Fabrication of TiO₂ compact layer precursor at various reaction times for dye sensitized solar cells

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A R T I C L E   I N F O
Article history:
Received 18 November 2014
Received in revised form 21 April 2015
Accepted 8 May 2015
Available online 24 August 2015

Keywords:
Compact layer
TiO₂
DSSCs
Titanium isopropoxide
Acetylacetone

A compact layer is used to increase the photoelectric conversion efficiency on DSSCs due to it can improve the transparent conduction oxides (TCOs) surface and prevent the electrolyte from directly contacting the ITO (Indium Tin Oxide) substrate. In this study, DSSCs with compact layer reacting for three hours are compared to those without compact layer, where the short-circuit current and solar energy conversion efficiency are improved by 22%, and 26%, respectively. Based on electrochemical impedance spectra (EIS) measurements, we clarify that the compact layer can decrease the charge interfacial resistance and the leakage current due to the fact that the dense TiO₂ nanoparticles can effectively prevent charge transport from the photoanode to the ITO substrate.

1. Introduction
Solar energy is one of the most important renewable energy. Dye-sensitized solar cells have first proposed in 1991 by O’Regan and Gratzel [1–3]. The compact layer can be fabricated by spray-pyrolysis method [17], sputter deposition [18] and sol–gel method [6] and TiCl₄ treatments method [15] to improve the TCO surface. But the spray-pyrolysis method needs high temperature to deposit on the TCOs and the sputter deposition requires high vacuum systems. The cost to fabricate the solar cell will be much higher than the sol–gel method. Although the TiCl₄ treatments are low cost and convenient, but the TiCl₄ will produce chlorine and HCl. HCl will etch the TCOs to cause surface structural damage [16]. TiO₂ compact layer can improve the short-circuit current and decrease the series resistance [4,5]. The compact layer is fabricated by spray-pyrolysis, sputter deposition and sol–gel methods [6]. The sol–gel precursor of titanium isopropoxide (TTIP) has high hydrolysis and polycondensation reaction rates to synthesize the TiO₂ nanoparticles with H₂O. To prevent a high hydrolysis rate, acetylacetone (Acac) is added to slow down the hydrolysis process and to control the gelation time of TiO₂ precursor [7,8]. In this research, the reaction time of the compact layer precursor was 3 and 24 h. According to the results, the efficiency of DSSCs with TiO₂ compact layer are higher than those without compact layer, and DSSCs with a compact layer of reacting for 3 h have the highest efficiency. After the compact layer was finished, it had to be annealed to form the anatase titanium at 450 °C. The conductivity of the ITO thin film was decreased and this caused the decrease of the efficiency after annealing. We prepared the FTO thin film as the substrate to make the photoanode. The FTO substrate has better heat-resistance and conductivity after secondary annealing [10,11]. To control the gelation time and hydrolysis, we fabricated the precursor solution at various molar ratios with 1 M and 2 M. The colloid will become sticky because of increasing the titanium isopropoxide. The thick colloidal will cause the surface edge stacking by using spin coating.

2. Experimental section

2.1. Preparation of the TCO substrate

The ITO substrate and FTO substrate were washed with acetone, ethanol and deionized water in an ultrasonic cleaner for 10 min. Finally, the substrates were dried and blown the excess water by nitrogen gas.

2.2. Preparation of the compact layer solution

Titanium isopropoxide was mixed with acetylacetone according to the 1:1 molar ratio. The solution was stirred for a period of time to become well-distribution. The compact layer solution is dropped on the TCO glass with an initial speed 1000 rpm for 10 s and a final speed...
2000 rpm for 20 s with an active area of 1.1 cm². The sample is dried in oven at 90 °C for 5 min, washed with absolute ethanol in an ultrasonic cleaner for 1 min, and blow-dried with nitrogen gas. Finally, the sample is annealed at a heating rate of 5 °C/min and holding at 450 °C for 30 min.

2.3. Preparation of the TiO₂ colloidal

The TiO₂ colloidal solution was mixed and dispersed by TiO₂ nanoparticles, the Triton X-100 and 2, 4-Pentanedione in deionized water. The TiO₂ solution was placed in an ultrasonic cleaner for 30 min. Finally, the stirrers were set at 300 rpm by running for 4–5 h. The TiO₂ colloidal solution is dropped on the compact layer/TCO glass with an initial speed 1000 rpm for 10 s and a final speed 2000 rpm for 20 s. The sample is dried in oven at 100 °C for 10 min, and then the sample is annealed at 450 °C for 30 min. The compact layer/TiO₂ layer was immersed in N719 dye for 24 h at room temperature.

2.4. The instruments of experimental measurements

The photoelectric performances of DSSCs such as the open-circuit voltage (V_{oc}), short-circuit density (J_{sc}), fill factor (F.F) and conversion efficiency (η) were measured under AM 1.5 (100 mW/cm²) by the solar light simulator (XES-40S2-CE). The electrochemical impedance spectroscopy (EIS) was measured by the potentiostat/galvanostat (SP-150, Bio-logic) and the frequency range was chosen from 1 MHz to 50 m Hz with AC amplitude of 10 mV. The sheet resistance was measured by the four-point probe (S-301-6, Signatone).

3. Result and discussion

3.1. Effect of various hydrolysis reaction times on solar cell performances and electrochemical impedance spectroscopy

As shown in Table 1 and Fig. 1, the J–V characteristics for DSSCs, the cell with TiO₂ compact layer is increased from 0.73 V to 0.76 V with a rise of around 4% for the open-circuit voltage (V_{oc}), from 4.81 mA/cm² to 5.87 mA/cm² for the short-circuit current density (J_{sc}), and from 1.77% to 2.24% for the photoelectric conversion efficiency, respectively. When the hydrolysis reaction time increased to 24 h, the short-circuit current density decreased from 5.87 mA/cm² to 5.39 mA/cm² with a decline of around 9%, and the efficiency decreased from 2.24% to 2.06%. Fig. 2 shows the SEM of the compact layer on the ITO substrate with reaction time of 3 and 24 hours, respectively.

Electrochemical impedance spectroscopy was used to investigate the electron transport and recombination in DSSC. As shown in Fig. 4 and Table 2, the EIS data included the DSSCs without compact layer and with TiO₂ compact layers of reacting in 3 h and 24 h. The start point to the first semicircle’s plot is the series resistance (R_s). It is mainly about the contact with the TCO substrate and the charge transference with DSSC [12]. The first semicircle on the left in Fig. 4 is the impedance (R_s) related to the charge transport at the Pt counter electrode and TiO₂/conducting layer [13,14]. The second semicircle represents the resistance (R_2) at the TiO₂/dye/electrolyte/ITO interface [9]. As shown in Fig. 3, since the transparent conductive thin film is formed by sputtering on the glass, the TCO film surface has the defects [6]. It will increase the resistance and the voids to cause the TiO₂ not to be evenly distributed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>V_{oc} (V)</th>
<th>J_{sc} (mA/cm²)</th>
<th>F.F%</th>
<th>Eta (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No compact layer</td>
<td>0.73</td>
<td>4.85</td>
<td>0.5</td>
<td>1.77 ± 0.05</td>
</tr>
<tr>
<td>Compact layer (3 h)</td>
<td>0.78</td>
<td>5.87</td>
<td>0.5</td>
<td>2.24 ± 0.06</td>
</tr>
<tr>
<td>Compact layer (24 h)</td>
<td>0.75</td>
<td>5.39</td>
<td>0.5</td>
<td>2.06 ± 0.03</td>
</tr>
</tbody>
</table>

Table 1

Photoelectric performances of DSSCs fabricated without compact layer, and with compact layers of 3 h and 24 h.
competing the ITO substrate with the FTO substrate, the FTO substrate has better conductivity and low sheet resistance. Therefore, the electron transfer is easier because of its good electrical conductivity.

3.3. Effect of various molar ratio on solar cell performances

In this part, the precursor of compact layer has been fabricated at various molar ratios (TTIP: Acac = 1:1, 2:1). As shown in Table 5 and Fig. 7, the $J$–$V$ curves for DSSCs, where the molar ratio is increased from 1 M to 2 M, the short-circuit current density ($J_{sc}$) is decreased from 6.09 mA/cm² to 5.86 mA/cm², and the photoelectric conversion efficiency from 2.67% to 2.49%, respectively.

**Table 2**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_1$ (Ω)</th>
<th>$R_2$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No compact layer</td>
<td>11.2</td>
<td>21.7</td>
</tr>
<tr>
<td>Compact layer (3 h)</td>
<td>5.2</td>
<td>7.4</td>
</tr>
<tr>
<td>Compact layer (24 h)</td>
<td>7.8</td>
<td>9.6</td>
</tr>
</tbody>
</table>

**Table 3**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>F.F%</th>
<th>Eta (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO substrate</td>
<td>0.76</td>
<td>5.87</td>
<td>0.5</td>
<td>2.24 ± 0.06</td>
</tr>
<tr>
<td>FTO substrate</td>
<td>0.76</td>
<td>6.09</td>
<td>0.57</td>
<td>2.67 ± 0.22</td>
</tr>
</tbody>
</table>

3.3. Effect of various molar ratio on solar cell performances

In this part, the precursor of compact layer has been fabricated at various molar ratios (TTIP: Acac = 1:1, 2:1). As shown in Table 5 and Fig. 7, the $J$–$V$ curves for DSSCs, where the molar ratio is increased from 1 M to 2 M, the short-circuit current density ($J_{sc}$) is decreased from 6.09 mA/cm² to 5.86 mA/cm², and the photoelectric conversion efficiency from 2.67% to 2.49%, respectively.
From the previous experiments, we see that the mixing of the TTIP and Acac as the compact layer precursor can effectively prevent the electron recombination from the electrolyte directly contacting the photoanode’s voids on the FTO surface. Here we compared the results with various molar ratios of 1 M and 2 M, with the increase of TTIP molar concentration, the viscosity of the precursor solution will be increased [7]. With a too thick colloid, it will cause the surface edge stacking by using spin coating [6]. The stacking of surface edge will increase the electronic transmission path and results in the increase of the resistance.

3.4. Comparison of the compact layer methods on the different literature

As shown in Table 6, compared with other literature, we can find that all of the DSSCs with the compact layer can efficaciously increase the photoelectric conversion efficiency.

In the literature [5], the TiCl4 is used to form the compact layer. In the literature [9], the TiO2 compact layer is used to reduce the recombination reaction and prevent the N719 directly contacting the ZnO layer. The ZnO compact layer as the second stage of the electron transfer reaction and prevent the N719 directly contacting the ZnO layer. Performance parameters of DSSCs fabricated on 1 M compact layer and 2 M compact layer.

Table 5
Performance parameters of DSSCs fabricated on 1 M compact layer and 2 M compact layer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M compact layer</td>
<td>0.76</td>
<td>6.09</td>
<td>0.57</td>
<td>2.67 ± 0.22</td>
</tr>
<tr>
<td>2 M compact layer</td>
<td>0.74</td>
<td>5.86</td>
<td>0.56</td>
<td>2.49 ± 0.07</td>
</tr>
</tbody>
</table>

4. Conclusion

The DSSCs fabricated with TiO2 compact layer have much better short-circuit density and photoelectric conversion efficiency. The compact layer can decrease the contact resistance and increase the solar cell efficiency. By adding the compact layer in DSSCs, the short-current density and the photoelectric conversion efficiency have a rise of around 22% and 26%, respectively. From the EIS measurements, the R2 (TiO2/dye/electrolyte/ITO interface) is decreased from 21.7 Ω to 7.4 Ω. By comparisons of DSSCs with the compact layer of different reaction time, the solar cell energy efficiency for compact layer of 24 h was reduced around 8%. For various annealing temperatures, the ITO sheet resistance is increased from 13 (Ω□) to 41 (Ω□), the FTO sheet resistance remained at around 25 (Ω□) and the efficiency is increased from 2.24% to 2.67%. The FTO substrate has nice heat-resistance and stability on the sheet resistance after annealing. Where the compact layer molar ratios increased, the viscosity of precursor increased. It caused the stacking of surface edge and decreased the efficiency from 2.67% to 2.49%.

References


