Fabrication of high quality TiO₂ thin films for high conversion efficiency dye-sensitized solar cells by multiple electrophoresis depositions

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1. Introduction
During the past decade, dye-sensitized solar cells (DSCs) are one of the potential photovoltaic (PV) devices for flexible device applications with high light-to-energy conversion efficiency. [1] The fluorine-doped tin oxide (FTO) glass substrate is replaced with a light-weight substrate, such as polyethylene naphthalate coated with indium-doped tin oxide (ITO/PEN), which requires all fabrication process designed in a temperature range below the 150°C. This flexible PV device has achieved an efficiency of 4.1% with 100 mW/cm² illumination. [2] In 2001, Hagfeldt et al. introduced a new method to prepare the TiO₂ photoanode at room temperature (RT) and obtained the efficiency to 5.2% under 0.1 sun irradiation. [3]

The electrophoresis deposition (EPD) method is a concern technique in which charged nanoparticles (NPs) in a suspension move toward an oppositely charged electrode and deposit onto a substrate under an applied DC electric field. However, when the EPD films dry at RT, the micro-cracks (µ-cracks) would appear on the surface of the film to lower the performance of the DSCs. In this report, the multiple EPD method is suggested to prepare a crack-free photoanode to improve the DSCs performance.

2. Experimental detail
The TiO₂ suspension for EPD consisted of 0.25g TiO₂ NPs in 100 mL IPA. The P-90 TiO₂ NPs is a kind gift from Degussa AG, Germany. The scattered TiO₂ NPs with ca. 100nm diameter were synthesized through sol-gel method in a basic solution containing mixing 58.6g titanium isopropoxide and 20 mL tetramethylammonium hydroxide (TMAH) with 290 mL distilled water in the autoclave at 250°C for 12 hours. A Keithley 2400 Source Meter was applied as a power supply for different currents and deposition durations at the constant current mode. The mesoporous TiO₂ photoanode was immersed in a solution of 0.5 mM N719 dye solution in ACN/t-BuOH (v/v=1:1) at 40 °C for 4 hrs. The dye-sensitized photoanode was rinsed with ACN to remove the remaining dye, and dried at RT under atmosphere. A platinum-sputtered ITO/PEN film was served as the counter electrode. A two-electrode sandwich cell separated by a 60 µm spacer (Surlyn) was filled with the electrolyte consisted of 0.4 M LiI, 0.4 M tetrabutylammonium iodide (TBAl), 0.04M I₂ and 0.5 M N-methylbenzimidazole (NMBI) in ACN/MPN mixture (v/v=1:1). As for the stability test, the electrolyte was changed to LiI free and used MPN as the electrolyte solvent.

3. Results and discussion

Table 1. DSCs performance with one-step or two-steps EPD.

*EPD process: EPD current density [time] (µA/cm² [min])

<table>
<thead>
<tr>
<th>Method*</th>
<th>JSC (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>One-step</td>
<td>8.81</td>
<td>0.780</td>
<td>0.595</td>
<td>4.09</td>
</tr>
<tr>
<td>Two-steps</td>
<td>8.94</td>
<td>0.784</td>
<td>0.690</td>
<td>4.83</td>
</tr>
</tbody>
</table>

For low-temperature fabricated DSCs, especially the electrophoretic deposition (EPD) method, the volatile organic compounds (ex: IPA, EtOH) are used as the solvent of the binder-free suspension; therefore the film easily cracks after air-drying to lower the device performance. The surface morphology shown in Fig. 1 illustrates the interconnected P-90 TiO₂ film in use of the optical microscopy. These results suggested that the 2nd deposition could fill the cracks on the 1st deposition to form a better quality photoanode. Three photoanodes were prepared to assemble into devices. Their performances were listed in Table 1. The DSCs with two-steps EPD process slightly improved the filling factor (FF) from 0.595 to 0.690, due to the less cracks of EPD film. The efficiency of the plastic-based DSCs with two-steps EPD photoanode has achieved 4.83%. It is believed that the two-steps EPD photoanode has better film quality to improve the efficiency of device.
Because the applied current density may affect the deposition rate of the TiO₂ film, we prepared three DSCs devices with different deposition rates in the 2nd step having the same 1st EPD condition (20 μA/cm²; 5 mins). Figure 2 shows the current density–voltage (J–V) curves of DSCs with the TiO₂ film deposited by different 2nd deposition rates. Corresponding thickness of TiO₂ film after 100MPa pressure (t), short-circuit current (Jsc), open-circuit voltage (Voc), fill factor (FF) and solar-to-electricity conversion efficiency (η) are summarized in Table 2. The results indicate that the slow EPD rate provides filling up more cracks caused by drying the 1st EPD layers, so the increase of TiO₂ film thickness in the 2nd EPD is directly proportional to the deposition rate. It is expected that Voc has decreased from 0.781 V to 0.723V with increasing photoanode thickness from 4.9 to 10.1 μm. Although the TiO₂ film thickness of the fastest deposition rate (20 μA/cm²) is almost twice thicker than the other ones that is mainly ascribed to the enlargement of the surface area for dye adsorption, the Jsc of DSCs with the thickest TiO₂ photoanode is only about 1 mA/cm² greater than the other two devices. The maximum FF (0.721) and conversion efficiency (5.54%) for the DSC device with the slowest 2nd deposition rate (5 μA/cm²) is obtained. The EIS data is shown in Fig. 3 and the fitting results are summarized in the inset table. It suggests that the charge-transfer resistance (Rw) decreases by about 1 order of magnitude with reducing the 2nd deposition rate from 20 μA/cm² to 5 μA/cm² due to the slow 2nd deposition rate may have filled up the cracks. Because the competition between the collection and the recombination of electrons can be expressed in terms of the electron diffusion length, the obtained effective electron diffusion time in TiO₂ photoanode (τe) decreases from 118.8 to 18ms and Ln/L increases about three times with decreasing the 2nd deposition rate from 20μA/cm² to 5μA/cm².

All above parameters from EIS analysis indicated that higher quality TiO₂ film deposited by the slower deposition rate (5μA/cm²) possess more efficient electron transport. As a result, through multiple EPD, including slow 2nd EPD to fill up the cracks after drying the 1st EPD layer and scattering layer deposited by 100nm TiO₂ NPs (20 μA/cm²; 5 mins) to enhance the light scattering, a high quality photoanode with thickness of ca. 8.5 μm was obtained. Figure 3 shows the excellent photovoltaic performance without antireflection layer under AM 1.5G one sun irradiation. Its Jsc, Voc, and FF are 12.06 mA/cm², 0.763 V, and 0.72 respectively, yielding efficiency (η) of 6.63%.

By using the LiI free electrolyte and ACN/MPN mixture (v/v=1:1) as the electrolyte solvent substituting for MPN, a minor decrease in cell performance is shown in Fig. 3 under illumination of approximately 1 sun at moderate temperatures (60 °C). The efficiency (η) of DSCs with a UV cutoff filter retained over 80% of its initial value after 1100 h. The optimal concentration of each chemical compounds in the electrolyte and the stability of DSCs under various testing conditions regarding accelerated aging are in progress.

3. Conclusion

EPD at RT with compress treatment was used to prepare TiO₂ thin films on ITO/PEN. Filling up the cracks caused by drying the previous EPD film was achieved by the two-steps deposition under slow 2nd deposition rate. The great enhancement of the electron collection has been confirmed by the EIS. It shows about 1 order of magnitude improvement of the electron diffusion coefficient in the crack-less multiple-EPD TiO₂ films. A conversion efficiency of 6.63% can be achieved for DSCs with the scattering layer on EPD transparent TiO₂ film as the flexible photoanode. The DSCs devices with UV-cut filter show good stability under continuous full sunlight illumination at 60°C and only about 20% reduction in conversion efficiency after 1100 h of continuous illumination.

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References