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# Preparation of platinum-free tubular dye-sensitized solar cells by electrophoretic deposition

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**Abstract**

Tubular dye-sensitized solar cells (DSSCs) were developed by replacing expensive materials with those of lower cost as follows: (1) substituting conductive glass electrodes for titanium (Ti) wires, and, (2) use of a mixture of multi-walled carbon nanotubes, MWCNTs and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate), and PEDOT-PSS in place of a platinum (Pt) catalyst. Platinized counter electrodes were used as the standard counter electrodes for comparison. The effects of the chemical treatment of a titanium wire substrate and electrophoretic deposition conditions on the efficiency of the resulting DSSCs were also investigated. Chemical treatment of titanium wires was done by soaking the wires in HF-$HNO_3$ solutions at three different concentrations, 0.8, 1.6 and 2.4 M, for three different soaking durations, 5, 10 and 15 min. The optimal condition was found to be a HF-$HNO_3$ concentration of 0.8 M and a soaking duration of 10 min. Film coating on working electrodes was performed using an electrophoretic technique at three different voltages, 5, 8 and 10 V, and four different coating durations, 1, 3, 5 and 7 min. Then, the optimal voltage of 5 V and deposition duration of 5 min was applied for film deposition on counter electrodes. The efficiency of the resulting DSSC with a CNTs/$TiO_2$ counter electrode was 0.03%. The addition of PEDOT-PSS improved the efficiency of this DSSC to 0.08%.

**Keywords:** Tubular dye-sensitized solar cell, Platinum-free solar cell, Electrophoretic deposition, Carbon nanotubes, PEDOT-PSS

## 1. Introduction

Dye-sensitized solar cells (DSSCs) are emerging as low cost alternatives to conventional silicon and other thin film solar cells because of their simple structure, low fabrication cost, low incident-light dependence and environmentally friendly properties. However, there are obstacles to be overcome including electrolyte leakage, cell sealing difficulties, low stability, high cost transparent conductive materials and platinum catalyst [1-2].

The problem related to electrolyte leakage of conventional flat DSSCs is due to the large contacting are between liquid electrolyte and sealing materials around the cells. To overcome the problems, tubular/wire-shaped DSSCs were proposed [3-6]. Experimental results showed that the new designed DSSCs had the potential to solve the problems related to the encapsulation of liquid electrolyte, attributed to their easy sealing, small sealing area and thus reduced electrolyte leakage possibility. Only one end of capillary tube needs to be sealed, so that total sealing areas are independent of the length of cell. Moreover, the high cost transparent conductive glass can be replaced by the lower cost conductive metal materials including stainless steel and commercial titanium wires [4-6]. In addition, the conductivities of the alternative electrodes are greater than that of transparent conductive glass.

In some conventional flat DSSCs, alternative cheaper catalysts were employed such as carbon black [7] carbon nanotubes (CNTs) [8] graphite [9] and conductive polymers [10-12] instead of high cost platinum. Carbon nanotubes are ones of the most promising alternative catalysts for DSSCs due to their large good catalytic activity, surface area and good conductivity. Recently, it was reported that Poly(3,4-Ethylendioxythiophene)–Poly(Styrene Sulfonate) (PEDOT–PSS) and titanium dioxide ($TiO_2$) composite offered comparable performance to Pt as the catalysts in DSSCs [12]. In addition, PEDOT–PSS not only showed good catalytic performance but also improved connection between $TiO_2$ particles, resulting in the reduction of cell resistance.

Dip coating was applied for the film preparation on electrode wires of tubular DSSCs [5-6]. However, the dip coating and sintering have to be repeated several times to obtained the film with adequate thickness, resulting in time and energy consuming. On the other hand, electrophoretic deposition (EPD) has a fast deposition rate, simple apparatus, no restriction on the substrate shape, and no binder required [13-16]. The coating can be finished in single step and the film morphology and thickness are simply controlled by

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adjusting coating voltage and duration.

In DSSCs fabrication, substrate pretreatment is an important step which affects the properties of the resultant DSSCs. The common pretreatment of Ti substrate is the chemical treatment by using hydrofluoric acid- nitric acid (HF-$HNO_3$) solution as a pickling solution [17- 19]. The acid solution not only etches Ti surface but also removes a passivating film. The XRD result by Yun *et al*. [19] revealed that the passivating film found in untreated Ti consisted of oxides with several forms including anatase $TiO_2$, rutile $TiO_2$ and titanium oxides. However, only rutile $TiO_2$ was detected after the chemical treatment. This indicated that most substances in the passivating film were eliminated during the chemical treatment. Their field-emission transmission electron microscopy (FE-TEM) and a fast Fourier transformation (FFT) diffractogram results also showed that the passivating film of the non-treated Ti substrate possessed disordered grain structure (low degree of crystallinity) while the surface of HF- $HNO_3$ treated Ti substrates had a single crystalline structure. It was also reported that the acid treatment of Ti substrate apparently helped to reduce an electrical resistance and improve the efficiency of DSSCs.

To our best knowledge, the use of alternative catalysts and electrophoretic deposition in tubular DSSCs has not been reported. The present work aims to develop tubular DSSCs by using carbon nanotubes and PEDOT-PSS composite as alternative catalysts and using commercial titanium (Ti) as substrate. To overcome the tedious repletion of dip coating, electrophoretic deposition is chosen for film deposition. Since the acid (HF- $HNO_3$) treatment of Ti substrate showed a positive effect on the property of DSSCs, the method is adopted in the present work. The effects of acid solution concentration and treatment duration are reported.

## 2. Materials and methods

### *2.1 Preparation of working and counter electrodes*

Commercial Ti wires with diameter of 0.5 mm (Prologtitanium, Thailand) were polished using abrasive paper and subsequently subjected to a chemical treatment in hydrofluoric acid- nitric acid (HF-$HNO_3$) solution as recommended in the previous paper [17]. The acid concentration varied from 0.8 to 2.4 M, the duration of the chemical treatment in the acid solutions varied from 5 to 15 min while the volume of acid solution for the treatment of each Ti wire was kept constant at 20 ml. After immersing in acid solutions, Ti wires were cleaned in DI water for three times, followed by ultrasonic cleaning in acetone, isopropyl alcohol and ethanol, respectively (10 min. for each step). Subsequently, the wires were dried at 100°C and then treated in 50 mM titanium (IV)isopropoxide solution at 70°C for 50 min and sintered at 450°C for 30 min. The working electrodes are obtained by coating $TiO_2$ nanoparticle film from $TiO_2$ colloids on the treated Ti wires via electrophoretic deposition. The $TiO_2$ colloid was prepared by dispersing 0.5 g P25 $TiO_2$ nanoparticles (Degussa) and 0.04 g iodine in 50 mL acetyl acetone. The colloid was sonicated for 30 min. Ti wires were employed for both negative and positive electrodes, the distance between two electrodes was kept constant at 1 cm. Deposition voltage varied from 5 to 10 V and deposition duration varied from 1 to 7 min. The schematic diagram of the electrophoretic deposition (EPD) setup is shown in Figure 1. Then, the coated wires were post-treated in 50 mM titanium (IV)isopropoxide solution at 70°C for 50 min and sintered at 450°C for 30 min. The coated wires were subsequently immersed in the dye solution (N719 dye, $5\times10^{-4}$ M in ethanol, Solaronix SA) for 24 h at room temperature. The sensitized electrodes were then rinsed with anhydrous ethanol and dried in air.

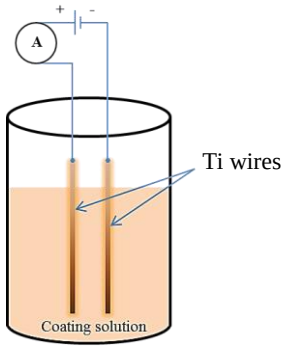


**Figure 1** The schematic diagram of the electrophoretic deposition (EPD) setup

To fabricate counter electrodes, multiwall carbon nanotubes (MWCNTs, Sigma –Aldrich) with OD of 7-15 nm and length of 0.5-10 μm were treated with mixed sulfuric acid-nitric acid solution ($H_2SO_4$:$HNO_3$= 3:1) for 8 h at 70°C to introduce functional groups onto the surfaces of the nanotubes. MWCNTs were rinsed with deionized water and dried at 80 °C under ambient condition. The $TiO_2$ – MWCNTs colloid was prepared by the same procedure for the $TiO_2$ colloid, except MWCNTs were added with 0.3% wt. The low concentration of MWCNTs is used in order to avoid aggregation problem [20]. The deposition process was also in the same manner of that for the working electrodes. Then, some coated wires were optionally immersed in PEDOT: PSS solution (0.54% in $H_2O$, high- conductivity grade, Sigma-Aldrich) at 70°C for 2 h and then dried at 80°C for 6 h. In addition, the attempt to incorporate polyethylene glycol (PEG, MW=4000) as a binder into deposited film was also made by adding PEG into a coating solution with PEG:$TiO_2$ = 3:1 by weight. For comparison, platinized counter electrodes as standard counter electrodes were also prepared by dipping deposition of platinum (Pt) compound solution (Platisol T/SP, Solaronix SA) on treated Ti wires at room temperature and dried at 100°C. The deposition and drying processes were repeated for 10 times. After deposition process, the coated films were sintered at 450°C for 30 min.

### *2.2 Cell assembly*

A working electrode was twisted with a counter electrode. Then, both electrodes were inserted into capillary glass tube with a diameter of 1.5 mm and a length of 10 cm. Then, the electrolyte (Iodolyte TG-50, 50 mM, Solaronix SA) was filled into the glass tube The end of the tube was sealed with Amosil 4R and 4H (Solaronix SA) at weight Amosil 4R : Amosil 4H ratio of 100:80.

### *2.3 Measurement and characteristics*

The photocurrent–voltage characteristics of samples were measured with a solar simulator (Model 92250A, Oriel) at an illumination intensity of 100 mW/cm$^2$. The experiments at each condition were all duplicated. The surface morphologies and film thickness were characterized by scanning electron microscopy (SEM, FEI, VERSA 3D) at 5.0 kV.

## 3. Results

### *3.1 Effect of chemical treatment of Ti electrodes*

The surface morphologies of Ti electrodes with and without chemical treatment are shown in Figures 2-3. The results revealed that Ti surface was dissolved and etched by the chemical treatment. The chemical reactions taking place when a titanium sample is immersed in HF-$HNO_3$ solution, are shown as follows [18].
The chemical dissolution of $TiO_2$ passivating film (reaction (1)):

$$TiO_2 + nHF \rightarrow TiF_n^{(n-4)-} + (n-4)H^+ + 2H_2O \quad (1)$$

The oxidation of Ti atom (reaction (2)):

$$Ti + 3/2HNO_3 + 3H^+ \rightarrow T^{3+} + 3/2HNO_2 + 3/2H_2O \quad (2)$$

Then, $Ti^{3+}$ cation is oxidized to form soluble titanium fluorides (reaction (3)):

$$T^{3+} + 3/2HNO_3 + nHF \rightarrow TiF_n^{(n-4)-} + 1/2HNO_2 + (n-1)H^+ + 1/2H_2O \quad (3)$$

Evidently, the longer duration and higher concentration of acidic solution led to more corrosion and further reduction of wire diameters. Efficiencies of DSSCs with untreated substrate and treated substrates at different acid solution concentrations and treatment durations are shown in Figure 4. Note that in this subsection, platinized counter electrodes as the standard counter electrodes were applied for all cells. The DSSCs consisted of most treated electrodes yielded higher efficiency than the ones prepared from an untreated electrode. This can be attributed to the increased surface roughness/area and less impurities on the treated surface (Figure.3) which help to increase film loading and reduce electrical resistance. This result agrees with that reported by Yun *et al.* [19]. However, the excess treatment (with too long duration and too high concentration of acidic solution) suppressed the efficiencies of DSSCs due to the significant reduction of wire diameters. For the studied range, the optimum treatment was achieved by using acid solution at acid concentration of 0.8 M and duration of 10 min. The optimum condition was adopted for the further study.

### *3.2 Effect of electrophoretic deposition condition*

Efficiencies of DSSCs with anodes coated at different applied voltages and deposition durations are shown in Figure 5. Note that all counter electrodes applied for the study in this subsection, were platinized counter electrodes. The efficiencies of DSSCs related to the film thicknesses (Figure 6). Apparently, film thickness slightly increased with increasing deposition voltage but considerably increased with increasing deposition duration. The increase of deposition duration from 1 to 3 min resulted in the increase of film thickness from 5-7 μm to around 14-17 μm, leading to the improvement of cell efficiency from 0.04-0.06% to 0.13-0.15%. This can be attributed to the increase of dye loading and larger interfacial area between a working electrode and an electrolyte. The further increase of deposition duration from 3 to 7 min resulted in the increase of film thickness from 14-17 μm to around 20-22 μm. However, the efficiency of DSSC insignificantly changed. In addition, the increase of deposition duration from 3 to 7 min resulted in a slight decrease of the efficiency of DSSCs. This can be explained that as film thickness increases beyond the optimum point, the effect of the increased carrier recombination (negative effect) is dominant over that of the increased dye loading (positive effect) [13]. For the studied range, the DSSC with anode prepared at deposition voltage of 5 V and deposition duration of 5 min yielded the maximum efficiency of 0.15%. The condition was adopted for the further study. It is noteworthy that micro-cracks were found on all coated films including the one at the optimum condition as shown in Figure 7. The attempt to reduce crack formation was made by incorporating polyethylene glycol (PEG, MW=4000) as a binder into a coating solution with PEG:$TiO_2$ = 3:1 by weight. However, it was found that no film deposited on a Ti wire during the coating process. This is possibly attributed to the repulsion of functional group (-OH) on $TiO_2$ surface and that on the tails of PEG molecules.

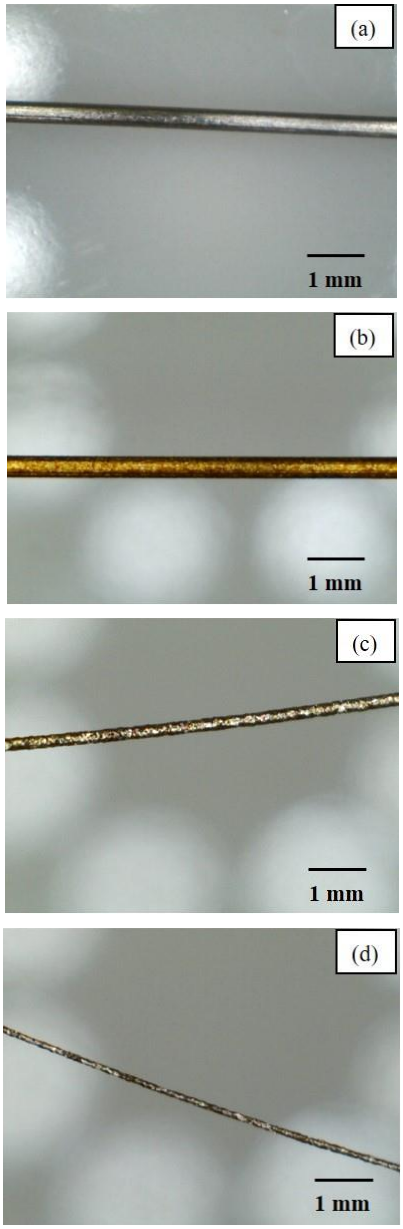


**Figure 2** Photographs of Ti wires with different pretreatment conditions (a) untreated Ti (b) treated at 0.8 M and 10 min (c) treated at 3.2 M and 10 min (d) treated at 3.2 M and 15 min.

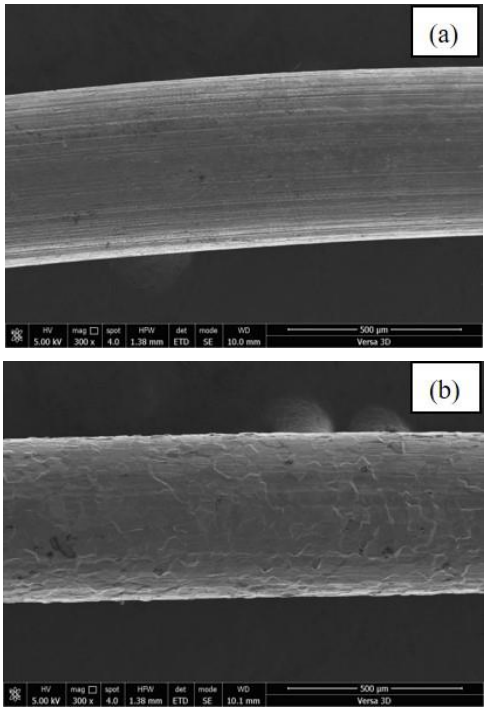


**Figure 3** SEM images of (a) untreated Ti (b) Ti treated at 0.8 M and 10 min.

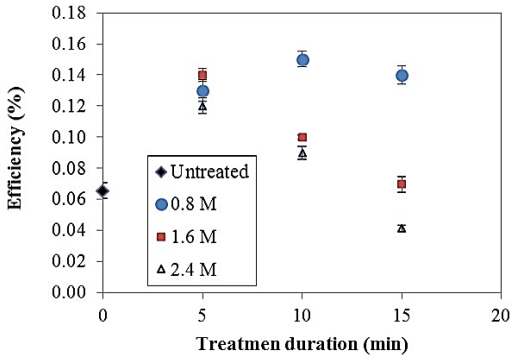


**Figure 4** Efficiencies of DSSCs with untreated substrate and treated substrates at different acid solution concentrations and treatment durations (all working electrodes were prepared by deposition of $TiO_2$ films at 5 V for 5 min while all counter electrodes were prepared by dipping deposition of Pt compound)

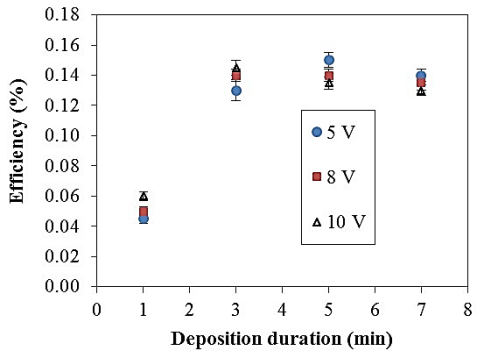


**Figure 5** Efficiencies of DSSCs with anodes coated at different applied voltages and deposition durations (all counter electrodes were prepared by dipping deposition of Pt compound).

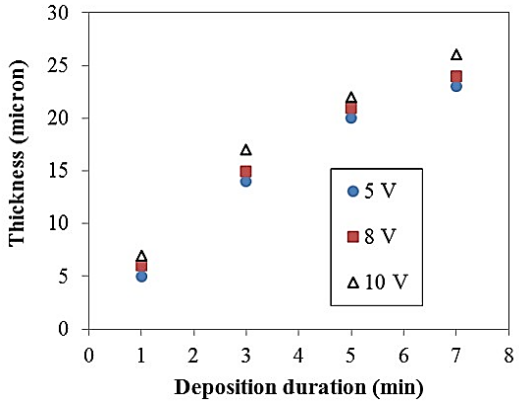


**Figure 6** Thicknesses of films coated at different applied voltages and deposition durations.

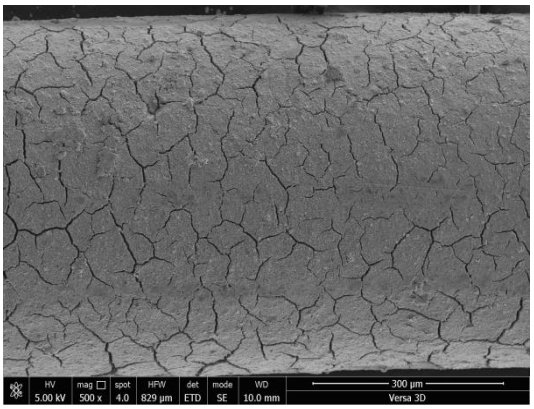

**Figure 7** SEM image of $TiO_2$ film prepared at deposition voltage of 5 V and duration of 5 min**.**

*3.3 Effect of counter electrode composition*

Current-voltage curves of DSSCs with different counter electrodes are shown in Figure 8 and Table 1. Apparently, the DSSCs with Pt-free counter electrodes gave considerably poorer photovoltaic performance than the one with Pt coated counter electrode. This can be attributed to the higher resistance because of the poorer adhesion of electrophoretically deposited films ($TiO_2$/CNTs/PEDOT-PSS and $TiO_2$/CNTs films) on Ti wires as compared to dip-coated Pt films. The poor film adhesion is indicated by the loose- packed structure of a film layer, as shown in Figure 9 (a) [3,5-6]. The addition of PEDOT-PSS improved cell efficiency as the conductive polymer filled the voids in $TiO_2$/CNTs film (Figure 9 (b)). This helps to improve electron transfer by suppressing electron recombination which usually occurs at interface between film/electrolyte. The improved electron transfer is indicated by the increased open circuit voltage (Voc), short-circuit current (Jsc) and also fill factor (FF) [7-9].

It is noteworthy that although the efficiencies of the Pt-free DSSCs (0.03-0.08%) prepared by electrophoretic deposition in the present work are significantly lower than that of the outstanding flat DSSC which is as high as 11% [21] and also lower than those of the tubular DSSCs prepared by dip coating (2%-4%) [3, 5-6]. However, the efficiencies of the Pt-free DSSCs in the present work are comparable to that of the wire-shaped flexible DSSCs prepared by spray coating [4]. This indicates that DSSC efficiency is strongly independent on material and deposition technique.

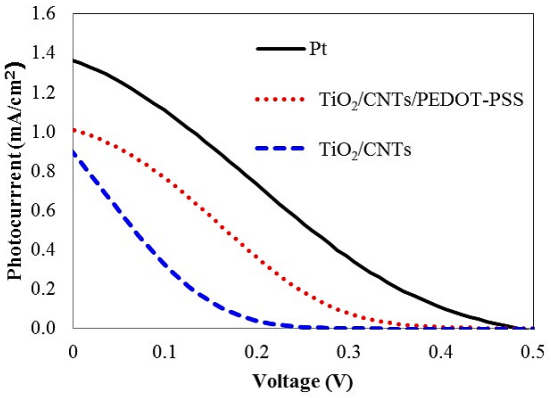


**Figure 8** Current-voltage curves of DSSCs with different counter electrodes.

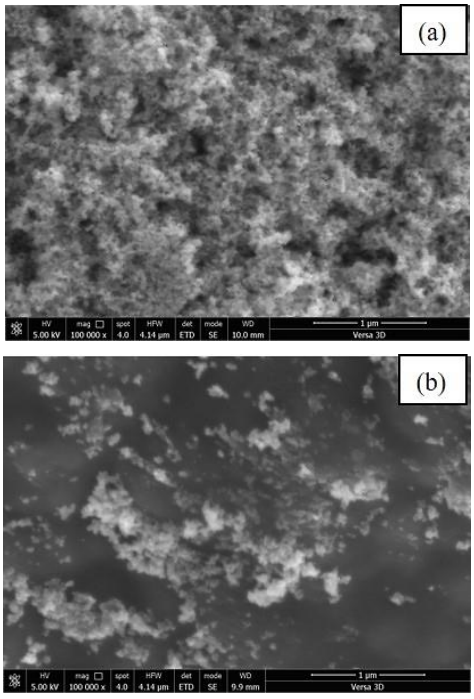


**Figure 9** SEM images of coated films on counter electrodes (a)$TiO_2$/CNTs and (b)$TiO_2$/CNTs/PEDOT-PSS (films prepared at deposition voltage of 5 V and duration of 5 min).

**Table 1** The photovoltaic performances of DSSCs with different counter electrode compositions

| Counter electrode | Voc(V) | Jsc (mA/cm$^2$) | FF | η (%) |
|---|---|---|---|---|
| Pt | 0.485 | 1.35 | 0.223 | 0.15 |
| CNTs+PEDOT-PSS | 0.467 | 1.00 | 0.181 | 0.08 |
| CNTs | 0.298 | 0.84 | 0.135 | 0.03 |

## 4. Conclusions

Titanium surface was cleaned and etched by the chemical treatment in HF-$HNO_3$ solution. The optimum condition of chemical treatment of titanium wire substrate was found at HF-$HNO_3$ concentration of 0.8 M and soaking duration of 10 min. Films obtained from an electrophoretic deposition had loose-packed structure. Thus, resultant DSSCs showed low efficiencies. The addition of PEDOT-PSS to $TiO_2$/CNTs film helped to improve cell efficiency. However, The DSSCs with Pt-free counter electrodes (Ti/$TiO_2$/CNTs with or without PEDOT-PSS) gave poorer photovoltaic efficiencies (0.03-0.08%) than the one with platinized counter electrode (0.15%).

## 5. Acknowledgement

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