

# Influences of Surface Morphology of Nanostructured Rutile TiO<sub>2</sub> Nanorods/Nanoflowers as Photoelectrode on the Performance of Dye-sensitized Solar Cell

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## Abstract

Aligned Rutile TiO<sub>2</sub> nanorods (r-TNRs) and TiO<sub>2</sub> 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<sup>-2</sup> (1.5 AM).

## Abstrak

**Pengaruh Morfologi Permukaan dari Nanorod/Nanoflower TiO<sub>2</sub> Rutil Berbentuk Nanostruktur sebagai Fotoelektroda pada Kinerja Sel Surya Tersensitisasi-Pewarna.** Penyejajaran nanorod TiO<sub>2</sub> Rutil (*Rutile TiO<sub>2</sub> nanorods* atau r-TNRs) dan Nanoflower TiO<sub>2</sub> Rutil (*Rutile TiO<sub>2</sub> nanoflowers* atau r-TNFs) telah berhasil dihasilkan melalui metode hidrotermal. Dengan menggunakan asam hidroklorida (HCl) sebagai media penghasil *chelate* dan titanium butoksida (TBOT) sebagai media perintis, r-TNRs yang disejajarkan dengan r-TNFs telah berhasil dikembangkan di dalam timah oksida bercampur fluorin (*fluorine-doped tin oxide* atau FTO) dengan morfologi yang berbeda-beda. Makalah ini membahas pengaruh-pengaruh morfologi permukaan terhadap efisiensi sel surya tersensitisasi-pewarna (*dye-sensitized solar cell* atau DSC) berbasis rutil. Efisiensi konversi energi tertinggi dari cahaya ke listrik, yaitu 1,80%, dicapai menggunakan konsentrasi yang berbeda-beda di bawah paparan cahaya matahari simulasi sebesar 100 mWcm<sup>-2</sup> (1.5 AM).

*Keywords: dye sensitized solar cell, hydrothermal, nanoflower, nanorod, TiO<sub>2</sub>*

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## 1. Introduction

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

In this study, we prepared rutile based DSC with different surface morphology. In the preparation of DSC, aligned TiO<sub>2</sub> (r-TNR)nanorods and nanoflowers (r-TNF) were grown on the substrate and used in DSC characterization.

## 2. Eksperiment

**Preparation of rutile phase TiO<sub>2</sub> 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 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]. 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.

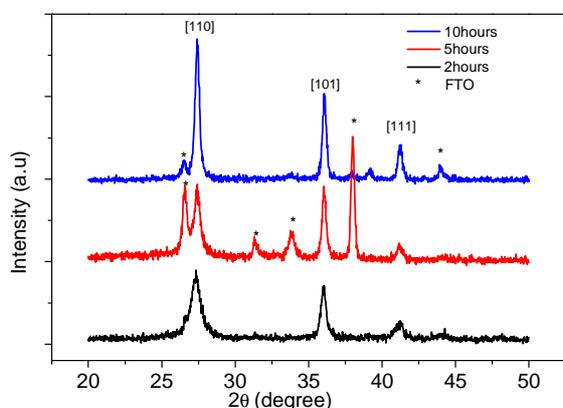
After the hydrothermal process, FTO substrates were rinsed into deionized water for 5 min and then annealed for 30 min at 450 °C.

**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).

**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 I<sub>2</sub>

### 3. Results and Discussion

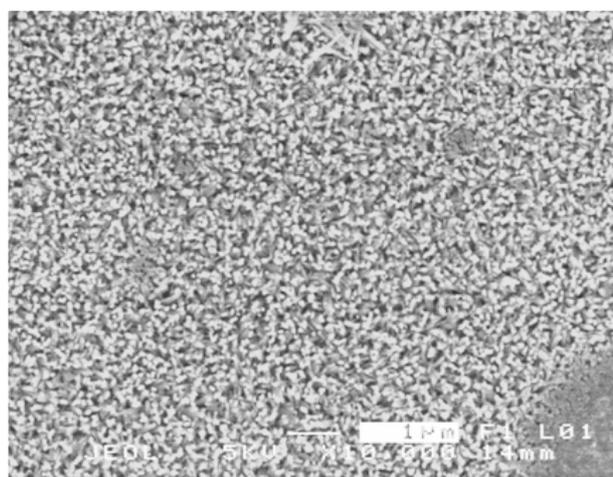
The structural properties of TiO<sub>2</sub> thin film were carried out using Rigaku RINT Ultima III with Cu-K $\alpha$  radiation and 2° grazing angle. Fig. 1 shows XRD pattern of r-TNR/r-TNF TiO<sub>2</sub> prepared at 150 °C for 2 h, 5 h and 10 h. From the XRD pattern, it confirmed that prepared



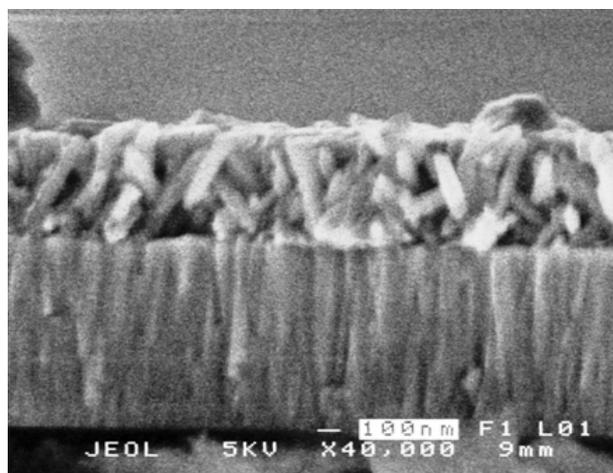
**Fig. 1. XRD Pattern of r-TNR/r-TNF TiO<sub>2</sub> Thin Film Prepared at 150 °C for 2 h, 5 h and 10 h of Reaction Times**

TiO<sub>2</sub> 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.

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 TiO<sub>2</sub> 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



**Fig. 2(a-1). SEM Image of r-TNR Thin Film Prepared at 150 °C for 2 h**



**Fig. 2(a-2). Cross Section Image of r-TNR Thin Film Prepared at 150 °C for 2 h**

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  $\mu\text{m}$  with different orientations. Fig. 2(c-2) indicates that the thickness of nanorods layer also increases upto 1.3  $\mu\text{m}$ .

Fig. 3 shows the I-V characteristics of cells based on the rutile-phased  $\text{TiO}_2$  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  $\eta$  energy conversion efficiency. It is found from the results that the cell based on the  $\text{TiO}_2$  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  $\text{TiO}_2$  surface due to an existence of r-TNFs. Estimated amount of adsorbed dye is also listed in Table 1.

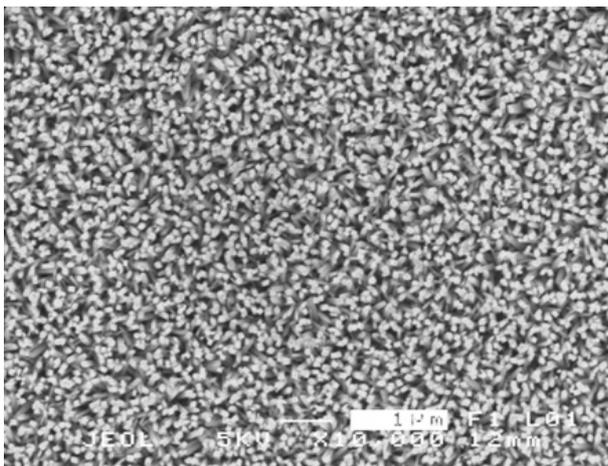


Fig. 2(b-1). SEM Image of r-TNR Thin Film Prepared at 150 °C for 5 h

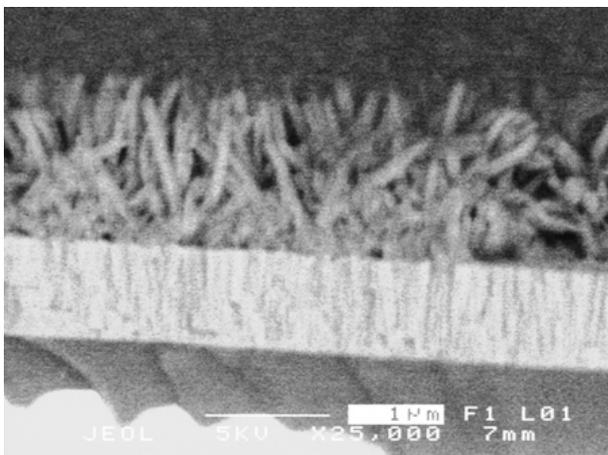


Fig. 2(b-2). Cross Section Image of r-TNR Thin Film Prepared at 150 °C for 5 h

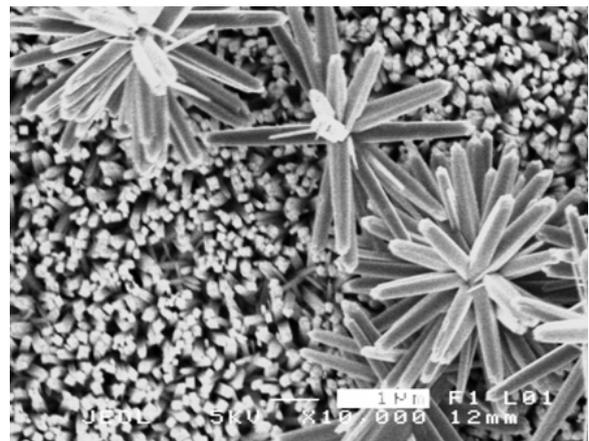


Fig. 2(c-1). SEM Image of r-TNR/r-TNF Thin Film Prepared at 150 °C for 10 h

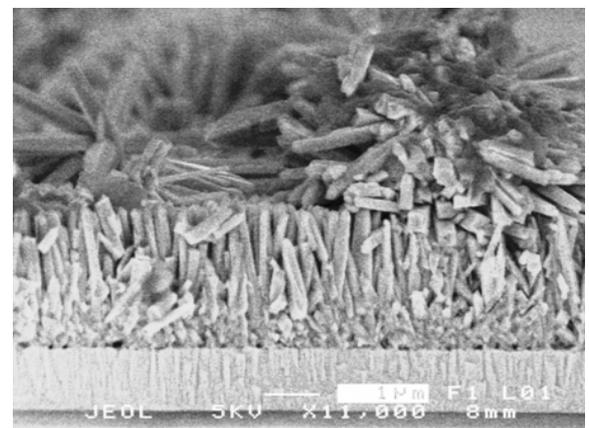


Fig. 2(c-2). Cross Section Image of r-TNR/r-TNF Thin Film Prepared at 150 °C for 10 h

Table 1. I-V Measurement Result of r-TNR/r-TNF  $\text{TiO}_2$  Thin Film Prepared Different Reaction Times

Sample	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA}/\text{cm}^2$ )	Fill factor (%)	Efficiency (%)	Dye adsorption ( $\times 10^{-8} \text{mol}/\text{cm}^2$ )
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

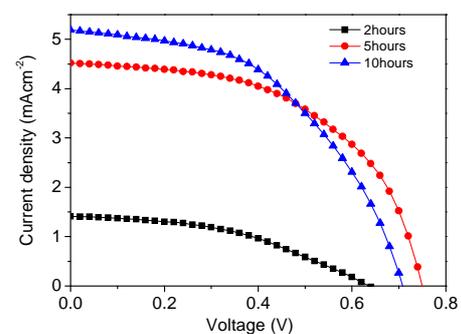


Fig. 3. I-V Measurement of r-TNR/r-TNF  $\text{TiO}_2$  Thin Film Prepared at 150 °C for 10 h

#### 4. Conclusions

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.

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