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Effect of the adsorbed concentration of dye on charge recombination in dye-sensitized solar cells

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1. Introduction

Dye-sensitized solar cells (DSCs) are one of the most promising technologies for sunlight to electricity conversion. DSCs have obtained 12.3% of the photoelectric conversion efficiency ( Voc, Isc and ff, and thus is one of the principal factors limiting power conversion efficiency [3].

The charge recombination in DSCs could take place between the injection electrons and triiodide in electrolyte at the semiconductor/electrolyte interface or oxidized dye at the semiconductor/electrode interface. As the former is calculated to take priority kinetically to the latter [4], the oxidized dye molecules have been neglected in the charge recombination of DSCs. However, some evidences implied that dye molecules could have great influence on the charge recombination in DSC.

The studies on the dependence of electron transport property on the incident light intensity in DSC indicated that the recombination of the injection electrons with oxidized dye molecules (D +) becomes important at high light intensity under the open-circuit condition where stationary electron densities in excess of 10 17 cm -3 (corresponding to more than one electron in a nanoparticle) [5,6]. In addition, the dye molecules are not independent from the electrolyte related electron recombination. Grätzel et al. [7] reported that the local l1 concentration had important influence on the electron lifetime. Under illumination, l1 is formed “in situ” by dye regeneration at the TiO 2/electrolyte interface, which is also proved by Raman spectra of dye-sensitized solar cells in situ investigated by Shi et al. [8]. The high local l1 concentration produced in the porous network under light is expected to accelerate the recapture of conduction band electrons by the local l1 and shortens their lifetime within the TiO 2 film. Peter and Wijayantha [9] reported that the recombination of electrons with tri-iodide was faster under high light intensity than under low light intensity and the electron lifetime depended inversely on the square root of the light intensity, i.e. \( \tau_l \propto \frac{1}{I_0^{0.5}} \) . High local l1 concentration may result not only from high light intensity but also from high adsorbed concentration of dye on the surface of TiO 2 film. It is reasonable to wonder if the adsorbed concentration of dye has similar effects on the charge recombination in DSC.

In this paper, the dye-adsorption capacity of anatase nanocrystalline film was first investigated to control the adsorbed concentration of dye in TiO 2 photoanode. The effect of the adsorbed concentration of dye on the charge recombination in DSCs was investigated by means of electrochemical impedance spectroscopy (EIS). And the photoelectric conversion performance characteristics of the DSC with different adsorbed concentrations of dye were measured.
2. Material and methods

2.1. Materials

All chemicals used are analytical grade. Tetrabutyl titanate, anhydrous ethanol, Nitric acid, acetylacetone (ACA), polyethylene glycol 2000, ultra pure water and Triton X-100 were used as received. cis-dithiocyanato-N,N-bis(2,2‘-bipyridyl-4-carboxylate-4’-tetrabuty ammonium carboxylate)ruthenium(II) (N719 dye), liquid electrolyte solution DHS-E23 (mixed by LiI, I₂, tert-buthyl pyridine (TBP), acetonitrile (ACN)) and Conducting glass plates (FTO, sheet resistance is 25 Ω/cm²) (used as a substrate for deposition of TiO₂ films) were purchased from Dalian Heptachroma Solar Tech. Co. Ltd.

2.2. TiO₂ photoanode preparation and cell assembly

The TiO₂ photoanode was prepared by the hydrothermal method according to the literature [10]. A TiO₂ nano-particles were first synthesized in an autoclave at 200 °C. The porous TiO₂ films were prepared from the TiO₂ nanoparticle paste on FTO glass by annealing at 450 °C for 30 min. After annealing process, the TiO₂ films were cooled to about 80 °C and then immersed in an ethanol solution of N719 over night for adsorbing dye to obtain the TiO₂ photoanodes. The TiO₂ photoanodes 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. The effective size of the DSC is 0.25 cm².

2.3. Measurements and characterizations

The photoelectric conversion performance characteristics of DSCs were measured with IV Test Station 2000 (Crowntech, 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 electrochemical impedance spectroscopy (EIS) measurements were performed with a computer-controlled potentiostat (CH1604D, USA). The frequency range is 0.01 Hz–100 kHz. The magnitude of the alternative signal is 10 mV. All impedance measurements were carried out under a bias illumination of 100 mW cm⁻² (calibrated using a standard silicon solar cell) from a 500 W xenon light source and under open-circuit conditions. The obtained spectra were fitted with ZSimpWin software (v3.1, Princeton Applied Research) in terms of appropriate equivalent circuits.

The morphology and microstructure of TiO₂ films were characterized by field-emission scanning electron microscopy (FE-SEM) (Leo-Supra35, Germany). The crystal structures of the samples were characterized by X-ray diffractometer (XRD) (Phillips PW 1830) using Ni-filtered Cu Kα radiation (λ = 1.54056 Å).

The TiO₂ film thickness was measured by a Stylus Profiler (Dektak8, Veeco, USA). The dye-loading of TiO₂ film was determined by desorbing the dye from the TiO₂ surface into NaOH aqueous solution (pH = 13) and measuring its adsorption spectrum by UV–Vis spectrophotometer (SP-2102UV, China). And then the concentration of desorbed dye was analyzed with the pre-measured concentration-absorbance curve of N719 dye to obtain the amount of dye adsorbed on the surface of TiO₂ film.

3. Results and discussion

3.1. Microstructure and dye-adsorption capacity of TiO₂ films

Fig. 1 shows the FE-SEM image of the microstructure of the TiO₂ film prepared. The TiO₂ film is composed of interconnected nanoparticles of ~20 nm in diameter. The XRD pattern of the TiO₂ 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 [11].

After immersing the resultant TiO₂ nanocrystalline film into the N719 dye ethanol solution with different concentrations or for different soaking time, the dye-loading of TiO₂ film varies within a certain range. The adsorption of dye molecules on the surface of TiO₂ film is known as a chemical adsorption process [12], which means that the dye-adsorption reaches a saturation state when the dye-loading does not increase any further. Fig. 2 shows the dye-loading of TiO₂ film obtained in different adsorption conditions. By soaking the TiO₂ film in the dye solution for 24 h, the dye-loading increased with the concentration of dye solution increasing and became constant when the concentration of dye solution exceeded 0.3 mM, as shown in Fig. 2a. Alternatively, by soaking TiO₂ film in the dye solution with a concentration of 0.5 mM, the dye-loading increased with the soaking time increasing and remained unchanged when the soaking time exceeds 24 h, as shown in Fig. 2b.

The adsorbed amount of dye (D₀) in unit specific surface area of TiO₂ film (S) by:

\[
C_0 \text{ (mol m}^{-2} \text{ kg}^{-1}) = \frac{D_0 \text{ (mol)}}{S \text{ (m}^2 \text{ kg}^{-1})}
\]  

(1)

For TiO₂ films composed by the nano-particles with a certain size and shape, thus the same specific surface area and pore structure, the available surface area for dye molecules adsorption
increases linear with the thickness of the TiO\textsubscript{2} film \cite{13}. \(C_0\) could be represented by the ratio (\(C\)) of dye-loading (\(D\)) to the TiO\textsubscript{2} film thickness (\(F\)) and calculated by:

\[
C = \frac{D \times 10^{-8} \text{mol cm}^{-2}}{F \text{lm}^{-1}}
\]  

(2)

Fig. 3 shows the increased dye-loading and the corresponding adsorbed concentration of dye obtained with increased TiO\textsubscript{2} film thickness. In saturated dye-adsorption state, the dye-loading of TiO\textsubscript{2} film increased proportionally with the increase in TiO\textsubscript{2} film thickness, as the available surface area for dye molecules adsorption increases linear with the thickness of the TiO\textsubscript{2} film. And the adsorbed concentration of dye, which is \(\sim 0.4\) mol \(\text{lm}^{-1}\), remained almost constant.

If the dye adsorption process stops before saturation, unsaturated state would be obtained. The unsaturated state with different amount of loaded dye can be achieved by using low concentration dye solution and insufficient dye loading time. By immersing TiO\textsubscript{2} films with different film thickness into the N719 dye ethanol solution with a concentration of 0.1 mM with which the TiO\textsubscript{2} film absorbs dye unsaturatedly, the different adsorbed concentration of dye can be obtained with the similar dye-loading while different film thickness, as shown in Fig. 4a. Alternatively, by soaking TiO\textsubscript{2} films with the similar thickness for the time shorter than the 8 h when the TiO\textsubscript{2} film adsorbs dye unsaturatedly, the different adsorbed concentration of dye can be obtained with the similar film thickness while different dye-loading, as shown in Fig. 4b.

3.2. EIS analysis

EIS has proven to be useful for studying electron transport and charge recombination in DSCs. Applying appropriate equivalent circuits, the interfacial electron transport resistance and lifetime of the electron in TiO\textsubscript{2} photoanode can be derived from the EIS analysis \cite{14}. The equivalent circuit for DSC is shown in Fig. 5. From left to right, \(R_{ct1}\) is the resistance of the FTO/TiO\textsubscript{2} contact...
and CPE1 is the capacitance of this interface; $R_{ct2}$ is the charge transport resistance at the TiO$_2$/electrolyte interface; CPE2 is the capacitance of this interface; $Z_{w1}$ is the impedance describing the diffusion of the electron in the mesoscopic TiO$_2$ film; $Z_{w2}$ is the impedance describing the diffusion of I$_3^-$ in the electrolyte; $R_{ct3}$ is the charge-transfer impedance at the counter electrode; CPE3 is the double layer capacitance at the electrolyte/Pt–FTO interface.

The EIS data can be analyzed by the Nyquist diagram and Bode phase plot. The resistance values of the interfaces in DSC can be fitted by the Nyquist diagram and the lifetime of the electron in TiO$_2$ photoanode can be calculated from the Bode plot. The Nyquist diagram features typically three semicircles that in the order of increasing frequency are attributed to the Nernst diffusion within the electrolyte, the electron transfer at the TiO$_2$/electrolyte interface and the redox reaction at the platinum counter electrode [15]. And the Bode phase plot features three characteristic frequency peaks in low-frequency, mid-frequency and high-frequency range according to those three processes respectively. The lifetime of electrons within the TiO$_2$ photoanode ($\tau_e$) can be estimated from the maximum angular frequency ($\omega_{\text{max}}$) of the impedance semicircle arc at middle frequencies, according to the relation:

$$\tau_e = \frac{1}{\omega_{\text{max}}} = \frac{1}{2\pi f_{\text{max}}}$$  \hspace{1cm} (3)

where $f_{\text{max}}$ is the maximum frequency of the mid-frequency peak [16].

The EIS is measured under illumination at open circuit voltage because (1) the oxidized dye molecules are produced by incident light; (2) I$_3^-$ is formed “in situ” by dye regeneration at the TiO$_2$/electrolyte interface, which is more suitable for interpreting the effect of dye on the electron recombination. In addition, at open circuit voltage and under illumination, there is no net current flowing through the cell. All the injected electrons are recaptured by I$_3^-$ at the FTO/electrolyte interface before being extracted to the external circuit. Meanwhile, the oxidized dye is regenerated by I$^-$. The adsorbed photon energy is converted to heat through the two coupled redox cycles involving sensitize electron injection, dye...
regeneration and electron recapture by $I_3$ [7]. Under this circumstance, the electron life time within the TiO$_2$ film could largely depend on the film thickness. In thin TiO$_2$ films, the actual diffusion length of electrons is too short that the electrons quickly reach the back of TiO$_2$ film and complete their transfer process to investigate the effect of the charge recombination on the electron life time within the TiO$_2$ electrode. So the thick TiO$_2$ films in which the actual diffusion length of electrons is compared to or slightly longer than their free diffusion length ($L_d$) should be used to investigate the influence of the adsorbed concentration of dye on the electron recombination in DSCs. In general, the optimal TiO$_2$ film thickness is 10–15 μm [17], so the TiO$_2$ films with the thickness greater than 15 μm were used for the EIS analysis.

Fig. 6 shows the impedance spectra of the DSCs with different adsorbed concentration of dye. The calculated $\tau_e$ and measured $R_{ct2}$ are listed in Table 1. The impendence due to electron transfer from the conduction band of TiO$_2$ film to $I_3$ in the electrolyte is presented by $R_{ct2}$, i.e. the radius of the semicircle in intermediate-frequency regime [18]. When the adsorbed concentration of dye decreasing, $R_{ct2}$ increases evidently, indicating that the charge recombination in DSC decreases. And no matter the film thickness of TiO$_2$ photoanodes were different or not, the same tendency was observed. $\tau_e$ increases with the adsorbed concentration of dye decreasing, $\tau_e$ is known determined by the charge recombination between the injection electrons transported within the TiO$_2$ film and $I_3$ in electrolyte [19]. Since $I_3$ is formed “in situ” by dye regeneration at the TiO$_2$/electrolyte interface, under a certain incident light intensity, the decrease of the adsorbed concentration of dye leads to the concentration of local $I_3$ increasing, which accelerates the recombination between the injection electrons and $I_3$. It is intriguing that under the circumstance of the TiO$_2$ film thickness increasing, $\tau_e$ still increases with the adsorbed concentration of dye decreasing, which indicates that $\tau_e$ depends more on the adsorbed concentration of dye than on the TiO$_2$ film thickness. When TiO$_2$ film saturatedly adsorbed dye and was with a high adsorbed concentration of dye of 0.398 mol μm$^{-3}$, the TiO$_2$ photoanode obtained the smallest $R_{ct2}$ and the shortest electron life time ($\tau_e$). It suggested that decreasing the adsorbed concentration of dye could improve the charge recombination in DSC as well as the electron transport properties of TiO$_2$ film.

### 3.3. Investigation of energy conversion performance

Charge recombination determines both the current and the open circuit voltage that are generated in DSCs. The fill factor ($ff$) is a measure of increase in recombination (decreased in photocurrent) with increasing photovoltage. An obvious possible cause for a low fill factor is increased electron transfer rate from the TiO$_2$ to the triiodide, i.e. charge recombination, during the process of injection electrons transported within TiO$_2$ layer [20]. The EIS analysis indicated that the charge recombination in DSC decreased with the adsorbed concentration of dye decreasing. The photoelectric conversion characteristics of the DSCs with different adsorbed concentration of dye, shown in Table 2, were measured to investigate how the effect affected the energy conversion performance. It can be seen that the fill factors ($ff$) increased significantly with the adsorbed concentration of dye decreasing. High $ff$ of 0.73–0.78 were obtained at C = 0.031–0.177 mol μm$^{-3}$. This concurs with the EIS analysis above, i.e. resulting from the decrease of the electron recombination occurring at the interface of TiO$_2$/electrolyte. And the lowest $ff = 0.6$ was obtained by the DSC with the highest adsorbed concentration of dye under the condition of the TiO$_2$ film saturatedly adsorbing dye. In DSCs, the optimum TiO$_2$ film thickness is known to be 10–15 μm which is in the range of the diffusion length of electrons within TiO$_2$ layer. And increasing film thickness results in electrons incapable of diffusing through the TiO$_2$ layer to reach the conductive substrate and causes the electron loss. Consequently, the photocurrent decreases significantly with the photovoltage increasing, which leads to an obvious decrease in fill factor [21]. However, when the adsorbed concentration of dye decreased, the TiO$_2$ photoanodes with the film thickness over 20 μm still obtained the high fill $ff$ of 0.75–0.78. It implies that electrons could diffuse a longer distance within TiO$_2$ layer when the adsorbed concentration of dye is lower.

$V_{oc}$ fluctuated with the adsorbed concentration of dye slightly and the highest $V_{oc}$ was obtained at low C = 0.141–0.290 mol μm$^{-3}$, no matter for the optimum film thickness (~15 μm) or the thick one (over 20 μm). $I_{sc}$ increased with the adsorbed concentration of dye increasing. It is still required of high dye-loading to generate high $I_{sc}$. However, for the optimum film thickness of ~15 μm, the highest $I_{sc}$ was obtained at C = 0.345 mol μm$^{-3}$ not at C = 0.411 mol μm$^{-3}$, the highest adsorbed concentration of dye obtained under the condition of the TiO$_2$ film saturatedly adsorbing dye. Grätzel [22] analyzed the dynamics of redox process involved in the conversion of

### Table 1

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<tr>
<th>C (mol μm$^{-3}$)</th>
<th>TiO$_2$ film thickness (μm)</th>
<th>$R_{ct2}$ (Ω)</th>
<th>$\tau_e$ (ms)</th>
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<td>0.889</td>
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### Table 2

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<th>C (mol μm$^{-3}$)</th>
<th>Dye-loading (10$^{-6}$ mol cm$^{-2}$)</th>
<th>TiO$_2$ film thickness (μm)</th>
<th>$I_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (mV)</th>
<th>$ff$</th>
<th>η (%)</th>
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light to electric power in DSCs and reported that for top quality cells, the electron diffusion length \((L)\) in TiO₂ photo-electrode could attain values in the 50–100 \(\mu m\) range. If this is true, the increased dye-loading and simultaneously decreased adsorbed concentration of dye as a result of increased film thickness would lead to an increased short circuit current density.

The energy conversion efficiency \(\eta\) of 5.34\% was obtained at \(C = 0.345\) mol \(\mu m^{-3}\). 13\% higher than that of 4.74\% at \(C = 0.411\) mol \(\mu m^{-3}\). Although only \(~10\%\) enhancement of energy conversion efficiency was obtained in this study, there would be bigger improvement space on the performance of DSC by the modification of the TiO₂ surface, other than simply decreasing the concentration of dye solution where TiO₂ films soaking, to achieve the best dispersity of dye molecules.

4. Conclusions

A significant effect of the adsorbed concentration of dye on charge recombination in DSCs was observed. Owing to this effect, the DSC kept the fill factors as high as 0.78 even though the TiO₂ film thickness exceeded 20 \(\mu m\), which is intriguing in the study of the charge recombination in DSCs. As the adsorbed concentration of dye was just altered by changing the concentration of dye solution that TiO₂ films soaking in or the soaking time, there might be aggregation of dye molecules, which limited the improvement of cell performance. In our future studies, the adsorbed concentration of dye will be adjusted through the modification of TiO₂ surface chemistry. By improving the dispersity of dye molecules on the surface of TiO₂ films, the TiO₂ photoanode could decrease the adsorbed concentration of dye and keep high dye-loading as well, which makes the DSC obtain high \(I_sc\).

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