Fabrication and characterization of TiO$_2$ & SnO$_2$ nanoparticles as a photoanodes in dye sensitized solar cell

Nurrisma Puspitasari$^1$, Gatut Yudoyono, Gontjang Prajitno, Sudarsono, Iim Fatimah, Susilo Indrawati, Diky Anggoro, Hasto Sunarno, Yono Hadi Pramono, Darminti

Physics Department of Natural Science, Institut Teknologi Sepuluh Nopember
Surabaya
Kampus ITS Sukolilo Jalan Raya ITS, Sukolilo, Surabaya 60111, INDONESIA.

E-mail: nurrismapuspitasari@gmail.com / nurrisma@physics.its.ac.id

Abstract. The third generation of solar cells that found by Gratzel in 1991 was called Dye Sensitized Solar Cell (DSSC). DSSC is composed of five parts namely Indium Tin Oxide (ITO) as a substrate; TiO$_2$ and SnO$_2$ nanoparticles as semiconductor materials; natural dyes (chlorophyll alfalfa) as an electron donor; gel electrolyte as electron transfer; active carbon as a catalyst which can convert light energy into electrical energy. The layer of two semiconductors was deposited on top of an substrat by doctor-blade method. Characterization of DSSC photoanoda materials that will be carried out in this research are: electrical characterization using Keithley I-V meter, optical characteristic characterization and bandgap analysis using UV-Vis Spectrophotometer, DSSC efficiency using TiO$_2$ as a semiconductor highest than DSSC using SnO$_2$ as a semiconductor. Characterization of photoanoda layer with X-Ray Diffraction (XRD). From the research, DSSC with a TiO$_2$ photoanoda capable of producing a higher efficiency than with SnO$_2$ photoanoda. The results shows 0, 05% for DSSC using TiO$_2$ photoanoda and 0,022% for DSSC using SnO$_2$ photoanoda.

1. Introduction
Solar cell is a p-n junction semiconductor device, which can convert solar light energy into electrical energy. This change 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 be expanded 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 composed 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 Dye Sensitized Solar Cell. 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

$^1$ To whom any correspondence should be addressed.
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 (TiO$_2$) 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 TiO$_2$ 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 TiO$_2$ 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 TiO$_2$ as its semiconductor. Next we will be research about material SnO$_2$ and TiO$_2$ as photoanode in DSSC.

2. Experimental Method

2.1. Synthesis of TiO$_2$ Nanoparticles and making the paste of photoanode materials

The TiO$_2$ synthesis nanoparticles was performed by coprecipitation method. The synthesis process of TiO$_2$ nanoparticle powder [7]: 20 mL TiCl$_3$ mixed with 100 ml of aquades and stirred for 1 hour. The solution sterilized NH$_4$OH 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$^\circ$ C with a holding time of 3 hours [7]. The TiO$_2$ paste is made by adding 1.4 ml of aquades into TiO$_2$. 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 Preparation of SnO$_2$ paste begins by dissolving 0.13 g of ethylcelulose into 3 mL of isopropanol and stirring for 1.5 hours. Further 0.25 g of SnO$_2$ powder is added to the solution and stirring is continued for 2 hours[9].

2.2. Preparation of Dye Sensitized Solar Cell

Semiconductor paste (TiO$_2$,SnO$_2$) is positioned over an area already formed by the Doctor-Blade method. After that heated above hot plate with temperature 450$^\circ$ C for 15 minutes. Dye used in this study is dye chlorophyll from alfalfa leaves (Medicago Sativa). Adsorption of dye in TiO$_2$ 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$^\circ$. The solid 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 nanocrystalline TiO$_2$ and SnO$_2$ structure was characterized by X-Ray diffraction (XRD). The absorption spectrum of chlorophyll dye solution was measured using a UV-Vis Spectrophotometer. Current and voltage (I-V) Characterization 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 (%).

\[
FF = \frac{V_{MPP}I_{MPP}}{V_{oc}I_{sc}}
\]
\[ \eta = \frac{P_{\text{max}}}{P_{\text{light}}} \times 100\% \]  

(2)

3. Results and Discussion

3.1 Photoanode Layer Characterization
The XRD result for photoanode layer was shown in Figure 1. With qualitative analysis using software match !, Figure 1, that TiO\(_2\) anatase phase with tetragonal structure has been successfully formed and located at 20 25.3°, 38.3°, 48°, 54°, 55°, 62°, 69°, 71° dan 75°.

![Figure 1. Crystal diffraction pattern of TiO\(_2\) and SnO\(_2\) layer](image)

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

The SEM micrograph of Figure 3 shows the particle shape of all samples are spherical. The morphology of TiO$_2$ layer (a) shows a porous structure with few cracks and agglomeration on its surface. As seen in figure (b) The SnO$_2$ layer surface has a particle size distribution that looks smooth, looks rather dense, and has a slightly porous structure. The same morphology was obtained by Camacho-Lopez M. A. et al. The porous structure of the photoanode surface is desirable because the presence of pores allows more dye molecules to be absorbed and the resulting photo current becomes larger [9]. Particle size information from pure TiO$_2$ films was obtained from SEM analysis. The TiO$_2$ particle size ranges from 15-60 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](image.png)

**Figure 3.** The films surface morphology shown in SEM micrograph (a). TiO$_2$ Co-precipitation film, (b). SnO$_2$ at 500x magnification (right row) and 5000x (left row)

3.4 Characterization of I-V Curves

| Cell Names | $V_{OC}$ (Volt) | $J_{SC}$ (mA/cm$^2$) | FF (%) | $\eta$ (%) |
|------------|-----------------|----------------------|--------|-----------|
| TiO$_2$    | 1.401           | 0.124                | 28.53  | 0.05      |
| SnO$_2$    | 1.182           | 0.082                | 22.63  | 0.022     |

Current and photo voltages measurements are performed using I-V Keithley Meter using halogen lamps on a 1 cm$^2$ area. The I-V characteristic curve of the under the simulation of light with an intensity of 100 mW cm$^2$ shown in Figure 4. Table 1 shows that the DSSC using the TiO$_2$ photoanoda shows a larger Jsc value compared to the DSSC using the SnO$_2$ photoanoda so that the efficiency value generated by the DSSC with the solvent TiO$_2$ is also higher. The higher Jsc values indicate the greater concentration of electrons in the TiO$_2$ conduction bands injected by dye [16] so that this leads to an increase in efficiency and produced by the DSSC with the TiO$_2$ 0.05% and 0.022% for SnO$_2$ photoanode. As shown in the Figure 3, the surface of the SnO$_2$ layer has a homogeneous particle size distribution, the structure is flat and looks rather dense but also does not contain agglomeration and has a slightly porous structure. Porous surface structure of the photoanoda is desirable, since the presence of pore allows more dye molecules to be absorbed and the resulting photo stream becomes larger.
4. Conclusion
DSSC with a TiO$_2$ photoanoda capable of producing a higher efficiency than with SnO$_2$ photoanoda. The results show 0.05% for DSSC using TiO$_2$ photoanoda and 0.022% for DSSC using SnO$_2$ photoanoda.

5. Acknowledgments
The author would like to thank the Institut Teknologi Sepuluh Nopember Surabaya for supporting the research.

6. 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 Effisiensi 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.