

Synthesis of TCO-free Dye-sensitized Solar Cells with Nanoporous Ti Electrodes Using RF Magnetron Sputtering Technology

Doo-Hwan Kim*, Jong-Hyun Heo*, Dong-Joo Kwak* and Youl-Moon Sung[†]

Abstract – A new type of dye-sensitized solar cell (DSC) based on a porous type Ti electrode without using a transparent conductive oxide (TCO) layer is fabricated for low-cost high-efficient solar cell application. The TCO-free DSC is composed of a glass substrate/dye-sensitized TiO₂ nanoparticle/porous Ti layer/electrolyte/Pt sputtered counter electrode. The porous Ti electrode (~350 nm thickness) with high conductivity can collect electrons from the TiO₂ layer and allows the ionic diffusion of I⁻/I₃⁻ through the hole. The vacuum annealing treatment is important with respect to the interfacial necking between the metal Ti and porous TiO₂ layer. The efficiency of the prepared TCO-free DSC sample is about 3.5% (*ff*: 0.48, *V_{oc}*: 0.64V, *J_{sc}*: 11.14 mA/cm²).

Keywords: Transparent conductive oxide, TCO-free dye sensitized solar cells, Porous Ti, RF sputtering

1. Introduction

Dye-sensitized solar cell (DSC) technology has been proposed as a promising new photovoltaic device [1-3]. The transparent conductive oxide (TCO) layer used for DSCs is an important component in their construction, and of the TCO materials available, the most commonly used for DSCs is fluorine-doped tin-oxide (FTO). However, FTO glass is very expensive and the use of two pieces of TCO glass for DSCs is not suitable in terms of cost-effectiveness [4]. It has been reported that one piece of TCO glass can be replaced with a Ti metal plate [5]. The DSC system uses a Ti plate/a TiO₂ porous layer stained with dye molecules/electrolyte/a Pt sputtered TCO glass configuration. Kroon et al. have reported a TCO-free DSC [6]. The cell is composed of a glass substrate/a TiO₂ porous layer stained with dye molecules/a Ti electrode/electrolyte/a Pt sputtered TCO glass, and showed an efficiency of 3.6%. Fuke et al. have studied a TCO-free DSC configuration using a Ti electrode prepared by a vacuum process and reported 7.1% efficiency [7]. Recently, Hayase et al. have reported an all-metal-electrode-type TCO-free DSC using tetrapod-shaped ZnO particles and an electro-spray technique. The reported efficiency of their cell could reach about 8% [8].

In order to promote DSCs for commercial application, it is necessary to improve the cell structure based on a simpler and lower-cost process. In this work, a fabrication process combining RF magnetron sputtering and sol-gel combustion methods has been set up in an effort to seek simple processing routes for TCO-free DSC synthesis based on a porous Ti electrode configuration. The porous TiO₂ glass substrates were prepared using a screen-printer method allowing the spray deposition of ethyl-cellulose

particles as the template, followed by RF sputtering Ti growth. Experimental results for porous Ti layer fabrication and the photovoltaic performance of the resulting TCO-free DSC samples were investigated.

2. Experimental

2.1 TCO-free DSCs Concept and Geometry

The cell structures of typical DSCs and TCO-free DSCs are schematically shown in Figs. 1(a) and 1(b), respectively. Typical dye-sensitized solar cells (DSCs), as shown in Fig. 1(a), use a layer of TiO₂ nanoparticles attached on a transparent conducting oxide (TCO) as an electron collecting layer. TiO₂ nanoparticles 15~20 nm in size are interconnected in three dimensions on the TCO. The large number of dye molecules injected into the layer of TiO₂ nanoparticles becomes attached to the large surface area of nanoparticles, which enables efficient light harvesting. The use of TCO in photo-electrode limits the competitiveness of DSCs due to the reasons mentioned above. Fig. 1(b) shows a TCO-free DSC structure with a porous-Ti electrode. In order to facilitate the photo-electrode performance without a TCO layer, a modification of the Ti electrode structure is required because the Ti monolayer is neither light transparent nor permeable to electrolyte molecules. The best photo-electrode must satisfy both the requirements of swift ion diffusion and high conductivity. Thus, a porous Ti-metal electrode on a porous TiO₂ layer is arranged in order to collect electrons from the TiO₂ layer effectively and to maintain the diffusion of I⁻/I₃⁻ through the porous Ti electrode as shown in Fig. 1(b). The electron behavior in the TCO-free DSC configuration (Fig. 1(b)) can be summarized as follows. Firstly, upon illumination of the cell, the dye molecule is excited by light. Hence, charge separation occurs by electron injection from the excited state dye

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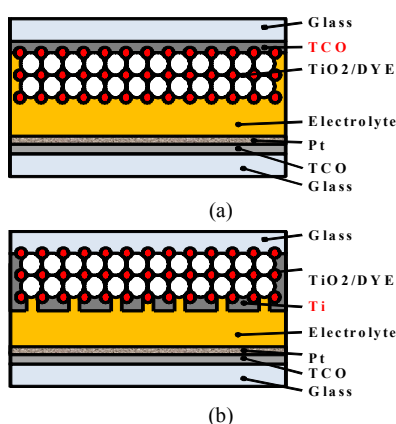


Fig. 1. Cell structures of typical DSCs and TCO-free DSCs, respectively. (a) Typical DSCs (b) TCO-free DSCs with porous-Ti layer.

molecule into the conduction band of the TiO_2 . In the long run, the electron is picked up on its way and transmitted by a porous Ti electrode, and becomes electrical energy. On the other hand, the dye molecule is reduced with an electron transferred by the redox couple of the electrolyte, which can easily be diffused through the porous Ti electrode. It is important that the porosity in the Ti electrode allows the charge-carrying I^-/I_3^- electrolyte to flow to the dye molecules.

2.2 TCO-free DSCs Synthesis Procedure

Fig. 2 shows the preparation procedure of TCO-free DSCs using ethyl-cellulose spray particles as a template and RF magnetron sputter methods. The TCO-free DSC sample is prepared in the following process. Firstly, the TiO_2 paste was prepared using the sol-gel combustion method, and the glass was screen-printed with a coating 10 μm thick.

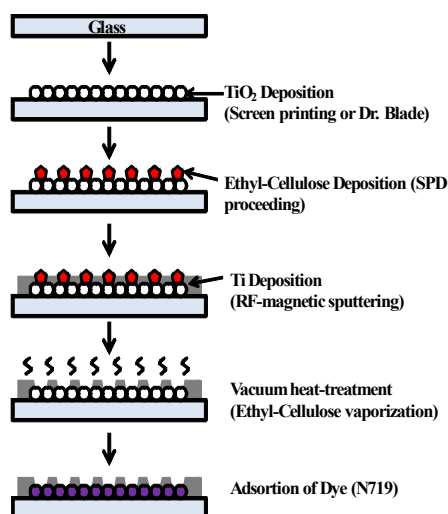


Fig. 2. Preparation procedure of TCO-free DSCs using ethyl-cellulose spray particles as a template and RF magnetron sputter methods.

The preparation method of spray material can be briefly described as follows: 1 g of commercial organic polymeric particles (ethyl-cellulose, Kanto Chemical Co. Inc.) several tens~hundreds in size was mixed with 100 g ethanol to make the solution, which was then dispersed well in a mortar. The sprayed Ti/ TiO_2 substrate was subsequently annealed at a maximum temperature of 450°C for 30 min to fabricate a porous Ti/ TiO_2 nanoparticle layer. Fig. 3 shows the XPS wide spectra of the ethyl-cellulose material used as a template for the formation of the porous Ti layer. The O (1s) and C (1s) photoelectron peaks were evidently detected at binding energies of about 529 and 282.5 eV, respectively. Additional peaks of Sn (3ds) and Ti (2p) on the sample were detected at the binding energies of about 483 and 455 eV, respectively, and these were the contained components in the sample.

Fig. 4 shows the SEM images of the sprayed ethyl-cellulose particles on the TiO_2 nanoparticles layer using the spray method (a) and the porous Ti/ TiO_2 nanoparticles layer after vacuum annealing treatment (b). As shown in Fig. 4(a), the porous Ti layer was deposited on the sprayed ethyl-cellulose/ TiO_2 nanoparticles layer using the RF magnetron sputtering method. The deposition conditions are listed in Table 1. The Ti film was deposited in Ar gas pressure of 5.0×10^{-3} Torr, substrate temperature of 250°C , RF power of 300 W and a deposition time of 30 min. After the Ti deposition, the chamber was purged for a few minutes with flowing Ar gas prior to the in situ annealing treatment. To perform the annealing treatment, the chamber pressure, substrate temperature and treatment time were set at 5×10^{-6} Torr, 500°C and 30 min, respectively. The annealing treatment was performed under vacuum conditions for the purposes of erasing the ethyl-cellulose component of the Ti/ TiO_2 nanoparticles layers, as well as strengthening the structural necking in the interface between the metal Ti and TiO_2 nanoparticles layers. As shown in Fig. 4(b), some ethyl-cellulose-like clusters were still observed on the porous Ti surface layer after the annealing process. The Ti/ TiO_2 substrate was subsequently washed with 0.1 M HCl solution to remove the remaining ethyl-cellulose component and to make straight holes in the sputtered Ti layer. The substrate was then rinsed with ethanol to remove residual HCl and water. Dye staining and cell preparation

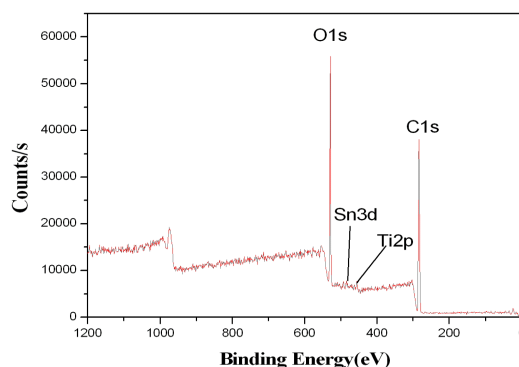


Fig. 3. XPS wide spectra of the ethyl-cellulose material used as a template for the formation of porous Ti layer.

were carried out in the following way after the Ti electrode was fabricated on the TiO₂ nanoparticles layer. The porous Ti on the TiO₂ nanoparticles substrate was immersed for 8 hours in an N3 dye solution (Solaronix, Switzerland). Counter electrodes were prepared by coating a solution of H₂PtCl₆·6H₂O and 2-propanol dihydruate (v/v=1:1) followed by drying at 450 °C for 30 min. Electrode spacing was ensured with the use of Surlynfilm spacers, 60 μm in thickness. The electrolyte used in the solar cell contained 0.5mM iodide, 0.005M LiI, 0.0058M 4-tert-butylpyridine, and 5 ml acetonitrile. The electrolyte was introduced into the clamped electrode by capillary action.

Table 1. Optimum deposition condition of porous Ti Film prepared by rf magnetron sputtering

Variables	Conditions
Pressure	Ar 5mTorr
rf power	300 Watt
Substrate temperature	250C
Deposition time	30 min
Distance between target and substrate	10 cm

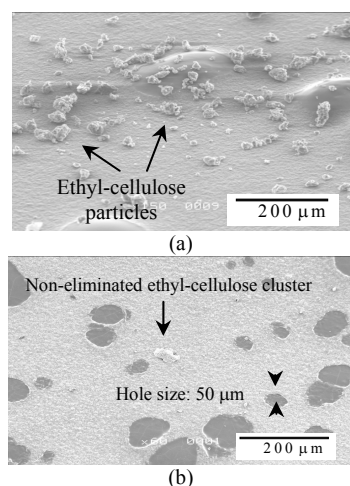


Fig. 4. SEM images of the sprayed ethyl-cellulose particles on the TiO₂ nanoparticles layer (a) and the porous Ti/TiO₂ nanoparticles layer after vacuum annealing treatment (b).

3. Results and Discussion

Figs. 5(a) and 5(b) show the side-view and top-view SEM images of the porous Ti deposited on the TiO₂ nanoparticles layer after annealing. The thickness of the prepared porous Ti layer was about 350 nm, and thus the deposition rate of Ti film was ~11 nm/min. The investigation on the film's conductivity was also performed using the four-point probe method. The sheet resistance decreased with increased film thickness, and the lowest sheet resistance (~2 Ω/□) was obtained from a Ti layer of 350 nm

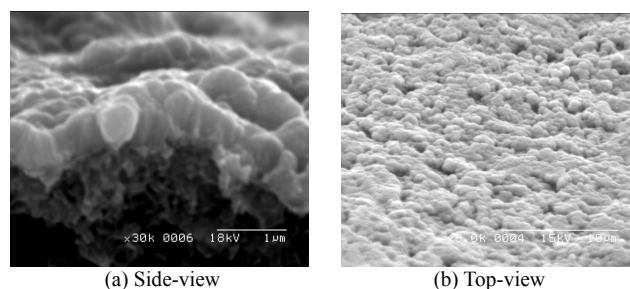


Fig. 5. Side-view (a) and top-view (b) SEM images of the porous Ti deposited on TiO₂ nanoparticles layer after annealing, respectively.

thickness. Considering that the sheet resistance of FTO glass is in the range of 10-30 Ω/□, the porous Ti film with a thickness of more than 350 nm is suitable for the photo-electrode.

Figs. 6(a) and 6(b) show the dye adsorption images of the porous Ti/TiO₂ nanoparticles substrate with and without HCl treatment, respectively. From Figs. 6(a) and 6(b), the effect of HCl treatment can be seen. Some ethyl-cellulose-like clusters were observed on the porous Ti surface layer after the annealing process as mentioned above in Fig. 4(b). This indicates that the ethyl-cellulose-like clusters remained in spite of the annealing treatment; this is not dependent on the other treatment parameters such as annealing time and operating gas. Thus, the additional treatment was subsequently performed with 0.1 M HCl solution to remove the remaining ethyl-cellulose component and to make straight holes in the Ti/TiO₂ substrate. The substrate was then rinsed with ethanol to remove the residual HCl and water. As shown in Fig. 6(a), the Ti/TiO₂ substrate with HCl treatment was stained with dye molecules, while the N3 dye was not adsorbed on some areas of the Ti/TiO₂ substrate without HCl treatment because the dye could not pass the Ti layer owing to the remaining ethyl-cellulose components as shown in Fig. 6(b). When only the HCl treatment was performed on the Ti/TiO₂ substrate without vacuum annealing, the Ti layer was detached and washed away during the HCl treatment. This is caused by the poor adhesion between the porous Ti metal and TiO₂ nanoparticles layers. Therefore, it can be found that the annealing treatment under vacuum conditions enables effective erasing to the ethyl-cellulose component as well as strengthening the structural necking in the interface between porous Ti metal and TiO₂ nanoparticles layers.

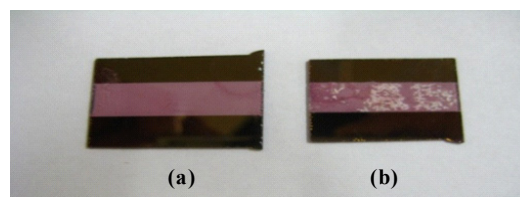


Fig. 6. Dye adsorption images of the porous Ti/TiO₂ nanoparticles substrate with and without HCl treatment, respectively. Left (a): with HCl treatment, Right (b): without HCl treatment.

The photocurrent (I) and the photovoltage (V) of the cell were measured with an active area of 0.2 cm^2 porous Ti using simulated sunlight at AM-1.5 produced by a 150-W Solar Simulator. I - V characteristics of the cell are shown Fig. 7. The efficiency of our TCO-free DSC sample was about 3.51 % (ff : 0.48, V_{oc} : 0.64V, J_{sc} : 11.14 mA/cm^2), which was also lower than that of conventional DSCs with TCO. This can be attributed to two major factors. The first is the photocurrent density, 11.14 mA/cm^2 , under 1.5AM illumination. The relatively large size (\sim hundreds μm) of the pores may have a significant affect on the photocurrent. The electrons diffuse through the networks of TiO_2 nanoparticles. however, if the electron life-time is not long ($\sim 30\mu\text{m}$) enough to avoid hole capture during diffusion, the current density will decrease. As the hole size of the porous Ti increases, the length of TiO_2 particle networks becomes longer. The longer the distance for electron diffusion, the less electrons reaching the porous Ti metal resulting in less photocurrent density. Thus, by controlling the hole size and thickness of the porous Ti, cell performance can increase significantly. The second factor for improvement is the fill factor of 0.48 in this work, which is reduced with increased series resistance. The series resistance will be increased, hence the fill factor is reduced with increased thickness of the porous Ti layer and poor contact between the TiO_2 particle and the porous Ti metal. For high-efficiency performance, it is important to ascertain pore size and thickness dependency. We will include the related study that is within our means in our next plans.

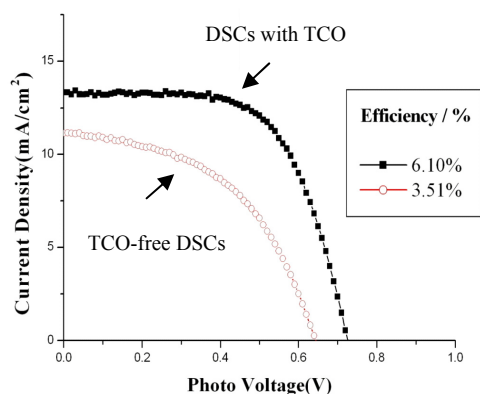


Fig. 7. Current-voltage characteristics curve of the prepared TCO-free DSCs. The sample was measured with an active area of 0.2 cm^2 porous Ti using simulated sunlight at AM-1.5 produced by a 150-W Solar Simulator.

4. Summary and Conclusion

TCO-free Dye-sensitized solar cells (DSCs) using a porous Ti layer is fabricated for high-efficient low-cost solar

cell application. The porous Ti metal can replace TCO in the photo-electrode part of DSCs. Porous Ti ($\sim 350 \text{ nm}$ in thickness) layers with high conductivity, processed using the rf magnetron sputtering method, can collect electrons from the TiO_2 layer and allows the ionic diffusion of I^-/I_3^- through the hole. It can be found that the annealing treatment under vacuum condition enables effective erasing to the ethyl-cellulose component as well as strengthening the structural necking in the interface between the metal Ti and the porous TiO_2 layers. The efficiency of the prepared TCO-free DSC sample is about 3.51 % (ff : 0.48, V_{oc} : 0.64V, J_{sc} : 11.14 mA/cm^2). Although the photocurrent and fill factor are low, the TCO-free configuration shows a high potential for DSC application in terms of cost-effectiveness.

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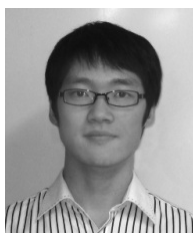
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