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The influence of surface morphology of TiO₂ coating on the performance of dye-sensitized solar cells[☆]

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Abstract

The optimization of solar energy conversion efficiency of dye-sensitized solar cells (DSSCs) was investigated by the tuning of TiO₂ photoelectrode's surface morphology. Double-layered TiO₂ photoelectrodes with four different structures were designed by the coating of TiO₂ suspension, incorporated with low and high molecular weight poly(ethylene glycol) as a binder. Among these four systems, P2P1, where P1 and P2 correspond to the molecular weight of 20,000 and 200,000, respectively, showed the highest efficiency under the conditions of identical film thickness and constant irradiation. This can be explained by the larger pore size and higher surface area of P2P1 TiO₂ electrode than the other materials as revealed by scanning electron microscopic (SEM) and Brunauer–Emmett–Teller (BET) analyses. Electrochemical Impedance Spectroscopy (EIS) analysis shows that P2P1 formulation displayed a smaller resistance than the others at the TiO₂/electrolyte interface. The best efficiency (η) of 9.04% with the short-circuit photocurrent density (J_{sc}) and open-circuit voltage (V_{oc}) of 18.9 mA/cm² and 0.74 V, respectively, was obtained for a solar cell by introducing the light-scattering particles to the TiO₂ nanoparticles matrix coated on FTO electrode having the sheet resistivity of 8 Ω /sq.

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1. Introduction

The dye-sensitized solar cells (DSSCs) have attracted considerable attention over the past decade because they offer the possibility of low cost production of devices [1,2]. Excellent photo-electron conversion efficiencies have been reported for regenerative photoelectrochemical cells based on nanocrystalline titanium dioxide (TiO_2) films, sensitized by Ruthenium-dyes using triiodide/iodide (I_3^-/I^-) redox couple in an organic solvent as the electrolyte [3,4]. Performance of the DSSCs depends on many factors such as the TiO_2 surface morphology, solvent-supporting electrolyte and the nature of the dye. In a recent study, a better performance of DSSCs was obtained by the tuning of the TiO_2 photoelectrode morphology using multi-layers under various particle sizes as light-scattering layers [5,6]. Shen et al. [7] had studied the optical absorption and electron transport properties of the TiO_2 particles having different pore sizes and proposed that the use of small TiO_2 particles and large pore size always led to the good electron transport and high current efficiency. In addition to this, particle size and surface area influence the efficiency of DSSCs significantly [8].

Based on these above studies, we prepared two kinds of the TiO_2 paste using poly(ethylene glycol) (PEG) as a binder with two different molecular weights ($\text{MW} = 20,000$ and $200,000$). Four different kinds of nanostructure of the TiO_2 photoelectrodes were fabricated by using each TiO_2 paste, which followed a simple preparation method. The internal resistance and the cell performance of the four different composite layers of the TiO_2 electrode surface were investigated in this work along with the employment of light-scattering layers using SiO_2 particles having two different sizes. The scattering of light increases the photon's path length inside the cell and increases the probability to interact with the dye molecule in the red light region where the dye is not efficient [8].

2. Experimental

2.1. Materials

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

2.2. Preparation of the TiO_2 pastes and fabrication of DSSCs

The preparation of TiO_2 precursor and the electrode fabrication were carried out based on previous reports [8,9] except after autoclave treatment, where the solution was concentrated to 13 wt% and two types of pastes namely P1 and P2 were prepared by the addition of 30 wt% (with respect to TiO_2) of PEG with the corresponding molecular weights of 20,000 and 200,000 respectively, to the above solution in order to control the pore diameters and to prevent the film from cracking during drying. These two TiO_2 pastes (P1 and P2) were coated on a fluorine-doped tin oxide (FTO) glass plate using glass rod. Using these two types of pastes, four different kinds of film structures of the TiO_2 material

were obtained by different coating procedures. For example, P1P1 and P2P2 represent the coating of P1 over P1 or P2 over P2, respectively, whereas P1P2 and P2P1 represent the coating of P1 over P2 and vice versa.

An active area of 0.25 cm^2 was selected from sintered electrode and the electrodes were immersed in $3 \times 10^{-4}\text{ M}$ solution of cis-di(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium (II) (N3) containing acetonitrile and tertiary butanol (in the volume ratio of 1:1) overnight. Pt (100 nm thick) sputtered on FTO was used here 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 tertiary butylpyridine (TBP) in CH_3CN .

2.3. Photovoltaic measurements

The TiO_2 film thickness was measured by using a profilometer (Sloan Dektak 3030). The TiO_2 surface area, pore diameter, pore volume, and particle diameter were measured by Brunauer–Emmett–Teller (BET) method, using accelerated surface area and porosimetry (Micrometrics Instruments ASAP 2010). 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).

Photoelectrochemical characteristics and the AC-impedance measurements of the DSSCs were recorded with a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie, Netherlands) under constant light illumination of 100 mW/cm^2 .

3. Results and discussion

3.1. Properties of P1 and P2 TiO_2 electrodes

The SEM micrographs of the TiO_2 electrodes with the corresponding coating material of P1 and P2 were shown in Fig. 1(a) and (b), respectively. Highly porous nanostructure could be observed for both the thin films from the SEM micrographs. However, from this figure, it is also observed that the TiO_2 electrode coated with P2 shows higher porosity and denser structure than those of P1. Further analysis of various parameters such as surface area, pore volume and pore diameter obtained from the BET measurement of these two TiO_2 electrodes confirm the results of the previous SEM measurement. The surface area and the pore diameter of P1 were found out to be $80.4\text{ m}^2/\text{g}$ and 11.5 nm and P2 to be $67.1\text{ m}^2/\text{g}$ and 18.9 nm, respectively (Table 1). The average pore diameter of P1 was lower than that of P2 and the pore diameter distribution of P1 was narrower than P2. Since the coating of these TiO_2 nano-particles had been carried out under identical conditions, the diameter of the particles obtained from the SEM and BET measurements were noted as the same (20 nm). These results indicate that the morphology of the TiO_2 electrodes depends greatly on the composition and the addition of the PEG.

3.2. Electrochemical impedance spectroscopy (EIS) analysis

Fig. 2 shows the equivalent circuit and the typical impedance spectrum of a DSSC having the two types of the TiO_2 film namely P1P1 and P2P1. Three semicircles were observed clearly in the measured frequency range of 10 mHz–65 kHz. The ohmic serial

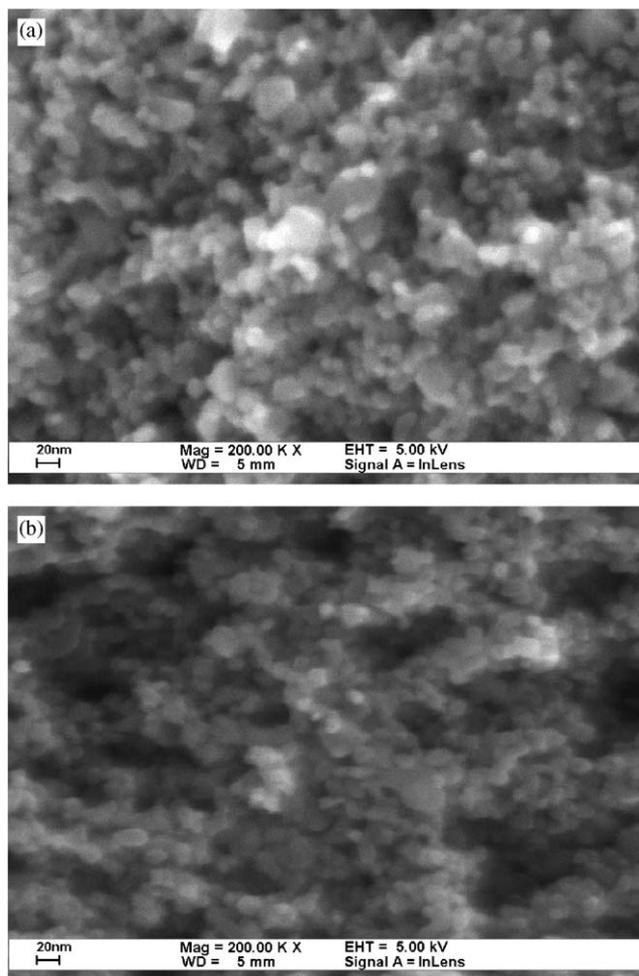


Fig. 1. The SEM images showing the surface morphologies of (a) P1 and (b) P2 TiO₂ electrodes, where P1 and P2 contain the binder PEG with molecular weights of 20,000 and 200,000, respectively in the TiO₂ paste.

Table 1

The specific surface area, pore diameter, pore volume and average particle diameter of P1 and P2 TiO₂ photoelectrodes obtained from BET measurements and SEM micrographs

Sample	Surface area (m ² /g)	Pore diameter (nm)	Pore volume (cm ³ /g)	d_{BET} (nm)	d_{SEM} (nm)
P1	80.4	11.5	0.29	19.2	20
P2	67.1	18.9	0.38	19.2	20

resistance (R_s) in the high-frequency region corresponds to the electrolyte and the FTO resistance, while the resistances R_1 , R_2 and R_3 relate to charge-transfer processes occurring at the Pt counter electrode in the high-frequency region, resistance for TiO₂/electrolyte

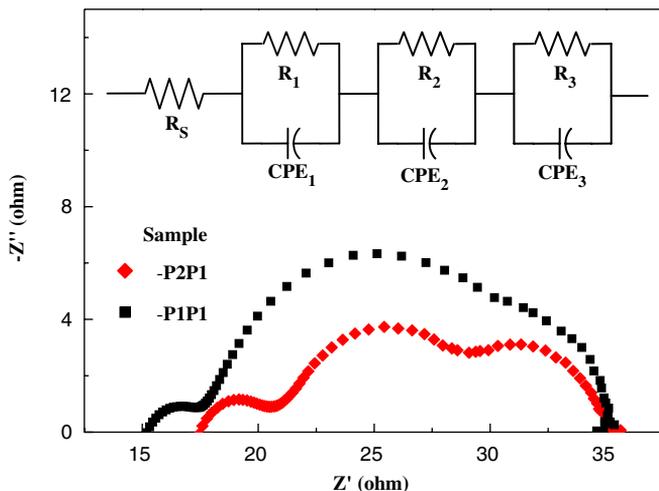


Fig. 2. EIS analysis of a DSSC, where solid square is the cell with P1P1 TiO₂ film and solid diamond is the cell with P2P1 TiO₂ film. Inset is equivalent circuit for a DSSC.

Table 2

Comparative performances of DSSC with various TiO₂ composite electrodes

Type of structure	Thickness of TiO ₂ (μm)	J_{sc} (mA/cm ²)	V_{oc} (V)	η (%)	FF
P1P1	17.2±0.5	12.84	0.75	4.71±0.2	0.49
P2P2	17.2±0.5	12.40	0.79	4.74±0.2	0.50
P2P1	17.2±0.5	14.44	0.77	5.31±0.2	0.48
P1P2	17.2±0.5	13.53	0.74	4.43±0.2	0.44

interface and Nernstian diffusion within the electrolyte in the low-frequency region, respectively [10,11]. If we compare the impedance spectra of these two TiO₂ materials, R_2 of P2P1 was smaller than that of P1P1 (Fig. 2). This proves that though the surface area of P2P1 electrode is smaller than that of P1P1 electrode, adequate pore sizes are available in the case of P2P1 for the facile transport of the redox couple in the TiO₂/interface thereby reducing the corresponding resistance at the interface [12–14].

3.3. Photoelectrochemical characteristics

Table 2 shows the comparative performances of DSSC associated with the different TiO₂ electrodes under the identical thickness of 17.2 μm. Among these different types of coated materials, P2P1 shows better efficiency than all the other TiO₂ electrode materials (the short-circuit current density (J_{sc}) is 14.44 mA/cm² and the open-circuit potential (V_{oc}) is 0.77 V with the cell efficiency η (%) of 5.31). The reason for this behavior is due to the presence of large pores in the electrode materials coated with P2 which may allow the diffusion of more redox species inside the pores. The DSSC performance also depends on the thickness of the TiO₂ film. By varying the thickness between 5 and 33 μm, there is a linear increase of J_{sc} , however, further increase in thickness, lowers the efficiency. Based on

these, we had prepared P2P1 electrode materials having the optimum thickness of 25 μm and found out its performance. The best efficiency is about 5.5–5.7% on FTO glass with the resistance of 25 $\Omega/\text{sq.}$, and the errors in the efficiency of three devices were within 0.3%. With the same sheet resistivity of FTO (R_{FTO}), the photocurrent is directly related to IR drop and for this reason, fabricating the device with less sheet resistant FTO will improve the FF and enhance the cell efficiency. For example, under identical conditions, if we decrease the sheet resistivity of FTO material from 25 to 8 $\Omega/\text{sq.}$ leads to an increase in DSSC efficiency of 8.67%.

In order to decrease the loss of light ascribed to the back-scattering, mono-dispersed light-scattering particles (SiO_2 particles of two different sizes such as 250 and 450 nm) were introduced to the TiO_2 matrix and the corresponding photocurrent action spectra is illustrated in Fig. 3 (The structures of these solar cells containing the light-scattering layers have been depicted as P1' and P1''). The response of simple P2P1 structure without light-scattering particles is also shown in the figure for comparison. The extension of photocurrent onset from 750 to 780 nm along with remarkable improvement in the incident photon conversion efficiency (IPCE, average value 7.1%) from 570 to 750 nm was noticed for both the SiO_2 nanoparticles which reveal that the efficient light scattering is responsible for this red shift in the action spectra. Solar cell made of SiO_2 nanoparticles having the size of 250 nm exhibits a better performance when compared to the other counterpart and as a result of this, an increase in the efficiency η (%) from 5.91 to 7.38 was noted (approximately an increase of 24.9% value). Similarly, in the case of TiO_2 particles as light-scattering layer with the sizes of 50–100 nm from the original d 25 nm, the increases in efficiencies of 28.2% [5] and 11.9% [6] were noted, respectively and the corresponding percentage of enhancement in efficiency is found to be reasonable in this work. From these investigations, it is understandable that the employment of light-scattering particles is also necessary besides the tuning of TiO_2 matrix for enhancing the performance of DSSC.

The best performance of DSSC incorporated with 250 nm SiO_2 light-scattering particles under the same conditions (R_{FTO} value of 8 $\Omega/\text{sq.}$) is shown in Fig. 3 as inset. A high solar

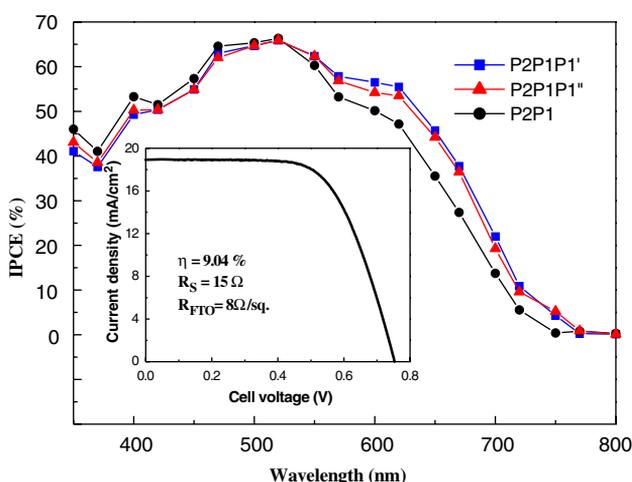


Fig. 3. Photocurrent action spectra of IPCE of DSSC having P2P1 electrode with and without the light-scattering particles and the inset shows the I - V curve for the DSSC exhibiting the best performance.

energy conversion efficiency of 9.04% along with J_{sc} of 18.8 mA cm^{-2} , V_{oc} of 0.74 V and fill factor (FF) 0.64 was attained.

4. Conclusions

From the above investigations, it is concluded that the DSSC performance depends strongly on the TiO_2 film morphology. Nano-particles are essential for increasing the surface area of the film in order to adsorb sufficient dyes. Adjusting pore size distribution is also an important parameter for improving the performance of the device. It is impossible to increase the surface area and to reduce resistance simultaneously, as both of them are opposite to each other. With the enough pore size distribution control, P2P1 electrode has better electron transport and less diffusion resistance than the other electrodes and it shows the optimum conditions to exhibit the best performance. Using multi-layer structure in combination with light-scattering particles, an energy conversion efficiency of 9.04% was obtained. Consequently, further detailed study of the nanostructures of TiO_2 surfaces could give better pathway for improving the performance the DSSCs.

Acknowledgments

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