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Titanium oxide Films Prepared by Sputtering, Sol Gel and Dip Coating Methods for Photovoltaic Application

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Abstract

Dye-sensitized solar cells (DSCs) without using transparent conducting oxides (TCO) electrode can be produced at much lower cost with a flexible structure. A new type of DSCs using flexible stainless steel mesh sheets based electrode is reported in this research. The working electrode of DSCs is processed with conductive and flexible stainless mesh coated with metal oxides (TiO_2) layer either by sputtering, sol gel or dip coating methods. Structures of the TCO-less DSCs sample is a stainless mesh for working electrode / dye sensitized TiO_2 layer / liquid type electrolyte with polymer film / Pt doped Ti plate for counter electrode. The metal oxide coated stainless mesh sample showed higher photo-current conversion efficiency in general. The best cell performance in this experiment showed the efficiency of 3.11% (V_{oc} = 0.58 V, J_{sc} = 11.98 mA/cm^2, ff = 0.45).

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Keywords: Dye-sensitized solar cell; Photoanode; Sputtering; Sol gel; Dip coating

1. Introduction

Transparent conductive oxide (TCO) film is an important part in the synthesis of DSCs [1, 2]. However, it makes very difficult to produce flexible structure of DSCs. In addition, the fluorine-doped tin oxide (FTO) layer as a TCO has its limitations in their infrared ray (IR) transmission and thermal resistance as a transparent conductor [3]. The use of TCO glass for the two DSC electrodes also results in significant cost increase for the less effective DSCs compared to Si based solar cell [4, 5]. Therefore, the replacement of TCO is required for the commercial production of DSCs. In this work, a new type of DSCs

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photoanode replacing TCO layer is developed to produce highly efficient low-cost solar cell. Typical dye-sensitized solar cells (DSCs) use a layer of TiO_2 nanoparticles attached on a transparent conducting oxide (TCO) as an electron collecting layer. 15-20 nm sized TiO_2 nanoparticles are interconnected in three dimensions on TCO. The large number of dye molecules injected into the layer of TiO_2 nanoparticles becomes attached to the large surface area of nanoparticles, which enables efficient light harvesting. Use of TCO in photoanode limits the competiveness of DSCs due to the reasons mentioned above. Thus, the typical photoanode layer structure of TCO/TiO_2 nanoparticles is less competitive. A completely different structure of photoanode is proposed in this report. The DSCs structure using new photoanode electrode is composed of a stainless mesh for working electrode/ dye sensitized TiO_2 layer/ liquid type electrolyte with polymer film/ Pt doped Ti plate for counter electrode.

Stainless steel sheet in a form of mesh can replace TCO as an anode electrode, where the TiO_2 nanoparticles are attached to Stainless steel sheet mesh. However, to facilitate the stainless steel sheet mesh metal as an anode electrode, a modification of photoanode structure is required since the stainless steel metal is neither light transparent nor permeable to electrolyte. DSC using this hybrid structure is schematically shown in Fig. 1. The photoanode is the layers of TiO_2-nanoparticles/stainless steel mesh. The electron collecting layer in photoanode is TiO_2-nanoparticles (around 15-20 nm in diameter) attached with dye molecules. The collected electrons diffuse into the stainless steel mesh metal and transport to counter electrode. The electrons at the counter electrode are transferred to I^-/I_3^- electrolyte, which subsequently transport electrons to dye molecules. The stainless steel mesh allows the charge-carrying electrolyte to flow to dye molecules on TiO_2. Processing and electrical characterization of the DSCs using this photoanode cell structure are also presented in this report.

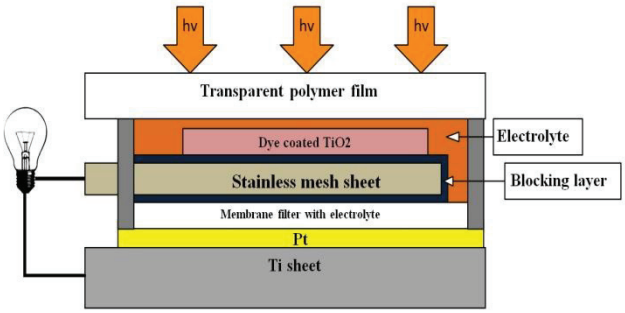

Fig. 1. Structure of the stainless steel mesh based DSCs.

2. Experimental

The DSCs structure with new photoanode electrode is composed of a stainless steel with a 635 mesh using wire diameter of 25 μm, as shown in Fig. 2. Nanoparticles and thin film of TiO_2 were coated either by three different processes of sol-gel coating and dip coating, and by sputtering of TiO_2 directly onto the stainless steel mesh, respectively. These three different processing procedures are schematically illustrated as shown in Figs. 3(a), (b) and (c). First, TiO_2 sol gel was produced with Ti-isopropoxide dispersed in 2-propanol, followed by drop addition of NH_4OH [6, 7]. Then, the stainless steel mesh was

immersed in the solution with stirring, followed by heat treatment at 500°C for 60 minute. Second, for the dip coating process, ethylene glycol heated at 60°C was mixed with Ti-isopropoxide and citric acid. The solution was then stirred at 90°C until its color turned clear. Then, the stainless steel mesh was dip coated and dried followed by heat treatment at 500°C for 60 minute. TiO_2 thin film was also coated by sputtering with a thickness of less than 1.0 nm on the stainless steel mesh.

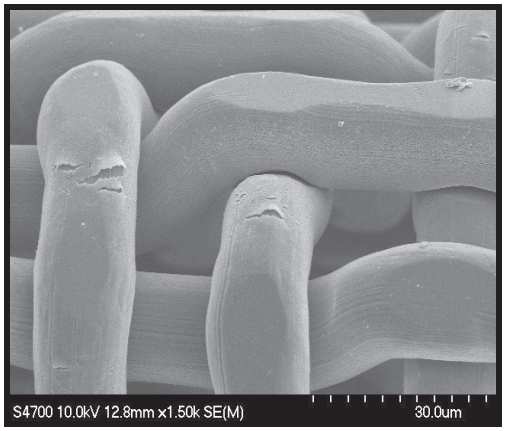

Fig. 2. Scanning electron micrograph (SEM) show the stainless steel mesh.

TiO_2-nanoparticles on the stainless steel mesh were immersed for 8 hours into N3 dye (Solaronix, Switzerland) solution. Pt doped Ti plate counter electrode were prepared by coating a solution of $H_2PtCl_6H_2O$ and 2-propanol dyhydnate (v/v=1:1) followed by drying at 450°C for 30 minute. Electrode spacing was maintained by the use of Surlyn film spacers. The electrolyte used in the solar cell contained 0.5 mM iodide, 0.005 M LiI, 0.0058 M 4-tert-butylpyridine, and 5 ml acetonitrile. The electrolyte was introduced into the clamped electrode by capillary action.

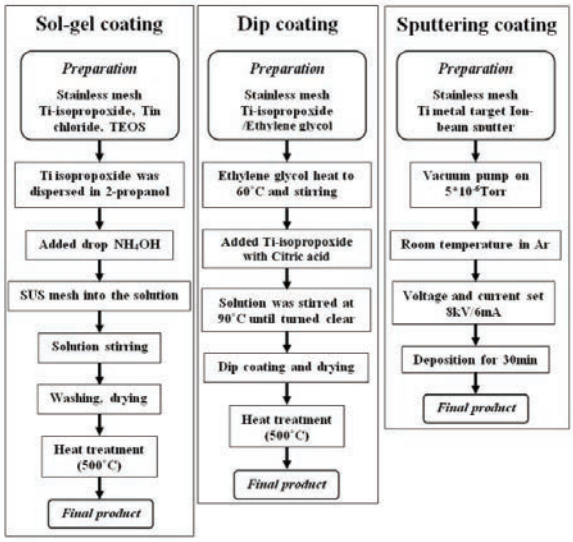

Fig. 3. Illustrating procedures of the three different methods of TiO_2 coating on stainless steel mesh.

3. Results and Discussion

DSCs using no TCO layer were fabricated with the hybrid structure of TiO_2-nanoparticle/stainless steel mesh as photoanode. TiO_2-nanoparticle arrays on stainless steel mesh are the electron collecting layer, in which dye molecules are attached to the nanoparticles. The stainless steel mesh as an anode, made of wires with ~25 nm in diameter, has ~50% porosity (Fig. 2). The porosity in the stainless steel mesh allows the charge-carrying I^-/I_3^- electrolyte to flow to dye molecules. Figure 1 shows the schematic structure of DSCs using a glass/ TiO_2-nanoparticle/ stainless steel mesh/electrolyte/ counter-electrode/ glass structures. The stainless steel mesh electrodes coated with TiO_2-nanoparticle by tree different methods are shown in Fig. 4.

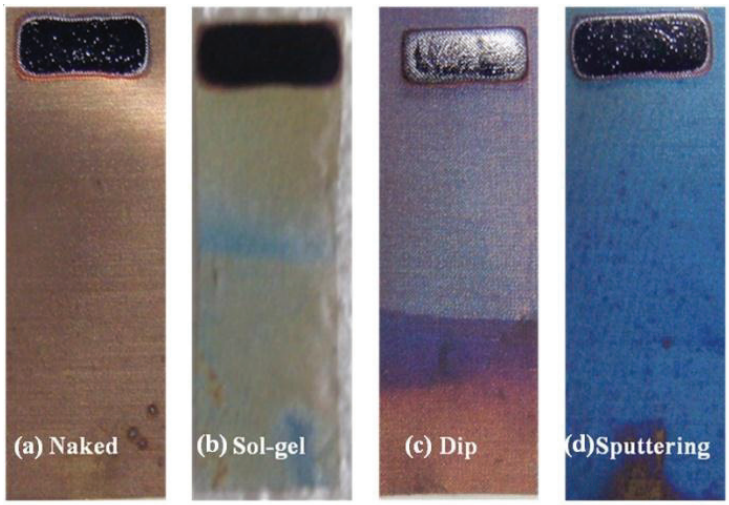

Fig. 4. Optical micrographs showing the stainless steel mesh coated with a layer TiO_2 either by (a) Naked wire, (b) Sol-gel, (c) Dip and (d) Sputtering.

The photocurrent (I) and the photovoltage (V) of the cell were measured with an active area of 0.2 cm^2 stainless steel mesh using simulated sunlight at AM-1.5 produced by a 150-W Solar Simulator. I-V characteristics of the devices are shown in Fig. 5 and Table 1. Overall photo-conversion efficiency is low (<3.11%). This can be attributed to two major factors. The first is the photocurrent magnitude, ~11.0 mA/cm^2, under 1.5AM illumination. The relatively large size of mesh pores may affect significantly on the photocurrent. The electrons are injected from the dye molecules to TiO_2 nanoparticles by photo energy. Then, the electrons diffuse through the networks of TiO_2 particles, however if the electron life time is not long enough to avoid hole capture during diffusion, the current density will decrease. As the hole size of the stainless steel mesh increases, the length of TiO_2 particle networks becomes longer. The longer the distance for electron diffusion, the less electrons reaching to stainless steel mesh metal

resulting in less photocurrent density. Thus, by controlling the hole size and wire diameter of stainless steel mesh, the cell performance can increase significantly [8].

Second factor for improvement is the fill factor of 0.42 to 0.45 in this work. The fill factor is reduced with increasing series resistance [9]. The series resistance will be increased, hence fill factor is reduced with increasing the thickness of stainless steel mesh and poor contact between the TiO_2 particle and stainless steel mesh metal. The thickness of stainless steel mesh can be easily further reduced either by a chemical or mechanical thinning of mesh, and employing thinner wires. The solid contact between the TiO_2 particle oxide and stainless steel mesh metal can only be accomplished by sintering, however high temperature sintering for longer time is not possible due to the glass and dye molecules vulnerable to heat. Adhesion between the oxide and metal at lower temperature can be enhanced by forming TiO_2 nano layer on stainless steel mesh, which can be done easily by simple electrochemical anodic oxidation of stainless steel mesh. As mentioned above, both the photocurrent and fill factor can be improved by the control of mesh dimension and anodized oxide formation, which are the focus of going on research.

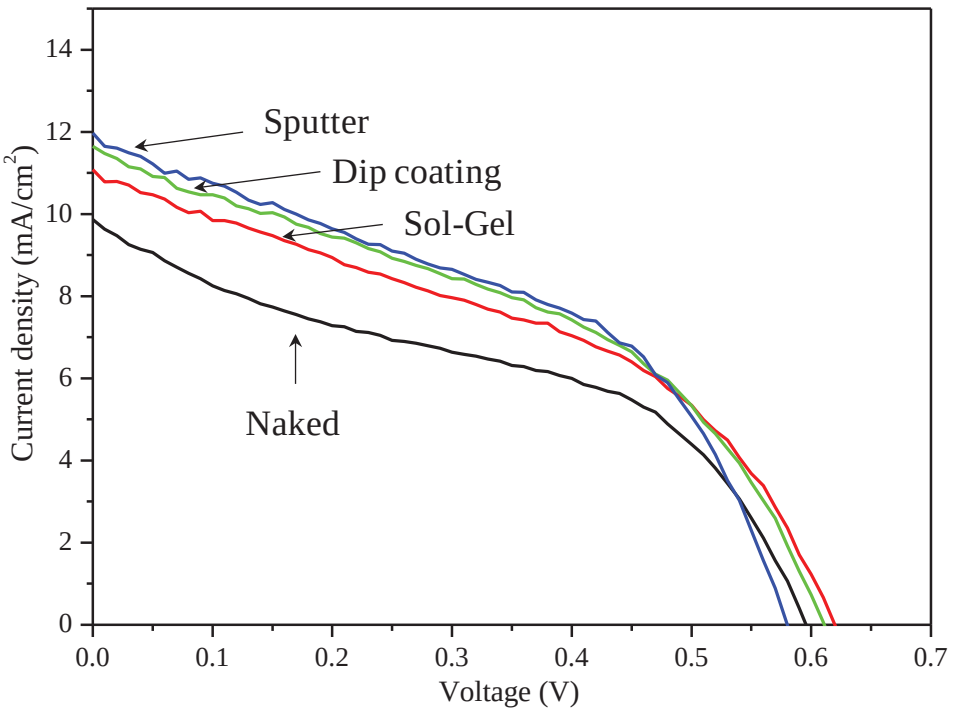

Fig. 5. I-V characteristic of the DSCs with different photoanode electrode structures.

Table 1: Photo-conversion efficiency of the DSCs with different photoanode electrode structure.

Coating method	Jsc (mA /cm^2)	V_{oc} (V)	ff	η (%)
Without layer	9.87	0.59	0.42	2.48
Sol-gel	11.08	0.62	0.42	2.89

Dip coating	11.64	0.61	0.42	2.99
Sputtering	11.98	0.58	0.45	3.11

In DSCs, the four important interfaces: TCO/TiO_2; TiO_2/dye; dye/electrolyte; and electrolyte/counter electrode play an important role in the performance of the cell. The unidirectional flow of charge without any electron leakage at the interfaces plays an important role in the high energy conversion efficiency of DSCs. An understanding of the different interfacial mechanisms can be used to enhance the performance of DSCs, as reviewed recently. Earlier 4-tert butyl pyridine was added to the electrolyte to decrease the carrier leakage of the direct electron acceptance from the TiO_2 electrode but this method is not very effective. The charge recombination is a common process in DSCs which takes place at the TiO_2/sensitizer and TCO/TiO_2 interfaces and limits the performance of the cell. The charge transfer process in DSCs shows that charge recombination at the TiO_2/sensitizer interface is negligible whereas the charge recombination at the TCO/TiO_2 interface takes place due to the physical contact between the electrolyte and the TCO surface. The mesoporous nature of the TiO_2 layer also helps in the percolation of the electrolyte and as a result electron transfer by the TCO surface becomes possible. The physical contact between the TCO and the electrolyte can be avoided by using a compact oxide layer on the TCO before the TiO_2 mesoporous layer. This blocking layer reduces the reaction of the photo-injected electrons and the I_3^- ions at the TCO/electrolyte interface. Recently the blocking layer introduced between the TCO and the porous film has been reported to show better results. The blocking layer prevents direct physical contact between the TCO and the electrolyte and this result in an increase in the overall efficiency of the cell. When metal mesh electrode was used as a photo electrode electron collector, the blocking layer formation is much important because the charge recombination reaction (back electron transfer reaction) is increase between Metal/electrolyte interfaces. In this study, three different method of sputtering, dip coating, sol-gel coating to form a blocking layer on stainless steel mesh electrode have been compared for the enhancement of flexible dye solar cell performance. The formation of dense of blocking layer, which comes from the back reaction, is the most efficient under the sputtering method. However, in terms of commercialization, the production of solar cells by sputtering method incurs higher costs. Therefore, dip coating and so-gel coating methods have comparative advantage of production costs.

In this work, the dense of metal mesh electrode which is formed on the surface structure of TiO_2 and it characteristics are investigated in each method, i.e. sputtering coating, dip coating and sol-gel coating. Figure 6 presents SEM of dense of metal mesh electrode which is formed on the surface structure of TiO_2. According to the figure, the sputtering method yields the highest dense structure of oxide layer of TiO_2, compared to dip coating and sol-gel coating method. The TiO_2 layer composed of holes and the thickness of TiO_2 layer is longer than 150 nm, under the dip coating and sol-gel coating method. However, by comparing to the dip coating method, the sol-gel coating method generates the hole which has the bigger size. In addition, the number of holes is higher under the sol-gel coating method.

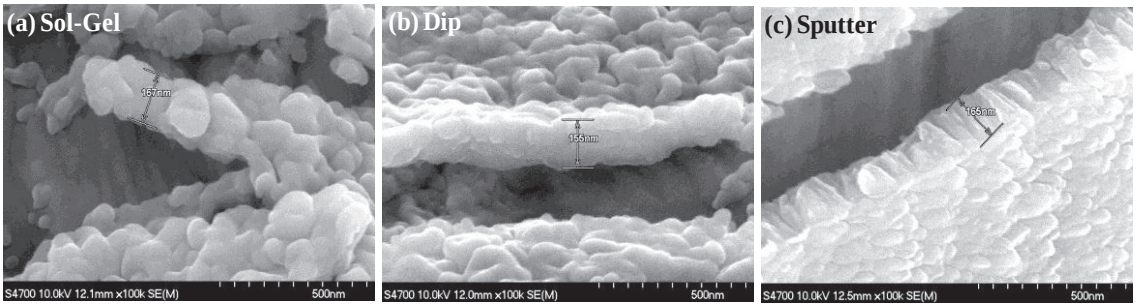

Fig. 6. FE-SEM of dense of metal mesh electrode which is formed on the surface structure of TiO_2 by (a) sol-gel, (b) dip and (c) sputtering coating.

Based on the I-V characteristic of the DSCs with different photoanode electrode structures, the sputtering method shows the highest efficiency in blocking the back reaction, follows by the dip coating method. In the other way, there is the electrolyte reaction at the middle of the hole under the sol-gel coating method. This makes the sol-gel coating method lacks of efficiency.

4. Conclusion

Dye-sensitized solar cells (DSCs) using stainless steel mesh electrode is fabricated for flexible and low-cost solar cell application. The stainless steel mesh can replace TCO in photoanode of DSCs, thus the cell structure is composed of a glass/ dye sensitized TiO_2 layer/ stainless steel mesh electrode/ electrolyte/ metal counter electrode. Thin stainless steel mesh (~25 μm in thickness) electrode material was coated with TiO_2 either by sol-gel, dip coating and sputtering process. Electrical performance of as-fabricated DSCs is characterized. Both the photocurrent and fill factor are low, which are attributed to the large pore size of the mesh, and the thickness of stainless steel mesh and poor contact between the TiO_2 particle and stainless steel mesh metal, respectively.

Acknowledgements

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