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The reversal constituent structure of photo-electrode in dye-sensitized solar cells

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ABSTRACT

This article presents significant experimental data about the dye-sensitized nano solar cells (DSSCs) using the new developed photo-electrode with reversal constituent structure in our CCT laboratory. The conventional constituent structure of a photo-electrode arranged in sequence from the incident light is the transparent conductive glass, the nano TiO_2 semi-conductive porous film, and the dye. In process, the photons energy of the incident light is mainly absorbed by the dye for DSSCs. This causes excited electrons in the dye to jump into conductive band of the TiO_2 and further to transfer into the outer circuit through the conductive glass. That is, a correct constituent structure of the photo-electrode arranged in sequence from the incident light in terms of the working principle should be the dye, the nano TiO_2 film, and the conductive substrate. The conventional constituent structure of the photo-electrode causes the incident light to be hindered by the TiO_2 layer. To reduce the light hindrance for the dye, this work used copper mesh as the conductive substrate and the nano TiO_2 was coated on it. In this way, the copper mesh connects the nano TiO_2 layer with the outer circuit and the holes of the copper mesh also allow the dye to contact with the electrolyte. The new developed constituent structure of the photo-electrode arranged in sequence from the incident light is the dye, the nano TiO_2 film, and the copper mesh. This new constituent structure, which increases amounts of the absorption light in the dye and further improved the short-circuit current as well as the photoelectric conversion efficiency of DSSCs is reverse to the conventional constituent structure.

1. Introduction

Dye-sensitized nano solar cell (DSSC) is a photoelectric chemical solar cell and is mainly composed of the photo-electrode, the electrolyte, and the counter electrode. The photo-electrode is generally built in layer with nano semiconductor of metallic oxide and dye. In process, the incident light is first absorbed by the dye for DSSC. The excited electrons in dye then jump into conductive band of the semiconductor and further run away from the semiconductor through outer circuit to the counter electrode. The electrolyte connects the dye with the counter electrode for electrons transportation through oxidation–reduction reactions [1–3]. Fig. 1 shows schema of the working procedure in DSSCs.

In principle, the constituent structure as shown in Fig. 1 should be made for a DSSC, but the conventional constituent structure of DSSC is rearranged in sequence as shown in Fig. 2 due to the technical reason. In comparison with Figs. 1 and 2, a conductive glass is applied in the conventional DSSC and the semiconductor is in front of the dye due to the dye has to contact with the electrolyte and the semiconductor must connect with the counter electrode though the outer circuit. This conventional constituent structure of DSSC has some disadvantages, e.g. the conductive glass has large electric resistance, the semiconductor in front of the dye hinders the incident light to reach the dye, etc.

Most of studies on DSSC are focused on developing the constituent materials, especially the dye. Today, the maximum reached photoelectric conversion efficiency of DSSC is over 11% [4–6]. Studies on structure of DSSC are relatively few. Liu et al. [7] presented a three-dimensional DNA-like structure of DSSC. The nano semiconductor is first coated on Ti metallic lines and then immersed into dye solution to build its photo-electrode. In comparison with conventional flat-type DSSC, the DNA-like DSSC shows superiority of light utilization due to its symmetrical double-helix structure [7]. Ito et al. [8] presented a bifacial structure of DSSC. The bifacial DSSC can capture the incident light with two surfaces and therefore increases its photoelectric conversion efficiency with ca. 6%.

Moreover, replacing the conductive glass with metallic substrate can reduce electric resistance. The sheet resistance of metallic substrate is more stable after annealing at 500°C, whereas the conductive glass has generally a low ability to withstand heat during the annealing process. Onoda et al. [9] used the Ti sheet as conductive substrate to coat the TiO_2 layer due to it has low sheet resistance. Okada et al. [10] presented a transparent substrate with

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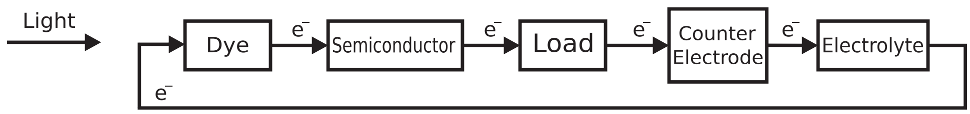


Fig. 1. Schema of the working procedure in DSSCs.

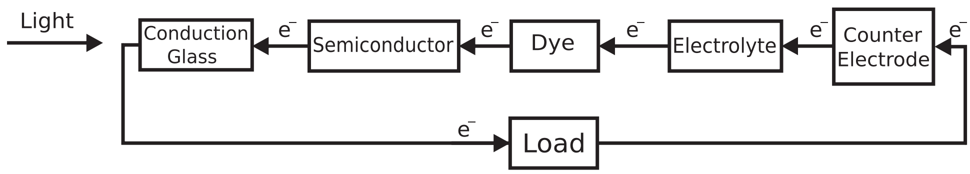


Fig. 2. Schema of the conventional constituent structure in DSSCs.

high conductive rate, which was made with nickel grids formed by an electroplating process and fluorine doped SnO_2/ITO double layered transparent conductive oxides.

This work presents a new developed photo-electrode with reversal constituent structure in DSSCs. The name of reversal constituent structure is relative to the conventional constituent structure of photo-electrode in DSSCs. It is actually the constituent structure in terms of the working principle of DSSC as shown in Fig. 1. The dye is in front of the semiconductor and directly faces to the incident light. A copper mesh is applied as the conductive substrate and coated by the nano TiO_2. In the new constituent structure, the holes of copper mesh allow the electrolyte to run through and to contact with the frontal dye. This new developed photo-electrode with reversal constituent structure in DSSCs can increase absorption of the incident photons by the dye and reduce the electric resistance. The results show good photoelectric conversion efficiency and also lower fabrication cost for DSSCs.

2. Theory

DSSC is mainly composed of three parts, the photo-electrode, the electrolyte, and the counter electrode, where the photo-electrode is normally made by using semiconductor of metallic oxide mixed with dye to coat on conductive glass [2,3]. Fig. 3 schematically shows constituent structure of the DSSC arranged in sequence from the light injection, which are the transparent conductive substrate, the nano TiO_2 layer, the dye, the electrolyte, and the counter electrode. The photons energy of the incident light is mainly absorbed by the dye and causes excited electrons of the dye to jump into conductive band of the TiO_2. These free electrons are further transferred into the outer circuit. The counter electrode receives electrons from the outer circuit and provides them to the dye through the electrolyte with oxidation–reduction reactions. Fig. 4 schematically illustrates the electric circuit in DSSCs. The electric potential energy difference between photo-electrode and counter electrode determines the output voltage of DSSCs.

The photo-electrode of DSSC determines the absorption spectrum and amounts of the incident light which further influence the photoelectric conversion efficiency of DSSC. In other words, the photo-electrode strongly influences the photoelectric conversion efficiency of DSSCs. Moreover, the dye helps the nano TiO_2 to expand its absorption spectrum from region of ultraviolet to region of visible light. In process, the incident light is mainly absorbed by the dye, so that the dye should directly face to the incident light for increasing the absorption of photons. In fact, the dye is unfortunately built behind the nano TiO_2 layer in the conventional constituent structure of the photo-electrode due to the following technical reasons: the dye must contact with electrolyte and the TiO_2 layer has to transfer the electrons through the outer circuit into the counter electrode. The conductive glass is applied in the conventional photo-electrode of DSSCs for light transmittance and electrons transportation from the TiO_2 layer. The conventional constituent structure of photo-electrode in DSSC causes the TiO_2 layer

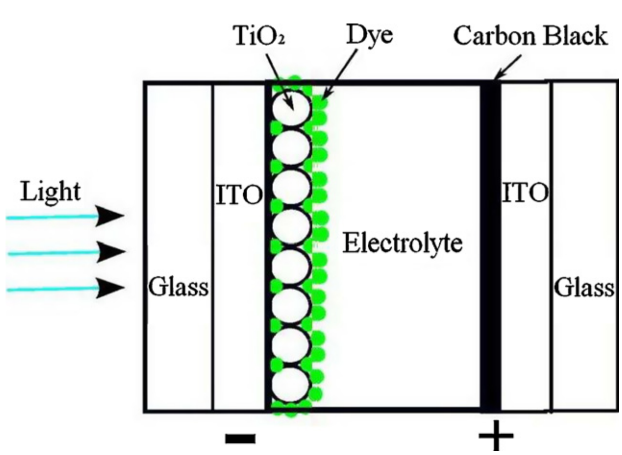


Fig. 3. Constituent structural schema of the conventional DSSCs.

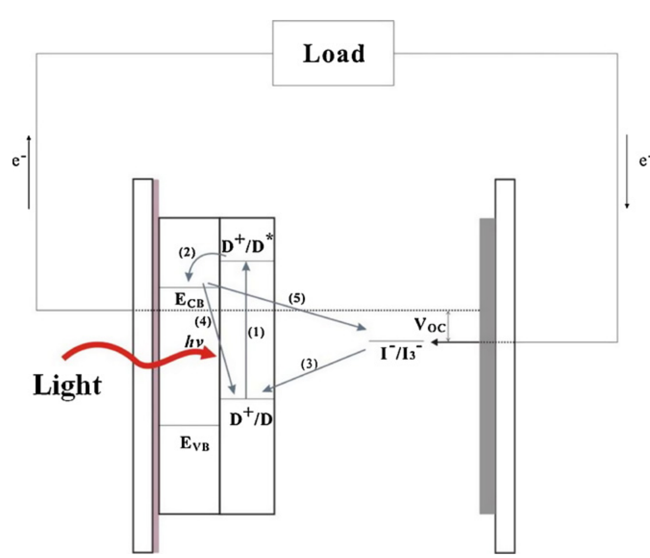


Fig. 4. Schematic description of electric circuit in DSSCs.

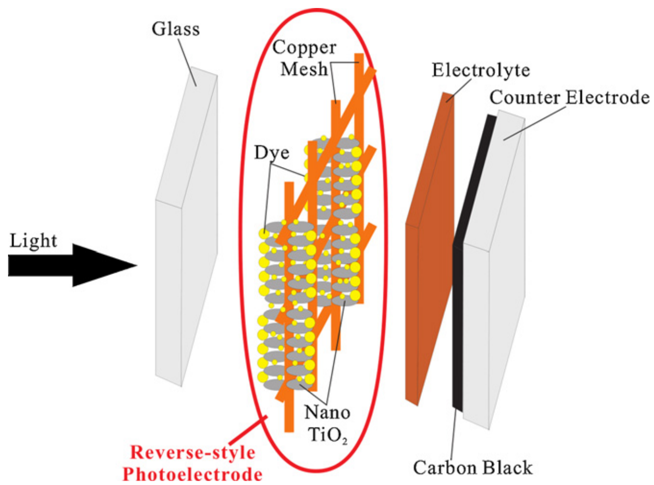


Fig. 5. Schema of DSSC with the photo-electrode of reversal constituent structure.

to hinder the light transmittance for the dye and further reduces amounts of the absorbed photons by the dye.

This work presents a new developed photo-electrode with reversal constituent structure, which uses the copper mesh as the conductive substrate for the nano TiO_2 coating. Fig. 5 shows schema of DSSC with the photo-electrode of reversal constituent structure. Fig. 5 indicates that the dye directly faces to the light incidence and is built in font of the nano TiO_2 layer, so that the electrolyte can run through the holes of copper mesh to contact with the frontal dye. This new developed photo-electrode with reversal constituent structure of DSSC can increase amounts of the absorbed photons and the copper mesh has lower electric resistance than any conductive glasses.

3. Experiments

This work develops a photo-electrode with reversal constituent structure of DSSC, which uses the copper mesh as conductive substrate for the nano TiO_2 coating. In process, the nano TiO_2 particles are first coated on the copper mesh using electrophoresis method. The coated TiO_2 layer with copper mesh is then sintered by 400 °C for 60 min. The sintered copper mesh with TiO_2 layer is continuously immersed into the dye solution for 24 h to absorb the dye. The constituent structure of the finished photo-electrode arranged in sequence from the light injection is the dye, the nano TiO_2 film, and the copper mesh. This new arrangement of constituent structure for the photo-electrode is reverse to the conventional constituent structure.

A homemade electrophoresis apparatus was built for the nano TiO_2 coating on the copper mesh with input voltage of 40 V and current of 20 mA. The distance between the copper mesh and the anode is 1 cm and the coating time is 6 min. The adjustable conditions for studying influence of the photo-electrode with reversal constituent structure in DSSCs are concentration of the nano TiO_2 solution for electrophoresis and mesh point number of the copper mesh. The coated area of the copper mesh is 3 cm × 4 cm and area of the made DSSC is 2 cm × 2 cm. Fig. 6 shows photo of the homemade electrophoresis apparatus. The main constituents of the new developed DSSC arranged in sequence from the light injection are the glass, the dye and TiO_2 layer, the copper mesh, the TiO_2 and dye layer, the electrolyte, and the counter electrode. Fig. 7 shows constituent structure of the new developed DSSC and Table 1 is its structural specifications [2]. Preparing the nano TiO_2 solution for electrophoresis first mixes the 0.3, 0.6, 1.0, 1.5, 2.0 g TiO_2 nanopowder (P25, Degussa) with dispersant of Triton X-100 and isopropyl alcohol respectively, then gives 2 h for ultrasonic shaking.

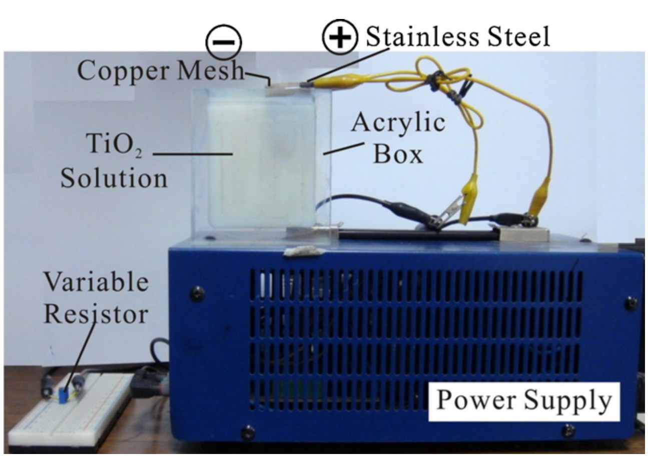


Fig. 6. Photo of the electrophoresis apparatus.

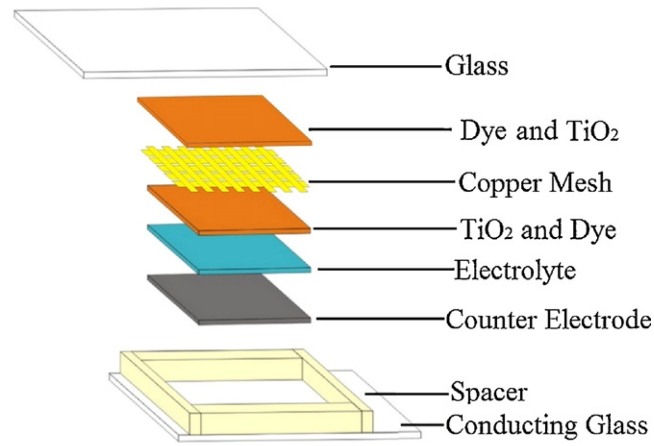


Fig. 7. Constituent structure of the new developed DSSC.

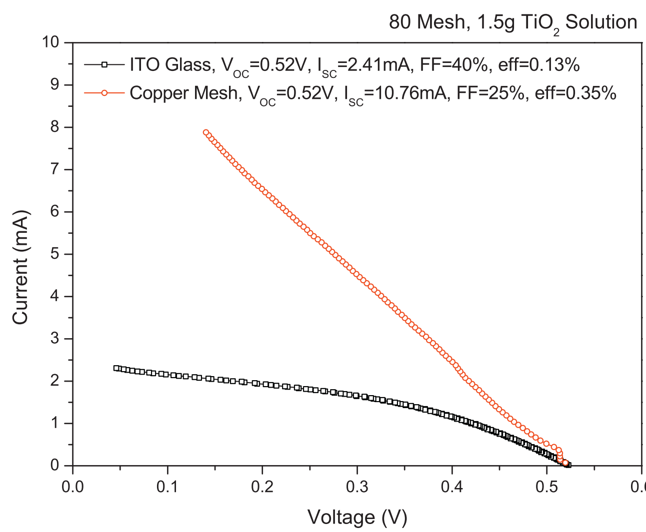


Fig. 8. *I–V* curves of DSSCs influenced by different photo-electrode.

Table 1
Structural specifications of the new developed DSSC.

Component	Specification
Copper mesh	60, 80, 100, 120, 150 mesh.
Semiconductor electrode	0.3, 0.6, 1.0, 1.5, 2.0 g, ϕ = 21 nm TiO_2 nanopowder (P25, Degussa), 100 ml Isopropyl alcohol, 0.1 g TritonX-100, 60 min and 400 °C heating.
Dye	2.5mM alizarin yellow.
Electrolyte	0.05 M I_2 and 0.5 M KI in solvent with ethylenecarbonate and propylenecarbonate.
Counter electrode	0.8 g Seedchem ϕ = 22 nm, 0.2 g TiO_2 nanopowder(P25, Degussa), 4 ml deionized water, 0.1 g ELASOL AS, 60 min and 400 °C heating.

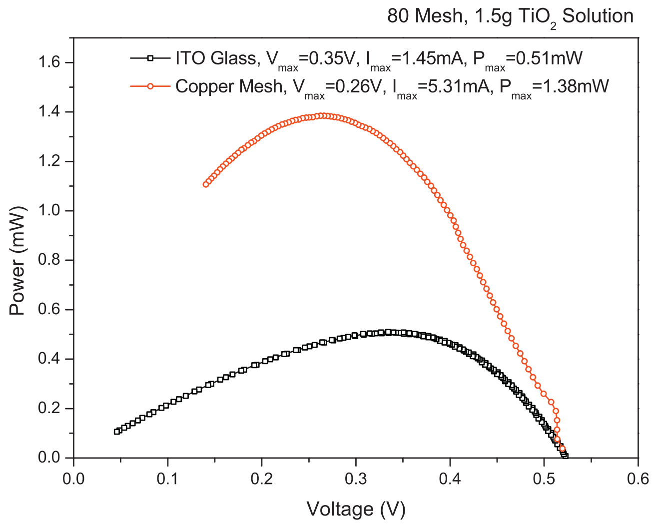


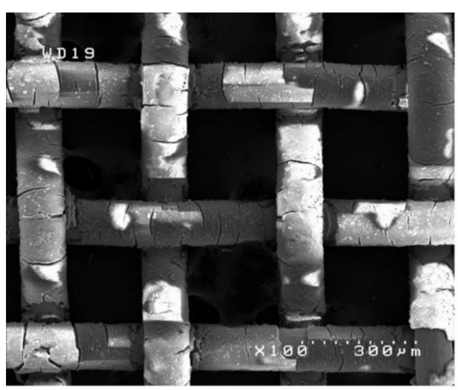
Fig. 9. *P–V* curves of DSSCs influenced by different photo-electrode.

4. Results and discussion

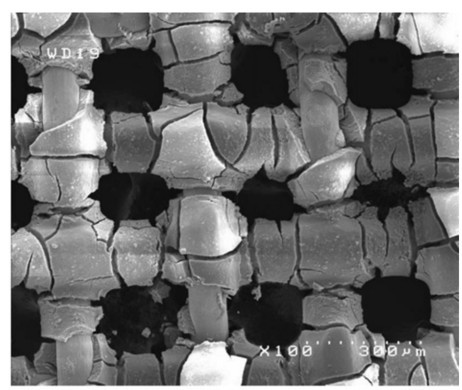
A photo-electrode with reversal constituent structure of DSSC uses copper mesh as conductive substrate. The nano TiO_2 particles are first coated on the copper mesh overall and the dye particles are then absorbed around the nano TiO_2 particles. The new arrangement from light injection is the dye, the nano TiO_2, and the copper mesh, which is reverse to the conventional constituent structure of photo-electrode using conductive glass as substrate. Applying the photo-electrode with reversal constituent structure can increase amounts of the incident light to reach the dye and therefore increases its absorption of photons. Moreover, using the copper mesh as conductive substrate has also reduced its energy loss due to the copper mesh has lower electric resistance.

Fig. 8 shows measured *I–V* curves of DSSCs influenced by different photo-electrode, where the curve with symbols of circle is the photo-electrode with reversal constituent structure and the curve with symbols of rectangle is the conventional constituent structure using the ITO glass as conductive substrate. Aera of the made DSSCs are 2 cm×2 cm, copper mesh is 80 mesh, and TiO_2 solution for electrophoresis is with 1.5 g TiO_2 additive. Fig. 8 indicates that the short-circuit current (I_{sc}) of DSSC using the photo-electrode with reversal constituent structure has clearly increased in comparison with the conventional constituent structure. The reason comes from the increased amounts of the absorbed photons and the reduced electric resistance for the photo-electrode with reversal constituent structure, which causes the increased output current. Moreover, the same nano TiO_2 particles and the dye of alizarin yellow are applied in the photo-electrode for both structures, their open-circuit voltages (V_{oc}) are therefore approximate. This result gives good agreement to the theoretical prediction. Fig. 9 further shows output power vs. output voltage (*P–V*) curves of DSSCs influenced by different photo-electrode.

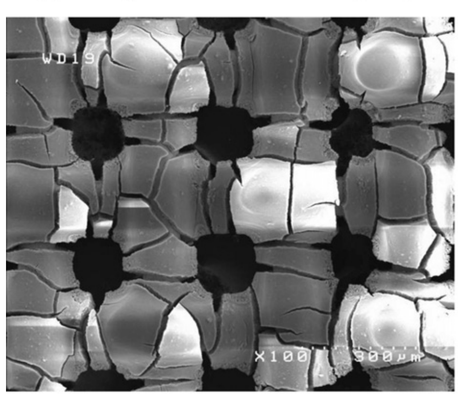
This work is focused on discussing influences of the coated amounts of the nano TiO_2 particles and the applied mesh point number of the copper mesh. In principle, a larger coated amounts of nano TiO_2 particles can increase the contact area with the dye, but a maximum limitation exists due to the contact necessity between the dye and the electrolyte. Too large coated amounts of the nano TiO_2 particles will block off holes of the copper mesh and hinder the access between the dye and the electrolyte. The similar situation also happens on influence of the mesh point number of the cop-



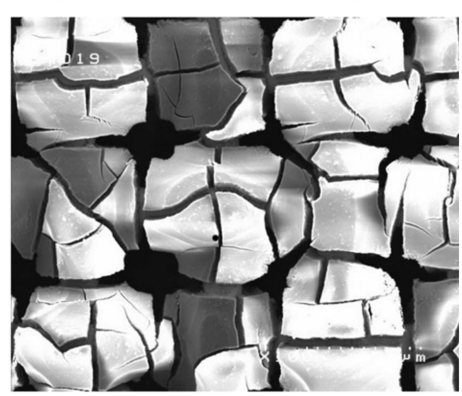
(a) Electrophoresis solution with 0.3 g TiO_2.



(b) Electrophoresis solution with 0.6 g TiO_2.



(c) Electrophoresis solution with 1.5 g TiO_2.



(d) Electrophoresis solution with 2.0 g TiO_2.

Fig. 10. SEM images of TiO_2 layer on copper mesh with different amounts of TiO_2 additive. (a) Electrophoresis solution with 0.3 g TiO_2. (b) Electrophoresis solution with 0.6 g TiO_2. (c) Electrophoresis solution with 1.5 g TiO_2. (d) Electrophoresis solution with 2.0 g TiO_2.

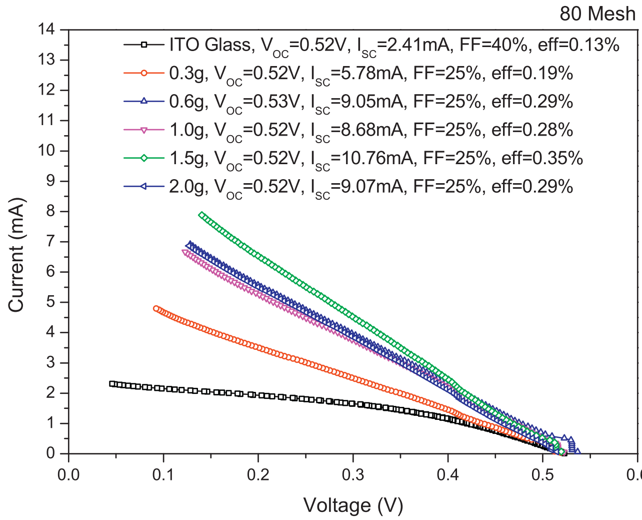


Fig. 11. *I–V* curves of DSSCs with different amounts of TiO_2 additive for photo-electrodes with reversal constituent structure in comparison with the conventional photo-electrode.

per mesh. A larger mesh point number can cover more nano TiO_2 particles, but it also exists an optimum limitation. Fig. 10 shows SEM images of TiO_2 layer on copper mesh with different amounts of TiO_2 additive. The SEM images show that the more the coated TiO_2 particles, the smaller pass holes of the copper mesh. Fig. 10(d) shows that holes of the copper mesh is almost blocked off.

Preparing the photo-electrode with reversal constituent structure used the electrophoresis technique and the 80 mesh copper mesh as conductive substrate for the nano TiO_2 coating. In process, the input voltage and current are individually 40 V and 20 mA, the coating time is 6 min and the distance is 1 cm from the copper mesh to the anode. The different concentrations of the nano TiO_2 solution will determine the coated amounts of the nano TiO_2 particles. Fig. 11 shows measured *I–V* curves of DSSCs with the different photo-electrodes of reversal constituent structure in comparison with the conventional photo-electrode, where the nano TiO_2 solutions for electrophoresis are individually with the nano TiO_2 particles of 0.3, 0.6, 1.0, 1.5, 2.0 g. Fig. 11 indicates that the electrophoresis solution with nano TiO_2 additive of 1.5 g has the maximum short-circuit current of DSSC. Fig. 12 further

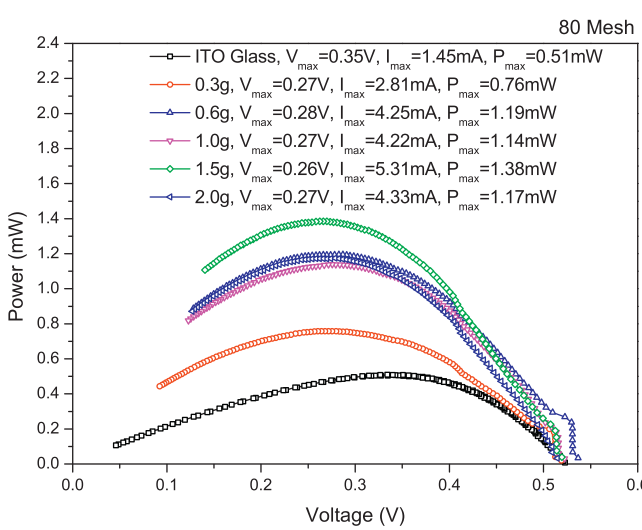


Fig. 12. *P–V* curves of DSSCs with different amounts of TiO_2 additive for photo-electrodes with reversal constituent structure in comparison with the conventional photo-electrode.

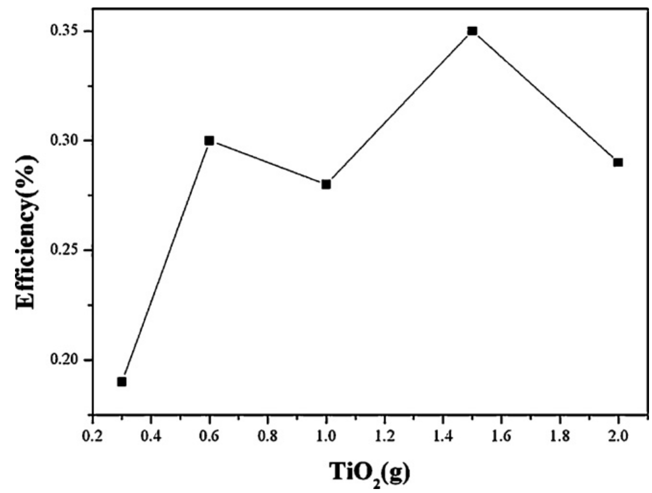


Fig. 13. Photoelectric conversion efficiency of DSSCs with different amounts of TiO_2 additive for photo-electrodes with reversal constituent structure.

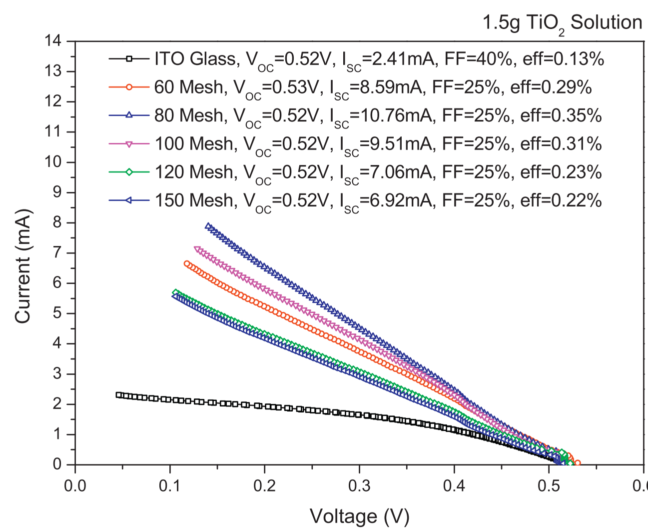


Fig. 14. *I–V* curves of DSSCs with different mesh point number of the copper mesh in comparison with the conventional photo-electrode.

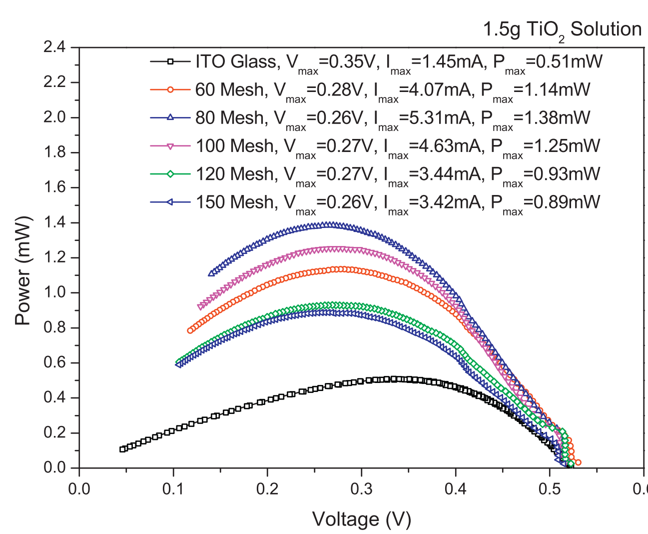


Fig. 15. *P–V* curves of DSSCs with different mesh point number of the copper mesh in comparison with the conventional photo-electrode.

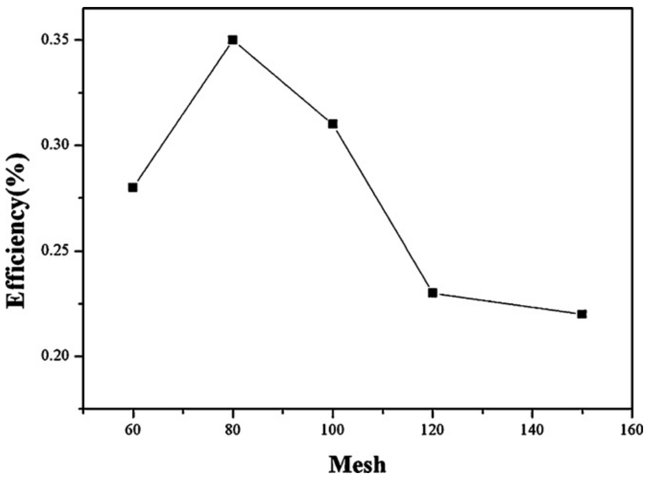


Fig. 16. Photoelectric conversion efficiency of DSSCs with different mesh point number of the copper mesh.

shows output power vs. output voltage curves of DSSCs with different amounts of TiO_2 additive for photo-electrodes with reversal constituent structure in comparison with the conventional photo-electrode.

Although the short-circuit currents (I_{sc}) of DSSCs in Fig. 11 clearly shows increment, the *I–V* curves approach to lines due to their lower fill factor (FF) of ca. 25% [11–13]. The lower fill factor of a DSSC will cause the instability of its maximum output voltage and current, which further influences the photoelectric conversion efficiency. Fig. 13 further shows relationship of the photoelectric conversion efficiency for DSSCs vs. the added amounts of TiO_2 additive. Fig. 13 indicates that the electrophoresis solution with 1.5 g TiO_2 additive integrated with the 80 mesh copper mesh receives the maximum photoelectric conversion efficiency of ca. 0.35%, which is ca. 3 times increment in comparison with the conventional DSSC. The previous studies on the DSSC using alizarin yellow as the dye in our CCT laboratory received the maximum photoelectric conversion efficiency of ca. 0.13% [3].

Fig. 14 shows measured *I–V* curves of DSSCs with different copper mesh point numbers of the photo-electrode with reversal constituent structure in comparison with the conventional photo-electrode. Fig. 14 clearly indicates that the optimum copper mesh point number in this work is 80 mesh. The smaller mesh point number means the fewer nano TiO_2 particles on copper mesh, which further receives the smaller current. Oppositely, the larger mesh point number means the more nano TiO_2 particles on copper mesh, which could hinder the contact between the dye and the electrolyte. The results show that the too large or the too small mesh point number receives the smaller photoelectric conversion efficiency for DSSCs. Fig. 15 further shows output power vs. output voltage curves of DSSCs with different copper mesh point number of the photo-electrodes with reversal constituent structure in comparison with the conventional photo-electrode. Fig. 16 shows relationship of the photoelectric conversion efficiency for DSSCs vs. the mesh point number of the copper mesh.

In this work, applying the copper mesh to build new photo-electrode with reversal constituent structure has clearly improve its photoelectric conversion efficiency, but it exists risks to get the copper surfaces oxidized to CuO through calcination and corroded to CuI with I^-/I^{3-} electrolyte, which will seriously reduce its working life. Moreover, alizarin yellow cannot effectively adhere to the TiO_2 also causes the low fill factor of the DSSCs. A future work will develop new technique using special adhesion agent mixed in TiO_2 solution for electrophoresis to remove calcination process. A suitable metal mesh and the N 719 ruthenium dye will further be used to improve the photoelectric conversion efficiency and the fill factor of the DSSCs.

5. Conclusions

Replacing the conductive substrate of ITO glass with the copper mesh to build the photo-electrode with reversal constituent structure of DSSC as well as its analysis of photoelectric conversion efficiency influenced by mesh point numbers of copper mesh and electrophoresis concentrations of TiO_2 solution have been successfully carried out. The results show that a ca. 3 times increment of photoelectric conversion efficiency has been received. The best reached photoelectric conversion efficiency of DSSC in this work is ca. 0.35%. The applied photo-electrode with reversal constituent structure is made with ca. 1.5 g TiO_2 additive and 80 mesh copper mesh. This work indicates that it exists an optimum condition about the mesh point number of copper mesh and the electrophoresis concentration of TiO_2 solution. Far from the optimum condition, the fabricated DSSC will reduce its photoelectric conversion efficiency.

6. Acknowledgement

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