

Effect of pore size/distribution in TiO₂ films on agarose gel electrolyte-based dye-sensitized solar cells

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Abstract This study develops a simple method to change the distribution of the pore size in a TiO₂ layer, using polyethylene glycol (PEG), while maintaining nearly the same surface area and porosity to clarify how large pores affect the performance of dye-sensitized solar cells (DSSCs). Specifically, a heating step at 100 °C for a specific duration is added prior to PEG removal and TiO₂ sintering at 400 °C. This process transforms the role of the PEG from a surfactant to a pore generator (porogen) and forms larger pores, depending on the loading and aggregation time for the PEG to gain larger pores. The effect of larger pores in TiO₂ films under 30 % PEG loading, on the performance of an agarose gel electrolyte-based DSSC, was further investigated using the ionic liquid, 1-allyl-3-ethylimidazolium iodide (AEII). The *I*-*V* characteristic and the electrochemical impedance spectroscopy analysis show that larger pores readily improve redox couple diffusion in a TiO₂ porous electrode and modify the interface between electrolyte and TiO₂. Using the optimized TiO₂ film with larger pores (30 % PEG loading, 100 °C/60 min), an efficiency of 7.43 % is achieved for the agarose gel electrolyte-based DSSC, which represents a 26.1 % improvement over TiO₂ without the addition of PEG.

Keywords Dye-sensitized solar cell · Pore size distribution · Polyethylene glycol · Agarose gel · Ionic liquids

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Introduction

In recent years, dye-sensitized solar cells (DSSCs) have been the subject of much scientific research and have found many industrial applications, because of their high efficiency, simple fabrication process, and low cost [1]. In 2011, a photo-to-electricity conversion efficiency of 12.3 % was achieved and reported [2]. DSSCs are expected to become a viable alternate to conventional silicon solar cells.

To date, extensive research involving DSSCs has focused on the key constituents, such as the semiconductor electrode [3–5], the dye [6–8], the electrolyte [9–11], and the counter electrode [12, 13], to improve the performance of DSSCs. Specifically, liquid electrolyte loss caused by leakage and volatilization has been one of the major problems limiting the long-term use of DSSC. Gel and solid state electrolytes are the viable solutions to make the sealing process easier and to minimize the loss of electrolytes for enhanced durability [10, 14]. When gel or solid electrolyte is introduced in DSSCs for enhanced cell durability, the pore morphology of TiO₂ films is even more critical because the viscous and steric effects of the gel or solid electrolytes make it especially difficult to fill the porous TiO₂ films completely [14, 15]. Moreover, it is found that large pores result in a higher electron lifetime in the TiO₂ electrode [16]. The pore morphology, which involves the pore size/distribution, surface area, and the porosity, of the porous films utilized in fuel cell [17] and lithium air battery [18], has great impact on their performance. Similarly, the pore morphology of a TiO₂ film also greatly influences the efficiency of a DSSC [19]. To date, the pore morphology of TiO₂ film has been modified by using (1) porogens, such as ethyl cellulose [20], [poly(ethylene oxide)₁₀₆-poly-(propylene oxide)₇₀-poly(ethylene oxide)₁₀₆] (Pluronic® F127) [21] and poly(methyl methacrylate) (PMMA) [22] with different molecular weights and loadings, (2) binders such as polyethylene glycol (PEG) under various loadings [23] and molecular weights [24], and

(3) different TiO₂ particle sizes [16, 25]. However, in modifying the TiO₂ particle size, the loading and molecular weight of any binders or porogen can simultaneously change the surface area, porosity, and pore size. This makes it difficult to quantitatively analyze the impact of pore morphology (surface area, porosity, and pore size/distribution) on DSSC performance.

This study develops a simple method to control the distribution of the pore size in the TiO₂ layer, using polyethylene glycol as the porogen, while maintaining the surface area and porosity. Specifically, a heating step at 100 °C for a specific duration is added prior to PEG removal and TiO₂ sintering at 400 °C, to modulate the pore morphology. The effects of the PEG loadings and isothermal heating time on the pore morphology (pore size/distribution, porosity, and surface area) are firstly investigated. The correlation between the pore size/distribution and the DSSCs performance is then examined, using agarose gel electrolyte and the ionic liquid, 1-allyl-3-ethylimidazolium iodide (AEII) [26, 27]. In addition, the pore properties, the photocurrent vs. voltage ($I-V$) curve, and the AC impedance are measured and analyzed, in order to determine the factors that affect the conversion efficiency of DSSCs.

Experimental

Titanium dioxide (25 nm, anatase phase) and poly(ethylene glycol) (PEG; molecular weight=100,000 g/mol) were purchased from Sigma Aldrich. N719 (ruthenium 535-bis TBA) was procured from Uni-Region Biotech. Guanidinium thiocyanate (99 %) (GuSCN), N-methylbenzimidazole (99 %) (NMBI), and 3-methoxypropionirile (MPN) were obtained from Alfa Aesar. Lithium iodide (LiI) was purchased from Merck. Titanium tetrachloride (TiCl₄) was purchased from Showa Chemicals. Glass substrates coated with a fluorine-doped tin-oxide (FTO) layer, with a sheet resistance of 8Ω/□, were obtained from Hartford Glass Co. All chemicals were used as received, without further purification, unless otherwise stated. The synthesis procedure for AEII followed a previously reported methodology [28].

PEG was added to de-ionized water (4.5 g) in a specific ratio relative to the weight of TiO₂. The solution was then stirred for 1 h. Anatase TiO₂ nanopowder (0.9 g) was then added to the PEG/water solution and stirred for another 48 h. The FTO-coated glass was cleaned with acetone and ethanol, prior to use. The nano-crystalline TiO₂ thin film (~10-μm thickness) was coated onto the FTO glass using the doctor-blading technique and then dried under vacuum. The as-prepared TiO₂ films were dried in air and then heated at 100 °C on a hot plate, for a specific duration, to allow the aggregation of PEG, in order to modulate the PEG size/distribution inside the TiO₂ matrix. Finally, the porous

TiO₂ thin films were formed by removing PEG and sintering at 400 °C for 30 min.

The N₂ gas adsorption–desorption curves for the TiO₂ films were plotted using a NOVA 1000e Surface Area Analyzer (Quantachrome instrument, USA). The specific surface area was determined from the linear portion of Brunauer–Emmet–Teller (BET) equation ($P/P^0=0.05–0.30$). The pore size distribution was calculated using a non-local density functional theory (NLDFT) model [29]. The film thickness was measured using a field-emission scanning electronic microscope (FE-SEM), JSM-6700F (JOEL, Japan).

The solution for the scattering layer was produced by adding TiO₂ anatase nanopowder of 400-nm diameter (0.4 g, ECOH) and poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (PI23) (0.5 g, Sigma Aldrich) into n-butanol (4 g) and stirring well. Subsequently, a 4-μm-thick scattering layer was deposited by spin-coating onto the sintered TiO₂ working layer, followed by sintering at 400 °C for 30 min. The dual-TiO₂-layer (scattering TiO₂ on working TiO₂ electrode) was immersed in an aqueous 0.1 M TiCl₄ solution for 30 min, using an ice bath. The dual-TiO₂-layer was then annealed at 450 °C for 1 h, to ensure excellent binding between the TiO₂ particles and the conversion of any remaining amorphous TiO₂ to anatase phase. Finally, the FTO/TiO₂ photo-anode was sensitized in a N719 dye/ethanol solution (3×10^{-4} M) at room temperature for 24 h. The DSSC cell was fabricated by sealing the dye-sensitized TiO₂ photo-anode and a Pt-sputtered cathode at approximately 100 °C, using a 25-μm hot-melt sealing foil (SX1170-25, SOLARONIX), which also served as a spacer. The agarose gel electrolyte consisted of 1.5 M AEII, 0.1 M GuSCN, 0.2 M NMBI, 0.05 M I₂, and 0.5 wt% agarose in low toxicity PC/DMSO co-solvents (volume ratio, 8:2). A DSSC cell (active area: 0.28 cm²) was produced upon the injection of the gel agarose electrolyte into the cell. Ionic liquid AEII-based agarose gel electrolyte was selected because its performance is comparable to MPN-based (3-methoxypropionirile) liquid electrolyte [30].

An AM1.5G Solar Simulator (Newport 3A) was used as a light source, with the incident light at 100 mW cm⁻², and calibrated using a standard Si solar cell (ORIEL), to evaluate the photocurrent conversion efficiency. The conversion efficiency was calculated from the photocurrent vs. voltage ($I-V$) curve, which was measured using a Keithley 2,400 source meter. The impedances between the interfaces inside the DSSC were measured by electrochemical impedance spectroscopy (EIS) and are shown in Nyquist plots. The EIS measurements were performed using a potentiostat/galvanostat (PGSTAT100; Autolab) over the frequency range from 0.01 to 10⁶ Hz, with an amplitude of 10 mV. All measurements in this study were performed at 25 °C.

Results and discussion

The distribution of the pore size in the TiO₂ films prepared using various PEG loadings, with direct sintering at 400 °C, was firstly examined. Using direct sintering at 400 °C for 0.5 h, the pore size distributions, based on a NLDFT model, of the porous TiO₂ films prepared using different PEG loadings are shown in Fig. 1a. When PEG is added to the TiO₂ film, the peak pore size shifts slightly from ~18 nm (no PEG) to 22–25 nm, for PEG loadings ranging from 20 to 100 %. A peak pore size of ~36 nm results from a PEG loading ≥40 %. The relative percentage of the 36-nm peak increases as the PEG loading increases up to 80 %, then drops slightly at a 100 % PEG loading. In short, when there is PEG loading of the TiO₂ at less than 40 %, the pore size distributions are slightly increased over those of TiO₂ films without PEG addition. These pores are mainly constructed from the crevices of the TiO₂ particle crevices. In the TiO₂ nanoparticle/PEG paste, PEG acts as a surfactant and is coated onto the TiO₂ nanoparticle surface via hydrogen bonding, which inhibits the aggregation of nanoparticles [31]. Little extra volume is occupied by the PEG in the TiO₂ thin film, prior to burning out at 400 °C. When the PEG loading is ≥40 %, the pore size is larger (~36 nm) and its relative percentage increases with PEG loadings. This indicates that in the TiO₂ nanoparticle/PEG paste, PEG is not only coated onto the TiO₂ nanoparticles but also occupies extra volume. Therefore, PEG serves as a porogen [28], which is transformed into additional larger pores after PEG burn-out. As the PEG loading increases, the amount of larger pores increases, as demonstrated by the increased peak height at ~36 nm.

The surface areas and porosity of the TiO₂ films are summarized in Table 1. The surface area is mainly controlled by

the size of the TiO₂ nanoparticles. Without PEG, the surface area of the TiO₂ film is 50.15 m² g⁻¹, in this study, which is close to the published data, 53 m² g⁻¹ [32]. The surface area and porosity are slightly reduced to ~49 m² g⁻¹, when the PEG loading is raised to less than 40 %, presumably due to a slightly larger distribution of pore size and insufficient packing under direct sintering. At a PEG loading ≥40 %, but less than 80 %, surface area and porosity reach 50.50–51.75 m² g⁻¹ and 49.6–51.1 %, respectively. At 80 % loading and above, while the surface area remains at approximately 50.93 m² g⁻¹, the porosity decreases from 50.52 to 47.46 %, due to film collapse, namely, the decrease in the film thickness, from 10 to 6 μm, after PEG burn-out.

The rheological behavior of PEG as a function of temperature was then determined (supporting data, Appendix 1). The viscosity of PEG ($T_{\text{melting}}=60$ °C) drops significantly from 1.1×10^6 poises to nearly 8×10^4 at $T \geq 65$ °C, so the mobility is substantially enhanced. An isothermal heating step at 100 °C was thus added to control the pore morphology of the TiO₂ films by taking advantage of the PEG's high mobility and ability to aggregate, without decomposition. Figure 1b illustrates the pore size distribution of TiO₂ films with various initial PEG loadings, prepared using an additional heating step at 100 °C for 1 h and then sintering at 400 °C for 0.5 h. The pore size distribution of the TiO₂ film with 0 % PEG loading is not obviously different to that with an intermediate heating step at 100 °C. When the loading is increased to 30 %, larger mesopores (~36 nm) are formed with the additional heating step. When the PEG loading is 40 % or higher, the amount of larger mesopores (~36 nm) increases and macropores with a diameter >50 nm also appear.

After the aggregation process for a PEG loading ≤40 %, the surface areas of the TiO₂ films decreases a little, but still

Fig. 1 The pore size distribution of TiO₂ layer under different PEG loadings (20–100 % relative to TiO₂ weight) based on NLDFT model: **a** sintered at 400 °C for 0.5 h directly and **b** kept at 100 °C for 1 h, then sintered at 400 °C for 0.5 h

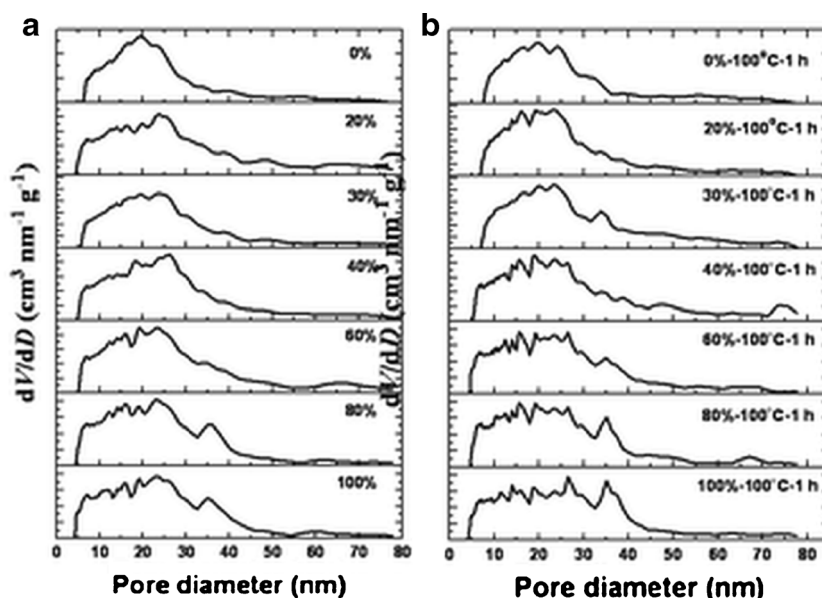


Table 1 The surface area and porosity in TiO₂ thin films prepared by using various PEG loadings with different sintering processes

Heating condition	Sample properties	0 %	20 %	30 %	40 %	60 %	80 %	100 %
Direct 400 °C sintering for 0.5 h	Surface area (m ² g ⁻¹)	50.15	48.97	49.27	50.85	51.75	50.93	51.57
	Porosity (%)	52.35	50.62	49.64	51.14	50.52	47.46	47.13
100 °C/1 h, then 400 °C/0.5 h	Surface area (m ² g ⁻¹)	48.20	48.45	48.90	49.77	49.99	51.14	49.06
	Porosity (%)	52.33	51.32	53.99	54.28	47.19	47.46	46.97

remains around 50 m² g⁻¹, as listed in Table 1. Meanwhile, the porosity increases slightly, compared with the TiO₂ films prepared by direct burn-out at 400 °C. However, when PEG loading is ≥60 %, the porosity decreases, similar to the case for ≥80 % PEG loading with a direct sintering process. The PEG aggregation deteriorates the structural integrity of the TiO₂ films and causes the film to collapse at PEG loadings, ≥60 %, which phenomenon is not evident for loadings ≥80 % with direct sintering. The results confirm that larger pores are introduced readily through PEG aggregation at 100 °C, because of the enhanced diffusivity at a reduced viscosity, as described by the kinetic molecular theory of Brownian motion, based on the Einstein–Stokes equation [33, 34]. With higher PEG loadings (≥60 %), macropores with a diameter >50 nm and interconnected pores weaken the skeleton of the TiO₂ and cause the film to collapse.

In addition to PEG loadings, isothermal heating time is another factor that controls pore morphology through the extent of PEG aggregation. A 30 % PEG loading was selected

in this study to determine the effect of heating time (0–150 min) at 100 °C on the pore size distribution in the TiO₂ films, as illustrated in Fig. 2, because this loading provides enough PEG to modulate the pore morphology via PEG aggregation at 100 °C, but avoids serious film shrinkage. Meanwhile, the images of SEM of these TiO₂ films showed no obvious difference in surface morphology (supporting data, Appendix 2). From Fig. 2, there is a peak pore size of ~32 nm, due to PEG aggregation into the larger pores, after heating at 100 °C for 30 min. At 100 °C, the interaction

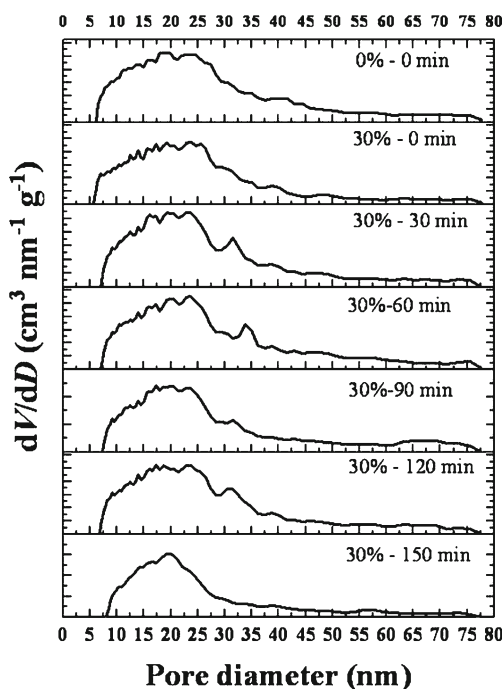


Fig. 2 The pore size distributions of TiO₂ layer at 30 % PEG loadings based on NLDFT model: various isothermal heating time at 100 °C, followed by sintering at 400 °C/0.5 h

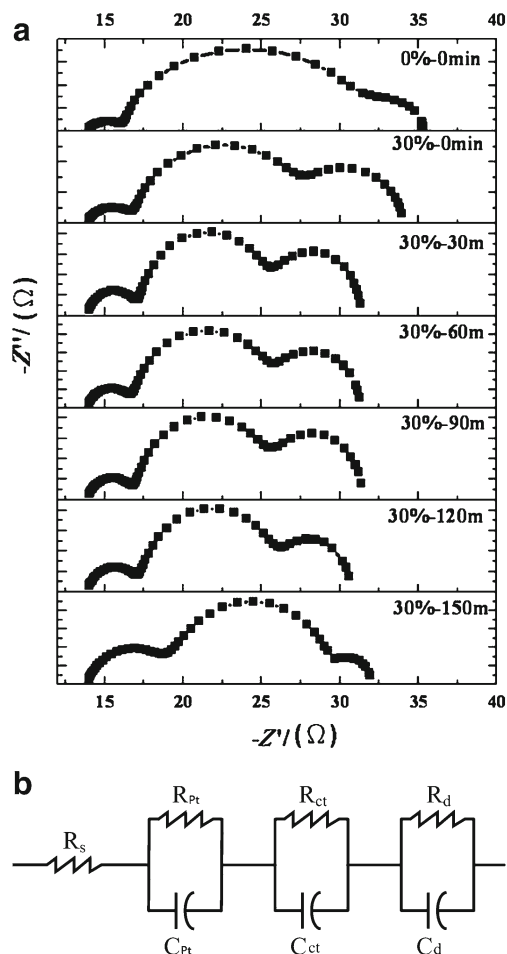


Fig. 3 **a** The Nyquist plots from EIS for DSSC cells with TiO₂ working electrodes fabricated by using (a) no PEG/no aggregation, and 30 % PEG loading with various isothermal heating time: (b) 0 min, (c) 30 min, (d) 60 min, (e) 90 min, (f) 120 min, and (g) 150 min. **b** The equivalent circuit for the DSSC

Table 2 Photovoltaic properties (J_{sc} , V_{oc} , FF, and η) for aragose gel electrolyte-based DSSCs using TiO_2 working electrodes using 30 % PEG under different heating time at 100 °C

Sample properties	0%—0 min	30 %—0 min	30 %—30 min	30 %—60 min	30 %—90 min	30 %—120 min	30 %—150 min
Surface area ($m^2 g^{-1}$)	50.15	49.42	48.61	48.90	49.66	49.73	49.98
Porosity (%)	52.35	52.24	52.91	53.99	54.50	53.38	53.50
V_{oc} (V)	0.80	0.74	0.74	0.75	0.73	0.74	0.68
J_{sc} ($mA cm^{-2}$)	10.39	13.29	14.18	14.32	14.57	13.89	11.36
FF	0.71	0.66	0.69	0.69	0.68	0.68	0.65
η (%)	5.89	6.54	7.18	7.43	7.28	7.04	4.98

between the PEG and the TiO_2 is weaker, so the highly mobile PEG molecules aggregate and collide with the TiO_2 particles, which leads to larger pores after sintering at 400 °C. When the heating time is increased to 60 min, the peak pore size continues to increase to 34–35 nm and larger pores >50 nm appear. After a longer PEG aggregation time of 120 min, larger mesopores remain and there is a peak pore size of ~32 nm, with less percentage. Up to 120 min, the TiO_2 film thickness remains at ~10 μm , with little shrinkage. These results indicate that increased heating time results in the formation of larger pores and the pore size distribution is increased because of increased PEG aggregation, due to the enhanced diffusivity of PEG at a reduced viscosity. As heating time is increased to 150 min, the approximately 32-nm pore size peak disappears and there is a narrow distribution, as seen in Fig. 3g. The decrease in the pore size distribution is attributed to the collapse of the TiO_2 film (from 10 to ~6 μm), after a heating time of 150 min.

The pore properties, such as the surface area and the porosity of the TiO_2 films prepared using a 30 % PEG loading and various isothermal heating times, are summarized in Table 2. The surface area and the porosity are virtually unchanged at approximately 49–50 $m^2 g^{-1}$ and 53.0–54.5 %, respectively. It is seen that TiO_2 films with different pore size distributions but similar surface area are produced by using a simple heating step at 100 °C for various durations. The TiO_2 films prepared by this method provide more defined conditions for the determination of the effect of the pore size distribution in TiO_2 films on the performance of DSSCs.

The $I-V$ results for an agarose gel electrolyte-based DSSC with TiO_2 films of various pore morphologies, prepared using 30 % PEG and different isothermal heating time, i.e.,

aggregation time, under AM 1.5, 1 sun ($100 mW cm^{-2}$) solar simulator illumination, are summarized in Table 2. Adding PEG into TiO_2 film and directly sintering at 400 °C results in an improvement in conversion efficiency (from 5.89 to 6.54 %) and J_{sc} (from 10.39 to 13.29 $mA cm^{-2}$), but a reduction in V_{oc} from 0.80 to 0.74 V. Increasing the aggregation time from 0 to 30 min results in further improvements to conversion efficiency and the J_{sc} value, to 7.18 % and 14.18 $mA cm^{-2}$, respectively. The form factor is increased to 0.69, but the V_{oc} value remains unchanged. An increase in the isothermal heating time to 90 min results in an improvement in the conversion efficiency of DSSCs, while the V_{oc} , FF, and J_{sc} values are relatively unchanged. An isothermal heating time of 120 min or more results in a decrease in the efficiency to a mere 4.98 % for a 150-min treatment time, as evidenced by the decreasing J_{sc} , V_{oc} , and FF values. The best performance for a DSSC is 7.43 %, for a 60-min aggregation time, which represents a 13.6 and 26.1 % improvement over the absence of aggregation (30 % PEG) and no addition of PEG, respectively. Since the surface areas of these TiO_2 films are approximately equal, these results indicate that the pore size and distribution both play a critical role in controlling DSSC performance. The dye loadings in various TiO_2 films are determined by desorption of the dye from the dyed TiO_2 after immersing in NaOH aqueous solution. This indicated that the adsorption of the TiO_2 films under different isothermal time was close and the TiO_2 film without isothermal treating owns more dye molecules due to the a little bit higher surface area than the others (Appendix 3). This does not bay the trend of the efficiency.

To determine the effect of the pore size distribution of the TiO_2 film on DSSC performance, the electron transport in the

Table 3 R_{pt} , R_{ct} , and R_d resistances obtained from Nyquist plots for gel electrolyte-based DSSCs using TiO_2 films using 30 % PEG under different heating time at 100 °C

	0 %—0 min	30 %—0 min	30 %—30 min	30 %—60 min	30 %—90 min	30 %—120 min	30 %—150 min
R_{pt} (Ω)	2.44	3.18	3.34	2.94	3.10	3.42	5.35
R_{ct} (Ω)	15.11	10.64	8.51	9.01	8.80	8.94	10.52
R_d (Ω)	3.98	6.33	5.65	5.44	5.74	4.49	2.28

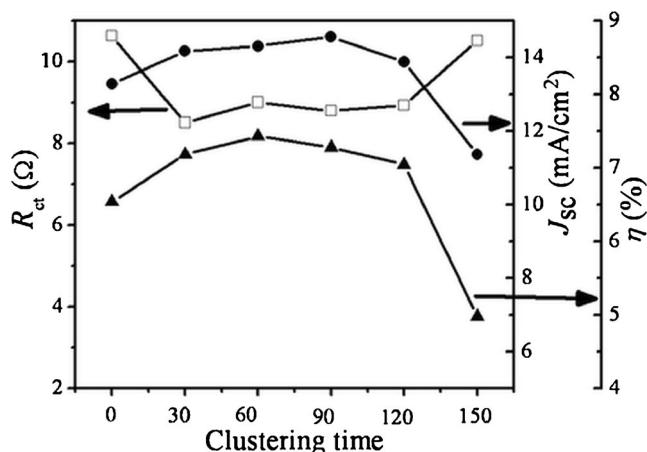


Fig. 4 The η , J_{sc} , and R_{ct} of agarose gel electrolyte-based DSSCs using TiO_2 working electrodes prepared by using 30 % PEG and under different isothermal heating time at 100 °C

TiO_2 /dye/electrolyte interface and the electron diffusion within the electrolyte were examined using electrochemical impedance spectroscopy (EIS). Figure 3a, b shows the Nyquist plots and the equivalent circuit for the agarose gel electrolyte-based DSSCs with a TiO_2 electrode of various pore morphologies, with a 30 % PEG loading and using an intermediate heating step, as illustrated in Fig. 2. C_{pt} , C_{ct} , and C_d are the interface capacitances of the DSSC. The series resistance (R_s) is related to the sheet resistance of the FTO and the resistance in electrolyte and the TiO_2 film, the resistance (R_{pt}) is related to the charge transfer at the platinum counter electrode, the resistance (R_{ct}) is related to the electron transport in the TiO_2 /dye/electrolyte interface, while the resistance (R_d) is related to the Nernst diffusion within the electrolyte at low frequency. The corresponding values for the resistances, R_{pt} , R_{ct} , and R_d , derived from the Nyquist plots, are summarized in Table 3. For 0 % PEG/no aggregation, three semicircles, relating to the R_{pt} , R_{ct} , and R_d values for a typical DSSC, are seen in Fig. 3a. When 30 % PEG is added, the absolute value of the second semicircle in the x-direction (R_{ct}) decreases significantly from 15.11 to 10.64 Ω but R_d increases slightly and R_{pt} remains relatively unchanged. These results indicate that the charge transfer impedance at the TiO_2 /dye/electrolyte interface is reduced, but charge recombination is slightly increased. As the heating time is increased from 0 to 120 min, R_{ct} decreases from 10.6 to ~9.0 Ω , which is attributed to a larger pore size and distribution. When the heating time is further increased to 150 min, the value of R_{ct} increases, presumably due to the slightly reduced pore size/distribution that results from the film collapse, as shown in Fig. 2.

The porous TiO_2 electrode with no PEG addition provides narrower pathways for electrolytic diffusion into the inner TiO_2 layer, which results in a higher value for R_{ct} and a lower value for J_{sc} . When 30 % PEG is added into the TiO_2 and there is an additional isothermal heating step to enable PEG

aggregation, the larger pores in TiO_2 -working anode provide a wider pathway for electrolytic diffusion. This leads to faster charge transport, as evidenced by the lower value for R_{ct} , i.e., there is better contact at the interface of the TiO_2 /dye/electrolyte, but there is a slight increase in the value of R_d , i.e., charge recombination. Therefore, a decreased resistance at the interface of the TiO_2 /dye/electrolyte enhances the photocurrent (J_{sc}). As the aggregation time is increased to 150 min, the porous TiO_2 film collapses and there is a reduction on the pore size/distribution, which inhibits the diffusion of the electrolyte and results in an increase in the value of R_{ct} and a lower J_{sc} value.

Based on the pore morphology and conversion efficiency, the PEG aggregation process with an isothermal heating step at 100 °C effectively increases the pore sizes/distribution of the TiO_2 films, which results in an increase in the efficiency, for an aggregation time of less than 120 min, as shown in Fig. 4. The best DSSC performance is obtained by using TiO_2 film with a 60-min aggregation treatment. Impedance analysis, using EIS, shows that the enhanced efficiency is attributable to a reduction in the value of R_{ct} , i.e., the resistance at the interface between the electrolyte and the TiO_2 and the improvement in the value of J_{sc} are due to enhanced diffusion in the TiO_2 layer with a larger pore size/distribution.

Conclusions

This study develops a simple method to control the pore size distribution in the TiO_2 layer, using polyethylene glycol (PEG), while maintaining a similar surface area and porosity. Meanwhile, the morphologies of the TiO_2 films were only slightly modulated, whose changes were not easily detected by SEM but BET and EIS.

Impedance analysis, using EIS, shows that the enhanced efficiency is attributable to a reduction in the value of R_{ct} , i.e., the resistance at the interface between the electrolyte and the TiO_2 and the improvement in the value of J_{sc} is due to enhanced diffusion in the TiO_2 layer with a larger pore size/distribution. For the optimized TiO_2 film with larger pores/distribution (30 % PEG loading, 100 °C/60 min), an efficiency of 7.43 % is achieved for an agarose gel electrolyte-based DSSC, which represents a 26.1 % improvement over TiO_2 without PEG addition. By minimizing the variation of the TiO_2 (surface area and porosity), larger pores modify the interface between the electrolyte and the TiO_2 and represent a 13.6 % improvement (6.54–7.43 %) of efficiency.

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