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Effect of heat treatment to the rutile based dye sensitized solar cell

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ABSTRACT

The effect of heat treatment of aligned titanium dioxide (TiO_2) nanorods and nanoflowers in the application of dye-sensitized solar cell were investigated. Both of these nanostructures were deposited on the fluorine-doped SnO_2 transparent conducting glass substrate using one step hydrothermal method. Characterizations of dye-sensitized solar cell (DSC) with rutile-phased TiO_2 nanorods and nanoflowers were performed such as surface morphology, structural property, dye-adsorption and energy conversion efficiency. In the DSC preparation, both TiO_2 nanorods/nanoflowers, platinum (Pt), ruthenium dye N719 and DPMII electrolyte were used as photo electrode, counter electrode, dye solution and liquid electrolyte, respectively. Concentration of 3 M cetyltrimethylammonium bromide (CTAB) was added in the preparation of rutile-phased TiO_2 nanorods and nanoflowers. All of the photo electrodes were heated at 150 °C, 250 °C, 350 °C, 450 °C, respectively. The thickness of TiO_2 nanorods and nanoflowers-layers were 5 μm and 15 μm, respectively. Lastly, power conversion efficiency of DSC was performed under the light intensity of 100 mW/cm^2. It was found that the highest power conversion efficiency was 3.27%, and heated at 450 °C.

1. Introduction

Nanostructured titanium dioxides (TiO_2) such as nanorods, nanotubes and nanoflowers have been widely studied nowadays due to their excellent properties for important applications. Compared to nanoparticle TiO_2, nanostructured TiO_2 has low recombination rate for electron-hole pair and good optical and electrical properties. A number of methods have been employed to prepare the nanostructured TiO_2 films including template assisted method [1], electrochemical method [2], hydrothermal method [3], chemical vapor deposition (CVD) [4] and sol–gel process [5]. One of the promising and cost effective methods to prepare a homogenous TiO_2 film is the hydrothermal method. Hydrothermal method is a liquid-deposit process using soft chemistry (bottom-up approach), and gives a homogeneous thin film assisted with stable temperature and pressure.

It is known that TiO_2 has three crystalline phases; rutile phase (tetragonal), anatase phase (tetragonal) and brookite phase (orthorhombic). Rutile is stable in high temperature region, whereas anatase and brookite are metastable and transforme to rutile when annealed at high temperature. Most researches have been performed for anatase phased TiO_2 in the DSC applications, even though some of the characteristics of these phases are same. There is only a few researches regarding the rutile phased TiO_2 nanorod or nanoflower for DSC applications [6–8], which has proven that the rutile phased TiO_2 also can be suitable candidate for the DSC applications.

Generally, nanorods provided us with good electron mobility which could be use in sensor devices application [9] meanwhile nanoflowers give high surface area for dye adsorption for dye-sensitized solar cell application. Annealing process is a heating process which enhanced the electron transportation in semiconductor materials. With the advantages of nanorods and nanoflowers structures and annealing process towards rutile phased TiO_2, we have prepared the rutile phased TiO_2 nanorods (r-TNRs) and nanoflowers (r-TNFs) and used them for the DSC application. In this paper, we discuss the effect of annealing process of r-TNRs and r-TNFs for the DSC application. At first, the growth of

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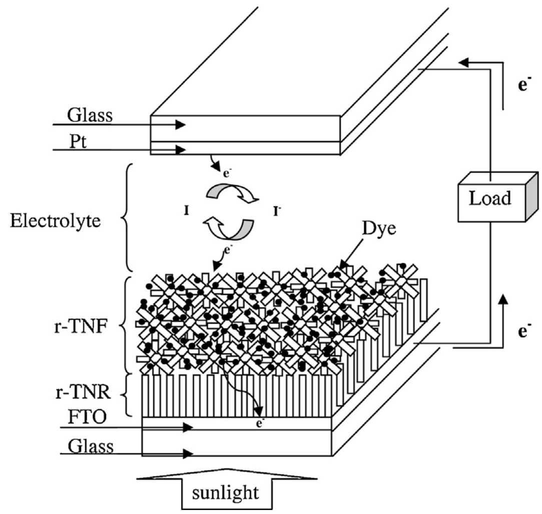

Fig. 1. Schematic diagram of dye-sensitized solar cell rutile phased TiO_2 nanorods (r-TNR) and rutile-phased TiO_2 nanoflower (r-TNF) deposited on top of FTO coated glass.

r-TNRs and r-TNFs with different amount of precursor was studied and then, we investigated the advantages of hybridization at different annealing temperatures to the performances of DSC.

2. Experimental

2.1. Synthesis of rutile phased nanorods/nanoflowers TiO_2 thin film

Diagram of the prepared DSC is shown in Fig. 1. Fluorine-doped SnO_2 (FTO) coated glass was used as a substrate with the thickness of 1.0 mm. Ethanol, acetone, hydrochloric acid and titanium butoxide (TBOT) (WAKO chemical) were used as received. Deionzed water was used to prepare all the solutions. FTO coated glass was cut into dimension of 10 mm × 25 mm and cleaned by sonicating method in acetone, ethanol and deionzed water with volume ratio of 1:1:1 for 30 min and finally dried in the air. The synthesis of the film was referring to our previous study with slight improvement [9]. The chemical solution in the process was obtained by dissolving 20 ml of concentrated hydrochloric acid (36.5–38%) in a 20 ml of deionzed water. The mixture was vigorously stirred for 5 min before drop wise amount of TBOT. The solutions were prepared at different concentrations, 0.5 ml, 0.7 ml, 1.0 ml and 1.5 ml. In order to enhance the film structure 3 M of cetyltrimethylammonium bromide (CTAB) was added into the solution as a surfactant [10]. The solution was stirred for 10 min before put into the Teflon steel autoclave for hydrothermal process. The FTO glass substrate was also put into the autoclave (50 ml volume) with facing the conducting side upward. The hydrothermal process was performed at 150 °C for 10 h. After hydrothermal process, the autoclave was taken out from oven and cooled down to room temperature. Prepared samples were taken out and immersed into deionized water for a few minutes and then rinsed extensively and dried in oven at 150 °C for 30 min. In order to study the effect of annealing temperature, prepared nanostructured films were annealing at 150 °C, 250 °C, 350 °C and 450 °C for 30 min.

2.2. Characterization

Surface morphology and cross-section of the prepared TiO_2 films were analyzed by using field-emission scanning electron microscopy (FE-SEM, JOEL JSM-6320F) at accelerating voltage of 20 kV. Thickness of the films was also determined by FE-SEM observation. X-ray diffraction (XRD) was performed by using RINT Ultima III (Rigaku) with Cu $K\alpha$ radiation (α = 1.5418 Å). The XRD profiles were measured in the 2θ range from 20° to 50° at a 2°/min scanning speed to investigate the crystal phases of TiO_2 films. The amount of adsorbed dye was determined as follows; desorbing the dye from the TiO_2 film surface into a mixed solution of 1.0 M NaOH and deionized water (1:1, in volume fraction) and measuring the absorption spectra of solution using UV–vis Spectrophotometer (V-630, Jusco) to determine the concentration of adsorbed dye.

Photocurrent versus voltage (*I*–*V*) characteristics was measured by using solar simulator under 1.5 AM (Bunkoh Keiki-Jusco). For photosensitization study, the prepared TiO_2 photoelectrode with working area of 0.25 cm^2 was immersed in 3 mM of N719 dye for about 14 h at room temperature. The Pt counter electrode with mirror finish was prepared by the sputtering method and used as counter electrode. In order to assemble the DSC, the electrolyte prepared from 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, 0.85 ml of acetonitrile, 0.5 ml of valeronitrile and 0.05 M of I_2 was inserted between the Pt electrode and the dye-coated r-TNR/r-TNF electrode to form a sandwich-type clamped cell for the solar cell measurement.

3. Results and discussion

3.1. Characterization of rutile phased TiO_2 nanorods/nanoflowers

The amount of precursor in the solution is a key factor to grow both r-TNR and r-TNF in this study. By using different concentrations, the amount of r-TNF can be controlled and optimized for the DSC application. Fig. 2(a)–(d) shows FE-SEM images of the prepared TiO_2 films composed of nanorods and nanoflowers on the FTO substrates through the hydrothermal method at 150 °C for 10 h. The inset in each figure shows the corresponding cross-section view. Fig. 2(a) shows the TiO_2 film prepared from 0.5 ml of precursor (TBOT). The film consists of mostly the vertically oriented nanorods with some mis-oriented nanorods. There are also a few of nanoflowers on top of nanorods layer. When the concentration of precursor increases to 0.7 ml, the amount of TiO_2 nanoflowers also increases as shown in Fig. 1(b). The amount of nanoflowers continually increases and the layer becomes denser with an increase in the concentration until 1.5 ml of TBOT. It is found from the cross-section views that the thickness of r-TNR layer is about 5 μm, which remains same until 1.5 ml of TBOT. On the other hand, the thickness of r-TNF layer increases with the concentration of precursor as shown in Fig. 2. From the results, the nanostructured TiO_2 film prepared using 1.0 ml of TBOT is chosen for further investigations. In order to apply the films to DSC application they are annealed at different temperatures from 150 °C to 450 °C for 30 min.

XRD profiles of the films annealed at different temperatures, 150 °C, 250 °C, 350 °C and 450 °C are shown in Fig. 3. The result shows that there are four peaks at 27.40°, 36.04°, 41.20° and 43.90° corresponding to (1 1 0), (1 0 1), (1 1 1) and (2 1 0) planes of the rutile phase (PDF No.98-000-0090). The main peak at 27.40° corresponds to [1 1 0] plane. As the annealing temperature increases, there is no additional peak observed in the XRD profiles. The peak intensities do not significantly increase either. It is confirmed from the results that the prepared TiO_2 films are single rutile phase and the peak intensities are not affected by the annealing temperature up to 450 °C due to thermodynamic stability of the rutile phase.

3.2. Application of rutile phase TiO_2 nanorods/nanoflowers to DSC

Photocurrent-voltage characteristics of the DSCs using r-TNR/r-TNF films are shown in Fig. 4 under the simulated full sunlight, 100 mW cm^{-2}. The configuration of DSC is FTO/r-TNR/

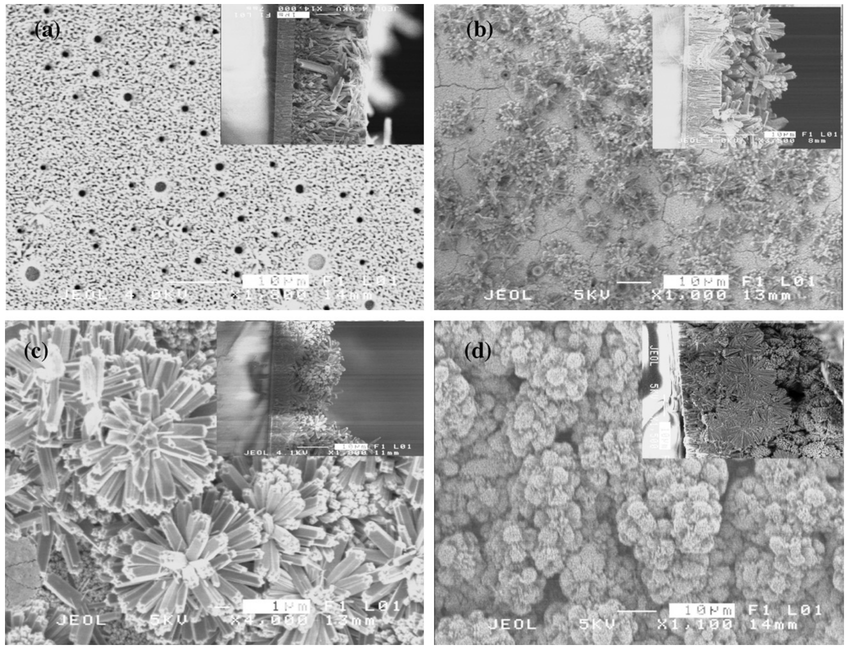

Fig. 2. FESEM images of TiO_2 nanorods and nanoflowers film prepared at different amount of precursors; (a) 0.5 ml, (b) 0.7 ml, (c) 1.0 ml and (d) 1.5 ml.

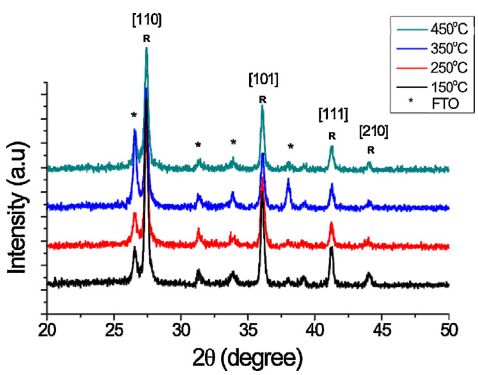

Fig. 3. XRD diffraction patterns of TiO_2 nanorods and nanoflowers film prepared at different annealing temperature; (a) 150 °C, (b) 250 °C, (c) 350 °C and (d) 450 °C.

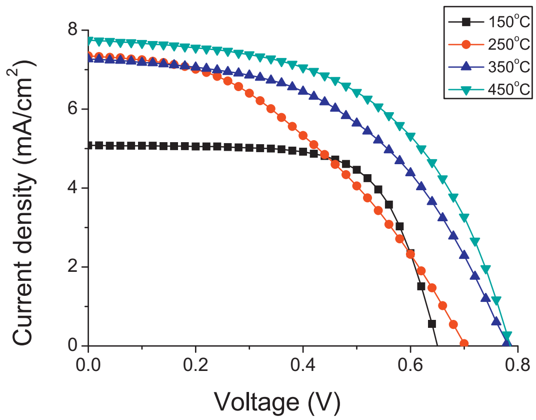

Fig. 4. *I–V* measurement of r-TNR/r-TNF TiO_2 thin film prepared with and without a-TiO_2 thin film.

r-TNF + dye + electrolyte/Pt. The r-TNR/r-TNF films are annealed at different temperatures, 150 °C, 250 °C, 350 °C and 450 °C. Photovoltaic performances of the DSCs are summarized in Table 1. It is found from the results that the short circuit current density (J_{SC}) and the open-circuit voltage (V_{OC}) increase with an increase in the annealing temperature. The energy conversion efficiency (η) of

Table 1
I–V measurement of DSC with different annealing temperature.

Sample (°C)	Dye absorption ($\times 10^{-8}$ mol cm^{-2})	V_{oc}	J_{sc} (mA cm^{-2})	Fill factor	Efficiency (%)
150	3.78	0.64	5.14	0.52	1.72
250	3.89	0.70	7.35	0.42	2.14
350	7.25	0.78	7.27	0.50	2.83
450	7.72	0.79	7.75	0.54	3.27

DSCs using the r-TNR/r-TNF films also increases with the annealing temperature and the DSC with the r-TNR/r-TNF film annealed at 450 °C gives the highest η of 3.27%. High efficiency is mainly attributed to the increased J_{SC}, in other words, amount of the dye adsorption on r-TNR/r-TNF films increases with the annealing temperature as shown in Table 1. The dye adsorption is closely related to surface morphology of the film. Morphology of the r-TNF layer can contribute to an increase in the surface area of the film resulting in the higher dye adsorption. Furthermore, surface contamination of the r-TNRs and the r-TNFs can be removed at higher annealing temperature which is formed during the hydrothermal process. Higher annealing temperature also improves interconnection between the r-TNRs and the r-TNFs resulting in enhancing of the electron mobility. Smaller surface area of the r-TNR film can lead to a reduction in the charge recombination [11], which suppresses the dark current and increases the V_{OC} [12]. More investigations on mechanism and structure of r-TNR/r-TNF could bring the rutile phased TiO_2 film to the same level as anatase phased one in the DSC application.

4. Conclusion

In summary, we have successfully prepared the DSCs using r-TNR/r-TNF TiO_2 films annealed at different temperatures and investigated the effect of amount of precursor on the structure of r-TNR/r-TNF film. The growth of r-TNF is enhanced by the amount of precursor (TBOT). High density of the r-TNF contributes to higher surface area of the film which could enhance the dye adsorption on the film. Better interconnection at r-TNR/r-TNF interface in the film is realized by annealing the film at higher temperature to improve the electron mobility. It is concluded that the hybridization of r-TNR and r-TNF is one of the promising way to improve the efficiency of DSC prepared from the rutile phased TiO_2 film.

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