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A study on the electron transport properties of TiO_2 electrodes in dye-sensitized solar cells

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Abstract

The influences of annealing temperature and different poly (ethylene glycol) (PEG) contents in nano-crystalline TiO_2 electrodes with and without N3 dye on the electron transfer in a dye-sensitized solar cell (DSSC) were investigated. It is found that the power conversion efficiency increases with the increase in annealing temperature and becomes saturated at 400–500 °C, and further increase lowers the performance which is consistent with the enhancement of the crystalline TiO_2 particles observed in X-ray diffraction (XRD) patterns and scanning electron microscopy (SEM) images. Electrochemical impedance spectroscopy (EIS) also confirms this behavior. These results have been further verified by studying the electron lifetimes (τ_e) and electron diffusion coefficients (D_e) of a bare TiO_2 and a dye-sensitized TiO_2 film using a pulsed laser spectrometer. It is noted that both the electron lifetime and the electron diffusion coefficient increase with the increase in annealing temperature. However, the evolution of rutile TiO_2 begins beyond 600 °C and this lowers the dye absorbance and the electron diffusion coefficients of TiO_2 electrodes. A similar study was made by varying the content of the PEG in the TiO_2 films. It is found that with the increase in the PEG content, a decrease in the electron lifetimes and a little hike in the electron diffusion coefficients are noted, where the cell performance remains almost the same. In addition, the dye adsorption decreases the electron lifetime and increases the electron diffusion coefficient of the TiO_2 films regardless of the PEG content and the annealing temperature.

Keywords: Dye-sensitized solar cells; Nanocrystallined TiO_2; Dye adsorption; Electron transfer

1. Introduction

Dye-sensitized solar cells (DSSCs) have been the subject of intense study on account of their high conversion efficiency and low cost [1]. These solar cells usually employ liquid electrolytes containing I^-/I_3^- redox couple as supporting electrolyte in order to reduce the dye cation, generated by the injection of the photo-excited electron. Though the electrons in the nano-TiO_2 film are surrounded by cations, it has been considered that no large electric field gradient is found in the film [2,3]. The transport of electrons in the TiO_2 electrode has been mainly related with their diffusion coefficient [4–6]. The electrons must travel a distance in the film to reach the transparent conductive oxide (TCO) layer before charge recombination. Several groups have developed trapping models, which assume that intraband charge trap sites exist in the films and electron travel through the events of trapping and de-trapping [7,8]. Studies on the lifetime of electrons in the TiO_2 electrode were performed in relation to employment of various dyes molecules [9] and electrolytes [10,11]. Further, the effects of TiO_2 surface treatment [12], applied bias voltage [13], TiO_2 crystalline type [14], nanoparticles size [15] and TiO_2 nanoparticles preparation methods and annealing temperature [16] on the performance of the DSSCs were also studied. In this work, we had investigated the influences of different annealing temperatures and weight percentages of poly (ethylene glycol) (PEG) on the performance of the DSSC as well as lifetime of electrons in the TiO_2 electrode.

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2. Experimental

Anhydrous LiI, I_2, PEG and 4-tertiary butyl pyridine (TBP) were obtained from Merck and titanium (V) isopropoxide (+98%) and deoxycholic acid (DCA) were purchased from Acros and used as such. CH_3CN and tertiary butanol were purchased from Merck and water molecules were removed by putting molecular sieves (4 Å) into the solvent. The N3 dye was the commercial product obtained from Solaronix S.A., Aubonne, Switzerland.

The preparation of TiO_2 precursor and the electrode fabrication were carried out based on previous literature [17] except after autoclave treatment, where the solution was concentrated to 13 wt% and PEG (M.W. 20,000) was added to the TiO_2 paste to prevent the film from cracking during drying. The TiO_2 paste was coated on a fluorine-doped tin oxide (FTO) glass plate ($R_{sh} = 25\,\Omega$/square, Sinonar Corporation, Hsinchu, Taiwan) using glass rod method.

An active area of 0.25 cm^2 was selected from sintered electrode and the electrodes were immersed in 3×10^{-4} M solution of *cis*-di(thiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium (II) (N3 dye) containing acetonitrile and tertiary butanol (in the volume ratio of 1:1) for 24 h. Pt (100 nm thick) sputtered on FTO was used as the counter electrode and the electrolyte was composed of 0.5 M lithium iodide (LiI)/0.05 M iodine (I_2)/0.5 M TBP in CH_3CN.

Micrographs were obtained using a Hitachi S-4700 scanning electron microscope (SEM). X-ray diffraction (XRD) patterns were monitored using a Rigaku RAD system with CuK_α radiation. The film thickness was measured using profilometer (Sloan Dektak 3030). The photoelectrochemical characterizations of the DSSCs were carried out by using an AM 1.5 simulated light radiation. The light source was a 450 W Xe lamp (Oriel, ♯6266) equipped with a water-based IR filter and AM 1.5 filter (Oriel, ♯81075).

The photovoltage transients of assembled devices were recorded with a digital oscilloscope (LeCroy, model LT322). Pulsed laser excitation was applied by a frequency-doubled Q-switched Nd:YAG laser (Spectra-Physics laser, model Quanta-Ray GCR-3-10) with 2 Hz repetition rate at 355 and 532 nm, respectively, and 7 ns pulse width at half-height. The beam size was larger than 0.25 cm^2 to cover the area of the device with an incident energy of 1 mJ/cm^2. The average lifetime of electron can be estimated approximately by fitting a decay of the open circuit voltage transient with $\exp(-t/\tau_e)$, where t is the time and τ_e is an average time constant before recombination. Electron diffusion coefficient was estimated by fitting a decay of the current transient with $\exp(-t/\tau_c)$ that was derived from the equation of continuity for electrons in the conduction band [18], where t and τ_c are the time and average time constant, respectively. Then, the apparent diffusion coefficient of electron can be estimated by

$$D_e = w^2/2.35\,\tau_c, \tag{1}$$

where w is the film thickness and the factor 2.35 arises from the geometry of the diffusion problem.

The photoelectrochemical characteristics and the AC-impedance measurements of the DSSCs were recorded with a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie, the Netherlands) under constant light illumination of 100 mW/cm^2. The applied bias voltage and AC amplitude were set at open-circuit voltage of the DSSCs at 10 mV between the FTO-Pt counter electrode and the FTO-TiO_2-dye working electrode, respectively, starting from the short-circuit condition [19]. The impedance spectra were analyzed by an equivalent circuit model interpreting the characteristics of the DSSCs [20].

3. Results and discussion

The effect of different annealing temperatures of the TiO_2 electrode on the crystalline nature of the TiO_2 particles was investigated using XRD and the results are shown in Fig. 1. Only the samples those were autoclaved at a temperature higher than 300 °C exhibits sharp peaks corresponding to anatase phase. However, at 600 °C, the evolution of rutile-TiO_2 is observed. Furthermore, the crystalline nature of the TiO_2 particles increases with the increase in annealing temperature. Surface morphology of the TiO_2 films obtained by SEM for different annealing temperatures is shown in Fig. 2. It reveals a porous structure of the TiO_2 particles with an average size of about 20 nm for sintering from 300 to 500 °C (Fig. 2a–c). However, the SEM image obtained at 600 °C (Fig. 2d) shows the formation of large TiO_2 particles and this may be correlated with the phase transformation of few TiO_2 nanoparticles from anatase to rutile [17]. The results obtained from the XRD data further support this (Fig. 1).

Table 1 shows the performance of the DSSC with the TiO_2 electrodes (only 5 μm) thickness annealed at different temperatures. From this table, it is observed that the

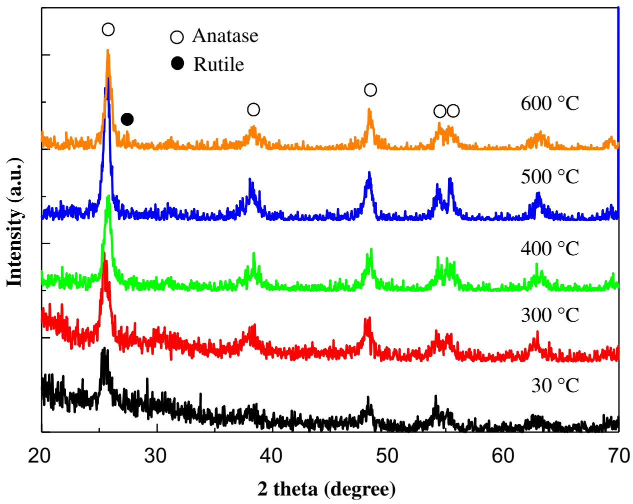

Fig. 1. XRD patterns of the TiO_2 film annealed at different temperatures.

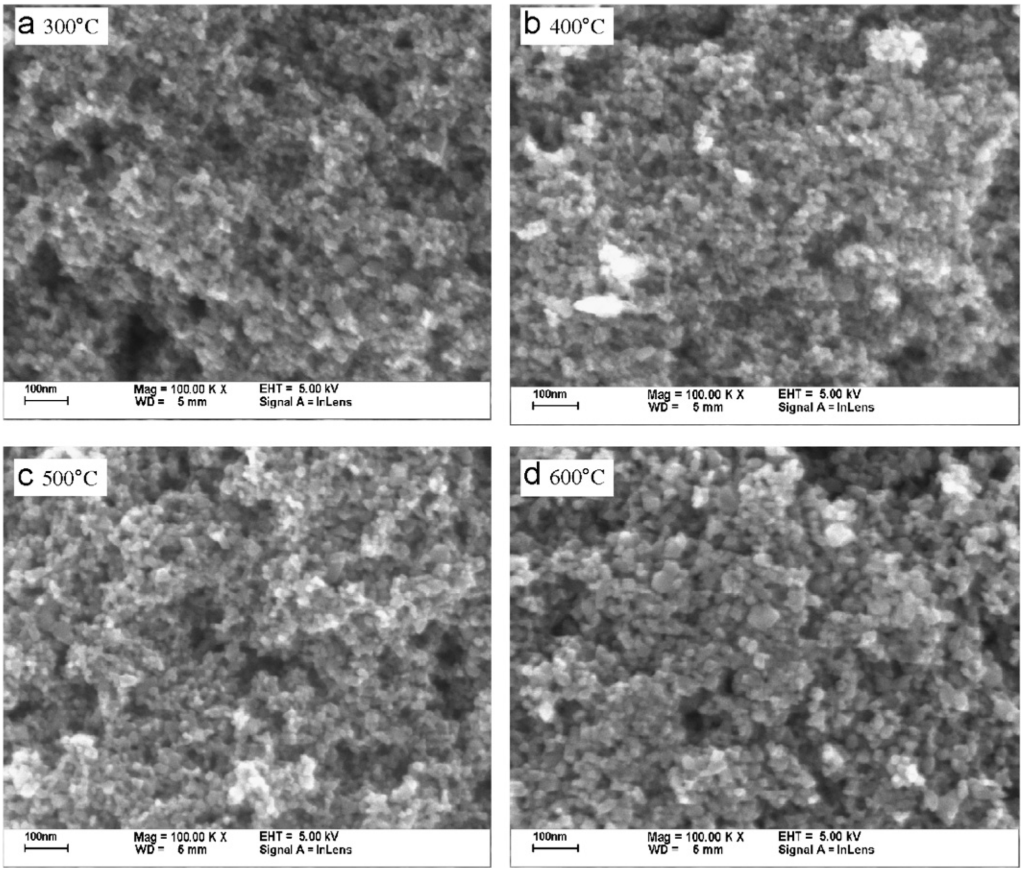

Fig. 2. SEM images of the TiO_2 film annealed at different temperatures.

Table 1
Cell performances of the DSSCs with TiO_2 films annealed at different temperatures

Sample[a] no.	Annealing temperature (°C)	J_{SC} (mA/cm^2)	V_{OC} (V)	η (%)	FF
1	—	1.76	0.645	0.57	0.498
2	300	9.80	0.781	5.01	0.655
3	400	11.76	0.783	5.72	0.622
4	500	11.20	0.763	5.35	0.626
5	600	7.72	0.824	4.23	0.666

[a] The thickness of TiO_2 was about 5 μm.

photoelectrochemical characteristics such as open circuit voltage (V_{OC}), short circuit current density (J_{SC}), fill factor (FF) and the conversion efficiency (η) of the DSSC containing un-sintered TiO_2 electrode is very low; however, these performance characteristics increase with the increase in annealing temperature and remains stable at 400–500 °C. The cell efficiency decreases at the annealing temperature of 600 °C. This may be correlated with the coarsening of TiO_2 anatase nanoparticles, and that the anatase particle size could start to increase at 600 °C, leading to a lower surface area. Alternatively, the evolution of rutile TiO_2, which possesses larger size, less surface area and slower electron diffusion rate, has been reported [14]. The low cell performance at 600 °C can also be related with the decrease in the dye adsorption onto the TiO_2 electrode. In connection with this, we studied the effect of dye adsorption onto the TiO_2 electrodes at different annealing temperatures. Our experimental results (not shown here) revealed that the amount of dye adsorption was found to be maximal up to 500 °C and it decreased with further increase in annealing temperature.

Fig. 3a shows electrochemical impedance spectroscopic (EIS) analysis of the DSSC associated with different annealing temperatures of the TiO_2 electrodes and the equivalent circuit is shown in Fig. 3b. In general, the EIS spectrum of the DSSC containing liquid electrolyte shows three semicircles in the measured frequency range of 10 mHz–65 kHz. The ohmic serial resistance (R_s) corresponds to the electrolyte and the FTO resistance and the resistances R_{ct1}, R_{ct2} and R_{diff} correspond to the charge transfer process occurring at the Pt counterelectrode, the TiO_2/dye/electrolyte interface and the Warburg diffusion process of I^-/I_3^- in the electrolyte, respectively. High interfacial charge transfer resistance (R_{ct2}) resulting from large semi-circle is observed for the DSSC containing un-sintered TiO_2 electrode and the R_{ct2} decreases with increase in annealing temperature from 300 to 500 °C (Fig. 3a). On the other hand, an increase in the R_{ct2} is noted at 600 °C (Fig. 3a). Presumably, this is due to the partial transformation of anatase TiO_2 to form rutile TiO_2 and results in a larger particle size and thus a slower electron diffusion rate.

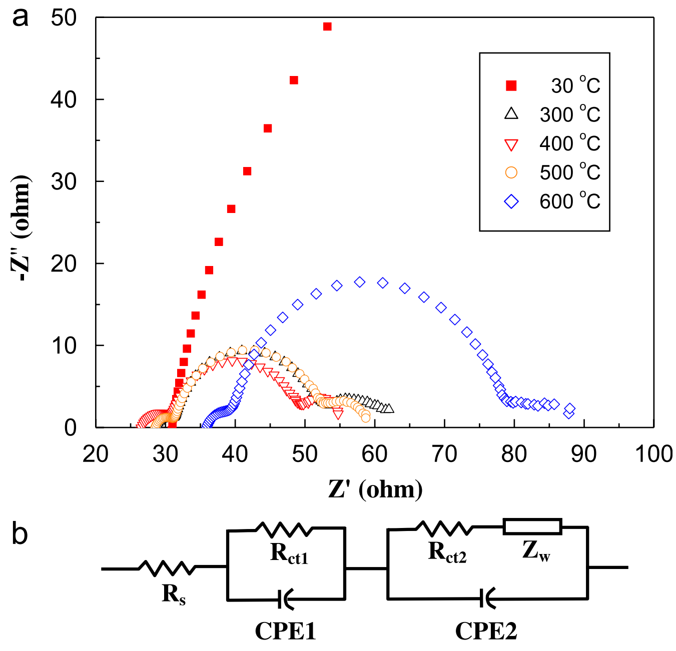

Fig. 3. (a) EIS spectra of the DSSCs with TiO_2 film annealed at different temperatures; (b) equivalent circuit for (a).

Laser-pulse induced photovoltage transients were recorded for bare and dyed TiO_2 electrode at different annealing temperatures (from 30 to 600 °C). All experiments were repeated for three times at each annealing temperature. The error bar represents the range of variation of the three data collected. The resultant electron lifetime (τ_e) and electron diffusion coefficients (D_e) were plotted as a function of increase in the annealing temperature (Fig. 4a and b). From Fig. 4a, it has been observed that the τ_e of bare TiO_2 electrode is higher than that of dyed TiO_2 and the τ_e in both cases increase from 300 to 600 °C. On the other hand, D_e of dyed TiO_2 electrode is higher than that of bare TiO_2 electrode and the D_e increases from 30 to 400 °C and then decreases at a high temperature of 600 °C (Fig. 4b). This is once again correlated with the formation of the rutile TiO_2 particles that has low electron diffusion coefficient. Further, this result also implies that the crystal structures of the particles in both bare and dyed TiO_2 electrodes influence the D_e obviously.

We had also measured the value of D_e of the TiO_2 films adsorbed with DCA, instead of N3 dye, and found that the value of D_e was higher for the former ($2.31 \times 10^{-4}\,cm^2/s$) when compared to the latter ($0.47 \times 10^{-4}\,cm^2/s$). This indicates that adsorption of carboxyl group increases the value of the D_e in the TiO_2 electrode.

It is well known that the addition of PEG to the TiO_2 colloidal solution, after autoclaving, influences the porosity

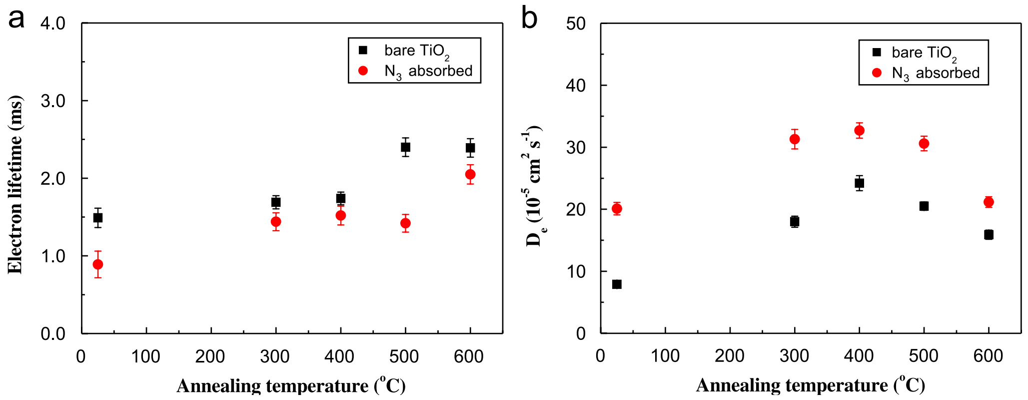

Fig. 4. Plots of (a) the electron lifetimes and (b) electron diffusion coefficients of bare and dyed TiO_2 films annealed at different temperatures.

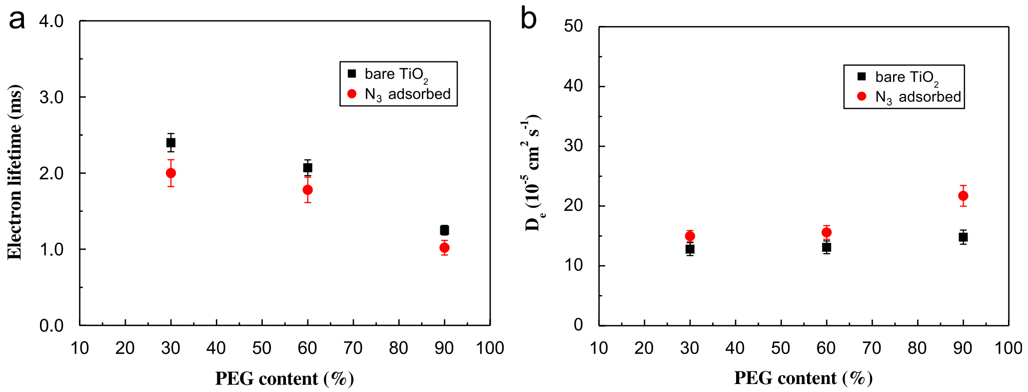

Fig. 5. Plots of (a) the electron lifetimes and (b) electron diffusion coefficients of bare and dyed TiO_2 films containing different contents of PEG.

Table 2
Cell performances of the DSSCs with TiO_2 films annealed at 500 °C containing different PEG contents

Sample[a] no.	PEG contents (%)	J_{SC} (mA/cm^2)	V_{OC} (V)	η (%)	FF
4–1	30	11.00	0.763	5.25	0.626
4–2	60	11.68	0.775	5.63	0.622
4–3	90	11.60	0.781	5.81	0.642

[a] The thickness of TiO_2 was about 5 μm and annealed at 500 °C.

of the TiO_2 electrode [21]. Herein, we have investigated the influence of lifetime of electrons in the TiO_2 electrode as well as the performance of the DSSC by varying the amount of PEG content in the TiO_2 electrode (the thickness of the TiO_2 electrode is kept at 5 μm and the annealing temperature is maintained at 500 °C). Once again, all experiments were repeated for three times at each PEG content. The error bar represents the range of variation of the three data collected. Fig. 5a and b brings the correlation between the electron lifetime and its diffusion coefficient in the TiO_2 electrode with and without dye for different PEG contents (30%, 60% and 90%) and Table 2 shows the performances of the DSSCs containing the TiO_2 electrodes with the above PEG contents. The electron lifetime (D_e) decreases and the value of the D_e increases with the increase in PEG content in both cases (Fig. 5); the conversion efficiency of the DSSC changes slightly (5–6%) (Table 2) and this shows that there is not much change in the electron diffusion lengths in hiking the PEG content.

4. Conclusions

From the above results, it is concluded that the conversion efficiency of the DSSC increases with the increase in annealing temperature of the TiO_2 and remains stable at 400–500 °C, however, further increase lowers the cell performance and this is correlated with the evolution of rutile phase of TiO_2 particles, as confirmed from SEM images, XRD patterns of the TiO_2 electrode and EIS studies of the DSSC. Further, our investigations on the electron lifetime and the electron diffusion coefficient also confirm these results. Moreover, it is also observed that with the increase in the PEG content of the TiO_2 films, the electron lifetime decreases, while the electron diffusion coefficient increases and changing the PEG content results in little variation on the performance of the cell.

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