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Back-Illuminated Dye-Sensitized Solar Cell Flexible Photoanode on Titanium Foil

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This paper reports the preparation and performance analysis on dye-sensitized solar cells (DSSC) using titanium (Ti) foil as flexible photoanode for back-illuminated measurement. Performance differences were also carried with the fluorine-doped tin oxide (FTO) glass photoanode using the back and front-illuminated technique. The hydrogen peroxide (H2O2) treated Ti foil surface was applied and the doctor blade method was used for deposition on photoanode during the process of fabrication. Surface morphology of the treated Ti Foil with H2O2 shows the formation of TiO2 nanostructure which results in significant attachment of TiO2 layer on Ti Foil. The results on measurement show that the fabricated flexible photoanode DSSC has an efficiency of power conversion at 1.00% under 1.5 A.M solar radiation by using back-illuminated while DSSC with solid-state glass photoanode has an efficiency power conversion at 0.53% (back-illuminated) and 2.22% (front-illuminated). However, the flexible photoanode DSSC has better power conversion efficiency than the solid-state glass photoanode DSSC under the condition of back-illumination. It is lower in result comparatively with front illumination DSSC due to the coated of platinum at the counter electrode that reflects light partially, while electrolyte iodine absorbs some photons and effects on DSSC performance.

Keywords: DSSC; Solar Cell; Ti Foil; Back-Illumination; Flexible Photoanode

I. INTRODUCTION

Renewable energy nowadays is experiencing an increment of worldwide attention due to various profits in an extended period as it is inexpensive and eco-friendly. Commonly, renewable energy was originated from resources which are renewable such as; hydro, wind, solar, and geothermal. Few supereminent among all and large scale utilization which started from small scale systems such as photovoltaic power station and the digital solar calculator, is the solar energy. Electricity is converted from photon to direct current via solar modules. The core of the sun emits nuclear fusion power committed to form the energy (Ellabban *et al*., 2014).

There are several peer groups of photovoltaic technologies in solar energy. First generation of the photovoltaic mono-crystalline also known as polycrystalline silicon, demonstrates typical efficiency of 15% to 25 % (Sharma *et al*., 2015). The good performance of this solar cell technology as well as high stability is the benefit of this PV Cell (Kranz *et al*., 2015). However, lots of energy and expensive production cost is needed. Thin-film solar cells are the next group using cadmium telluride (CdTe), copper indium gallium selenide (CIGS) including

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amorphous silicon (a-Si), where efficiency at 10% to 15% was achieved (Ferekides *et al.*, 1994). It also lowers the fabrication cost since it avoids the usage of silicon wafer processes. High-temperature treatment and vacuum involvement during production is associated with large energy consumption. Furthermore, low sufficient source of CdTe on second generation solar cells for the demand and this is the cause of the price restrain factor. The thin-film CdTe solar cell production must be handled carefully as it is toxic for human beings (Fthenakis *et al.*, 1999). Third generation solar cells are mostly polymers, and organic, consisting of tiny molecules. It contributes to a lower cost although its efficiency could go up to 20%. Perovskite solar cell is currently under investigation with great potential with efficiencies recorded at 20% on very small areas (Conibeer *et al.*, 2016). Despite that, perovskite vulnerability suffers from unstable processes, considering it should be fabricated in a strict, uncontaminated area with humidity temperature control.

Dye-Sensitized Solar Cell (DSSC) are in the third generation PV group that exchanges light energy to a voltaic energy constructed on the dye molecules absorption in wide-bandgap of a semiconductor film. Dye-sensitized Solar Cell received global attention due to its increasing energy conversion efficiency at 11.9% and it also has moderate cost of production (Tsai *et al.*, 2013; Buda *et al.*, 2017; Buda *et al.*, 2017). Important components for common DSSCs are wide band-gap semiconductor, synthetic sensitizer to act as a photoanode, catalyst, redox couple, and mechanical support. The photoanode is normally a dye particle coated together with the nanopore metal oxide semiconductor film deposited on the TCO glass substrate as the working electrode. The platinum (Pt) catalyst deposited on TCO substrate acts as the counter electrode and redox couple mediator is the iodide-triiodide ($I^-/I3^-$) electrolyte (Fan *et al.*, 2013).

Metal oxide semiconductor comprises of TiO2, ZnO and SnO. The semiconductor is engaged as a light absorber and photo-induced charge separation transport are different the functioning of a DSSC. In an ordinary DSSC, light is absorbed by a molecule in a synthetic dye sensitizer familiarly known as N719, which conducts to the n-type semiconductor wide band-gap surface (Cavallo *et al.*, 2017). The dye sensitizer is DSSC photographic component as when it is sensitized by any visible light, it will be converted to electricity. The dye excites electrons from the ground state and then injects the excited electron to the nanocrystalline TiO2 semiconductor after seizing photons from any visible source. TCO glass with Pt coating counter electrode performs the catalytic activity of $I^-/I3^-$ reduction (Tsekouras *et al.*, 2008). Electrolyte redox mediators assist to connect and reconstruct the oxidized dye. Most redox mediators with slow recombination rate with the injected electrons chosen are the $I^-/I3^-$ couple (Gu *et al.*, 2017). The electrolyte closes the circuit as the electrons yield to the sensitizer. These electrons create energy and gather them to the load appliances. Some alteration made to the common DSSC with regards to the substrates are flexible DSSC. As it has excellent electrical conductivity, metal materials were chosen. Besides, its bendability and pliable, at high thermal treatment stability matched to the plastic, surface resistivity lower than indium tin oxide/polyethylene tetraphlate (ITO/PET), plus as inexpensive production cost puts metal a good substitute (Lin *et al.*, 2010). The implementation of metal as a working electrode for DSSC substrates could minimize the internal resistance on substrates yet helps the productivity of the solar cell and mark down the cost of the devices. Various metals carried out nowadays as substitution include W, StSt, Ni, Ti, Co, Pt, Cu, Al, and Zn (Wu *et al.*, 2017).

The preliminary article studied such H2O2 treatment on Ti foil photoanode is an excellent example. This is because the H2O2-treated Ti foil shows a high device area due to the networked TiO2 nanosheets formed, which increases electrical correspondence between substrate and nanoparticles of TiO2 (Tsai *et al.*, 2013). The oxidized Ti foil layer surface property and treatments have been established to profoundly control surface adhesion and ideal electrical contact of Ti-wires coated TiO2 (Kapil *et al.*, 2014).

This paper discusses the surface treatment of Ti Foil and deposition method of TiO2 paste on Ti Foil as flexible photoanode for back-illuminated DSSC. This is very important because a suitable method is capable to make TiO2 layer properly attached to Ti Foil so it would not crack after annealing and detached while immersed in the dye. The step-by-step process in detail on flexible Ti foil fabrication as photoanode and the evaluation on the performance of the outcome are described in this paper.

II. MATERIALS AND METHOD

A. Material

The following materials were purchased from merchant

suppliers: pure metals (titanium (Ti) foil purity of 99.5%; The Nilaco Corporation), FTO conductive glass (> 83 % ;< 150hm/sq.; Zhuhai Kaivo Optoelectronic Technology Co., Ltd.), glacial acetic acid (ACS Analysis; 99.7%, J.T Baker), ethanol, ethyl alcohol, 2-propanol (Quality Reagent Chemical), chloroplatinic acid hexahydrate, ,titanium dioxide (TiO2) P25 anatase-nanopowder, hydrogen peroxide, H2O2 (Sigma Aldrich), redox mediator iodine-based electrolyte (Solaronix). Di-tetrabutylammoniumcis-bis (isothiocyanato) bis (2,2-bipyridyl-4-dicarboxylato) ruthenium(II).

B. Glass Substrates Preparation

Firstly, the FTO conductive glass with resistivity surface at 15 Ω/sq was chosen as the substrate, the glass slits to 20 mm × 25 mm with the usage of a Glass Cutter System (ZHKV-DT300) from the non-coated area. The slit glasses were cleaned with soap and sonicated to remove any surface contamination during slitting. Then, the glasses were placed in acetone and later the cleaning was repeated with ethanol and isopropanol and submitted to sonication for an additional 15 min respectively to eliminate organic contaminants. Finally, the excess fluid on glass substrates was dried after rinsing with de-ionized (DI) water deliberately.

C. Flexible Photoanode Substrates Preparation

Next, the Ti foil was cut into 20mm × 25mm. Then the foil was cleaned with detergent, acetone, ethanol and isopropanol in 15 min respectively using ultra-sonicator. The Ti foil was then immersed into H2O2 solution at (30 Wt. %, 20 mL) in a petri dish together with a magnetic bar depending on the diameter of the dish and spun 30 min with speed of 500 rpm at 70°C. Throughout immersing, H2O2 reacted with the Ti foil creating TiO2 networked nanosheets on the scratched side of the photoanode. To further improve the crystallization of TiO2 nanosheets, the Ti foil was annealed for 30 min at 450°C (Tsai et al., 2013). Figure 1 shows the preparation of Ti foil (a) the oxidized surfaces of Ti foil, (b) the sandpaper scratched surface and (c) the H2O2-treated annealed surface of Ti foil.

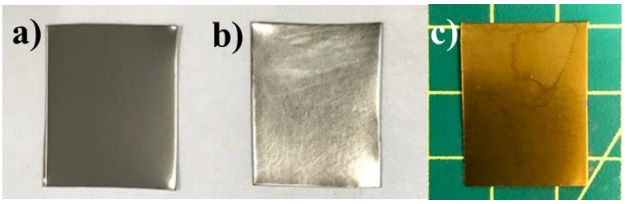

Figure 1. Preparation of Ti Foil (a) the oxidized surfaces of Ti foil, (b) the sandpaper scratched surface and (c) the H2O2-treated annealed surface of Ti foil

D. TiO2 Paste Preparation

The TiO2 P25 anatase-nanopowder was preheated for 30 min in a furnace at 400°C to eliminate organic impurities and any moisture. The heated TiO2 powder was mixed with 0.2ml of DI water and acetic acid respectively. The mixture was ground in a ceramic mortar. This is to lessen the particle size mean by extending the dispersion time. Also, by extending the time of grinding, the transparency of the coated film could be enhanced. This TiO2 solution went through ultra-sonication at 15 min to acquire homogenous paste of TiO2. The obtained homogenous white paste was stirred at a speed of 300 rpm in room temperature for 2 hours. Then, the runny paste was evaporated at 80°C for 15 min to obtain a viscous thick paste. The paste was transferred into a bottle and sealed with parafilm to avoid any moisture adsorbed in paste (Valsaraj *et al.*, 2016).

E. Deposition of TiO2 Layer

The TiO2 paste was deposited on the Ti foil using the doctor blade method. In the experiment, 3M scotch tape was placed at the edges of the scratched Ti foil to create a 10 mm2 square area for TiO2 paste deposition. Next, TiO2 paste was applied on the masked top edge of Ti foil and spread across the unmasked area using a squeegee. Then, the scotch tape was removed, leaving an uncoated area of Ti foil for electrical contact for solar measurement. To evaporate the solvents and binder presented in the paste, the films were sintered at 4500 C in 30 min inside the furnace. Following the cooling off to 80˚C, the films were directly immersed in the red dye N719 solution dissolved with ethanol at a volume ratio of of 1:1 and sealed at room temperature for a minimum of 24 hours. Figure 2 shows

(a) the sintered TiO2 film on Ti foil and (b) dye-immersed Ti foil.

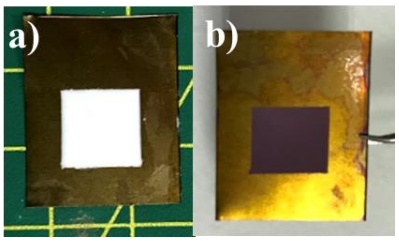

Figure 2. (a) Sintered TiO2 film on Ti foil, and (b) dye-immersed Ti foil

F. Counter Electrode Preparation

The FTO glass was used as a counter electrode and these glasses were cleaned. To prepare the Pt solution, 2 mM of hexachloroplatinic acid was dissolved in 20 mL of isopropanol solution. Then, the solution was dropped and spin-coated on FTO glass. Next, the glass was sintered at 450°C for 30 min.

G. DSSC Assembly and I-V Measurement

Figure 3 (a) shows the photoanode loaded with N719 being air-dried. The fabricated counter electrodes were sandwich together using 60 µm thick Surlyn polymer. The polymer film was cut as a spacer of 5 mm × 15 mm and framed around the area of TiO2 film. Later, iodine-based electrolyte was injected into the device. Figure 3 (b) shows the solar energy conversion efficiency was tested under the solar spectrum at AM1.5 densities using a solar simulator. An evenly maintained distributed incident power densities beam homogenizer was also incorporated into the device across the irradiation area. The plotted I-V characteristic was analysed to be measured the I-V characteristic, fill factor, power output, and efficiency using Keithley 2450 SourceMeter.

H. Surface Morphology Characteristics

Field Emission Scanning Electron Microscopy (FESEM) was used to characterize the surface morphology of Ti Foil before and after the surface treatment of H2O2. The magnification for the characterization was 2.5 kX and 50 kX. While the Atomic Force Microscopy (AFM) used to analyze the surface topography of the Ti foil includes the thickness and roughness of the Pt catalyst on FTO glass.

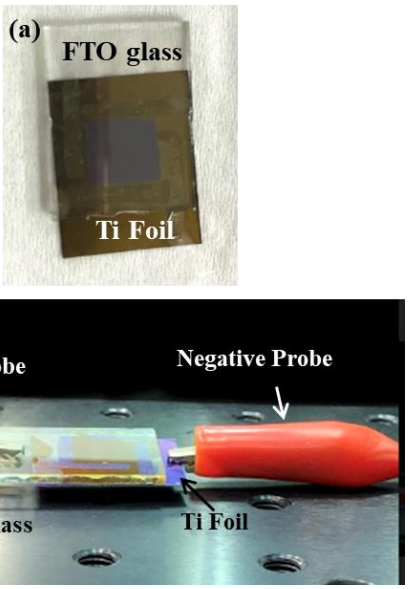

Figure 3. (a) Assembled Ti foil and Pt counter electrode and (b) setup on testing the DSSC

III. RESULTS AND DISCUSSION

A. Characterization

Figure 4 shows the FESEM image of (a) Ti foil without and (b) with H2O2 treatment. The untreated Ti and H2O2 treated surface roughness can be seen as shown in Figure 4 (a) and (b) with the formation of packed TiO2 nanosheets due to the oxidation reaction the Ti with H2O2. The TiO2 nanosheet is expected to increase the absolute area of Ti substrate because of its structure to enhance dye loading and the electrical contact between TiO2 nanoparticles and the Ti substrate compared to the untreated surface. Surface morphology of the treated Ti Foil with H2O2 shows the formation of TiO2 nanostructure which results in significant attachment of TiO2 layer on Ti Foil. (Kapil *et al.*, 2014; Tsai *et al.*, 2013).

Figure 5 (a) shows the atomic force microscopy (AFM) image of Pt-based counter electrode to measure the thickness of Pt catalyst layer. The thickness of Pt layer on FTO glass is important for back illumination due to a thicker layer can cause light reflection and reduce light transmission to the photoanode electrode (Mohammadpour *et al.*, 2015). The thickness of Pt was

measured to be approximately 3.11 nm.

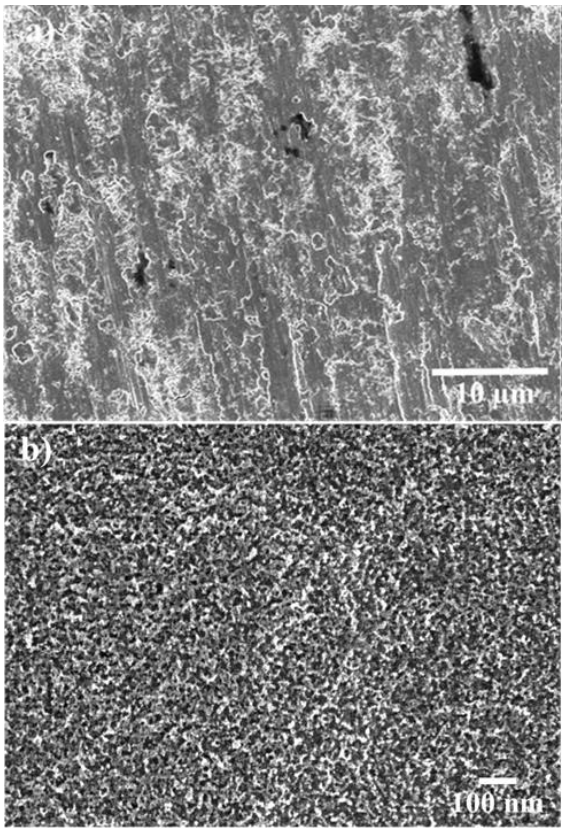

Figure 4: The Field Emission Scanning Electron Microscopy (FESEM) image of (a) Ti foil without H2O2 treatment at a magnification of 2.5 kX and (b) Ti foil with H2O2 treatment at a magnification of 50 kX

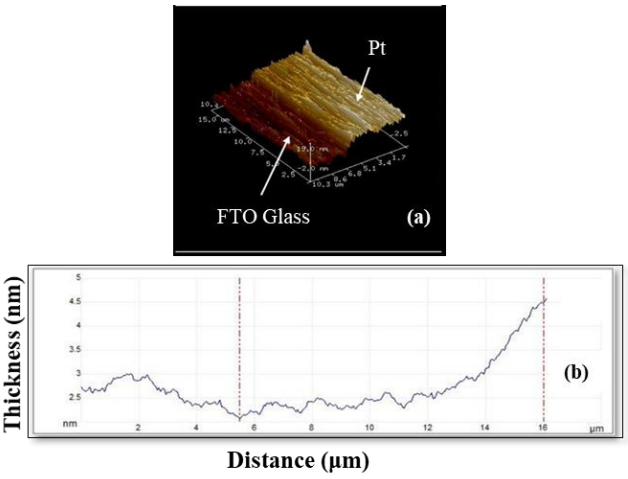

Figure 5. AFM of Pt-based counter electrode (a) 3D image and (b) thickness measurement

B. I-V Characteristic Performance

The investigation of fabricated Ti foil flexible photoanode is performed together with the glass solid-state photoanode with both illumination condition setup. Figure 6 shows I–V characteristics of Ti foil flexible photoanode DSSC in comparison with solid-state glass photoanode DSSC. From the plotted graph, the back-illuminated DSSC with flexible photoanode has better performance on short circuit current density, (J_{SC}), open-circuit voltage (V_{OC}) and the fill factor (FF), compared to glass-based DSSC. Despite that, the performance of glass-based DSSC through front illumination is highly considerable too. The transparency effect on the counter electrode gave impact to the DSSC performance (Balasingam *et al.*, 2013). The Pt and FTO layers on counter electrode reduced the transparency of the substrate. The only alternative for measurement are back-illumination hence the metal Ti photoanode based DSSC is opaque and no light can pass through with the front-illumination setup. To strengthen the performance, counter electrode transparency needs to be enhanced.

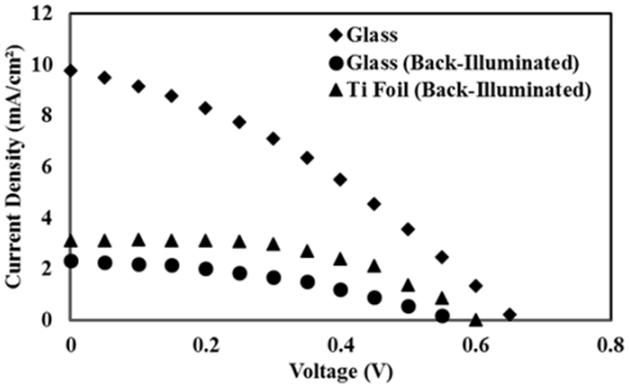

Figure 6: I-V characteristics measured (◆) the glass (front-illuminated), (●) the glass (Back-illuminated) and (▲) the Ti foil (Back-illuminated).The irradiation of solar simulator was AM 1.5 (100 mW/cm²).

Table 1 shows the performance details on DSSC with fabricated Ti foil photoanode. The measured V_{OC}, J_{SC}, FF, and also efficiency respectively are 0.6 V, 3.12 mA/cm², 0.51 and 1.00%,. The contrast of efficiency from back-illuminated glass DSSC reduced by half with the Ti foil DSSC and front-illuminated glass DSSC doubled with the Ti foil DSSC.

The notable drawback of this DSSC configuration is due to the losses of transmission of coated Pt at the counter electrode as well as the absorption by redox mediator electrolyte I^-/I_3^- (Jin *et al.*, 2017). The incident light was

cut by electrolyte at the back illumination slightly

Table 1: Details of DSSC Performance for front and back illumination

Parameter	Glass		Ti Foil
	Front	Back	Back
V_{OC} (V)	0.65	0.55	0.60
J_{SC} (mA/cm²)	9.77	2.32	3.12
Fill Factor	0.35	0.41	0.51
Efficiency (%)	2.22	0.53	1.00

from optical wavelength of 400 nm to 600 nm on Ti foil flexible photoanode DSSC while the absorbance of Pt is 540 nm to 680 nm (Ito *et al.*, 2006). The nanotube array DSSC exhibit consistently huge amount of V_{OC} typically 0.8 V incomparable to published values of 0.84V for front-illumination solar cell because of this limitation (Paulose *et al.*, 2006)

As reported in (Tsai *et al.*, 2013), the improvement of dye-loading also provides good absorption for the Ti foil photocurrent after the treatment of H2O2 networked with TiO2. The method generated from this paper was applying the method of screenprint rather than the method of doctor-blade. The method of doctor-blade is not preferable for the flexible substrate as it causes rupture during fabrication due to any curvature during fabrication which disengage it from the surface as a high density of paste is applied in the doctor-blade method. Some proposals for efficiency performance at back-side illumination are displacing the electrode with an extra translucent material. Varieties of Platinum catalyst thickness and solid-state electrolyte film could be implemented.

IV. CONCLUSION

The surface treatment for Ti Foil with H2O2 improves the surface bonding between TiO2 and Ti Foil. Titanium foil as flexible photoanode has been successfully assembled and measured by back-illumination under AM 1.5. The reassuring efficiency results at 1.00% with the setup for back-illumination testing. Loss of transmission due to Pt and $I^-/I3^-$ electrolyte is the main drawbacks for back-illumination configuration as the iodine electrolyte cuts the incident light from 400 nm to 600 nm while the absorbance of Pt is 540 nm to 680 nm. The shorter wavelength in solar spectrum sight was the reason for the lesser efficiency of the back-illuminated measurement.

V. ACKNOWLEDGEMENT

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