

Effect of surface morphology of nanostructured rutile TiO₂ nanorods/nanoflowers as photoelectrode on the performance of Dye-sensitized solar cell

Mohd Khairul Ahmad¹ and Murakami Kenji²

¹Microelectronics and Nanotechnology-Shamsuddin Research Centre (MiNT-SRC) &

Faculty of Electrical and Electronic Engineering

Universiti Tun Hussein Onn Malaysia

86400 Batu Pahat, Johor, Malaysia

Email: akhairul@uthm.edu.my

²Research Institute of Electronics

Shizuoka University

432-8011 Hamamatsu, Shizuoka, Japan

Email: rskmura@ipc.shizuoka.ac.jp

Abstract—Aligned Rutile TiO₂ nanorods (r-TNRs) and TiO₂ nanoflowers (r-TNFs) were successfully prepared by hydrothermal method. Using hydrochloric acid (HCl) as chelating agent and titanium butoxide (TBOT) as precursor, aligned r-TNRs with r-TNFs were successfully growth onto fluorine-doped tin oxide (FTO) with different morphologies. The influences of surface morphologies to the rutile based Dye-sensitized solar cell (DSC) efficiency are discussed. The highest light-to-electric energy conversion efficiency, 1.80% is achieved using different concentration under simulated solar light illumination of 100 mWcm⁻² (1.5 AM).

I. INTRODUCTION

In dye-sensitized solar cell (DSC), photo-excited electrons in the dye are injected into the conduction band of TiO₂ film and resulted holes in the dye and then the electrons moved in the TiO₂ films by diffusion. In order to increase the efficiency of DSC, there are attempts in investigating the nanostructured TiO₂ such as nanorod and nanoflower in DSC applications [1-2]. The researches on the rutile-phased TiO₂ based DSCs were also reported [3-4] and the problems for using

rutile-phased TiO₂ is the low energy conversion efficiency in DSC applications.

One of the way to enhance the performance of rutile based DSCs, is to improve the dye adsorption in TiO₂ film.

In this study, we prepared rutile based DSC with different surface morphology. In the preparation of DSC, aligned TiO₂ (r-TNR)nanorods and nanoflowers (r-TNF) were grown on the substrate and used in DSC characterization.

II. EXPERIMENTAL

A. Preparation of rutile phase TiO₂ nanorods/nanoflowers thin films

Fluorine-doped tin oxide (FTO) coated glass was used as substrate in this experiment. All of the substrates are cleaned with deionzed water, acetone and ethanol with volume ratio of 1:1:1 using ultrasonic cleaner.

Both r-TNR and r-TNF were prepared on top of FTO coated glass using hydrothermal method. The solution was prepared by dissolving 20 ml of concentrated hydrochloric acid (36.5 %~38 %) in a 20 ml of deionzed water. The mixture was then stirred for

5 min before drop wise amount of Titanium Butoxide (TBOT). TBOT was fixed at 1.0 ml. After the solution was stirred for 10 min, it is put into Teflon steel made autoclave for hydrothermal process [5]. In order to prepare various surface morphologies, we did the hydrothermal process at 150 °C for 2 h, 5 h and 10 h of reaction time.

After the hydrothermal process, FTO substrates were rinsed into deionized water for 5 min and then annealed for 30 min at 450 °C.

B. Characterization method

The structural properties was done using X-ray Diffractometer (RINT Ultima III-Rigaku) and the surface morphology image was observed using FE-SEM (JSM-7001F JOEL). The solar cell efficiency was measured using solar simulator under 1.5 AM (Bunkoh Keiki-JUSCO).

C. DSC preparation

DSC was prepared using FTO coated glass and Pt coated glass as electrode and counter electrode. The dye solution was prepared at 3 mMol which is contained of Acetonitrile, ButylAlcohol and Ruthenium Dye (N719). The electrolyte that we used called DPMM electrolyte which contained of 0.6 M of 1,2-Dimethyl-3-propylimidazolium iodide, 0.1 M LiI, 0.5 M of 4-tert-Butylpyridine, 0.1 M of Guanidine Thiocyanate, 0.85ml of Acetonitrile, 0.5 ml of Valeronitrile and 0.05 M of I₂

III. RESULT AND DISCUSSIONS

The structural properties of TiO₂ thin film were carried out using Rigaku RINT Ultima III with Cu-K α radiation and 2° grazing angle. Fig. 1 shows XRD pattern of r-TNR/r-TNF TiO₂ prepared at 150 °C for 2 h, 5 h and 10 h. From the XRD pattern, it confirmed that prepared TiO₂ thin film corresponded to rutile crystallinity phase. Fig.1 also shows that there are three main peaks at 27.40°, 36.04° and 41.20°

corresponding to (110), (101) and (111) planes of the rutile phase (PDF No.98-000-0090). Some peaks are also detected in the profiles originated from the FTO layer of substrate glass.

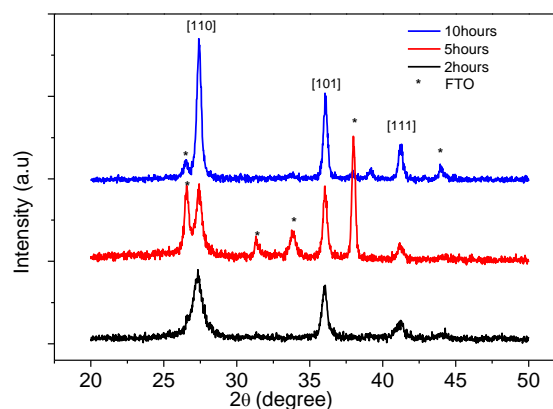


Fig. 1 XRD pattern of r-TNR/r-TNF TiO₂ thin film prepared at 150 °C for 2 h, 5 h and 10 h of reaction times

The surface morphology of the film was analyzed using Field Emission Scanning Electron Microscopy (FE-SEM). Fig. 2 shows surface morphologies and cross-sections of nanostructured TiO₂ films prepared at different hydrothermal reaction times 2, 5 and 10 h. As shown in Figs. 2(a-1) and (a-2), only nanorods layer is grown on the FTO layer of substrate glass with 300 nm in thickness for 2 h reaction. Diameter of the nanorods is found to be less than 100 nm. Growth of the nanorods looks like random. As we increase the reaction time to 5 h, both the diameter of nanorods and the thickness of layer become larger. It is also found from the cross-section of Fig. 2(b-2) that most of nanorods grow vertically and sparsely. When the reaction time reaches 10 h, we can see nanoflowers on the surface of film as shown in Fig. 2(c-1). The nanoflower consists of the nanorods whose diameter and length are 400 nm and 1.5 μ m with different orientations. Fig. 2(c-2) indicates that the thickness of nanorods layer also increases upto 1.3 μ m.

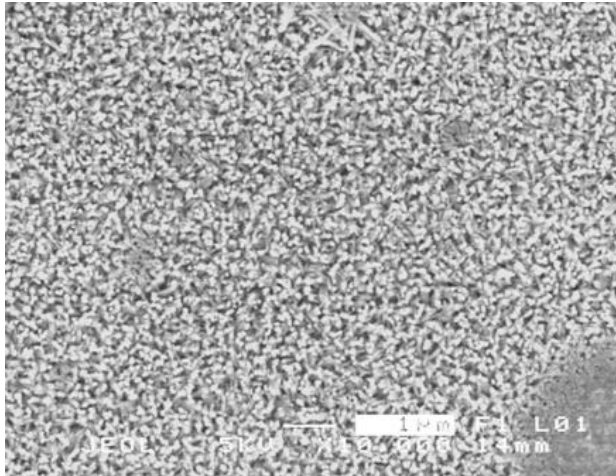


Fig. 2(a-1) SEM image of r-TNR thin film prepared at 150 °C for 2 h

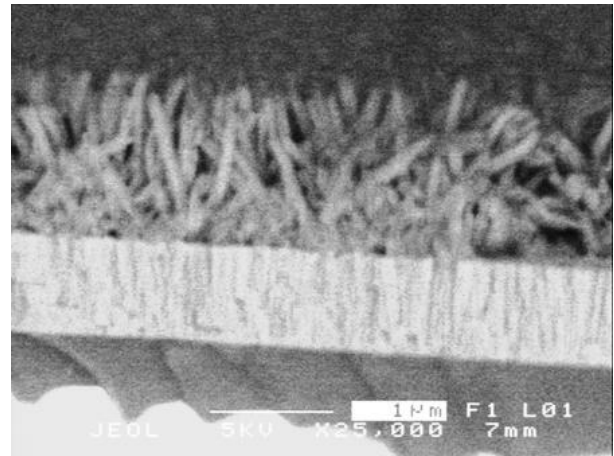


Fig. 2(b-2) Cross section image of r-TNR thin film prepared at 150 °C for 5 h

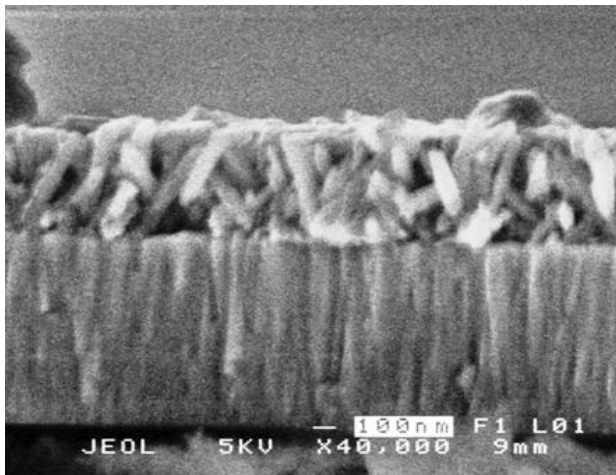


Fig. 2(a-2) Cross section image of r-TNR thin film prepared at 150 °C for 2 h

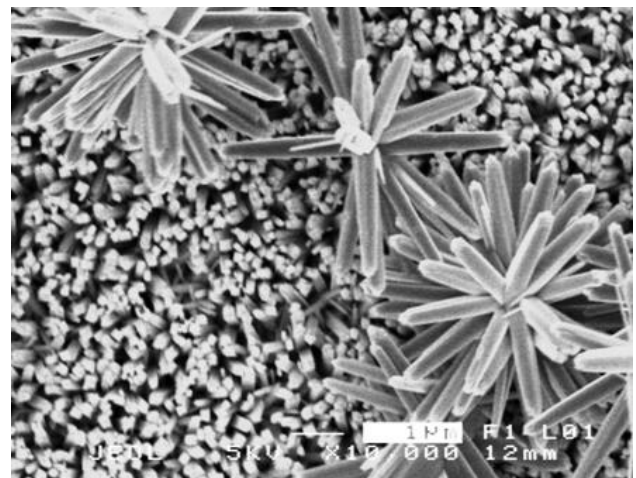


Fig. 2(c-1) SEM image of r-TNR/r-TNF thin film prepared at 150 °C for 10 h

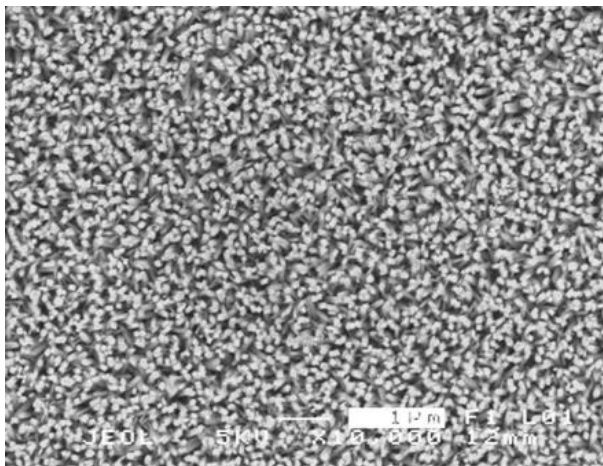


Fig. 2(b-1) SEM image of r-TNR thin film prepared at 150 °C for 5 h

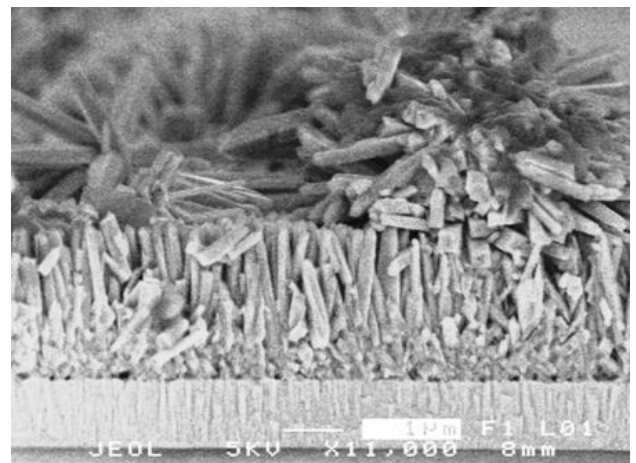


Fig. 2(c-2) Cross section image of r-TNR/r-TNF thin film prepared at 150°C for 10 h

Fig. 3 shows the I-V characteristics of cells based on the rutile-phased TiO₂ films. Photovoltaic performances of the cell are summarized in Table 1,

where V_{OC} is the open circuit voltage, J_{SC} short circuit current density and η energy conversion efficiency. It is found from the results that the cell based on the TiO_2 film synthesized hydrothermally for 10 h shows the highest conversion efficiency of 1.80%. The efficiency is originated mainly from the highest J_{SC} , which can be attributed to the increased amount of adsorbed dye molecules on TiO_2 surface due to an existence of r-TNFs. Estimated amount of adsorbed dye is also listed in Table 1.

Table 1 I-V measurement result of r-TNR/r-TNF TiO_2 thin film prepared different reaction times

Sample	V_{oc} (V)	J_{sc} (mA/cm ²)	Fill factor(%)	Efficiency(%)	Dye adsorption (x10 ⁻⁸ mol cm ⁻²)
2 hours	0.635	1.41	0.43	0.39	3.46
5 hours	0.750	4.51	0.53	1.78	3.90
10 hours	0.708	5.18	0.49	1.80	5.08

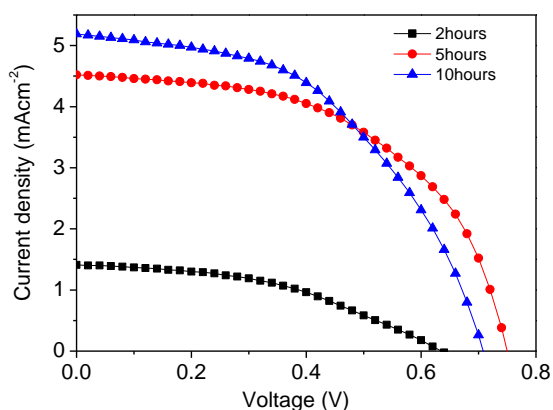


Fig. 3 I-V measurement of r-TNR/r-TNF TiO_2 thin film prepared at 150 °C for 10 h

IV. ACKNOWLEDGEMENT

The authors would like to thank Universiti Tun Hussein Onn Malaysia and Fundamental Research Grant Scheme (FRGS) for supporting this work

V. CONCLUSION

We had successfully prepared r-TNR/r-TNF thin film and used it in DSC application. Surface morphology of r-TNR can be changed with longer reaction time of hydrothermal process. For longer reaction time, r-TNF can be obtained at 10 h, and the performance of DSC was increased due to more dye adsorption in influence of r-TNF thin film.

REFERENCES

- [1] P. Charoensirithavorn, Y. Ogami, T. Sagawa, S. Hayase, S. Yoshikawa, 'A facile route to TiO_2 nanotube arrays for dye-sensitized solar cells', *Journal of Crystal Growth*, vol. 311, (2009), pp. 757.
- [2] Y. Zhang, Y. Gao, X.H. Xia, Q.R. Deng, M.L. Guo, L. Wan, G. Shao, 'Structural engineering of thin films of vertically aligned TiO_2 nanorods', *Material Letter*, vol. 64, (2010), pp. 1614.
- [3] D.U. Lee, S.R. Jang, R. Vittal, J. Lee, K.J. Kim, 'CTAB facilitated spherical rutile TiO_2 particles and their advantage in a dye-sensitized solar cell', *Solar Energy*, vol. 82, (2008), pp. 1042.
- [4] H.-Y. Byun, R. Vittal, D.Y. Kim, K.-J. Kim, 'Beneficial Role of Cetyltrimethylammonium Bromide in the enhancement of Photovoltaic Properties of Dye-Sensitized Rutile TiO_2 Solar Cells', *Journal of Surfaces and Colloids*, vol. 20, (2004), pp. 6853.
- [5] M.K. Ahmad, K. Murakami, 'Application of Titanium Dioxide Nanorods in DSC using Hydrothermal method', *Advanced Material Research* vol. 222, (2011), pp. 24