

Synthesis of Nanorods Titanium Dioxide via Anodic Alumina Membrane Template and their Applications in Dye-Sensitized Solar Cells

R Suryana, Sehati and Kusumandari

Department of Physics, Faculty of Mathematics and Natural Sciences, Sebelas Maret University, Jl. Ir. Sutami 36A Kentingan Surakarta 57126 Indonesia

E-mail: rsuryana@staff.uns.ac.id

Abstract. Titanium dioxide (TiO_2) nanorods have been successfully synthesized through sol-gel method via Anodic Alumina Membrane (AAM) as template. AAM template was removed using 6 M NaOH solution to obtain TiO_2 nanorods only. Then TiO_2 nanorods were annealed at 400°C for 2 h. Phase TiO_2 nanorods were characterized using X-Ray Diffraction (XRD) and morphology of TiO_2 nanorods were observed using Atomic Force Microscopy (AFM). In addition, the I-V meter was used to determine the DSSC efficiency. The XRD patterns showed that all peaks of synthesized- TiO_2 indicated anatase phase. AFM images confirmed that TiO_2 nanorods have diameters in range 18 – 30 nm. TiO_2 nanorods were mixed with TiO_2 nanoparticles having 21 nm in size then it was applied in the DSSC with β -carotene from carrot as dye. The efficiency of DSSC using TiO_2 mixed-nanorods and nanoparticles increase about 154.20% compare to using TiO_2 nanoparticles only. It is considered that TiO_2 nanorod structures can be effective in photon trapping thus many photon interact to dyes to produce many excited-electrons.

1. Introduction

At least, there are four parts of dye-sensitized solar cells (DSSC) which affect the performance, i.e., the dyes, the semiconductors for example titanium dioxide (TiO_2), the catalyst, and the electrolytes. Basically, processes occurring in the DSSC are the electrons transport. The process starts when the dye adsorbs the photons energy then the electrons in the dyes excite to the higher level energy. These electrons are injected to the conduction bands of the TiO_2 then diffuse to the electrodes. The electrons flow toward the catalyst through the external circuit. The electrons are attracted by the catalyst to supply electrons into the electrolyte. The electrolyte then transports the electrons back to the dye molecules. On the basis of electrons transport, the dyes are electron donors which the first responsible determines the performance of DSSC.

Many efforts have been done on TiO_2 to reach higher efficiencies. In this case of Ru-based dyes in DSSC, it is found that TiO_2 nanoparticles increase the dye absorption area to large scale which extends a wide range of optical absorption from the UV to the near IR [1]. In previous work, TiO_2 nanoparticles were synthesized using the sol-gel method with main materials of titanium tetrakisopropoxide (TTIP) and HClO_4 [2]. The performance of DSSC using this TiO_2 nanoparticles consisting the anatase and the rutile phases with beta carotene as dyes can be improved about ten times



compared to that using the pure-TiO₂ rutile phase [3]. However there are the factors that limit the performance of DSSC in absorption of low-energy photons. Some efforts have been made to develop dyes that absorb better at long wavelengths [4], but it was little success. Furthermore, the thickening the nanoparticles film to increase its absorption at long wavelengths can be performed. However, the film thickness comes to exceed the electron diffusion length through the nanoparticle network. In order to solve the electron diffusion length in the electrode by replacing the nanoparticles planar with modification of TiO₂ shapes i.e. nanowires [5], nanowhiskers [6], nanotubes [7], and nanorods [8]. In this paper, the TiO₂ nanorods will be synthesized using anodic alumina membranes (AAM). Then the TiO₂ nanorods are used in DSSC devices. In order to study the effect of TiO₂ nanorods to the DSSC efficiency, it is also performed the nanoparticles TiO₂ in planar shape as comparison.

2. Experimental Methods

TiO₂ nanorods were prepared by two steps. First step was the synthesis of TiO₂ solution using sol-gel method. Second step was formation of TiO₂ nanorods using anodic alumina membranes (AAM). Titanium tetraisopropoxide (TTIP), acetylacetone (ACAC), aquadest, and ethanol in ratio 1:1:3:20 were mixed and then magnetically stirred for 2 h at room temperature. AAM was heated at 75°C for 10 min to increase the hydrophilicity of the alumina porous to TiO₂ sol and then heated at 100°C for 8 h. Cleaned-AAM was immersed into the TiO₂ sol at 80°C for 10 min and cooled at room temperature for 24 h. In order to remove water or solvent, TiO₂-AAM was heated at 100°C for 8 h and then annealed at 400°C for 2 h to obtain the anatase phase only. Finally the TiO₂-AAM was treated with a 6 M NaOH solution to remove AAM template and it is obtained the TiO₂ nanorods only.

TiO₂ pastes were made in two types. First type, 0.25 g TiO₂ powders (Aldrich, 21 nm) was dissolved into 2 mL ethanol and then stirred in 300 rpm for 30 min. Second, 0.25 g TiO₂ powders was mixed with 0.025 g TiO₂ nanorods and then stirred in 300 rpm for 30 min. Each type was deposited on fluorine-doped tin oxide (FTO) glasses using spin coating at 1000 rpm and then hydrolyzed at 400°C for 10 min to evaporate organic materials [9]. While the beta-carotene as dyes, the I/I³⁻ solution as electrolytes, and the carbon as catalyst were prepared according to refs. [2, 3, 9]. The DSSC were fabricated in the sandwich structure using these two types.

Atomic Force Microscopy (AFM) was performed to confirm that the TiO₂ nanorods have formed. TiO₂ nanoparticles and nanorods were characterized using X-Ray Diffraction (XRD) to determine the phase. The performance of DSSC was obtained using I-V meter [3].

3. Results and Discussion

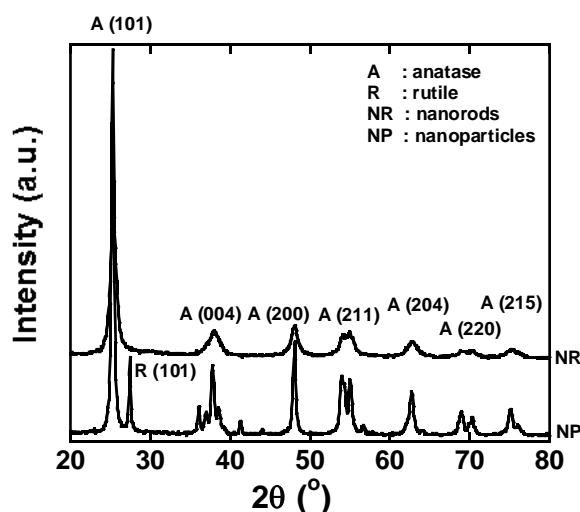


Figure 1. X-ray diffraction patterns of (a) TiO₂ nanoparticles (NP) and (b) TiO₂ nanorods (NR).

X-ray diffraction (XRD) patterns of TiO_2 nanoparticles and TiO_2 nanorods are shown in Figs. 1(a) and 1(b), respectively. Anatase phase appears at crystal orientations of (101), (004), (211), (220), and (215) for both TiO_2 nanoparticles and nanorods. Rutile phase appears at crystal orientation of (101) only with low intensity in TiO_2 nanoparticles. Therefore, it is considered that the DSSC efficiencies are dominantly affected by the anatase phases. Thus, it can be investigated the effect of the TiO_2 nanorods compare to the TiO_2 nanoparticles to the DSSC efficiency.

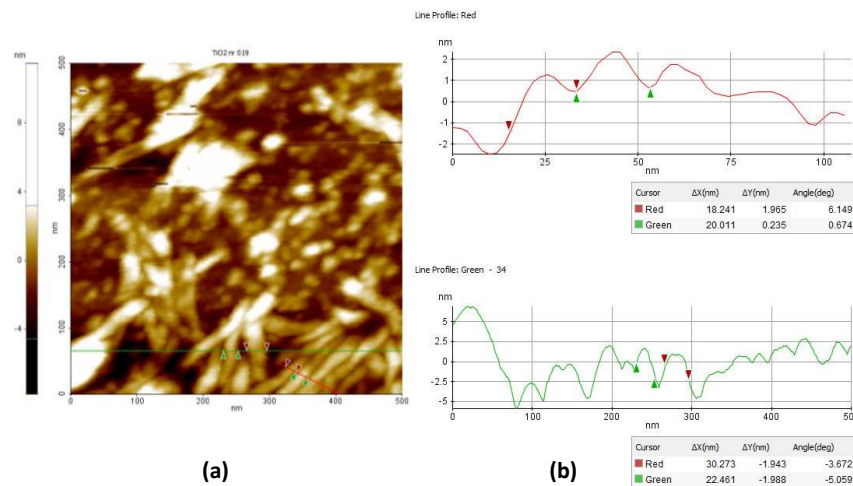


Figure 2. (a) Morphology image (500 nm x 500 nm) of TiO_2 nanorods surface on the FTO glass substrate and (b) line profile of TiO_2 nanorods surface correlating red and green lines.

Synthesization of the TiO_2 nanorods have been successfully formed using AAM templates. Figure 2 (a) shows the morphology image of TiO_2 nanorods deposited on the FTO glass substrate. The nanorods diameter are about 18-30 nm as shown in the profile lines correlating red and green lines (Fig. 2(b)). Nevertheless, there are many the TiO_2 grains that present in around the TiO_2 nanorods. It is speculated that when the AAM templates are immersed into the TiO_2 sol, the TiO_2 sol filled the membrane until saturated condition. Then, the remaining TiO_2 sol will attached on the membrane surface. After the rinsing treatment in 6 M NaOH solution to remove the AAM template, the TiO_2 sol inside the membrane holes will produce the nanorods while they TiO_2 sol on the membrane surfaces will produce the nanoparticles.

Table 1. I-V measurement parameters of the TiO_2 nanoparticles and the TiO_2 nanoparticles + the TiO_2 nanorods in DSSC applications as the work electrode.

Parameters	TiO_2 nanoparticles	TiO_2 nanoparticles+ TiO_2 nanorods
V_{oc} (Volt)	0.16	0.34
I_{sc} (Ampere)	4.98×10^{-4}	4.66×10^{-4}
V_m (Volt)	0.09	0.19
I_m (Ampere)	0.29×10^{-3}	0.35×10^{-3}
P_m (Watt)	2.61×10^{-5}	6.65×10^{-5}
η (%)	1.31×10^{-2}	3.33×10^{-2}

The performance of DSSC for each samples using the TiO_2 nanoparticles and mixed the TiO_2 nanoparticles and TiO_2 nanorods were determined through I-V characterization. The procedure to obtain the efficiency of DSSC from I-V characterization has been demonstrated in the previous work [3]. Table 1 summarize the I-V measurements consisting the open circuit voltage (V_{oc}), the current

short circuit (I_{sc}), the voltage maximum (V_m), the current maximum (I_m) to obtain the power maximum (P_m) and the efficiency (η). The DSSC efficiency increase about 154.20 % when the TiO_2 nanoparticles are mixed with the TiO_2 nanorods compare to the only TiO_2 nanoparticles in DSSC applications as the work electrodes. This is evidence that the TiO_2 nanorods can effectively traps the photon [8] so that the photon can stays in the DSSC system longer than if it is used the TiO_2 nanoparticles only. As consequence, many the photon will interact with the dyes to produce many the excited-electrons. Thus, the DSSC efficiency will increase significantly.

4. Conclusion

TiO_2 nanorods were successfully fabricated using AAM template method with 18-30 nm in a diameter. Adding TiO_2 nanorods into TiO_2 nanoparticles enhanced the DSSC performance about 154.20% compared with using TiO_2 nanoparticles only. It is suggested that mixed TiO_2 nanorods and nanoparticles might be favorable materials use as the electrode in DSSC device.

Acknowledgments

Authors wish to thank DIPA (PNBP) Universitas Sebelas Maret No. 501/UN27.11/PN/2014 for financial support through Unggulan Fakultas 2014.

References

- [1] O'Regan B and Gratzel M 1991 *Nature* **353** 737
- [2] Ardhani N, Supriyanto A, Yuwono A H and Suryana R, "Influence of mass ratio of aquadest and TTIP on the synthesis of TiO_2 nanoparticles to improve the performance of DSSC with beta-carotene as sensitizer", in *Advanced Material Research* **896**, eds by Triyana K *et al.* 17-18 September 2013 (Switzerland: Trans Tech Publications) pp. 481-484
- [3] Suryana R, Khoiruddin and Supriyanto A, "Beta-carotene dye of daucus carota as sensitizer on dye-sensitized solar cell", in *Materials Science Forum* **737**, eds Abdullah M *et al.* 20 September 2012 (Switzerland: Trans Tech Publication) pp. 15-19
- [4] Renouard T, Fallahpour R A, Nazeeruddin M K, Humphry-Baker R and Gorelsky S I *et al* 2002 *Inorganic Chemistry* **41**(2) 367
- [5] Law M, Greene L E, Johnson J C, Saykally R and Yang P 2005 *Nature Material* **4** 445
- [6] Ng J, Pan J H and Sun D D 2011 *J. Mater. Chem.* **21** 11844
- [7] Liu X, Guo M, Cao J, Lin J, Tsang Y H, Chen X and Huang H 2014 *Nanoscale Res. Lett.* **9**(1) 362
- [8] Liu J, Luo J, Yang W, Wang Y, Zhu L, Xu Y, Tang Y, Hu Y, Wang C, Chen Y and Shi W 2015 *J. Mater. Sci. Technol.* **31**(1) 106
- [9] Yulika D, Kusumandari and Suryana R 2014 *Jurnal Fisika Indonesia* **XVIII** (53) 66