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RESEARCH

Improvement in photo voltaic performance of rutile-phased TiO_2 nanorod/nanoflower-based dye-sensitized solar cell

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Abstract

An improved dye-sensitized solar cell (DSC) of rutile-phased titanium dioxide (TiO_2) electrode with increased power conversion efficiency was successfully fabricated. Rutile-phased TiO_2 nanorods and nanoflowers were grown directly on fluorine-doped SnO_2 (FTO) by simple aqueous chemical growth technique using one-step hydrothermal process. The solution was prepared by mixing hydrochloric acid, deionized water, and titanium butoxide used as precursor. In the preparation of DSC, both TiO_2 nanorods and nanoflowers, platinum (Pt), ruthenium dye N719, and DPMII electrolyte were used as photoelectrode, counter electrode, dye solution, and liquid electrolyte, respectively. The prepared rutile-phased TiO_2 nanorods and nanoflowers samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The DSCs were fabricated based on the rutile-phased titanium dioxide nanorod and nanoflower photoelectrodes. For their energy conversion efficiency, I-V characteristics and electrochemical impedance spectroscopy were studied. We also investigated the effect of cetyltrimethylammonium bromide (CTAB) reaction times 2, 5, and 10 h in the preparation of rutile-phased TiO_2 nanoflowers for DSC. CTAB is one of the capping agents that cover the refine surface of nanoparticles and prevent them from coagulation or aggregation. In our final result, the combination of rutile-phased TiO_2 nanorod- and nanoflower-based DSCs showed best efficiency at approximately 3.11% due to its good electron transport of TiO_2 nanorods and increased surface area by the TiO_2 nanoflowers that had increased dye absorption.

Keywords Titanium dioxide · Nanostructures · TiO_2? nanorods · TiO_2? nanoflowers · Hydrothermal method · Rutile phase · Dye-sensitized solar cell

Introduction

Nanostructured titanium dioxides (TiO_2) such as nanorods, nanotubes, and nanoflowers have been widely studied nowadays due to their excellent properties for various types of applications. Compared to TiO_2 nanoparticles, one-dimensional 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, 6]. One of the promising and cost-effective methods to prepare a homogenous TiO_2 film is the hydrothermal method. Hydrothermal method is a liquid-deposition process using soft

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chemistry (bottom-up approach) that gives a homogeneous thin film assisted with stable temperature and pressure.

It is well known that TiO_2 has three crystalline phases: rutile phase (tetragonal), anatase phase (tetragonal), and brookite phase (orthorhombic). Rutile is more stable in a high-temperature region, whereas anatase and brookite are metastable and transforms into rutile when annealed at high temperature. Most of the researchers have performed anatase-phased TiO_2 in the DSC applications, compared to rutile-phased, even though both rutile and anatase phases have some similar characteristics. There are small numbers of researchers who investigated the rutile-phased TiO_2 nanorod or nanoflower for DSC applications [7–9]. Their results have proven that the rutile-phased TiO_2 is a suitable candidate for the DSC applications.

Surfactant has been used to stabilize and control the unlimited nucleation growth and agglomeration of nanoparticles by adsorption on the surface of the head groups, lowering the mean particle size. Among the stabilizers, in the presence of cationic surfactant, cetyltrimethylammonium bromide (CTAB) is essential as a shape-directing agent for the synthesis of metal oxide nanomaterials [10, 11].

Generally, nanorods and nanotubes provide good electron mobility, which is used in sensor devices application [12, 13]. Meanwhile, nanoflowers have high surface area for dye adsorption, which is suitable for dye-sensitized solar cell application. Knowing the advantages of nanorod and nanoflower structures for the application of DSC, we prepared the rutile-phased TiO_2 nanorods (r-TNRs) and nanoflowers (r-TNFs) using the hydrothermal method. In this study, we discussed the growth mechanism of r-TNRs and r-TNFs using the hydrothermal method. The growth mechanism of r-TNRs and r-TNFs will be studied for different reaction times, and also, the effect of adding cetyltrimethylammonium bromide (CTAB) to the hydrothermal process was also investigated. Nevertheless, the advantage of r-TNFs deposited on the top of the r-TNR electrodes for the DSC application was also investigated.

Experimental

Materials

All chemicals used were of analytical reagent grade without any further purification. All aqueous solutions were prepared using deionized water.

Preparation of rutile-phased TiO_2 nanorod photoelectrodes

Rutile-phased TiO_2 nanorod (r-TNR) films were prepared on top of fluorine-doped tin oxide-coated glass (FTO-coated glass). The FTO-coated substrates were cleaned using acetone, ethanol, and deionized water of 1:1:1 volume ratio and then put into ultrasonic cleaner for 1 h. The FTO substrates were sandwiched between two soda lime glasses (10 mm × 25 mm). The first soda lime glass was put under the FTO substrate and the second glass with mask area (0.25 cm^2) was put on top of the FTO substrate. All of these glasses were sealed using Teflon tape and kept into the Teflon (300 ml)-aligned stainless steel autoclave for hydrothermal process [14].

The prepared solution for the growth of r-TNRs consist of titanium butoxide (TBOT) as a precursor, hydrochloric acid (36.5–38 wt%), and deionized water. The effect of surfactant cetyltrimethylammonium bromide (CTAB) was also studied in our experiments during hydrothermal process. All the above chemicals were mixed up to 10 min by stirring to form a homogeneous solution. Then, the solution was kept into the autoclave along with FTO substrate, which is prepared as mentioned earlier. The hydrothermal process was performed at 150 °C for different reaction times of 2, 5, and 10 h. After the hydrothermal process, FTO substrates were rinsed with deionized water for 5 min and then annealed for 30 min at 450 °C.

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 an accelerating voltage of 20 kV. The thickness of the films was determined by cross section of FE-SEM images. X-ray diffraction (XRD) pattern of the films were performed using RINT Ultima III (Rigaku) with Cu Kα radiation ($\lambda = 1.5418$ Å). The XRD profiles were measured in the 2θ range from 20° to 50° at a 2°/min of scanning speed to investigate the crystal phases of the TiO_2 films.

Photocurrent versus voltage (I-V) characteristics were measured by using solar simulator under 1.5 air mass (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 14 h at room temperature. The platinum (Pt) counter electrode with mirror finish was prepared by sputtering method and used as a counter electrode. As part of the assembly of DSC, the electrolyte was prepared using 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. The electrolyte was infused 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. The schematic diagram of the prepared DSC using rutile-phased TiO_2 film is shown in Fig. 1.

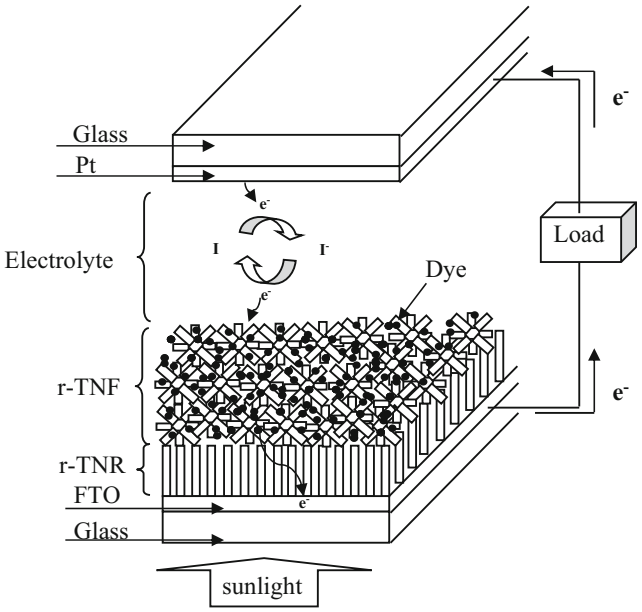

Fig. 1 Schematic diagram of dye-sensitized solar cell rutile-phased TiO_2 nanorods (r-TNR) and rutile-phased TiO_2 nanoflower (r-TNF) deposited on top of FTO-coated glass

The incident photon to current efficiency (IPCE) was measured using a monochromator (Bunkoh Keiki-Jusco), and the generated photocurrent signal was collected using a single-phase lock-in amplifier (NF Electronic Instruments 5600 A). The amount of adsorbed dye was calculated by the dye absorbance spectrum, which was measured using Jusco V-630 spectrophotometer. The impedance measurement of cell was carried out with a frequency of 0.01 to 20 kHz with ac amplitude of 10 mV (Solartron Analytical 1280C).

Results and discussion

The effect of hydrothermal reaction process time

The FTO substrate was placed facing upward in the autoclave. Then, the autoclave was kept into the hot oven at a fixed temperature of 150 °C, for different reaction times at 2, 5, and 10 h. Figure 1 reveals that the schematic representation for the growth of nanorods and nanoflowers on the top of the FTO substrate, respectively. The bilayer of nanorods and nanoflowers was annealed at 450 °C for 30 min and used as photoelectrode. DSCs were fabricated using these photoelectrodes, electrolyte, and Pt catalyst.

Figure 2 shows the surface morphology and cross section of r-TNR film prepared at different hydrothermal reaction times of 2, 5, and 10 h. At 2 h of reaction time, nanorods with less than 1 μm in length were deposited on top of the FTO substrate. The diameter of the nanorods was found to be less than 100 nm. Most of the nanorods grown on top of the FTO are vertical, and some, disoriented shapes. At the bottom of the nanorods, larger gaps between the nanorods were observed. As we increased the reaction time to 5 h, the diameter of the nanorods became larger and the gap between the nanorods also increased. This may be due to the increase of growth density for a longer reaction time. The increase in length of the nanorods can be observed from the cross section of Fig. 2b-2.

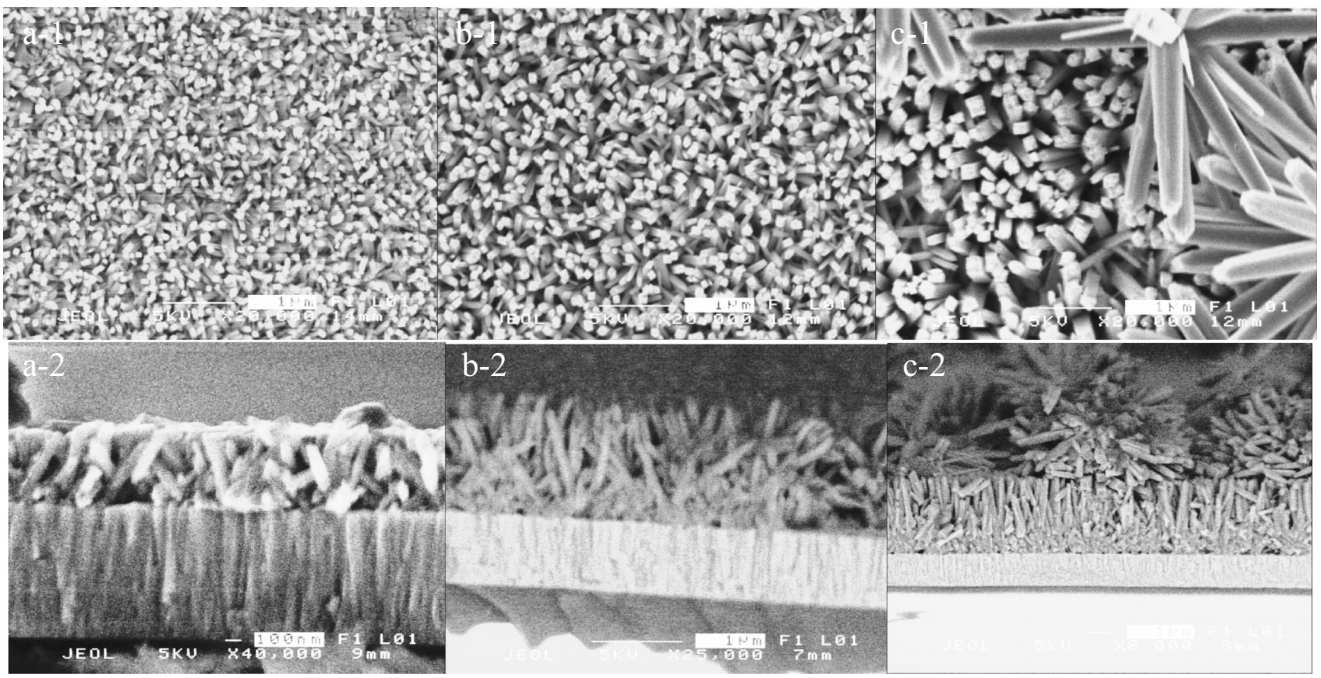

Fig. 2 a-1, b-1, and c-1 show the surface morphology of the r-TNR thin films prepared without using CTAB for 2, 5, and 10 h at 150 °C. a-2, b-2, and c-2 indicate their cross sections

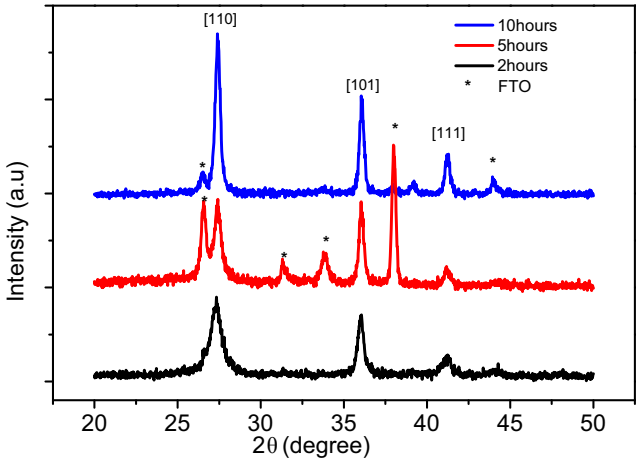

Fig. 3 XRD diffraction patterns of rutile-phased TiO_2 nanorod and nanoflower films prepared at different reaction times

Figure 2b-2 indicates that the film was denser and longer compared to 2-h reaction time and the thickness is about 1.2 μm. There is no rutile-phased nanoflowers (r-TNF) observed at 2 and 5 h of reaction times. For longer reaction time, we can see TiO_2 nanoflower shapes deposited on top of nanorods. The nanoflowers were exhibited at different orientations with small diameters of nanorods that have approximately 400 nm in diameter and 1.5 μm in length. At this stage, we could observe that the aligned nanorods with higher density and length are about 1.5 μm in Fig. 2c-2. From these observations, we confirmed that TiO_2 nanoflowers appeared only when hydrothermal process was performed at 10 h. The explanation of the growth mechanism of TiO_2 nanorods and nanoflowers was reported in our previous study [15].

XRD measurements indicate that the prepared TiO_2 films consisted of pure rutile-phased TiO_2 nanorods. Figure 3 shows that there are three peaks exhibited at 27.40°, 36.04°, and 41.20° corresponding to (110), (101), and (111) planes of the rutile phase (PDF No. 98-000-0090). The main peak at 27.40° corresponds to the (110) plane. These XRD results show that all of the TiO_2 films prepared are rutile phase. There are some FTO peaks that appeared in the pattern which is due to the low thickness of r-TNR thin films. However, for 10 h of reaction time, no FTO peaks were detected, which is due to all surfaces of FTO was fully covered by rutile-phased TiO_2 nanorods.

Table 1 I-V measurement of DSC prepared without CTAB at different reaction times

Sample	V_{OC} (V)	J_{SC} (mA cm^{-2})	Fill factor	η (%)	Dye adsorption ($\times 10^{-8}$mol cm^{-2})
2 h	0.635	1.41	0.43	0.39	3.46
5 h	0.750	4.51	0.53	1.78	3.90
10 h	0.708	5.18	0.49	1.80	5.08

Figure 4 shows the I-V measurement for DSC prepared at reaction times 2, 5, and 10 h. We found that 10 h of reaction time has the highest conversion efficiency at approximately 1.80%. We noticed that the 10-h reaction time samples give the highest current density which may be due to the improvement of the amount of dye molecules adsorbed and also to the increased light-harvesting effect within the existing of r-TNF films. I-V measurement parameters and the estimation of adsorbed dye amount are as shown in Table 1. For more understanding in the improvement of J_{SC}, we studied the incident photon to current efficiency (IPCE). Figure 5 shows that the IPCE spectra increased when the reaction times were increased.

The effect of adding CTAB surfactant in hydrothermal process

In the section "The effect of hydrothermal reaction process time," we understand that when we increased the reaction

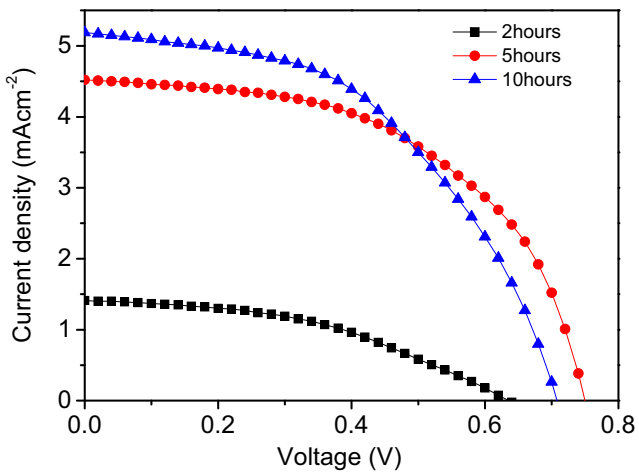

Fig. 4 I-V measurement of r-TNR and r-TNF TiO_2 films prepared at different reaction times

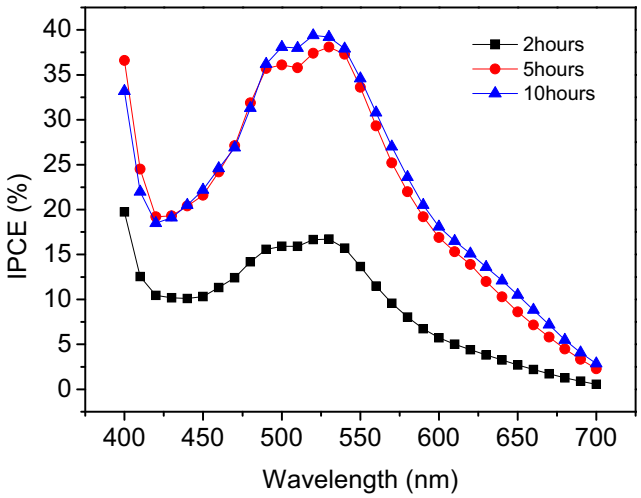

Fig. 5 IPCE spectra for 2, 5, and 10 h of reaction times prepared without using CTAB at 150 °C

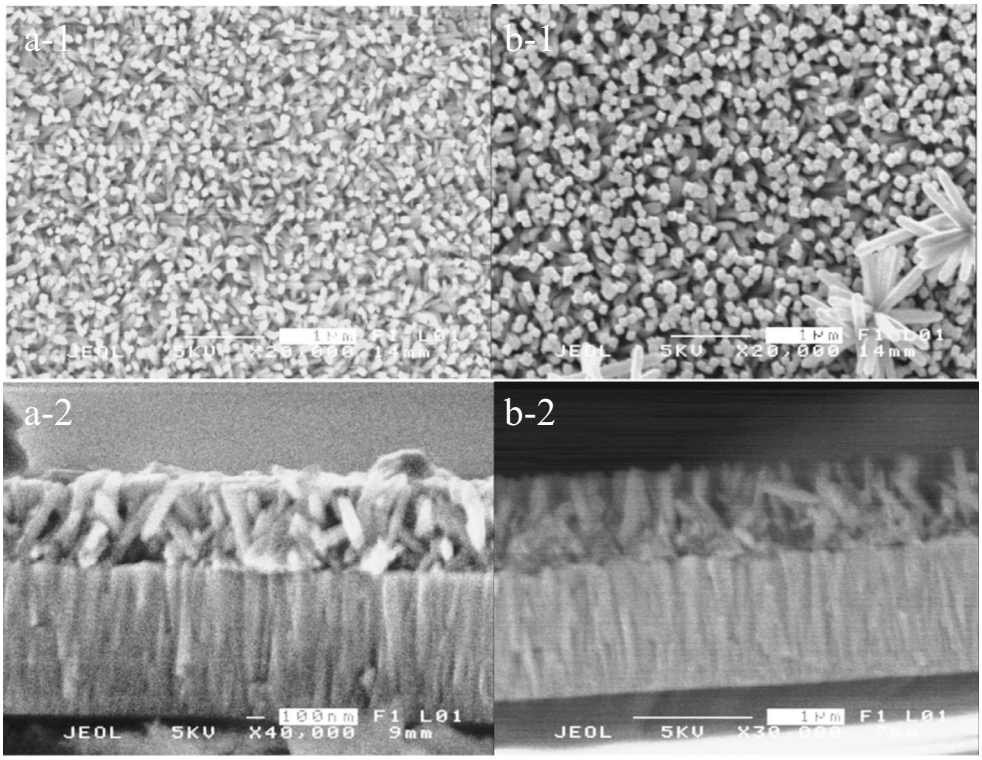

Fig. 6 a-1 and b-1 show the surface morphology of the r-TNR thin films prepared with and without using CTAB for 2 h at 150 °C. a-2 and b-2 indicate their cross sections

time up to 10 h, r-TNFs would grow and enhance the performance of DSC. It is important to know the growth mechanism of r-TNFs to improve the DSC performance. There are many ways to control the surface morphology of a film for DSC application. Mansourpanah et al. [16] have used cetyltrimethylammonium bromide (CTAB) to control the surface morphology of thin films. Based on Mansourpanah et. al's work, we added CTAB to study the effects to the growth of r-TNFs. The same amount of solution was taken as mentioned before with an

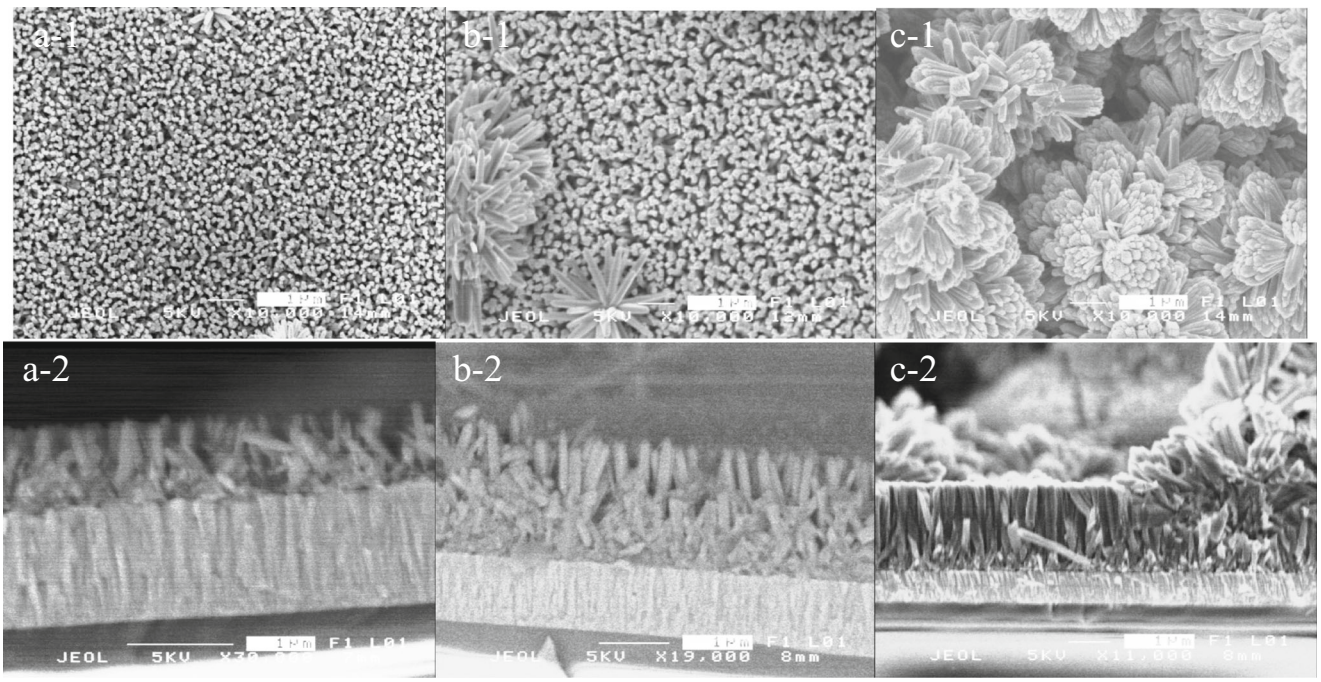

Fig. 7 a-1, b-1, and c-1 show the surface morphology of the r-TNR thin films prepared using CTAB for 2, 5, and 10 h at 150 °C. a-2, b-2, and c-2 indicate their cross sections

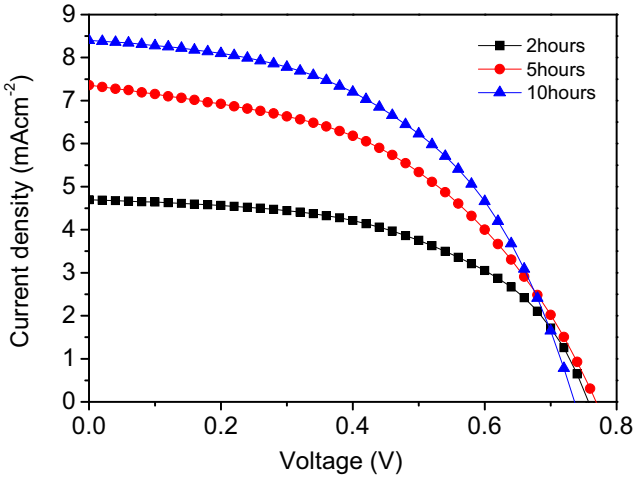

Fig. 8 I-V measurement of r-TNR and r-TNF TiO_2 films prepared at different reaction times with CTAB

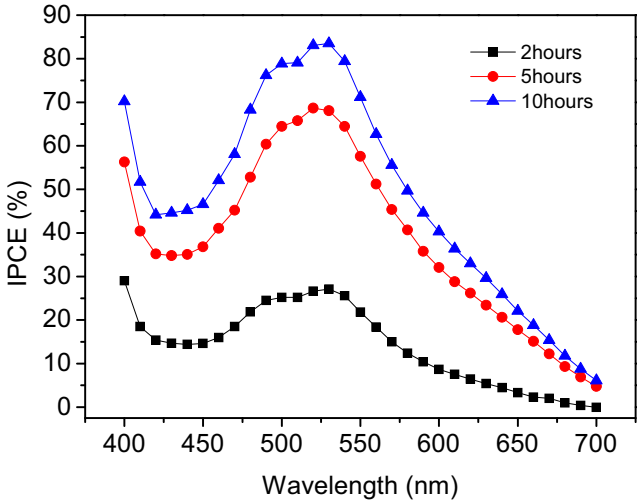

Fig. 9 IPCE spectra for 2, 5, and 10 h of reaction times prepared with CTAB at 150 °C

addition of 3 M of CTAB and stirred for 10 min. The hydrothermal process was carried out only for 2 h at 150 °C.

Figure 6 shows the surface morphology and cross section of r-TNR thin films prepared with and without CTAB. No r-TNFs appeared in the prepared samples after 2 h of reaction time. In this condition, we obtained r-TNRs with aligned and disoriented nanorods. The thickness is about 300 nm. Figure 7 shows the surface morphology and cross section of r-TNR thin films prepared with and without CTAB. When we introduced CTAB in the hydrothermal process, the r-TNRs in diameter and length are slightly increased to 200 and 500 nm, respectively. We also obtained r-TNFs with a diameter of 200 nm and a length about 500 nm. In the hydrothermal process, by introducing CTAB as a surfactant, we managed to grow r-TNRs and r-TNFs at the same time in a one-step process. Rutile-TNFs can be prepared as fast as 2 h of reaction time using this method.

The growth mechanism of rutile-phased TiO_2 nanoflowers assisted with CTAB

In this study, the cetyltrimethylammonium bromide (CTAB) was used due to its effectiveness in the changing of surface morphology [13]. Cheon et al. reported that there are four main parameters: (i) kinetic energy barrier, (ii) temperature, (iii) time, and (iv) capping molecules, which can affect the growth of nanocrystals under the non-equilibrium kinetic growth condition in the solution [17]. In our study, the capping molecule is the key factor for the formation of TiO_2 nanorods. CTAB can combine with the growth unit, i.e., $[Ti(OH)_3]^-$ due to coulomb force [18]. CTAB acted as a capping agent that increases stability of nanorods and nanoflowers, and it will also prevent the particle aggregation and keep the nanoflowers away from one another. This will contribute to the growth of both TiO_2 nanorods and nanoflowers. To investigate the growth of r-TNFs assisted with CTAB, we prepared hydrothermal process at different reaction times, using CTAB. Three molars of CTAB was included to the solution of hydrothermal process for 2, 5, and 10 h. Figure 7a-1 shows the aligned r-TNRs, disoriented nanorods, and also some r-TNFs deposited on top of r-TNRs. When we increased the reaction time, the r-TNR becomes denser and longer in the length of approximately 1.5 μm. The diameter of r-TNRs was slightly increased. The r-TNFs grown on top of the r-TNRs increased when the reaction time was up to 10 h. The r-TNFs' diameter and length are found to be 500 nm and 1.5 μm, respectively. The r-TNRs became denser and longer compared to those at 2-h reaction time. The length and diameter of r-TNRs are found to be 5 μm and 500 nm, respectively. By introducing CTAB, r-TNFs could be prepared at low reaction time and the r-TNFs substrates were used as photoelectrode in DSC application for the enhancement of DSC performance.

In order to study the improvement of DSC performance with r-TNFs, we measured I-V characteristics as shown in Fig. 8. The dye adsorption may also increase due to increasing

Table 2 I-V measurement of DSC prepared with CTAB at different reaction times

Sample	V_{OC} (V)	J_{sc} (mA cm^{-2})	Fill factor	η (%)	Dye adsorption ($\times 10^{-8}$mol cm^{-2})
2 h	0.757	4.696	0.530	1.88	2.84
5 h	0.768	7.358	0.471	2.66	4.28
10 h	0.736	8.396	0.503	3.11	7.72

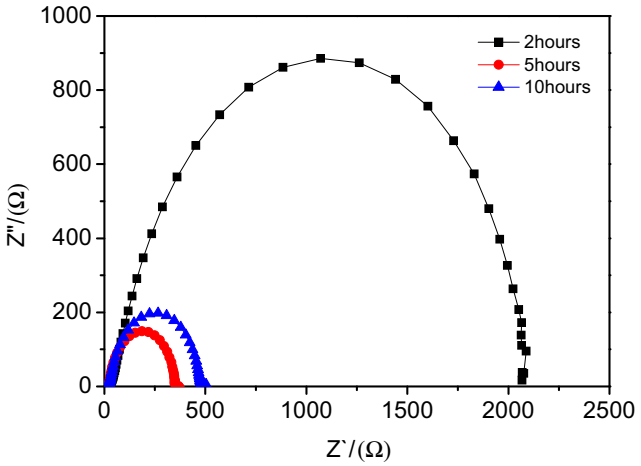

Fig. 10 EIS spectra for 2, 5, and 10 h of reaction times prepared without CTAB at 150 °C

of r-TNFs in the film. I-V measurement parameters and the amount of dye adsorbing data are shown in Table 2. The prepared r-TNR- and r-TNF-based TiO_2 films with CTAB give the highest conversion efficiency at about 3.11% at 10 h reaction time. The length of the aligned r-TNRs was increased up to 7 μm, and the total thickness of the film obtained was about 15 μm. The IPCE was increased with the increasing of reaction times as shown in Fig. 9. The results indicate that the J_{sc} of DSC increased for the r-TNR- and r-TNF-based photoelectrodes due to the improvement of dye adsorption as well as increased surface area.

Electrochemical impedance spectroscopy

Figures 10 and 11 show the electrochemical impedance spectroscopy (EIS) spectra of DSC based on r-TNRs and r-TNFs prepared with and without CTAB for 2-, 5-, and 10-h reaction times at 150 °C. As shown in Fig. 10, the second semi-circle

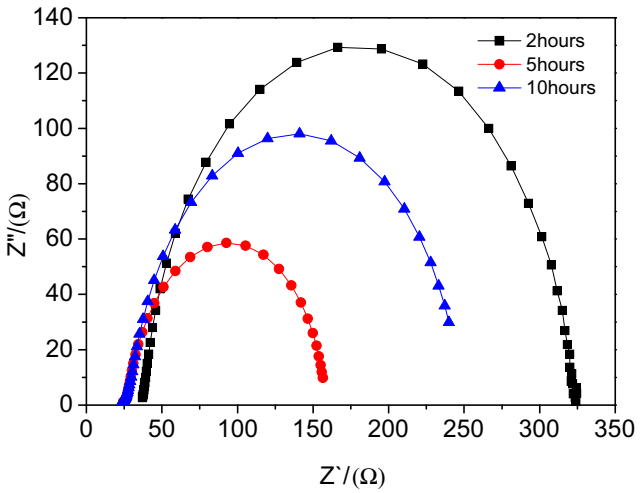

Fig. 11 EIS spectra for 2, 5, and 10 h of reaction times prepared without CTAB at 150 °C

of 2 h is the biggest among the other semi-circles. The second larger semi-circle is for 10 h of reaction time, and the smallest semi-circle is about 5 h of reaction time. In other words, the resistance related to the electron transport in the rutile TiO_2 /dye/electrolyte in 2 h has the biggest value about 2000 Ω. The resistance of 10 and 5 h is 442 and 325 Ω, respectively. The DSC prepared with CTAB results also shows similar EIS responses as in Fig. 10, in which a 2-h grown sample gave the highest internal resistance about 281 Ω, followed by 216 and 129 Ω for 10 and 5 h, respectively.

The reason for the highest internal resistance is may be due to the low crystallinity of r-TNRs. As we refer to the XRD pattern in Fig. 3, the crystallinity increased with the increases of reaction time. The higher crystallinity of the films always show better electron transport. The internal resistance of 10-h reaction films is slightly higher than that of 5-h grown films. It may due to the higher thickness obtained in 10 h by the formation of more r-TNFs. With the increasing larger amounts of r-TNFs, the electron diffusion and transport are slightly affected and it will increase the internal resistance in the performance of DSC.

Conclusion

In summary, we have successfully prepared DSC using rutile-phased nanostructures of TiO_2 films and improved the DSC performance by introducing r-TNFs on top of r-TNR films by using hydrothermal method at low temperature and shorter reaction time. Applying CTAB in the hydrothermal process can enhance the growth rate of r-TNFs. CTAB contributes to faster growth rate. When we increased the reaction time along with CTAB in the hydrothermal process, the amount of r-TNFs will be increased. The DSC prepared based on r-TNR and r-TNF TiO_2 films along with CTAB gives the highest conversion efficiency about 3.11% at 10-h reaction time. The current density of the DSC was increased due to the adsorption of more dye molecules.

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