Rutile-phased TiO₂ nanorods/nanoflowers based Dye-sensitized solar cell

Mohd Khairul Bin Ahmad^{1,a} and Kenji Murakami^{2,b}

¹Microelectronics & Nanotechnology-Shamsuddin Research Centre (MiNT-SRC), Faculty of Electrical and Electronics Engineering

University Tun Hussein Onn Malaysia (UTHM), Malaysia

²Research Institute of Electronics, Shizuoka University, Japan

^aakhairul@uthm.edu.my, ^brskmura@ipc.shizuoka.ac.jp

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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).

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.

Experimental

Fluorine-doped tin oxide (FTO) coated glass was used as substrate in this experiment. All of the substrates are cleaned with deionized 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 deionized 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]. 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. 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). DSC was prepared using FTO coated glass and Pt coated glass as electrode and counter electrode. The dye solution and electrolyte were prepared according to previous study [5].

Results and Discussion

Structural property study. 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

Surface morphology study. 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. 3(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. 4(c-1). The nanoflower consists of the nanorods whose diameter and length are 400 nm and 1.5 μ m with different orientations. Fig. 4(c-2) indicates that the thickness of nanorods layer also increases upto 1.3 μ m.

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

Fig. 3(b-1) and (b-2) SEM image of surface morphology and cross section of r-TNR thin film prepared at 150 °C for 5 h

Fig. 4(c-1) and (c-2) SEM image of surface morphology and cross section of r-TNR thin film prepared at 150 °C for 10 h

Electrical property study. Fig. 5 shows the I-V characteristics of cells based on the rutile-phased TiO_2 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.

Fig. 5 I-V measurement of r-TNR/r-TNF TiO₂ thin film prepared at 150 °C for 10 h

Table 1 I-V measurement of DSC with different TBOT concentrations.

Sample	V _{oc} (V)	J _{sc} (mA/cm ²)	Fill factor (%)	Efficiency (%)	Dye adsorption (x10 ⁻⁸ molem ⁻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

Summary. TiO₂ nanorods have been successfully deposited onto the FTO glass substrate using a hydrothermal method. DSC was also successfully fabricated without annealing process. From the results, the efficiency of DSC was still low compared to conventional TiO₂ thin film. Further improvement on thickness and TNF growth are required.

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