

Enhancement of Dye Sensitized Solar Cell Efficiency Using Chlorophyll as Dye Sensitizer by Adding The SnO₂ Material to TiO₂

Nurrisma Puspitasari*, Siti Rabi'atul Adawiyah, Muhammad Noer Fajar, Gatut Yudoyono, Gontjang Prajitno, Agus Rubiyanto, Endarko

Physics Department Faculty of Natural Science Institut Teknologi Sepuluh Nopember Surabaya

nurrismapuspitasari@gmail.com, nurrisma@physics.its.ac.id

Abstract. Dye-Sensitized Solar Cell (DSSC) is the third generation of solar cells. DSSC is formed by sandwich structure, there are five parts: ITO glass (Indium Tin Oxide) as the substrate; TiO₂ and SnO₂ as semiconductor material; natural dye from chlorophyll as an electron donor; gel electrolyte as electron transfer and active carbon as a catalyst in the counter electrode. The synthesis of nanometer-sized TiO₂ powder is obtained by coprecipitation method. The layer of TiO₂ was deposited on top of an ITO glass by doctor blade method. From the research, the DSSC efficiency has increased by nearly 100% after additions SnO₂ to TiO₂. The DSSC efficiency result is 0.05% for DSSC before additions and 0.1% after additions

1. Introduction

The solar cell is a p-n junction semiconductor device, which can convert solar light energy into electrical energy. This alteration is called the photovoltaic effect which is the basis of the process of converting sunlight (in the form of photons) into electricity [1]. Currently this type of solar cell is experiencing the development of conventional solar cells that require silicon material as the main ingredient up to dye-sensitized solar cells. The dye-sensitized solar cells developed by Gratzel are called Grätzel or Dye Sensitized Solar Cells (DSSC) cells or sensitized dye-based solar cells (SSPT) [2]. Simple production process and low cost of production is one of the main attraction of the development of research on DSSC. DSSC consists of five important parts, among others: transparent conductive glass, semiconductor material coated on transparent conductive glass, dye (dyestuff) made from synthetic materials as well as natural materials, and electrolytes. This cell consists of layers of semiconductor immersed in a photosensitizer (dye). Dye is used to replace inorganic semiconductor materials in solar cells. The process of photosynthesis that converts light energy into chemical energy is the basis of a chemical approach for the process of converting light energy into electrical energy in the DSSC. Dye on DSSC acts as a photon catcher which then occurs electron excitation process on dye molecule to produce electrical energy. The ability of dye to absorb photons is something that is very important, as well as semiconductor layer that serves as a place of absorption of dye (working electrode or photoanoda). Photoanoda in DSSC consists of a layer of semiconductors in nanostructures deposited on a TCO (Transparent Conducting Oxide) glass with a thickness of several microns[3]. Titanium dioxide (TiO₂) is the most widely used semiconductor material as photoanoda because it has high photoactivity characteristics, good chemical stability, non-toxic and easy to obtain [4]. The TiO₂ layer in the DSSC generally has a large surface and in the anatase phase allowing more dyes to be



absorbed and the resulting photo stream to become larger. One way to expand the surface is to reduce / reduce the size of TiO₂ particles on a scale of less than 100 nm (Yan et al., 2013). From a study by Nurul and Nurrisma [6], the semiconducting layers of ZnO and MgO materials yielded lower efficiency when compared to DSSCs that use TiO₂ as its semiconductor. Next will be done research about addition of material SnO₂ on TiO₂ to know its influence to DSSC performance.

2. Experimental

2.1. Synthesis of TiO₂ Nanoparticles and making the paste of photoanode materials

The synthesis of TiO₂ nanoparticles was performed by coprecipitation method. The synthesis process of TiO₂ nanoparticle powder [7]: 20 mL TiCl₃ mixed with 100 ml of aquades and stirred for 1 hour. The solution sterilized NH₄OH until the solution reaches pH 9. Furthermore, if the solution has settled, then washing the solution by adding 200 ml aquades. The washing was repeated until the solution was obtained with pH 7. After the precipitate was obtained with pH 7, calcination was done with a temperature of 400° C with a holding time of 3 hours [7]. The TiO₂ paste is made by adding 1.4 ml of aquades into TiO₂. Then added 0.3 gr of PEG 1000, 0.7 ml of acetic acid, 1 ml acetylacetone and 0.7 ml triton X-100 [8]. Thereafter, the first step of preparing the paste of TiO₂ / SnO₂ was done by mixing the powdered TiO₂ and SnO₂ nanoparticles and continued by heating to a temperature of 450 ° C for 30 minutes. The next step is making the solution by mixing 3 mL of ethanol, 0.13 g ethylcellulose and 0.89 mL terpineol stirred for 1.5 hours. The powder mixture of TiO₂ and SnO₂ nanoparticles was then added to the solution and stirred with a magnetic stirrer for 2 hours [9].

2.2. Preparation of Dye Sensitized Solar Cell

Semiconductor paste (TiO₂,SnO₂) is positioned over an area already formed by the Doctor-Blade method. After that heated above hot plate with temperature 450° C for 15 minutes. Dye used in this study is dye chlorophyll from alfalfa leaves (Medicago Sativa). Adsorption of dye in TiO₂ layer was done by immersing the coating into dye solution with the immersion time for 24 hours. In this study electrolytes were used in gel form because electrolyte with gel phase was more stable than liquid phase [10,11] The gel electrolyte used was made from 7 grams of PEG 1000, 25 mL of chloroform and liquid electrolyte at 80 °. The liquid electrolyte was prepared from 3 grams of KI dissolved in 10 mL acetonitrile and 3 mL iodine [11,12]. Subsequently, a comparative electrode was prepared from a carbon material superimposed on ITO conductive glass. DSSC Sandwich Making begins by arranging working electrodes and comparative electrodes arranged flip over where there is an electrolyte between the two electrodes. The working electrode, also called photoanoda, is an electrode consisting of ITO glass coated with a semiconductor material and immersed in a dye solution. Whereas the reference electrode is electrode coated by carbon material as catalyst..

2.3. Measurement

The synthesis of nanocrystalline TiO₂ and SnO₂ structure was characterized by X-Ray diffraction (XRD). The absorption spectrum of chlorophyll dye solution was measured using a UV-Vis Spectrophotometer. Characterization of current and voltage (I-V) using I-V meter. The output data and I-V meter device are the values of current and voltage. From the graph of the relationship can be known DSSC cell characteristics are made by analyzing solar cell parameters such as; Voltage open-circuit (Voc), Short circuit current (Isc), Maximum Power Point (MPP), voltage and current on MPP (VMPP and IMPP), Fill factor (FF) and Efficiency.

$$FF = \frac{V_{MPP} I_{MPP}}{V_{OC} I_{SC}} \quad (1)$$

Where *FF* is the fill factor (value should be between 0 and 1)

$$\eta = \frac{P_{\max}}{P_{\text{light}}} \times 100\% \quad (2)$$

Where η is efficiency (%), P_{\max} is the maximum power (Watt)

3. Result and Discussion

3.1. Characterization the layer of photoanoda materials

The XRD result for photoanode layer was shown in Figure 1. After the adding of SnO_2 to TiO_2 , produces anatase-rutile mixed phase. The results are also obtained by Li et al and chen et al . They explained that the emergence of the rutile phase was due to the addition of SnO_2 powder having a rutile phase.

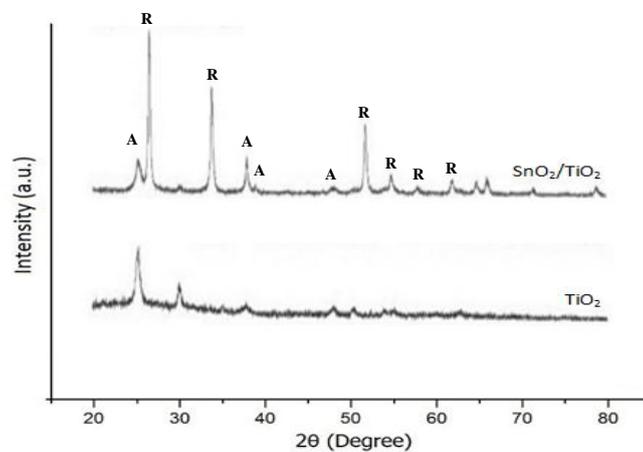


Figure 1. Crystal diffraction pattern of TiO_2 and $\text{SnO}_2/\text{TiO}_2$ layer

3.2 Absorbance Analysis of Chlorophyll Dye

The results of the chlorophyll dye absorbance test of light using the UV-Vis Spectrophotometer are shown in Figure 2. Based on the graph in Figure 2 it is known that chlorophyll dye has a wide absorbance spectrum ranging from 300 - 700 nm and has an optimum absorbance value at 290 nm and 400 nm wavelengths of 3.03 a.u and 2.2 a.u. The efficiency value of DSSC depends also on the absorbance of the wavelength used. The wider the spectrum of chlorophyll dye absorbance, the more light frequencies can be absorbed by the solar cells.

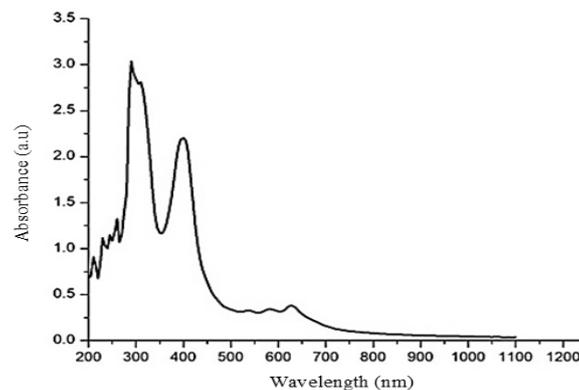


Figure 2. Absorption spectra of chlorophyll dye

3.3 Characterization the surface morphology analysis using Scanning Electron Microscopy (SEM)

The SEM micrograph of Figure 3 shows the particle shape of all spherical samples. The morphology of the thin layer TiO_2 Co-precipitation (a) shows many cracks (cracks) on its surface. A more uniform particle distribution is identified in the composite sample (c). In addition, the surface layer of the sample (c) is also more porous than the pure TiO_2 sample. This is thought to be due to the effect of the addition of SnO_2 which has porous particles. As shown in figure (b) the surface of the layer SnO_2 has a homogeneous particle size distribution, the structure is flat and looks rather dense but also has a porous structure and does not contain agglomeration. The same morphology was obtained by Camacho-Lopez M. A. et al. The porous surface structure of the photoanode is desirable since the presence of the pore allows more dye molecules to be absorbed and the resulting photo stream becomes larger [9]. The SEM analysis also provides particle size information from pure TiO_2 films located in the range of 15-60 nm. While the composite obtained a smaller size, which ranges from 10-30 nm. The SnO_2 film shows the surface looks very smooth, flat and somewhat dense causing the particle is not visible and the determination of particle size becomes difficult to do.

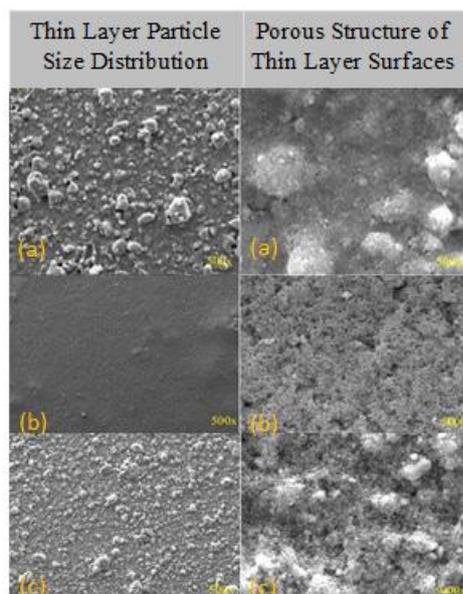


Figure 3. SEM micrograph shows the surface morphology of the film (a). TiO_2 Co-precipitation film, (b). SnO_2 , (c) $\text{TiO}_2/\text{SnO}_2$ at 500x magnification (right row) and 5000x (left row)

3.4 Characterization of I-V Curves

Table 1. Voc, Jsc, FF and Efficiency value of DSSC

Cell Names	V_{OC} (Volt)	J_{SC} (mA/cm ²)	FF (%)	η (%)
TiO ₂	1.401	0.124	28.53	0.05
SnO ₂ /TiO ₂	1.401	0.089	82.60	0.103

Current measurements and photo voltages are performed using I-V Keithley Meter using halogen lamps on a 1 cm² area. Figure 4 shows the I-V characteristic curve of the under the simulation of light with an intensity of 100 mW cm². Table 1 shows that the DSSC using the TiO₂ / SnO₂ photoanoda shows a larger Jsc value compared to the DSSC using the TiO₂ photoanoda so that the efficiency value generated by the DSSC with the solvent TiO₂/SnO₂ photo-solo gel is also higher, reaching nearly 100% (0.05% to 0.103%). The higher Jsc values indicate the greater concentration of electrons in the TiO₂ conduction bands injected by dye [16] so that this leads to an increase in efficiency of 0.103% produced by the DSSC with the TiO₂/SnO₂ photoanoda composite. In addition, surface morphology produced by a uniform TiO₂/SnO₂ thin film free of cracks may also affect the performance of the DSSC. The agglomeration and cracks on the surface of the photoanoda layer can affect the charge transfer process in the DSSC system. In addition, Mahshid et al in his journal on the manufacture of TiO₂ nanoparticles with anatase-rutile mixed phases, mentioned that photocatalytic and photovoltaic properties of TiO₂ nanoparticles containing anatase-rutile phase mixtures exhibit better performance compared to pure TiO₂ anatase phases [17]. This can also be one of the factors that can explain the DSSC with a TiO₂/SnO₂ composite photoanoda capable of producing a higher efficiency than with pure TiO₂ photoanoda.

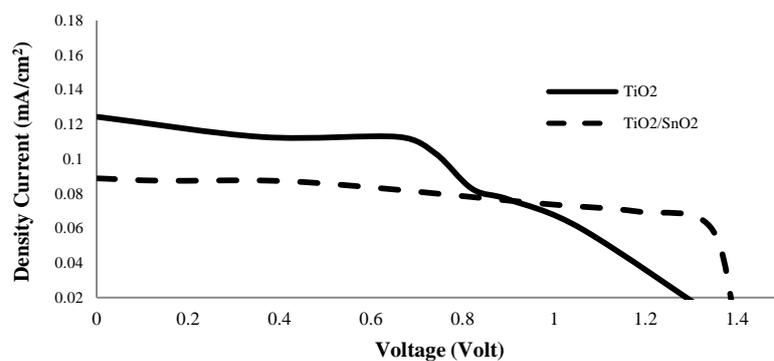


Figure 4. The I-V characteristic curve of the DSSC

4. Conclusion

The SEM results show a porous structure formed on a thin layer of photoanoda with the addition of SnO₂. The addition of SnO₂ to TiO₂ increased the efficiency of nearly 100% (from 0.05% to 0.103%) produced by DSSC with a composite photoanoda TiO₂ / SnO₂ using TiO₂ nanoparticle powders

Acknowledgments

The author would like to thank the Physics Department, Institut Teknologi Sepuluh Nopember Surabaya for supporting the research.

References

- [1] Konstantatos G, McDonald SA, Zhang S, Cyr PW, Klem EJ, Levina L, Sargent EH (2005). *Solution-processed PbS quantum dot infrared photodetectors and photovoltaics*. Nature Materials 4 (2): 138–42.
- [2] O’regan dan Gratzel, M. 1991. “*A Low-Cost, High Efficiency Solar Cell Based On Dye-Sensitized Colloidal TiO₂ Films*”. Nature Vol. 353. Issue 6346, 737 - 740.
- [3] Suhaimi, S., Shahimin, M.M., Alamed, Z.A., Chysky, J., and Reshak, A.H. (2015). Materials for Enhanced Dye-sensitized Solar Cell Performance: Electrochemical Application. Int. J. Electrochem. Sci. 10, 2859–2871.
- [4] Hashimoto, K., Irie, H., and Fujishima, A. (2015). TiO₂ Photocatalysis: A Historical Overview and Future Prospects. Jpn. J. Appl. Phys. 44, 8269–8285.
- [5] Yan, X., Feng, L., Jia, J., Zhou, X., and Lin, Y. (2013). Controllable synthesis of anatase TiO₂ crystal for high-performance dye-sensitized solar cells. J. Mater. Chem. A.
- [6] Nurul, A.S, Nurrisma P, dan Endarko. 2013. “*Analisa Perbandingan Efisiensi Dye Sensitized Solar Cell (Dssc) Dengan Bahan Semikonduktor TiO₂, ZnO dan MgO Sebagai Photoelektroda*”. Seminar Fisika dan Aplikasinya 2013. ISSN 2086-0773 2 2.
- [7] Nur Widaryanti, H., n.d. (2010), “Pembentukan Nanopartikel TiO₂ Fasa Anatase dan Rutile dengan Metode Bervariasi”, Buku Skripsi ITS Surabaya.
- [8] Kook, Lee Jin, Jeong Bo-Hwa, Jang Sung-il, Kim Young-Guen, Jang Yong-Wook, Lee Su-Bin, Kim Mi-Ra. (2009), “*Preparations of TiO₂ pastes and its application to light-scattering layer for dye-sensitized solar cells*”. Journal of Industrial and Engineering Chemistry 15 724-729.
- [9] Liu, J., Gu, Y., and Zhang, Y. (2013). Dye-sensitized solar cells with composite ZnO/SnO₂ nanoporous electrodes. 1.
- [10] H. Hug, M. Bader, P. Mair, T. Glatzel, Appl. Energy, 115, 216-255 (2014)
- [11] Nurrisma P, Nurul A.S, Gatut. Y, Endarko. 2017. “*Effect of Mixing Dyes and Solvent in Electrolyte Toward Characterization of Dye Sensitized Solar Cell Using Natural Dyes as The Sensitizer*” IOP Conf. Series: Materials Science and Engineering 214 (2017) 012022 doi:10.1088/1757-899X/214/1/012022.
- [12] Maddu, A., Zyhri, M., Irmasyah. (2010), “*Penggunaan Ekstrak Antosianin Kol Merah Sebagai Fotosensitizer Pada Sel Surya TiO₂ Nanokristal Tersensitisasi Dye*”, MST 11.
- [13] Li, H., Xie, C., Liao, Y., Liu, Y., Zou, Z., and Wu, J. (2013). characterization of Incidental Photon-to-electron Conversion Efficiency (IPCE) of porous TiO₂/SnO₂ composite film. jalcom 569, 88–94.
- [14] Chen, W., Ghosh, D., and Chen, S. (2008). Large-scale electrochemical synthesis of SnO₂ nanoparticles. J. Mater. Sci. 43, 5291–5299.
- [15] Camacho-Lopez M. A., J. R., G.-C., C., S.-P., and C. M., J. (2013). Characterization of nanostructured SnO₂ films deposited by reactive DC-magnetron sputtering. Superf. vacio 26.
- [16] Yuan, S., Tang, Q., He, B., Men, L., and Chen, H. (2014). Transmission enhanced photoanodes for efficient dye-sensitized solar cells. Electrochimia Acta 125, 646–651.
- [17] Mahshid, S., Askari, M., Ghamsari, S.M., Afshari, N., and Lahuti, S. (2009). Mixed-phase TiO₂ nanoparticles preparation using sol-gel method. jallcom 478, 586–589.