

Effect of TiO₂ dense layer thickness on efficiency improvement of dye sensitized solar cells

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Dye Sensitized Solar cells (DSSC) using Z907 Ru-dye were fabricated with different thickness of the TiO₂ dense layer. The optical, photovoltaic and structural properties of the DSSCs with the different thickness of dense layers are studied and compared. The experimental results show that the DSSC with TiO₂ layer thickness of 50 μm gives efficiency of 6.59%, the DSSCs with TiO₂ layer thickness of 100nm provides an efficiency of 1.35%. The IV characteristics were measured under solar radiation intensity of about 100W/cm². The DSSCs fabricated with TiO₂ layer thickness of 150 nm were showing short circuit. The DSSC with 50 nm TiO₂ layer transmit 80% of light to active layer while devices with 100 nm thick TiO₂ layer transmit less than 50 % of incident light.

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1. Introduction

In dye sensitized solar cells, a wide band gap semiconductor materials such as TiO₂ is a used as photo anode. Since DSSCs with TiO₂ were invented by Gratzel in 1991, they are smart alternatives for the development of a new generation of photovoltaic devices [1]. The DSSCs are a successful combination of materials, consisting of a transparent electrode like ITO, FTO etc coated with a dye-sensitized nanoporous film of wide band gap semiconductor such as TiO₂, SnO₂ etc. [2,3], an electrolyte containing a suitable redox couple and a Platinum or Carbon coated counter-electrode as shown in Fig. 1(a). The basic working principle of DSSCs is generation of excited electrons in the dye after absorption of sunlight. These generated electrons are injected from the excited dye molecules into the conduction band of the TiO₂. These electrons then move towards the external load through the nanoporous and dense TiO₂ layer. The electrolyte such as iodide/ tri-iodide donates electron to the dye for regeneration. Electron vacancy in iodide is filled by the transfer of electron from the counter electrode [4]. Conversion efficiency upto 11% has been achieved by DSSC devices fabricated using dense and nanoporous TiO₂ layers [4 5]. To further improve the conversation efficiency of these solar cells, more scientific research work is required for improving the design, stability and structure of the devices.

As shown in Fig. 1, sensitized nanoporous TiO₂ layer of the DSSCs contains small pores to make direct contact between the electrolyte and the working electrode. For

preventing the charge leakage, a dense layer of TiO₂ is used as blocking layer between the conducting electrode and the sensitized nanoporous TiO₂ layer. This dense layer of TiO₂ represses the electron back transport between electrolyte and ITO by blocking direct contact. Different types of materials and different film thickness of the TiO₂ dense layer (blocking layers) have been reported [6-12].

We report on the effect of thickness of TiO₂ dense layer on the performance of DSSCs. We fabricated DSSC with TiO₂ nanoporous layer and Z907 dye. The TiO₂ dense layer was deposited on the ITO glass substrate using spin coating method. The optical, photovoltaic and structural properties of the DSSCs with the different thickness of blocking layers are studied and compared.

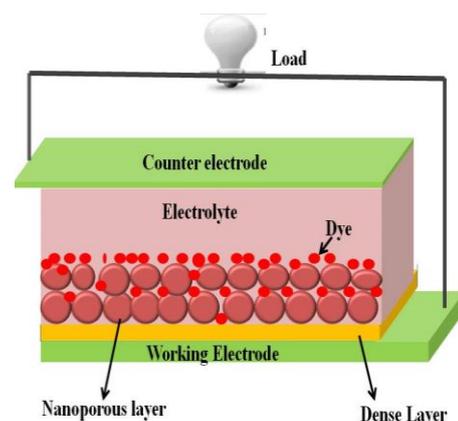


Fig. 1. Schematic of DSSCs with different layers

2. Materials and methods

The TiO₂ layers and the conductive glass substrates (working electrode) plays an important role in the efficiency of DSSCs since different thickness of TiO₂ layer affects the photo-conductive properties and transmission. TiO₂ dense layers with three different thicknesses (50 nm, 100 nm and 150 nm respectively) were deposited on the ITO substrates by spin coating technique and the nanoporous film was deposited by doctor blade method [13]. Details of the device fabrication and characterization are given in the following sections

2.1. Devices fabrication

ITO glass substrates (sheet resistance of 20 Ω per square and thickness of 100 nm) are cleaved into area of 5cm² and cleaned with washing powder, ethanol and DI water using ultrasonic bath. For deposition of TiO₂ dense films, solution of 10 ml Ti-Isopropoxide, 7 ml acetyl and 52 ml ethanol are applied using VTC-100 vacuum spin coater at 1000 rpm for 10 sec (for film thickness of 100 nm), 2000 rpm for 30 sec (for film thickness of 50 nm) and 2000 rpm for 10sec (for film thickness of 150 nm) on conducting side of ITO substrate. In the next step, the TiO₂ nanoporous film was deposited on the top of dense TiO₂ layer using doctor blade technique. The sample was annealed in a carbolite furnace at 400°C for 60 minutes.

The counter electrodes were made by coating carbon on ITO substrate with the help of lighting a candle. Allow both electrodes at room temperature for few hours and then dip TiO₂ coated electrode in a solution of Z907 dye in ethanol with 3×10⁻⁴ M. The electrodes are put together such that the active sides of the anode and the cathode are facing each other. The gap left between the two glass plates was filled with electrolyte in the next step. We assembled both electrodes with the help of clip board and injected iodide/tri-iodide solution between the electrodes. They were connected to external load using crocodile clips.

2.2. Results and discussions

After the devices were fabricated, they were electrically and optically characterized by measuring the short circuit current or current density, open circuit voltage, fill factor and conversion efficiency. The Current-Voltage (IV) plots were measured using Keithly 2420 source meter. The IV characteristics were measured under solar radiation intensity of about 100 W/cm². The UV transmittance and absorbance spectra were measured using a SPECORD 200 spectrometer.

The electrical properties of the DSSCs were studied by measuring the I-V (Current-Voltage) curves as shown in Fig. 2. Measuring the I-V curves, we calculated short circuit current or current density, open circuit voltage, fill factor and conversion efficiency. The short circuit current, open circuit voltage, fill factor and conversion efficiency obtained for the device with 50 nm thickness of TiO₂ dense layer are 5.88 mA, 0.76 V, 0.295 and 6.59 %

Similarly, the short circuit current, open circuit voltage, fill factor and conversion efficiency obtained for the device with 100 nm thickness of TiO₂ dense layer are 1.17 mA, 0.65V, 0.355 and 1.35%. The devices with TiO₂ dense layer thickness of 150 nm showed short circuit. For comparison purpose, these values are presented in Table 1.

The conversion efficiency obtained from the DSSC with 50nm thick dense layer is 4.8 times more than the device with 100nm thick dense layer. The performance of the device fabricated with 100 nm thick dense layer is far lower than the one fabricated with 50 nm thick window layer. To fully understand the behavior of the devices, transmittance and absorbance curves were measured which are presented in Fig. 3. Fig. 3a shows that the device with 50 nm thick dense layer transmit 80% of light to the active layer while cells with 100 nm thickness can transmit less than 40% of light, i-e maximum of photon are absorbed by window layer due to its thickness and hence does not reach the active layer. The surface morphology of the thin films plays a very important role in the device performance. Smooth and crack-less surface of the thin film is required for optimum performance of the device. Scanning electron microscope (SEM) images of different thickness of TiO₂ thin films were taken. The SEM analysis shows that the TiO₂ thin film has very smooth and crackless profile for thinner layers. As the thickness of blocking layer increases, cracks appear in its surface as shown in Fig. 4. Due to cracks in dense layer of TiO₂ the direct contacts that are produced in between the electrolyte and ITO (working electrode) results in leakage of charge carriers and results in decrease in performance of cell. Thus due to the cracks on the surface of thin film and lower transmission of light of 100 nm thick TiO₂ layer, the device with 100 nm thick dense layer exhibit poor performance. The dense layer of TiO₂ represses the electron back transport between electrolyte and ITO by blocking direct contact and therefore increasing the stability of the devices.

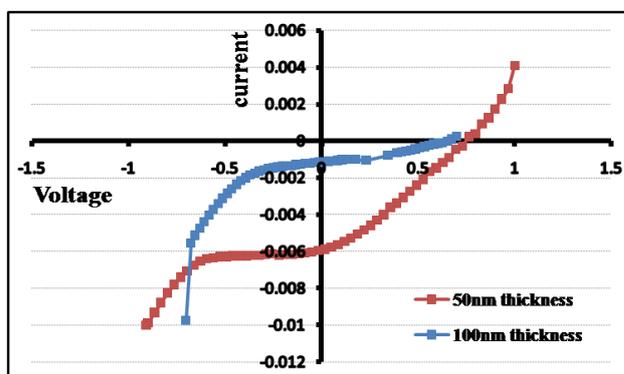


Fig. 2. I-V curve of the device with 50 and 100 nm thick TiO₂ dense layer

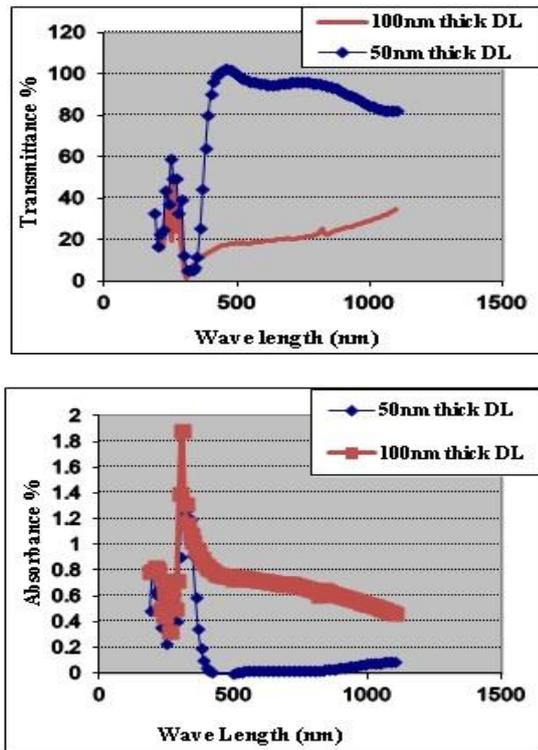


Fig. 3. (a) Blue curve shows 80% of light is transmitted to active layer while red line shows decrease in transmittance for 100 nm thick window layer (b) Absorption graph of 50 and 100 nm thick TiO₂ dense layers

Table 1. Performance parameters of solar cell fabricated with 50 and 100 nm thick TiO₂ dense layers

Thickness of dense layer	I _{sc} (mA)	V _{oc} (V)	J _{sc} (mA/cm ²)	F.F%	η (%)
50 nm	5.88	0.76	2.94	29.5	6.59
100 nm	1.17	0.65	0.585	35.5	1.35

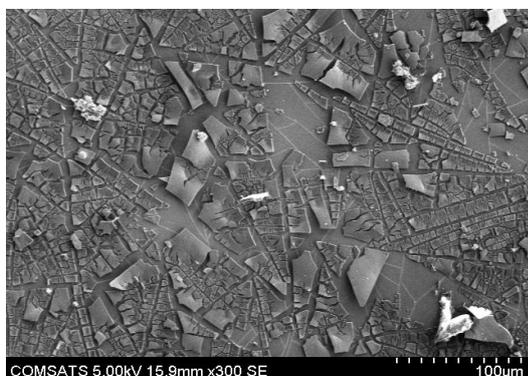


Fig. 4. SEM image shows cracks in TiO₂ dense layer that is the main reason of less efficiency and short circuit of devices with dense layer thickness of 150 nm

3. Conclusions

DSSC's were fabricated using Z907 Ru-dye (3×10^{-4} M solution in ethanol) with variation in dense/ window layer thickness (50 nm, 100 nm and 150 nm). The ITO glass was used as substrates for DSSC's upon which TiO₂ dense layer was deposited using spin coating technique. The TiO₂ nanoporous film was deposited on the top of the dense layer by the doctor-blade technique, it was followed by carbon-coated counter electrode and liquid Iodide/Iodine electrolyte solution. The efficiencies of solar cell having 50 nm thick dense layer is 6.59% which is greater than 1.35% for 100 nm thick dense layer under a 100 W/cm² solar irradiance. The devices with 150 nm thick dense layer exhibit short circuit. The decrease in efficiency with increase in thickness of dense layer is due to absorbance of photons in window layer and leakage of electron between electrolyte and working electrode. The dense layer of TiO₂ represses the electron back transport between electrolyte and ITO by blocking direct contact and therefore increased the stability of the devices

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References

- [1] B. O' Regan, Gratzel. Nature **353**, 737 (1991).
- [2] S. Konstantinidis, J. P. Dauchot, M. Hecq, Thin Solid Films **515**, 1182 (2006).
- [3] A. Mills, S. Le Hunte, J. Photochem. Photobiol. A Chem. **108**, 1 (1997).
- [4] M. Gratzel, Journal of Photochemistry and Photobiology C Photochemistry Reviews **4**(2), 145(2003).
- [5] K. J. Hwang, J. W. Lee, H. S. Yoon, H. D. Jang, J. G. Kim, J. S. Yang, S. J. Yoo, Bull. Korean Chem. Soc. **30**(10), 2365 (2009).
- [6] R. Hattori, H. Goto Thin Solid Films **515**(20-21), 8045 (2007).
- [7] J. N. Hart, D. Menzies, Y. B. Cheng, G. P. Simon, L. Spiccia, Comptes Rendus Chimie **9**(5-6), 622 (2006).
- [8] B. Yoo, K. J. Kim, S. Y. Bang, M. J. Ko, K. Kim, N. G. Park, J. Electroanal. Chem. **638**(1), 161 (2010).
- [9] M. Wu, Z. H. Yang, Y. H. Jiang, J. J. Zhang, S. Q. Liu, Y. M. Sun, J. Solid State Electrochem. **14**(5), 857 (2010).
- [10] J. Y. Kim, S. Lee, J. H. Noh, H. S. Jung, K. S. Hong, J. Electroceram. **23**(2-4), 422 (2009).
- [11] M. H. Kim, Y. U. Kwon, J. Phys. Chem. C **113**(39), 17176 (2009).
- [12] S. Lee, J. H. Noh, H. S. Han, D. K. Yim, D. H. Kim, J. K. Lee, J. Y. Kim, H. S. Jung, K. S. Hong, J. Phys. Chem. C **113**(16), 6878 (2009).
- [13] Andrew Mills, Nicholas Elliott, George Hill, David Fallis, James R. Durrant, Richard L. Willis. Photochem. Photobiol. Sci. **2**, 591 (2003).

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