Enhanced Photovoltaic Performance of Dye-Sensitized Solar Cells via Electrochemically Deposited TiO_2 Compact Underlayer

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Abstract

The TiO_2 compact layers produced by the electrochemical deposition method were employed as blocking underlayer in dye-sensitized solar cells (DSSCs). The galvanostatic deposition method was utilized to deposit TiO_2 compact layer (TiO_2-CL) onto FTO substrates from acidic titanium (III) chloride electrolytic solution. The formation-TiO_2 compact layers were affirmed by X-ray diffraction (XRD). The transparency of TiO_2 compact layer was examined by UV-vis absorption spectroscopy. The present work mainly investigated the effect of TiO_2-CL incorporation on the photovoltaic performance of the DSSCs where the photosensitizer is LEG4 organic dye and the redox mediator is CoII/CoIII based electrolyte. Incorporation of TiO_2-CL between transparent FTO electrode and meso-TiO_2 could increase efficiency of a device with an obvious increase in short circuit current density. The power conversion efficiency is 4.3% and 3.5% of the devices with and without TiO_2-CL.

Keywords: $TiCL_3$ solution, Blocking compact layer, DSSCs, Electrochemical Deposition, Recombination lossless

Introduction

With appearing photovoltaic technologies, dye-sensitized solar cells have been realized for manufacturing since it was discovered in 1991[7] with easy fabrication procedure and the applicability of colorful light absorbers. Typically, a dye sensitized solar cell (DSSC) consists of transparent conductive oxide (TCO) coated glass substrate, (normally FTO), metal oxide semiconductor (meso-TiO_2 layer), light absorber and redox mediator and a catalyst deposited FTO (standard, pt counter electrode).Upon light illumination, in a DSSCs, the light absorber can be excited and electrons were extracted from high occupied molecular level to lowest unoccupied molecular level and injected into the conduction band of TiO_2. Eventually, by collecting excited electrons from TiO_2 conduction band were at FTO substrates, the photocurrent is generated. Through the external load, the electrons reached the counter electrode, i.e, the inner circle is completed. The oxidized light absorber can be regenerated by a redox mediator. Therefore, in generating the photocurrent in DSSCs, not only electrons transport and junction engineering is also vital. Many studies showed that improving interface engineering is critical to improve performance of devices suppressing the unwanted back transfer reactions, mainly, interfaces between transparent photoanode and meso-TiO_2 film and meso-TiO_2 films and oxidized dye/oxidized redox mediator [1,2].

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Integration of a thin transparent compact layer in between transparent photoanode and meso-TiO_2 film is an efficient way to provide further overall efficiency improvement of devices [5]. There are several ways to prepare a compact layer including spray pyrolysis, DC sputtering, chemical vapor deposition methods and electrochemical deposition method and hydrolysis method. According to the best of our knowledge, there was a report applying similar electrochemical deposition method used in the dye-sensitized solar cell [8]. Another one was submitted by Su and co-workers. Nowadays, TiO_2 compact layer prepared by hydrolysis of titanium (IV) chloride is widely used for DSSCs. This method has been applied in perovskite solar cells (PSCs) research and provided a competitive performance compared to the spray pyrolysis method which is the most common used in PSCs area [3,8]. Therefore, in the present study, the TiO_2 compact layers were prepared by the electrochemical deposition (ED) method and performance of TiO_2 compact layers produced by the ED method in DSSCs were evaluated. Electrochemical deposition method was carried out with a three-electrode setup.The constant current method was utilized to control for the formation of a TiO_2 layer onto the FTO substrate following work by Kavan and co-workers in 1993[4].

Experimental Section

Materials

The materials used in this work are all commercially available. Fluorine-doped tin oxide (FTO) glasses were purchased from Nippon Sheet Glass Co., Ltd., Japan. Acidic titanium (III) chloride Solution ≥12% $TiCl_3$ (Sigma Aldrich) was used as the electrolyte. Organic dye LEG4 and CoII/CoIII redox media were purchased from Dyenamo, Sweden.

Preparation of $TiCl_3$ Precursor Solution

The acidic titanium (III) chloride solution was utilized as a precursor electrolyte in preparation of titanium oxide layer onto transparent Fluorine-doped tin oxide (FTO) glass substrates. The salt, sodium carbonate (Na_2CO_3) was used to adjust pH values. The pH value in the range of 2.0 – 2.5 was used for titanium oxide layer deposition. Required supporting electrolytes were obtained by adding some amounts of Na_2CO_3 into 3 mM $TiCl_3$ in DI water.

Electrochemical Deposition of Titanium Oxide Compact Layer (TiO_2-CL)

Before electrochemical deposition, the FTO (area – 3.3 cm x 8.0 cm, sheet resistance_10 ohm sq^{-1}) were ultrasonically washed with detergent for 30 minutes followed by washing with ethanol, DI water and acetone for 15 minutes each. Then the substrates were rinsed with DI water and dried under airflow. The electrochemical deposition was carried out on the pre-cleaned FTO. The electrochemical deposition was controlled by the constant current method in a three-electrode configuration and the electrochemical workstation Corr-Test CS 350 was used. The Ag/AgCl/saturated KCl was utilized as reference electrode while a titanium sheet with a surface area (4 cm ×12 cm) was used as a counter electrode. As a working electrode, a pre-cleaned bare FTO glass was used. The constant current 20 μA and deposition time 1000 s was applied for $Ti^{(IV)}$ oxide layer deposition onto pre-cleaned FTO. After rinsing solid residues of Ti, the samples were heated at 400℃ for 30 minutes for the formation of compact, dense TiO_2 anatase layer. After heating, obtained TiO_2 films were used for structural and optical characterization by XRD and UV-vis spectroscopy. They were incorporated as blocking compact layer in the fabrication of the DSSCs devices.

Fabrication of Dye-sensitized Solar Cells

For the preparation of working electrodes (WEs), FTO substrates with and without TiO_2-CLs were utilized to screen-print the meso-TiO_2 transparent layer ($\sim 5\mu m$) with active

area 0.25 cm^2 and sintered at 450 ˚C for 30 min and cooled down to 90 ˚C. Then the electrodes with and without TiO_2 were immersed 0.2 mM LEG4 in ethanol. In preparation of counter electrode, 5mM chloroplatinic acid, $H_2Pt\ Cl_6$ solution in ethanol were utilized as a catalyst and the predrilled hole FTO glass substrates were heated at 450 ˚C for 30 min for further cleaning. After cooling down to room temperature, by dropping 15 μl of chloroplatinic acid solution pt catalyst thin layer coated counter electrodes were prepared. The dried pt coated electrodes are heated at 450 ˚C for 30 min. Electrolytic solution composed with 0.3 M $Co(bpy)_3\ (PF_6\ )_2$, 0.04 M Co $(bpy)_3\ (PF_6\ )_3$,0.4 M TBP (Tert-butylpyridine, 0.25 M LiTFSI in acetonitrile were used. Then by using polymer, thermoplastic sealants frame working electrodes and pt coated counter electrodes were initially attached at 120 ˚C. Then, electrolyte were injected via predrilled holes and sealed back by using polymer films. The power conversion efficiencies of the complete devices are examined by recording the I-V characteristic under A.M 1.5 Solar illumination of intensity (1000 W/m).

X-ray Diffraction Spectroscopy (XRD)

X-ray diffractometer (RIGAKU Multiflex) was used to identify the structural formation of TiO_2. Under Cu K (alpha) (0.1541 nm) radiation source, measurements were performed at operating voltage 40 kV and current 20 mA. The intensity of the diffracted X-rays was recorded with the diffraction angle (2-theta) from 10 to 80 degrees and the obtained XRD data was interpreted.

UV-vis Absorption Spectroscopy

The optical transmittance of TiO_2-CLs was investigated by using UV-vis spectrophotometer (Thermo, Genesys 10S) in the visible region.

Current-voltage (J-V) Measurements

Upon illumination of AM 1.5 G spectral distribution, current-voltage (J-V) characteristics were measured using a Newport solar simulator in combination with a computer-controlled digital source meter. The certified Si solar cell (Fraunhofer ISE) was used to adjust the light intensity to 1000 W m^{-2}. A black mask with an aperture (0.5 × 0.5 cm^2) was used for accurate measurement.

Results and Discussion

X-ray diffraction spectroscopy (XRD) was used to investigate the formation of titanium oxide onto FTO substrates. From the investigation of XRD profile in Figure 1, the TiO_2 crystalline structure was identified. The strong diffraction peaks at 35° and 55° and the featuring of peaks at 63° and 68° confirmed TiO_2 anatase phase.

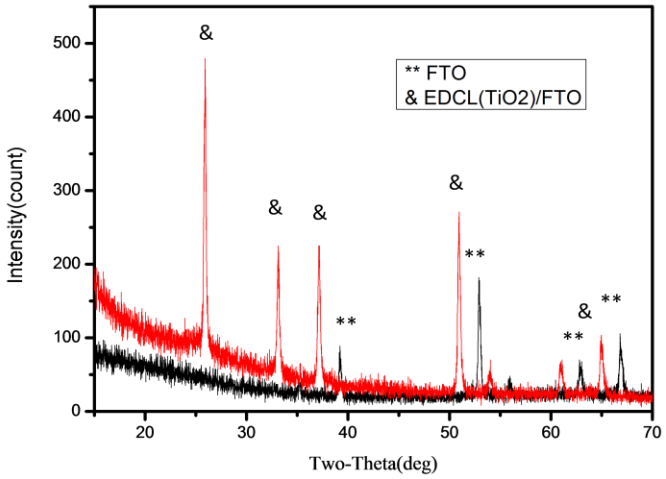

Figure 1. XRD spectrum of TiO_2 compact layer produced from acidic titanium (III) chloride at room temperature following sintering temperature 450 °C for 30 minutes. Applied current= 20 μA, deposition time = 1000s.

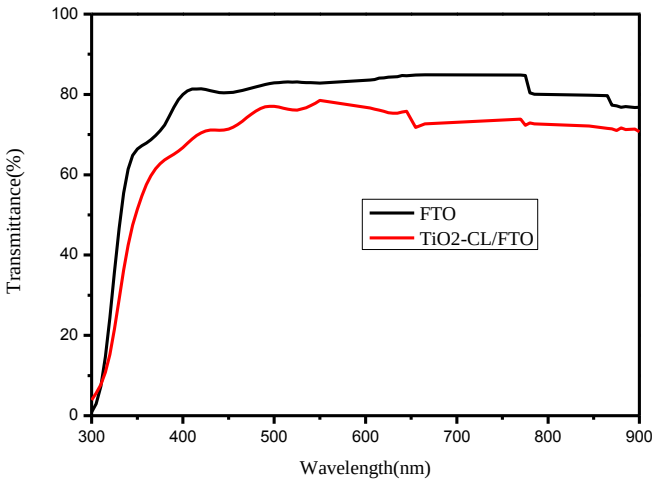

Figure 2. The transmission spectra of bare FTO and TiO_2-CL/FTO.

Furthermore, the transparencies of TiO_2 compact layers produced by the electrochemical deposition method were investigated in comparison with control FTO substrates. The transmission spectra of TiO_2 compact layers/FTO and FTO substrates were presented in Figure 2. The transparency of TiO_2 layer prepared by the electrochemical deposition method was not much different from that of FTO substrates, thus it can be used as a front electrode.

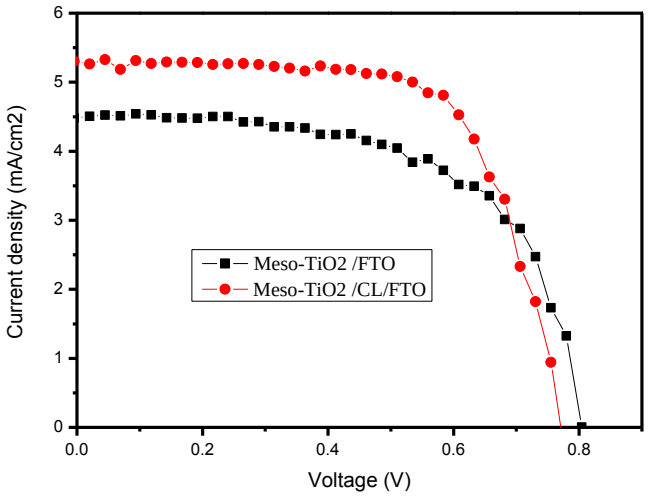

Figure 3. Current-voltage curves of DSSCs with and without TiO_2 compact layers incorporating with, Co(II/III) electrolyte (0.22 M Co(II) and 0.033 M Co(III), 0.1 M LiTFSI and 0.5M 4-tert-butylpyridine in Acetonitrile). Photo-sensitizer (LEG4).

Table 1. Photovoltaic parameters of DSSCs with and without TiO_2 compact layer. Short-circuit current (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF), and power- conversion efficiency.

Photoanode	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
Meso-TiO_2/FTO	0.80	4.5	0.61	3.4
Meso-TiO_2/CL/FTO	0.78	5.3	0.67	4.5

The current-voltage (J-V) curves for the two devices with and without the TiO_2 blocking under layer measured under AM 1.5 G illuminations were shown Figure 3. The photovoltaic parameters were summarized in Table 1. DSSCs with an incorporation of TiO_2 compact underlayer in photoanode has produced a higher power conversion efficiency (PCE) of 4.5% yielding V_{oc} (0.78 V), J_{sc} (5.3 mA/cm^2) and FF(0.67) while in the device without TiO_2 blocking underlayer, the PCE is 3.4% revealing V_{oc} (0.80 V), J_{sc} (4.5mA/cm^2) and FF(0.61). It is speculated that the recombination in between transparent FTO substrate and meso-TiO_2 could be reduced efficiently. Obviously, increase in J_{sc} and FF lead to a higher overall PCE of devices fabricated with TiO_2-CL deposited electrode which is in agreement with the previous report which studied the effect of blocking layer in different dye systems [5].

Conclusion and Outlooks

In summary, TiO_2 compacter layers prepared by the electrochemical deposition method were applied as an efficient blocking underlayer in DSSCs. The photosensitizer is an organic dye LEG4 and the redox mediator is Co (II/III) based electrolyte. With an improved J_{sc} and FF values, higher PCE of 4.5 % was achieved with an incorporation of TiO_2 compact layer. It is expected that using different additives in TiO_2 layers deposition in future experiment could enable further efficiency improvement in DSSC devices.

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