An Exploratory Study on TiO$_2$ Film Thickness Related Photocurrent Decreasing in Dye-sensitized Solar Cells

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Abstract. This paper studies the effects of titanium dioxide films with different thickness on the photocurrent. The results show that titanium dioxide itself is not able to reduce Isc as long as the film thickness is less than 50$\mu$m-100$\mu$m (the electron diffusion length). The real factors affecting the photocurrent is the number of photoelectrons which could be injected into the TiO$_2$ conduction band generated by dye adsorbed on the surface of TiO$_2$. The thickness of the film provides a huge space for the dye molecules, but dye molecules quenching might play an important role to prevent the photoelectrons from injecting into the conducting band of TiO$_2$. The improvement mechanism of Isc was discussed and an intriguing approach to enhance Isc was addressed.

Introduction

Dye-sensitized solar cells (DSCs) are one of the most promising technologies for sunlight to electricity conversion. The production cost of DSCs is about ten to thirty percent of that of silicon solar cells, permitting DSCs become the most widely spread technology for large scale power generation from renewable energy source [1]. However, the overall light-to-electricity conversion efficiency ($\eta$) of DSCs has been in 12.3% at the best, far below the 30% of theoretical photoelectric limit [2]. The power conversion efficiency is determined by:

$$\eta = \frac{I_{sc} V_{oc} ff}{V_{oc}^2}$$

(1)

Where $V_{oc}$ is the open circuit photovoltage; 750~850(mV) has been obtained and the maximum attainable $V_{oc}$ is 900(mV) according to the energy band structure in DSCs. $I_{sc}$ is the short circuit photocurrent density, which shows big variation, and is a major factor in determining $\eta$, as shown in Fig.1. $ff$ is the fill factor, the ratio of the maximum power over open circuit voltage times short circuit current density. Among the best DSCs, $ff$ of 0.7~0.85 has attained, and the limitation of $ff$ is 1. For the 30% of theoretical photoelectric conversion efficiency, the maximum $I_{sc}$ should reach 33(mA/cm$^2$). However, $I_{sc}$ is usually in the range of 10~15 (mA/cm$^2$) and the highest one is 20.83 (mA/cm$^2$) achieved by J. Chae et al. [3]. Obviously, there is a large room for enhancement in the short circuit current density.

$I_{sc}$ is dependent on the abilities of photon capturing, the generation of electron-hole pairs, the injection of electrons, and the regeneration of dye molecules combined. In addition, the charge recombination at the interface and the charge trapping by defects would reduce $I_{sc}$. So it is not surprised that it is difficult to enhance $I_{sc}$. Lots of efforts have been made to increase $I_{sc}$. For instance, a transparent nanocrystalline TiO$_2$ film was combined with a microcrystalline light-scattering layer, in conjunction with an anti-reflecting film, to enhance the incident photon-to-electricity conversion efficiency (IPCE) [5]. The molecular structure of dyes was designed or several kinds of dyes were mixed to extend the light absorption spectrum to the near infrared region [6].
Increasing TiO$_2$ film thickness is a conceptually straightforward way to enhance the amount of dye molecules adsorbed on the surface of TiO$_2$ film, so as to generate more photoelectrons, and thus possibly lead to higher Isc. However, the increase of Isc with increased TiO$_2$ film thickness is quite limited as the photoelectrons may not be able to diffuse to the charge collector. It is generally believed that this effect is resulted from the poor electronic conductivity and the light transmittance of the thick TiO$_2$ film. For instance, Huang et al. reported that when TiO$_2$ film became thick, the relative size of I$_3$/I diffusing into the TiO$_2$ matrix and the lifetime of injected electrons were reduced, which caused $I_{sc}$ and $ff$ to decrease [7]. Kao et al. suggested that the decrease of $I_{sc}$ with increased TiO$_2$ film thickness was due to decreased light transmittance and led to reduced light absorption [8].

This paper reports an experimental study on the dependence of short circuit current density on the dye loading and the dependence of short circuit current density on the photoelectrode thickness. The experimental results suggested that dye molecules quenching might play an important role to prevent the photoelectrons from injecting into the conducting band of TiO$_2$. The improvement mechanism of $I_{sc}$ was discussed and an intriguing approach to enhance $I_{sc}$ was addressed.

**Experimental**

**Preparation of TiO$_2$ Photo-electrode**

The TiO$_2$ photo-electrode was prepared by the following steps: firstly, use hydrothermal method to synthesize Anatase TiO$_2$ nanocrystalline according to the literature [9]. TiO$_2$ film were immersed in an ethanol solution of N719 over night for adsorbing dye to obtain the TiO$_2$ photo-electrode. The concentration of 0.25mM and 0.05mM of N719 ethanol solution were used to immerse the TiO$_2$ films for the TiO$_2$ photo-electrodes saturatedly and non-saturatedly adsorbing dye respectively. The former is the maximum concentration which N719 dye can be dissolved in ethanol.

**Fabrication of DSC**

The dye-adsorbed TiO$_2$ electrodes were clamped with the counter electrode (a platinised FTO) into a sandwich-type cell. A drop of electrolyte solution was injected into the space between the clamped electrodes to obtain a DSC for testing of the photoelectric conversion performance characteristics.

**Measurements and Characterization**

The photoelectric conversion performance characteristics of DSCs were measured with IV Test Station 2000 (USA) which consisted of Sourcemeter 2400 (Keithley, USA), Solar Simulator 92250A-1000 (Newport, USA) and Lamp power supply 69907 (Newport, USA). The light intensity corresponding to AM 1.5 (100 mW/cm$^2$) was calibrated using a standard silicon solar cell.
The bulk resistance of the TiO$_2$ photo-electrode was tested using LCR digital electric bridge (E4980A, USA) under the illumination of the solar simulator with the light intensity of 100n(W/cm$^2$), which was described in our previous article [19]. The absorbance of TiO$_2$ photo-electrode was measured by UV-vis spectrophotometer (SP-2102UV). The thickness of TiO$_2$ films was measured by a Stylus Profiler (Dektak8, Veeco USA). The amount of adsorbed dye was determined by desorbing the dye from the TiO$_2$ surface into NaOH aqueous solution (pH=13) and measuring its absorption spectrum by UV-vis spectrophotometer (SP-2102UV). And then the concentration of adsorbed dye was analyzed with the pre-measured concentration-absorbance curve of N719 dye.

**Results and Discussion**

**Microstructure of TiO$_2$ Film**

Fig.2 is the FE-SEM images showing the microstructure of the TiO$_2$ film prepared. The TiO$_2$ film is composed of interconnected nano-particles of ~20 nm in diameter. The XRD pattern of the TiO$_2$ film shows distinguishable peaks at 2$\theta$ of 25.5°, 38.0°, 48.0°, 54.0°, 55.1°, 62.7°, 69.1° and 75.0°, corresponding to the characteristic peaks of Anatase [10] shown in the insert.

![Fig.2 FE-SEM picture of TiO$_2$ film (a) and XRD pattern of the TiO$_2$ film (b)](image)

**Relationship of TiO$_2$ Film Thickness and $I_{sc}$**

Fig.3 shows the amount of dye adsorbed linearly increases with the increasing film thickness. This result is easy to understand. Assuming the film has a homogeneous porous structure and the same
surface chemistry, the increased film thickness would lead to a linear increase in the surface area for the dye molecules to adsorb. It should be noted that the amounts of dyes adsorbed presented in Y-axis is normalized to the nominal film area (or the device surface area), not the specific surface area (or typically the BET surface area). This result suggests that the dye solution can easily penetrate throughout the entire film and the dye molecules can diffuse and absorb to all the surface area equally regardless the film thickness. The result agrees well with the literature data. For example, for the film of 10 µm in thickness, the amount of dyes adsorbed is approximately 0.08 mg/cm².

Fig. 3 Amount of the dyes adsorbed as a function of the TiO₂ film thickness

Michael Grätzel analyzed the dynamics of redox process involved in the conversion of light to electric power in DSCs and suggested the electron diffusion length (L) in TiO₂ photo-electrode could attain values in the 50~100 µm range [13]. If this is true, the increased dyes adsorbed as a result of...
increased film thickness would lead to an increased short circuit current density. At least, there would be no decrease in short circuit current density when the film thickness is larger than 15 μm. If the theory is correct and the above reasoning is acceptable, the results presented in Figure 4 would suggest that the short-circuit current density is also determined by some factors other than the amount of dye molecules adsorbed and the electron diffusion length.

**Influence of TiO$_2$ film on $I_{sc}$**

Titania film is composed of the 15~30 nm sized anatase crystals sintered to form a mesoporous structure. The inherent huge surface and defects including the grain boundaries between adjacent nanocrystals may all raise electron scattering within the mesoporous TiO$_2$ film. This effect gets more pronounced with thick film to reduce the electronic transport property of the TiO$_2$ film and, consequently lead to reduced $I_{sc}$ and ff [14].

When TiO$_2$ film adsorbed dye in a saturated state, ff declined with the film thickness increasing, just as the other researchers thought. However, when TiO$_2$ film adsorbed dye in a non-saturated state, ff did not decrease with the film thickness increasing and kept as high as 0.8~0.85 even the film thickness over 30 μm.

It is well known that ff reflects photocurrent loss during the release of photovoltage in solar cells and is determined by the rate of the electron recombination occurring during the process of the photoelectrons transported in TiO$_2$ film. The fact that ff values kept as high as 0.8~0.85 and did not decrease with the film thickness increasing indicated that it was not TiO$_2$ film itself leading to the electronic transport properties getting bad. TiO$_2$ film itself wouldn’t cause $I_{sc}$ to decrease as long as the film thickness was less than the electron diffusion length which for DSCs was 50 ~ 100 μm.

![Fig.5 Relationships of ff and film thickness of TiO$_2$ photo-electrode with saturated and non-saturated adsorbing of dye](image)

A further experiment was carried out to verify this conclusion. The bulk resistance values under illumination (denoted as R) of TiO$_2$ photo-electrodes were tested. Fig.6 showed the variation trend of R with time under the conditions of TiO$_2$ films saturatedly adsorbing dye and non-saturatedly adsorbing dye. R of the TiO$_2$ film non-saturatedly adsorbing dye is two orders of magnitude lower than the one saturatedly adsorbing dye. And the non-saturatedly adsorbing dye TiO$_2$ film obtained a resistance of several thousands ohms, which showed a good semiconductivity of the TiO$_2$ photo-electrode. It indicated that TiO$_2$ film could be a good electron acceptor and transporter in DSCs even its film thickness was over the limitation of 10~15μm.
From the above two experiment results, we noticed that the reduction of the transport efficiency of photoelectrons in DSCs concerned to the adsorption state of dye. The factor leading to $I_{sc}$ decreasing more lied in dye molecules than in TiO$_2$ film.

![Graph showing R values varying with time under different adsorption conditions of dye](image)

**Fig.6** R values varying with time under the conditions of TiO$_2$ films saturatedly adsorbing dye and non-saturatedly adsorbing dye (the area of TiO$_2$ film is 1cm$^2$; the thickness of TiO$_2$ film is about 22μm)

**Influence of dye on $I_{sc}$**

When TiO$_2$ films become thick, there might be a possibility that most of the incident light could be absorbed by the dye molecules adsorb on the upper surface layer of TiO$_2$ film and there were hardly light absorbed by the dye molecules in the bottom layer of TiO$_2$ film. Therefore, with the film thickness increasing, more and more dye molecules could not absorb the incident light to be excited to produce photoelectrons. To figure that out, we measured the absorbance of TiO$_2$ photo-electrodes at 530nm (the absorption peak of N719 dye), which was varied with the increasing dye-adsorption amount owing to film thickness increasing, as shown in Fig.7. The dye-adsorption amounts were corresponding to those in Fig.5. We also investigated the absorption spectrums in the visible wavelength range of the dye-sensitized TiO$_2$ films whose film thickness increasing with the coating times, as shown in the insert of Fig.7. It could be seen in Fig.7 that the absorbance increased with the film thickness consistently due to the dye-adsorption amount being raised and the thicker a TiO$_2$ film was, the more incident light the dye molecules absorbed. It indicated that in thick TiO$_2$ films, it was no problem for the dye molecules to absorb the incident light to generate photoelectrons. The problem was why not all these photoelectrons contribute to $I_{sc}$.

As we know, $I_{sc}$ originates from the photoelectrons injected into the conducting band of TiO$_2$ and is determined by the rate of electron injection effect. In view of the numerous photoelectrons resource in DSCs owing to the high dye-adsorption amount, there was only one possibility leading to low $I_{sc}$ that most photoelectrons were not injected into the conducting band of TiO$_2$. And considering the good electron accepting and transporting properties of TiO$_2$ film, we inferred that when the TiO$_2$ film became thick, the effect that the excited dye molecules quenching each other became dominant to prevent the photoelectrons from injecting into the conducting band of TiO$_2$. And the adsorption state of dye on the surface of TiO$_2$ film had a major influence on the possibility of the excited dye molecules quenching each other.

In a high efficiently operating DSC, the dye molecules suppose to adsorb on the surface of TiO$_2$ film monolayely and high dispersedly. Otherwise, the oxidized dye molecules could easily capture the photoelectrons produced by the other ones overlapping or interconnecting to them (i.e. quenching each other). And this electron recombination effect tended to occur right before the photoelectrons...
injected into the conducting band of TiO$_2$ because it was more thermodynamically convenient for the electrons to transfer between two connected oxidized dye molecules than they did between the dye molecule and TiO$_2$ film. This recombination could reduce the quantity and the rate of photoelectrons injected into the conducting band of TiO$_2$, therefore, leaded to the photoelectrons not contributing to $I_{sc}$.

Fig.7 Absorbance (determined at a wavelength of 530nm which is the absorption peak of N719 dye) of dye-sensitized TiO$_2$ film with the increasing dye-adsorption amount obtained by the different thickness of TiO$_2$ films (the insert shows the absorption spectrums in the visible wavelength range of dye-sensitized TiO$_2$ film with different thickness due to the repeated coating times)

It is well known that Anatase has a high adsorption capacity to dyes and there are hundreds of adsorption sites for dye molecules on a single Anatase nanocrystalline whose size was about 15~30nm. When TiO$_2$ film became thick, numerous dye molecules could crowd on the surface of TiO$_2$ film. They could be stack up, connected or twisted together, which increased the chance of quenching each other. The thicker TiO$_2$ film was, the bigger the possibility of this recombination effect was bigger. As a result, $I_{sc}$ decreased with the film thickness increasing and so did $ff$. Fig.8 is the schematic illustration of the oxidized dye molecules capturing producing photoelectrons when they aggregate on the surface of a single Anatase nanocrystalline (as shown in (a)) and injecting the photoelectrons into TiO$_2$ when they highly dispersed on the surface of a single Anatase nanocrystalline (as shown in (b)).

Fig.8 Schematic illustration of the dye molecules quenching each other (a) and injecting the photoelectrons into TiO$_2$ (b)

**Conclusions**

There are necessary and sufficient conditions for DSCs to generate a high $I_{sc}$. The necessary condition for DSCs with the possibility of producing a high $I_{sc}$ is that there are enough dye molecules adsorbing on TiO$_2$ film to be excited to produce a large amount of photoelectrons. While the
sufficient condition for DSCs to actually generate a high $I_{sc}$ is that those photoelectrons are injected into the conducting band of TiO$_2$.

Based on the experimental results and analysis above, a potential strategy for enhancing $I_{sc}$ in DSCs is suggested. Since TiO$_2$ film itself do not cause $I_{sc}$ to decrease as long as the film thickness is less than 50μm~100μm (the electron diffusion length), there is a huge space for TiO$_2$ film to adsorb a large amount of dye. At the same time, increasing the film thickness also provides a large space for dye molecules to adsorb on the surface of TiO$_2$ film high dispersive. If the aggregation of dye molecules were improved by some technical means, such as TiO$_2$ surface modification etc., the possibility of dye quenching each other could be reduced to enlarge the quantity and the rate of photoelectrons injected into the conducting band of TiO$_2$, thus enhance $I_{sc}$.

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