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 50μm-100μm (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 (η) 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:

$$\eta = I_{sc} V_{oc} ff \tag{1}$$

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 photocurrency density, which shows big variation, and is a major factor in determining η, 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.

Isc 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 Isc. So it is not surprised that it is difficult to enhance Isc. Lots of efforts have been made to increase Isc. For instance, a transparent nanocrystalline TiO2 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].
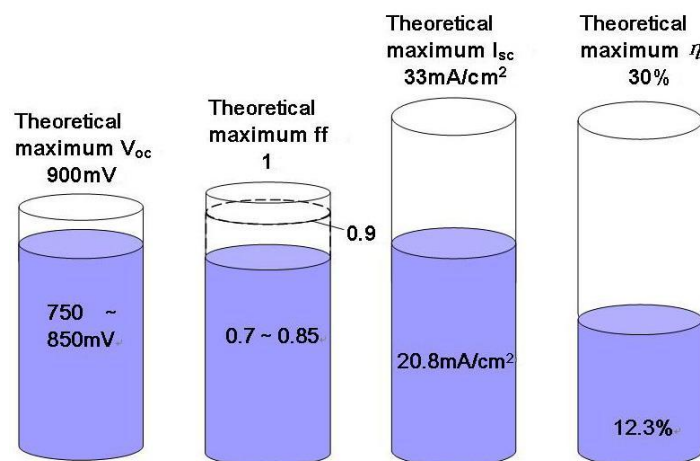
Fig.1 Room for improvement of the photoelectric conversion performances of DSCs [4]

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 theTiO_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 pervious 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 2θ 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.
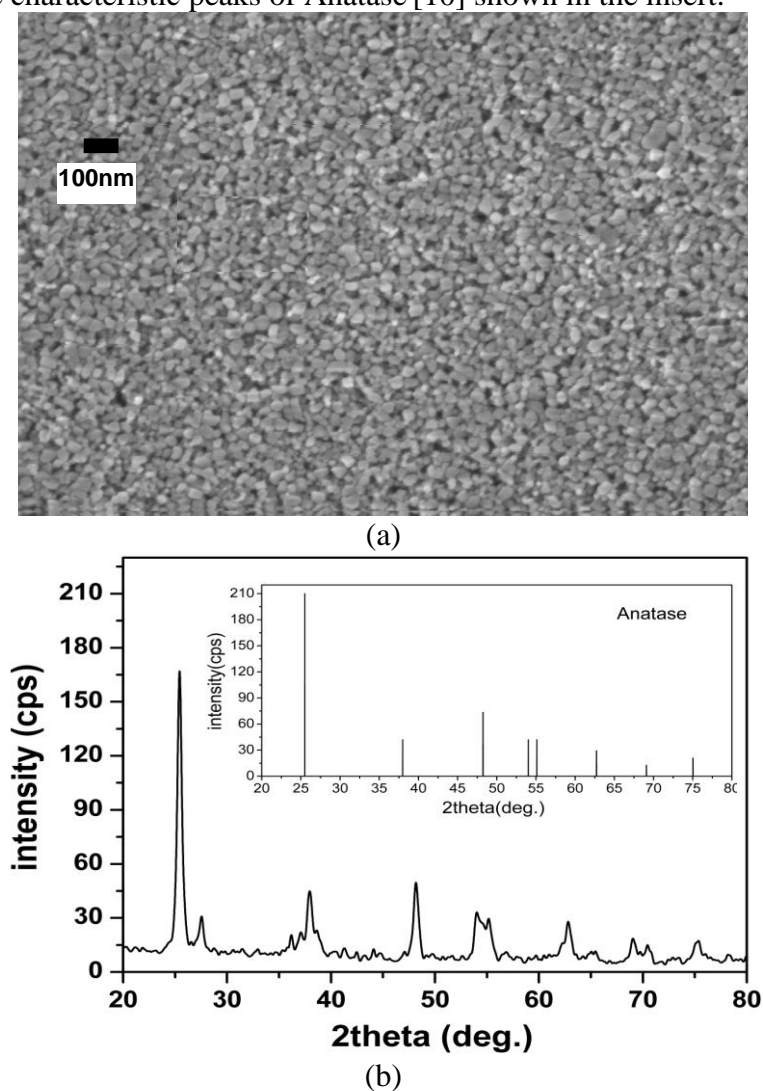

(a)

(b)

Fig.2 FE-SEM picture of TiO_2 film (a) and XRD pattern of the TiO_2 film (b)

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 of 0.08(mg/cm^2).
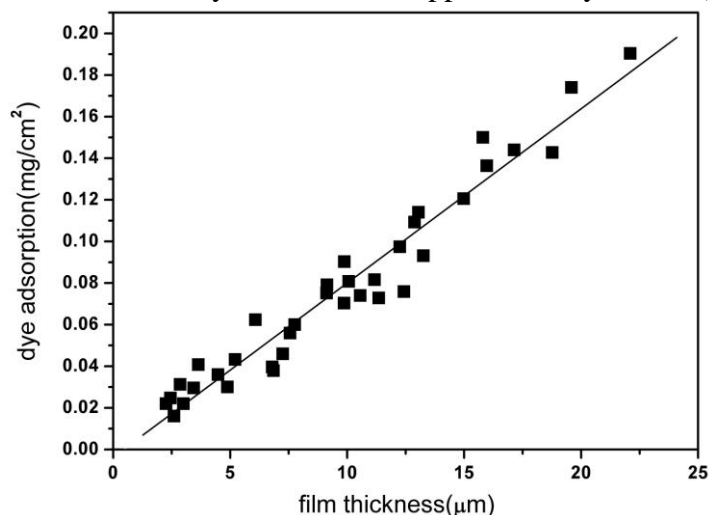

Fig.3 Amount of the dyes adsorbed as a function of the TiO$_2$ film thickness

Fig.4 shows the relationship between I_{sc} and the amount of dye adsorbed to the TiO$_2$ photoelectrode with increasing thickness, and revealed that I_{sc} did not increase with the increased amount of dye molecules adsorbed. I_{sc} reached its peak value at the amount of dyes adsorbed corresponding to a film thickness of ~12 μm; further increase in dyes adsorbed accompanied a decrease in I_{sc}. This finding is in a good agreement with the literature, the optimum film thickness is 10 ~ 15 μm [11]. It is generally accepted that the electrons generated by dye molecules through the capturing the photons, after injected to titania network can only diffuse a nominal distance of 10-15 μm. Further increase in TiO$_2$ film thickness would result in a reduction in both short circuit current density and fill factor [12].
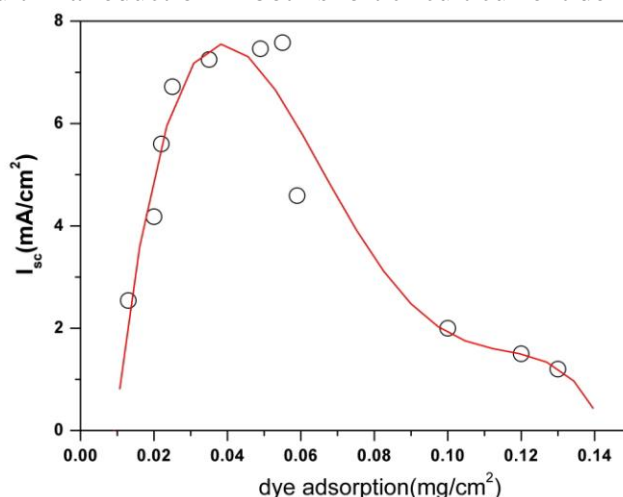

Fig.4 Variation of I_{sc} with the increasing dye-adsorption amount obtained by increasing thickness of TiO$_2$ films

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 TiO$_2$ 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.
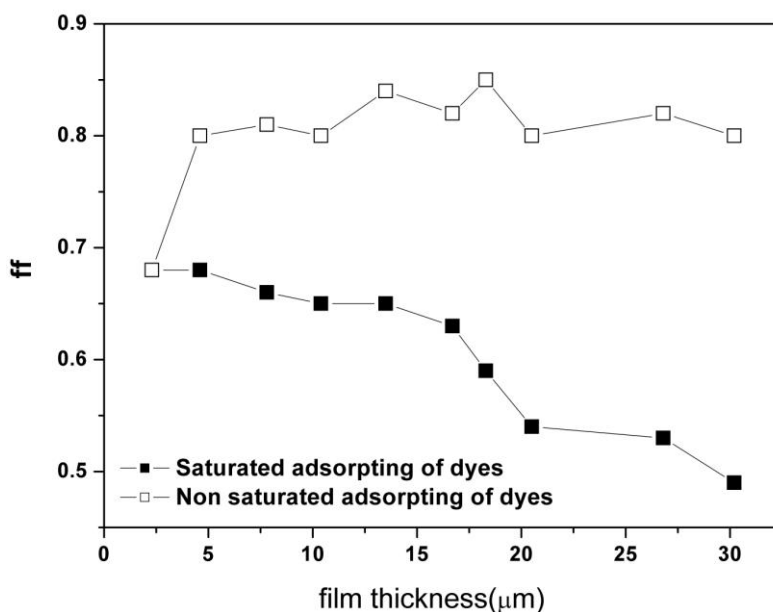

Fig.5 Relationships of ff and film thickness of TiO$_2$ photo-electrode with saturated and non-saturated adsorbing of dye

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 absorbing 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.
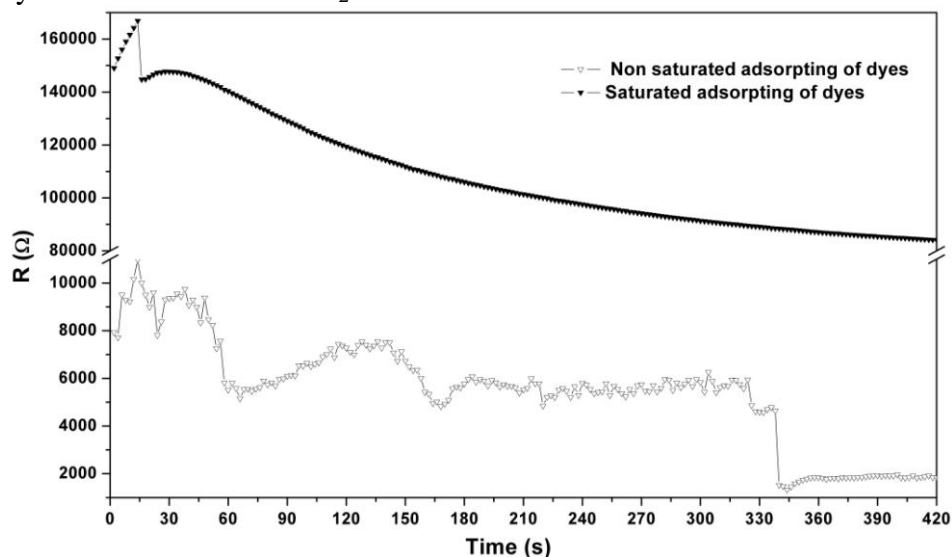

Fig.6 R values varying with time under the conditions of TiO$_2$ films saturatedly adsorbing dye and non-saturatedly adsorbing dye (the area of TiO$_2$ film is 1cm^2; the thickness of TiO$_2$ film is about 22μm)

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$_2$ was the reason leading to I_{sc} decreasing. 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}.
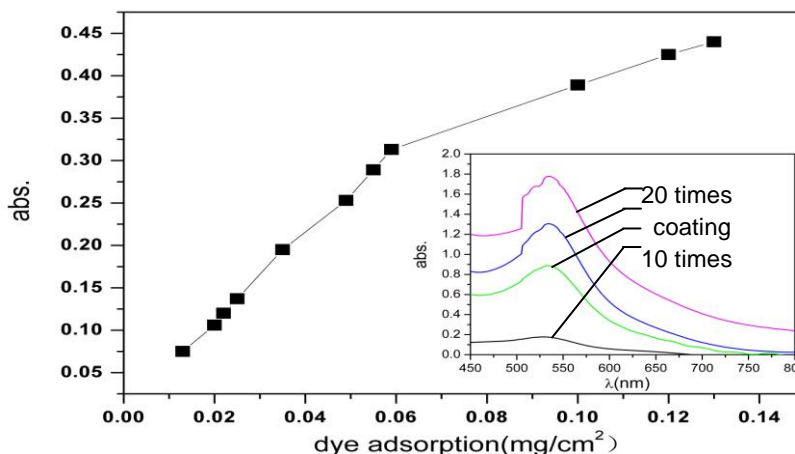

Fig.7 Absorbance (determined at a wavelength of 530nm which is the absorption peak of N719 dye) of dye-sensitized TiO_2 film with the increasing dye-adsorption amount obtained by the different thickness of TiO_2 films (the insert shows the absorption spectrums in the visible wavelength range of dye-sensitized 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)).
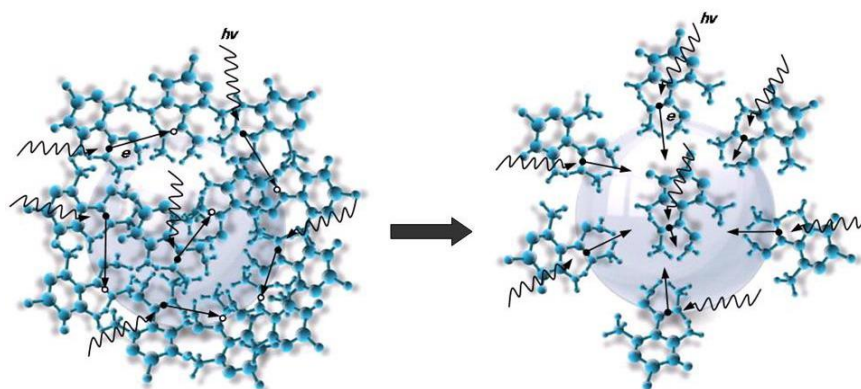

Fig.8 Schematic illustration of the dye molecules quenching each other (a) and injecting the photoelectrons into TiO_2 (b)

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}.

Acknowledgements

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