for DSSCs using R_0 values. A series of TiO_2/FTO photoanodes with different electron transport resistance were fabricated using conventional screen printing technique, surface modifications using titanium organic sol and TiCl_4 aqueous solution. R_0 values of the photoanodes were characterized and subsequently used to correlate with the important performance parameters of the corresponding DSSCs. The preliminary results suggest that these surface modifications do not significantly affect the surface area, film thickness, dye loading and optical properties of the TiO_2 film, but significantly decrease the R_0 values. Furthermore, the DSSCs photoanodes with lower R_0 values due to the organic sol or TiCl_4 modification bestow better photovoltaic performance than the corresponding non-modified photoanodes. Therefore, it can be concluded that the performance improvements were mainly attributed to the decrease of the R_0 values, which validates the proposed electrochemical evaluation method.

Introduction

Dye-sensitized solar cell (DSSC) is a very promising candidate for next-generation solar cells due to the prospects of low cost and high efficiency.¹ Recently, an overall energy conversion efficiency as high as 11% has been achieved.² Typically, a DSSC consists of a porous TiO₂ coated fluorine-doped tin oxide (FTO) working electrode (i.e., TiO₂/FTO photoanode), dye, a Pt thin film counter electrode and electrolyte normally containing I⁻/I₃⁻ redox couple.^{1, 3, 4} It is well-recognized that the nanoporous nature of the TiO₂ layer provides high surface area is of great importance for achieving high energy conversion efficiency, because it enhances dye loading for efficient solar light absorption.⁵ To generate meaningful electricity from DSSC, the photogenerated electrons need to pass through the nanoporous TiO₂ layer to reach the FTO and external circuit. The electron transport resistance of the TiO₂/FTO electrode, including the interfacial resistance of TiO₂/FTO and the resistance among TiO₂ nanoparticles, plays an important role on the overall electron collection percentage, and consequently on the energy conversion efficiency.⁶⁻⁹ Materials characterisation techniques, such as SEM,^{10, 11} TEM¹² and XRD,¹³ can provide supporting information for the connectivity among TiO₂ nanoparticles and contact area between TiO₂ and FTO surface. However, they cannot provide direct and quantitative information on the electron transport resistance. Intensity modulated photocurrent spectroscopy (IMPS),¹⁴ intensity modulated photovoltage spectroscopy (IMVS),¹⁵ electrical impedance spectroscopy (EIS)¹⁶ and open-circuit photovoltage decay (OCVD)¹⁷ methods have been used as effective tools in studying the electron transport process in DSSCs. These techniques can provide overall electron transport efficiency for all the interfaces of a complete DSSC, including: dye/TiO₂, TiO₂ particles/TiO₂ particles, TiO₂/FTO, electrolyte/counter electrode, and dye/electrolyte. Besides, many studies focused on the interpretation of the charge transport kinetics and derived diffusion length of electrons in the microporous semiconductor films in photoelectrochemical cells.^{18, 19} For this study, we attempts to derive and quantify the

intrinsic electron transport resistance of the photoanode for DSSCs. The evaluation of the electron transport resistance of the TiO_2/FTO electrode will provide useful and practical guidance to produce quality photoanodes for DSSCs.

In recent years, photoelectrochemical method has been widely used to characterize TiO_2 .²⁰⁻²² In our previous work,^{22, 23} under varying light intensities, an intrinsic electron transport resistance (R_0) at a TiO_2/ITO electrode could be obtained using a linear sweep voltammetry (LSV) technique and a simple curve fitting process. The photoelectrochemical method can be possibly used to characterise the electron transport resistance of the TiO_2/FTO electrode for the DSSCs. However, there are some obvious differences between the DSSC and the photoelectrocatalytic oxidation process when the TiO_2/FTO photoanodes are used. Firstly, these two processes occur in different physical and chemical environments. Secondly, in terms of electron injection mode, electrons are injected from the excited dye molecules to TiO_2 conduction band in DSSC process, while electrons are injected from TiO_2 valence band upon absorption of photons to the conduction band in the TiO_2 photocatalytic process. Nevertheless, we can also uncover the similarity of the two processes-they share the common electron pathways, i.e., TiO_2/FTO photoanode, through which the injected electrons are transported from TiO_2 conduction band to the FTO back contact. Therefore, the electrons should encounter the same electron transport resistance in these two processes regardless of the manner of electron injection, physical and chemical environment. Because the intrinsic R_0 is measured in the photoelectrochemical system that possesses the same electron transport pathway as the DSSC process, the electron transport information obtained can be directly used in a DSSC process. The measurement of R_0 would allow an accurate estimation of the electron transport capacity of a photoanode, determine if the electron transport is the limiting step of the overall process and calculate the ohmic drop. Additionally, this photoelectrochemical measurement can be carried out using an electrochemical station and Xenon light source for DSSC testing and does not

require other instrument. This method may provide DSSC researchers with a simple and rapid way to characterize the quality of the TiO₂/FTO electrode using the R_0 values.

In this work, the photoelectrochemical characterisation method is proposed to quantify the R_0 value of the TiO₂/FTO electrode for DSSC for the first time. The amount of electron injection was regulated by varying the UV light intensities in the measurement. In order to validate the proposed method, a range of TiO₂/FTO electrodes with different electron transport resistance were fabricated. This is achieved by varying the number of traditional TiO₂ porous layers (i.e., control films), and subsequent surface modifications using a titanium organic sol²⁴ and a conventional TiCl₄ aqueous solution.²⁴⁻²⁷ The organic sol modification is expected to broaden electron transport pathways and construct additional electron pathways from the bridging-gap effect²⁸ while TiCl₄ post-treatment is anticipated to improve the connectivity among TiO₂ nanoparticles.²⁴⁻²⁷ Both processes are used to reduce free electrons scattering among TiO₂ interparticles and therefore are expected to decrease the electron transport resistance. All the prepared films were subject to the resistance measurement using the proposed photoelectrochemical method. The obtained resistance values were subsequently used to correlate with the performances of the corresponding DSSCs.

Experimental

Chemicals and Materials

Titanium butoxide (97%), diethanolmine (99%), Hydrochloric acid (37%) and Titanium (IV) chloride (99%) were purchased from Sigma-Aldrich. Ethanol (99.5%) and isopropanol (99.7%) were supplied by Ajax Finechem and Merck, respectively. TiO₂ paste (DSL 18NR-T), N719 dye (RuL₂(NCS)₂(TBA)₂·(H₂O)₄, L=2,2'-bipyridyl-4,4'-dicarboxylic acid, TBA = tetrabutylammonium) and liquid electrolyte (EL141) containing I⁻/I₃⁻ redox couple were from Dyesol Co. Australia. Fluorine-doped tin oxide (FTO) glass (≤14 Ω/square) was from Pilkington.

TiO₂ Porous Film Preparation and Modification

TiO₂ porous films were prepared on pre-cleaned FTO glass using a screen-printing technique with a commercial TiO₂ paste and sintered in a furnace at 450°C for 30 min, designated as control films.²⁹ The coating process was repeated to obtain desirable number of TiO₂ layers. Control films with 1 layer, 2 layers and 3 layers were labelled as C1, C2 and C3, respectively.

A TiO₂ organic sol was prepared at room temperature (21°C) by a method illustrated in our previous work.²⁹ Briefly, 68 mL of tetrabutyl titanate, 16.5 mL of diethanolamine and 210 mL absolute ethanol were mixed and stirred vigorously for 1h at room temperature (Solution A). A mixture of 3.6 mL H₂O and 100 mL ethanol (Solution B) was added dropwise into the Solution A under stirring. The resulting solution was aged for 24h at room temperature resulting in the TiO₂ organic sol.

Control films were immersed in the organic sol for 1 min to achieve thorough sol pervasion into the porous structure. The resulting films were dried in an oven at 60°C in air atmosphere for 10 min and subsequently sintered at 450°C for 2h. The modified films after the sol modification originated from C1, C2 and C3 were marked as MS1, MS2 and MS3, respectively.

Post-treatment with TiCl₄ was carried out according to the procedures in literature.²⁷ Briefly, a 0.05 M TiCl₄ aqueous solution was prepared in 2M HCl solution. Freshly sintered TiO₂ control films were immersed into this solution and stored in an oven at 70°C for 30 min in a closed vessel. After flushing with distilled water and drying, the electrodes were sintered at 450°C in an oven for 30 min. The resulting TiO₂ films after the TiCl₄ modification originated from C1, C2 and C3 were designated as MT1, MT2 and MT3, respectively.

Physical Characterizations

Surface morphologies and cross-sectional structures of control and modified films were characterized by scanning electron microscopy (SEM, JSM 890). The dye loading measurement was conducted by measuring the absorbance of dye-sensitized films using the spectrophotometer (Varian, Cary 4500).

Photoelectrochemical Measurement

All photoelectrochemical experiments were carried out at 25 °C in 0.10 M NaNO₃ solution in a three-electrode cell. A TiO₂ working electrode was mounted in a special holder with an area of 0.78 cm² exposed to UV illumination via a quartz window. A scanning potentiostat (PAR 362, Princeton) was used to conduct the LSV measurements. The light source was a 150 W xenon lamp (Trusttech, Beijing, China) with regulated optical output and an UV-band-pass filter (UG-5, Schott). The output UV light intensity was measured at 365 nm wavelength using a UV irradiance meter (UV-A, Instruments of Beijing Normal University, China).

DSSC Characterization

Detailed DSSC preparation procedures and experimental setup of photovoltaic measurement can be found in our recent work.²⁹ Briefly, a series of DSSCs were assembled with traditional sandwich type configuration using N719 dye sensitized control films or modified films, liquid electrolyte (EL141) containing I⁻/I₃⁻ and a platinum counter electrode deposited on FTO glass.²⁹ A 500W xenon lamp (Trusttech, Beijing, China) with an AM 1.5G filter (Sciencetech, Canada) was used as the light source. The photovoltaic measurements of DSSCs were performed by the PAR 362 potentiostat.

Dye adsorption and dye loading measurement

The control and modified films were put into the dye solution (3×10⁻⁴ M in butanol and acetonitrile, 1:1, v/v) for 24 h. The dyed films were washed with anhydrous acetonitrile after the adsorption process and then dried in N₂ flow before measurements. The dye loading measurement was conducted by measuring the absorbance of the dye-anchored photoanodes using a spectrophotometer (Varian, Cary 4500).

Results and Discussion

Fig. 1 indicates the angle view SEM images of control film, sol modified film and TiCl₄ modified film, showing the morphology of the surface as well as the cross-sectional structure.

The control films have a typical porous structure with averaging particle sizes about 25 nm (see Fig. 1a). In a sharp contrast with the control films, the sol modified film in Fig. 1b has a more compact structure with an average particle size of ca. 10 nm. The average particle size of MT3 is about 18 nm as shown in Fig. 1c. In other words, the MS3 film possesses a smaller average particle size than the MT3 film. This is probably because the titanium organic sol has a lower viscosity than the TiCl_4 solution. Besides, Fig. 1c shows that only a portion of gaps between the porous particles are filled and some of the gaps remained. Thus, the SEM images show that the structures of the sol and the TiCl_4 modified films are more compact than that of the control film. Low magnification cross-sectional SEM analysis (images not shown) indicated that the thickness of control films for C1, C2, C3 electrodes are 5, 9, 12 μm , respectively. The thickness of the sol modified films and TiCl_4 modified film in comparison with the corresponding control films showed trivial changes (see Table 1) due to the low viscosity nature of the organic sol and the TiCl_4 aqueous solution. Hence, the effect of the sol modification and the TiCl_4 modification process on the film thickness can be ignored. Due to the effects of the different modifications on the control structure are not the same, various electron transport resistances and photovoltaic performances are expected for the photoanodes with different thicknesses and different modifications.

Photoelectrochemical Determination of R

All the TiO_2/FTO electrodes were subject to the LSV measurement under various UV intensities, leading to a series of LSV voltammograms for each electrode. Under UV illumination, electrons in TiO_2 semiconductor are injected from the valence band to the conduction band. In effect, the TiO_2/FTO electrode serves as a photoanode to seize electrons by splitting water into oxygen and hydrogen. Fig. 2a shows the typical voltammograms for MS3 under different UV light intensities. It can be observed that each voltammogram ($J_{ph}-E$) under a given light intensity consists of two stages (see Fig. 2a). From -0.3V to 0.0V of potential bias, the photocurrent

response increased monotonically with the applied potential bias. In contrast, when potential bias was greater than ca. 0.0V, the photocurrent levelled off, namely saturation photocurrent (J_{sph}). Most importantly, excellent linearity of $J_{ph}-E$ relationship can be observed in a certain potential range, for example, from -0.20 V to -0.15 V for MS3 film (see Fig.1). This observation implies that the rate of the reaction within this range was controlled by the electron transport inside the TiO_2 layer. Under such conditions, the photocurrent (the rate of the overall reaction) is determined by the rapidity of the photoelectron removal process from the layer.

In this study, the linear range of the $J_{ph}-E$ curves was selected by a specially designed program (Matlab software) to avoid arbitrary selection. For a given photocatalyst, the linear potential range will vary slightly depending on the type and the concentration of electron scavenger and light intensity. For different types of catalysts, the linear potential range may also depend on the conduction band edge potentials. However, the change in these linear potential ranges should not be a concern. This is because a linear $I-V$ relationship obtained within whatever potential range implies the electron transport inside the photocatalyst layer is a controlling step in the overall process. Under such conditions, the system behaves like a pure resistor.^{22, 23} Therefore, Ohm's law can be used to calculate the total resistance, i.e., $R=(E_2-E_1)/(I_2-I_1)=\Delta E/\Delta I$.²² Using computer linear regression fitting, the R values obtained were plotted against the reciprocal of the saturation current (i.e. $1/J_{sph}$), giving an excellent linear regression equation as Eq.1 (see Fig. 2b)

$$R = k / J_{sph} + R_0 = R_1 + R_0 \quad (1)$$

In which, k and R_0 are the slope and interception on y axis for a given electrode, respectively. The physical meaning of Eq. 1 is that R , is the sum of a variable resistance ($R_1=k/J_{sph}$) and a constant resistance (R_0).²²

For a given TiO_2 /FTO photoanode, R_1 is the interfacial reaction resistance that should not be dependent on potential. It depends on the parameters such as the type and concentrations of

electron scavengers, and the light intensity that affect the interfacial processes. Fig. 2a also shows the higher photocurrent (J_{ph}) and saturation photocurrent (J_{sph}) under stronger UV light intensities at the same potential bias. This is due to the fact that the stronger UV light intensity leads to the generation of more charge carriers (i.e., electrons and holes) and give rise to lower R_l . This explains why R_l is inversely proportional to J_{sph} . The k values can be considered as a quantitative measure of recombination tendency of electrons and holes, or the minimum potential to achieve 100% separation of photoelectrons and photoholes (i.e., 0% recombination). It is an intrinsic property of semiconductor materials that is independent of the film thickness and experimental conditions. As shown in Table 1, C1, C2 and C3 porous films had very similar k values (i.e., 139, 145, 150 $\Omega\cdot\text{mA}$, respectively) though they had different thickness (i.e., 5, 9, 12 μm , respectively). Likewise, MS1, MS2, MS3 films had a nearly constant average k values of 177.6 $\Omega\cdot\text{mA}$, despite the fact that they had various thickness (i.e., 5, 9, 12 μm , respectively). This also applies to the MT1, MT2 and MT3 films, which had average k values of 170 $\Omega\cdot\text{mA}$. It can be observed that the average k values of the sol modified film and the TiCl_4 modified film are higher than that of the control film. This was possibly because the TiO_2 surface of the sol and TiCl_4 modified films had more defects (and therefore more recombination centres) than that of the porous film.^{26, 29} Consequently, the photoelectrochemical system with the sol modified film and TiCl_4 modified film needs a slightly higher potential to offset the recombination tendency (k).

R_0 values obtained from the interception of the linear regression equations for all photoanodes are listed in Table 1. R_0 corresponds to the sum of ohmic resistance at the TiO_2/FTO interface and resistance among TiO_2 nanoparticulates during electron transport. More importantly, R_0 is independent of the experimental conditions (e.g., light intensity and applied potential bias) and chemical environments. Table 1 shows for both control films and modified films, R_0 is linearly dependent on the film thickness. This is expected because R_0 should be

closely related to the electron transport distance. For the photoanodes fabricated with the same starting materials and identical processing technique, the electron transport distance increases linearly with the film thickness, which is similar to the behaviour of typical electrical resistors. Therefore, the thicker the TiO_2 film of the same type, the higher the R_0 value (as shown in Table 1.)

The R_0 values of the sol modified films showed a significant decrease compared with that of the corresponding control films. In particular, The R_0 values of MS1, MS2 and MS3 were reduced by 29%, 36% and 40% compared with that of C1, C2 and C3, respectively. The reductions of R_0 for MT1, MT2 and MT3 compared with that of the corresponding control films were 26%, 26% and 25% respectively. This suggests that the modified films are more conductive than the corresponding control films. The decrease of the R_0 value or the increase in conductivity is because the formation of more effective electron transport network resulted from the modification process by the organic sol or the TiCl_4 solution. This is supported by the observation of the SEM experiments. As indicated in Fig. 1a, the porous structure has a large amount of gaps that will limit the number of effective electron pathways. In contrast, due to the gap-filling and particle-bridging effect of the organic sol on control films (see Fig. 1b), the sol modified films have a less rough surface morphology and more compact internal structure than the corresponding control films. Fig. 1b demonstrates that the modification process is able to bridge the gaps between TiO_2 nanoparticles, shorten the electron transport distance and create more effective pathways. Furthermore, Fig. 1b also shows that the original large TiO_2 particles were closely surrounded and interconnected by the modifying TiO_2 nanoparticles, which enlarged the inter-particle contact area and therefore expanded the electron pathways. This suggests that the organic sol modification could substantially reduce the electron transport resistances for the sol modified films. For the TiCl_4 modified film, as shown in Fig. 1c, the structure is more compact than the control film due to the partly filled gaps. But compared with

the structure of the sol modified film in Fig. 1b, the particle-bridging and gap-filling effect of the TiCl_4 modified film is less significant. As a result, the particle connectivity in the TiCl_4 modified film is improved but not as significant as that in the sol modified film. In other words, the R_0 values for TiCl_4 modified film are larger than that of the sol modified film.

Correlation of R_0 and DSSC Performance

The aforementioned control films and modified films were used to fabricate corresponding DSSCs using the identical fabrication process and reagents. The performance of the resultant DSSCs was characterized under the simulated AM 1.5 illumination ($100 \text{ mW}\cdot\text{cm}^{-2}$).²⁹ The photovoltaic parameters for all photoanodes were calculated from the I - V curves. The results are listed in Table 2 and the typical I - V curves of C3, MS3 and MT3 are displayed in Fig. 3. Table 2 shows that the DSSCs constructed with the sol and TiCl_4 modified films exhibit improved performance in comparison with the corresponding control films for all parameters studied. Among them, J_{sc} , FF and η show the most significant improvement while V_{oc} do improve but the changes appear to be relatively small. For example, in comparison with C3, J_{sc} , V_{oc} , FF and η for MT3 increased 5.1%, 3.2%, 6.2%, and 14.4%, respectively, while for MS3, the corresponding parameters improved 16.7%, 4.9%, 6.1% and 28% respectively. This suggests that the improvements in terms of FF of the MT3 and MS3 were comparable, but in strong contrast, the improvements in terms of J_{sc} , V_{oc} , and η for MS3 samples are substantially higher than that for MT3 samples, respectively.

For both the sol modified film and the TiCl_4 modified film, modification of the porous structure could improve the DSSC performance from two aspects. One is to enhance the photo efficiency to produce more photoelectrons, and the other is to improve the electron transport efficiency to transport more electrons to the external circuit. The former is mainly achieved by enhancing light absorption via boosting of dye loading and augmenting of light reflection, while the latter is realized by reducing the electron transport resistance (i.e., R_0) of the porous films.

In order to identify the causes of performance improvement, the light reflection property and dye loadings on the TiO₂ surface of all the electrodes were therefore analysed. The UV-Vis reflection spectra (not shown) indicated that the difference of the reflection properties was very limited (within experimental error) for control and modified films. This can be expected because the reflection effect is mainly caused by the large particle sized TiO₂, e.g., 125 nm³⁰ and the size of the modifying TiO₂ particles for sol modified film and TiCl₄ modified film was only ca. 10 nm and 15 nm, respectively.

Dye loadings of the control and modified photoanodes were characterized by the UV-Vis absorbance measurement. Fig. 4 shows the absorption spectra of the dye-sensitized control films and the modified films with different layers. The spectra indicate the absorption increase dramatically with the increased number of layers which coincides with the thicknesses of the TiO₂ films in Table 1. For example, the C3 (12 µm) sensitized film has 30% and 23% increase in absorbance at 535 nm, in comparison with the C1 (5 µm) and C3 (9 µm) sensitized films, respectively. In contrast, there are not significant differences in the adsorption spectra between the sensitized modified films and their corresponding control films regardless of the number of layers. This suggests that neither the sol modification nor the TiCl₄ modification significantly affects the dye loading compared with the control films. This is consistent with conclusion drawn from the dye loading measurements,²⁷ where the dye loading amount was determined by desorbing the adsorbed dye from the photoanode into NaOH ethanolic solution and measuring the absorbance of the solution.

The trivial change in light reflection and dye loading for the modified films suggests that they are not the major driver for the performance improvement in the corresponding DSSCs. Therefore, it is concluded that the DSSC performance is mainly dependent on the electron transport efficiency. Because photoanodes are the common electron pathways in both DSSCs

and photoelectrocatalytic oxidation processes, the electron transport resistances encountered by the photogenerated electrons from dye molecules in the DSSC process should be the same as R_0 .

J_{sc} is mainly influenced by dye loading amount and electron transport efficiency in the TiO_2 film.²⁵ Based on the dye loading amount measurement, the difference in dye loading amount between the control film and sol modified film is negligible. Therefore, the significant J_{sc} increase for modified films should be mainly related to the improved electron transport efficiency in the TiO_2 film. Apparently, this was largely attributed to the significantly decreased R_0 . Open-circuit potential of DSSC is the difference between the (quasi-) Fermi level of the TiO_2 and the redox potential of the electrolyte.³¹ The V_{oc} mainly depends on the concentration of electrons in the conduction band, which is limited by recombination of conduction band electrons with I_3^- ions in the electrolyte and also oxidised dye molecules. The continuous modified TiO_2 network reduces the electron leakage,²⁸ which helps maintain the electron concentration at the conduction band. This results in the increased V_{oc} . However, V_{oc} is the maximum potential output when the electrical circuit is open (i.e., current is zero), while R_0 is the electron transport resistance between the TiO_2 network and back contact. Therefore, no iR drop was involved. The effect of R_0 on the V_{oc} is consequently not as significant as that on the J_{sc} . The fill factor (FF), is defined as $(V_{mp}J_{mp})/(V_{oc}J_{sc})$, where J_{mp} and V_{mp} represent the current density and voltage at the maximum power (i.e., $V_{mp}J_{mp}$) point.²⁹ For the modified films in our study, the aforementioned reduced electron leakage as well as the decrease R_0 , is beneficial to the reinforcement of maximum power and consequently the increase of the FF .

As previously mentioned, due to the improved interfacial connectivity of the nanoporous TiO_2 particles in the sol modified films, the R_0 values decreased significantly - by 29%, 36% and 40% for C1, C2, and C3 respectively. In Table 2, the η of DSSCs with MS1, MS2 and MS3 photoanode had a remarkable increase of 30%, 22%, 29% compared with that of C1, C2 and C3 photoanodes, respectively. This corresponding relationship was further confirmed by correlating

the R_0 values of the TiCl_4 modified films with the performance of the corresponding DSSCs. In comparison with C1, C2 and C3 photoanodes, the R_0 value of the MT1, MT2 and MT3 films decreased by 26%, 26% and 25% respectively, while the corresponding energy conversion efficiency η increased by 26%, 13%, 15% respectively. The corresponding relationships for both the sol modified film and the TiCl_4 modified films suggest that reduction of the R_0 values of TiO_2/FTO photoanodes is strongly correlated to their performance improvement. In consideration of all the changes caused by the sol modification and TiCl_4 modification, including light reflection, dye loading and R_0 , the DSSC performance enhancement, in terms of η , was largely attributed to the significant reduction of R_0 . In other words, reduction of R_0 can enhance the performance of DSSCs. R_0 can be considered as an effective quality indicator of photoanodes for DSSCs.

Conclusions

The overall electron transport resistance of a TiO_2/FTO photoanode can be measured by the proposed photoelectrochemical method. It consists of a variable resistance (R_l) and constant resistance (R_0). The R_0 value measured in the photoelectrocatalytic process is an intrinsic property of the TiO_2/FTO photoanode and is considered as the electron transport resistance of the TiO_2/FTO photoanode when the photoanode is used in the DSSC process. The proposed method is validated by good correlation between the R_0 values of various photoanodes with the performance of their corresponding DSSCs. The preliminary results indicate that the DSSC photoanode with lower R_0 value imparts better photovoltaic performance. The proposed electron transport resistance measurement provides a simple and effective alternative to evaluate the quality of the photoanodes for DSSCs.

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References

- 1 L. M. Peter, *Phys. Chem. Chem. Phys.*, 2007, **9**, 2630.
- 2 M. Graetzel, *C. R. Chim.*, 2006, **9**, 578.
- 3 H. Pettersson, T. Gruszecki, R. Bernhard, L. Haeggman, M. Gorlov, G. Boschloo, T. Edvinsson, L. Kloo and A. Hagfeldt, *Prog. Photovoltaics*, 2007, **15**, 113.
- 4 E. Palomares, J. N. Clifford, S. A. Haque, T. Lutz and J. R. Durrant, *J. Am. Chem. Soc.*, 2003, **125**, 475.
- 5 I. Kartini, D. Menzies, D. Blake, J. C. D. da Costa, P. Meredith, J. D. Riches and G. Q. Lu, *J. Mater. Chem.*, 2004, **14**, 2917.
- 6 J. A. Maine, G. Phani, J. M. Bell and I. L. Skryabin, *Sol. Energy Mater. Sol. Cells* 2005, **87**, 133.
- 7 K.-M. Lee, V. Suryanarayanan, J.-H. Huang, K. R. J. Thomas, J. T. Lin and K.-C. Ho, *Electrochim. Acta* 2009, **54**, 4123.
- 8 W. Liu, L. Hu, S. Dai, L. Guo, N. Jiang and D. Kou, *Electrochim. Acta* **55**, 2338.
- 9 F. Fabregat-Santiago, J. Bisquert, L. Cevey, P. Chen, M. Wang, S. M. Zakeeruddin and M. Graetzel, *J. Am. Chem. Soc.*, 2009, **131**, 558.
- 10 U. Opara Krasovec, M. Berginc, M. Hocesvar and M. Topic, *Sol. Energy Mater. Sol. Cells*, 2009, **93**, 379.
- 11 Y. J. Kim, Y. H. Lee, M. H. Lee, H. J. Kim, J. H. Pan, G. I. Lim, Y. S. Choi, K. Kim, N.-G. Park, C. Lee and W. I. Lee, *Langmuir*, 2008, **24**, 13225.
- 12 J. H. Noh, S. Lee, J. Y. Kim, J.-K. Lee, H. S. Han, C. M. Cho, I. S. Cho, H. S. Jung and K. S. Hong, *J. Phys. Chem. C*, 2009, **113**, 1083.
- 13 J. Qu, X. P. Gao, G. R. Li, Q. W. Jiang and T. Y. Yan, *J. Phys. Chem. C* 2009, **113**, 3359.
- 14 F. Cao, G. Oskam and P. C. Searson, *J. Phys. Chem.*, 1996, **100**, 17021.
- 15 J. Bisquert and V. S. Vakhrenko, *J. Phys. Chem. B*, 2004, **108**, 2313.
- 16 R. Kern, R. Sastrawan, J. Ferber, R. Stangl and J. Luther, *Electrochim. Acta*, 2002, **47**, 4213.
- 17 A. Zaban, M. Greenshtein and J. Bisquert, *ChemPhysChem*, 2003, **4**, 859.
- 18 S. Soedergren, A. Hagfeldt, J. Olsson and S.-E. Lindquist, *J. Phys. Chem.*, 1994, **98**, 5552.
- 19 J. Bisquert, *Phys. Chem. Chem. Phys.*, 2008, **10**, 3175.
- 20 I. Mora-Sero, T. L. Villarreal, J. Bisquert, A. Pitarch, R. Gomez and P. Salvador, *J. Phys. Chem. B*, 2005, **109**, 3371.
- 21 Y. Kondo, H. Yoshikawa, K. Awaga, M. Murayama, T. Mori, K. Sunada, S. Bandow and S. Iijima, *Langmuir*, 2008, **24**, 547.
- 22 D. Jiang, H. Zhao, S. Zhang and R. John, *J. Phys. Chem. B*, 2003, **107**, 12774.
- 23 H. Zhang, H. Zhao, S. Zhang and X. Quan, *ChemPhysChem*, 2008, **9**, 117.
- 24 S. Ito, P. Liska, P. Comte, R. Charvet, P. Pechy, U. Bach, L. Schmidt-Mende, S. M. Zakeeruddin, A. Kay, M. K. Nazeeruddin and M. Graetzel, *Chem. Commun. (Cambridge, U. K.)*, 2005, 4351.
- 25 B. C. O'Regan, J. R. Durrant, P. M. Sommeling and N. J. Bakker, *J. Phys. Chem. C* 2007, **111**, 14001.
- 26 Q. Zhang, L. Gao and J. Guo, *Appl. Catal., B* 2000, **26**, 207.
- 27 P. M. Sommeling, B. C. O'Regan, R. R. Haswell, H. J. P. Smit, N. J. Bakker, J. J. T. Smits, J. M. Kroon and J. A. M. van oosmalen, *J. Phys. Chem. B*, 2006, **110**, 19191.
- 28 H. Yu, S. Zhang, H. Zhao, B. Xue, P. Liu and G. Will, *J. Phys. Chem. C* 2009, **113**, 16277.
- 29 H. Yu, S. Zhang, H. Zhao, G. Will and P. Liu, *Electrochim. Acta*, 2009, **54**, 1319.
- 30 S. Hore, C. Vetter, R. Kern, H. Smit and A. Hinsch, *Sol. Energy Mater. Sol. Cells*, 2006, **90**, 1176.
- 31 M. Graetzel, *Inorg. Chem*, 2005, **44**, 6841.

Table captions

Table 1. The film thickness, k and R_0 values of the TiO_2/FTO photoanodes measured in the photoelectrocatalytic process.

Table 2. Photovoltaic characteristics of the DSSCs.

Figure Captions

Fig. 1 Cross-section images of the C3 control film (a) and MS3 film (b) and (c) MT3 film

Fig. 2 (a) Voltammograms of the MS3 TiO_2 photoanodes under various light intensities in 0.1 M NaNO_3 solution. Scan rate 5 mV/s, light intensity for curves 1-8 were 9.8, 9.2, 8.2, 7.2, 6.2, 5.2, 4.2, 3.4 mW/cm^2 , respectively; (b) Relationship between calculated resistances and inversed saturation photocurrent of the photoanodes. Data were derived from Fig. 2a.

Fig. 3 The I - V curves of control films and modified films with 3 layers

Fig. 4 The absorption spectra of the dye-sensitized control films and modified films.

Table 1

Photoanodes	<i>Thickness</i> (μm)	<i>k</i> (mV)	<i>R_o</i> (Ω)
C1	5	139	148
C2	9	145	258
C3	12	150	395
MS1	5	175	105
MS2	9	179	164
MS3	12	179	235
MT1	5	166	109
MT2	9	181	190
MT3	12	169	296

Table 2

Photoanodes	<i>J_{sc}</i> (mA/cm ²)	<i>V_{oc}</i> (mV)	<i>FF</i> (%)	<i>η</i> (%)
C1	8.93	630	63.7	3.60
C2	11.62	628	64.2	4.68
C3	14.18	626	63.9	5.67
MS1	10.80	645	67.0	4.7
MS2	13.04	647	68.0	5.73
MS3	16.53	653	67.8	7.32
MT1	10.51	639	68.1	4.57
MT2	12.09	641	68.0	5.27
MT3	14.91	646	67.9	6.54

Fig. 1

Fig. 2

Fig. 3

Fig. 4