TiO₂ Nanowires Prepared by Anodization in Combination with Hydrothermal Method on the Ti Sheet for Dye-sensitized Solar Cell

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Abstract

In this work, we prepared a porous seed by anodization method and the prepared samples were prepared by nanowires method using hydrothermal method. The samples were selected for nanowires and nanopores for dye-sensitized solar cells fabricated. We found that the TiO₂ nanowires were prepared by two methods: anodization and hydrothermal methods. The prepared samples were characterized with X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis. The XRD pattern shows that both the nanostructures are anatase and rutile phases with good crystalline nature. The morphological results show that the nanoporous TiO₂ has a diameter of about 50 nm and the TiO₂ nanowires have diameters between $50 - 100$ nm with length of about 250 nm. The solar cell energy conversion efficiency of the nanoporous TiO₂ cell is about 4.2% with J_{sc} of 5.9 mA cm^{-2}, V_{oc} of 0.82 V and FF of 0.60. The solar cell energy conversion efficiency of the nanowires TiO₂ cell is about 5.8 % with J_{sc} of 8.4 mA cm^{-2}, V_{oc} of 0.85 V and FF of 0.57.

KEYWORDS: TiO₂ nanowire; anodization; hydrothermal; dye-sensitized solar cell

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Introduction

In the future, the global energy demand will double in the next 50 years. It will cause the world's oil reserves to be in danger of depletion and oil shortage. Recent public concern has been heightened by the foreseen reality of global warming caused by the greenhouse effect, a direct result of fossil fuel combustion [1]. Solar energy is another alternative to the study design: researchers have tried to develop smart material technology for applying to power. The dye sensitized solar cells (DSSCs) has been applied for enhancing the efficiency of solar cells due to its high energy conversion efficiency and low cost of their production process, combined with an easy and environmentally friendly [2,3]. Nanoscale materials exhibit a much greater surface area for a given mass or volume compared to conventional particles. Therefore, all applications involving surfaces and interfaces will benefit from nanosized particles, enhancing catalytic reactions and increasing interactions with surrounding media. In addition, new physical and chemical properties emerge when the size of the material is reduced to the nanometer scale, leading to quantum confinement effects, affecting the charge transport or causing band gap energy shifts [4, 5]. TiO₂ has three distinct crystalline structures: rutile, anatase, and brookite. Most studies on the photocatalytic reactivity were conducted with either rutile or anatase, which reported that the indirect band gap is 3.0 eV respectively. Although rutile has a lower band gap than anatase, it has been demonstrated that anatase structure TiO₂ exhibits a better photocatalytic performance than that of rutile [6 − 8]. Moreover, anatase becomes more stable than rutile when the particle size is decreased below 14 nm [9, 10]. General speaking, functional properties of nano-TiO₂ are influenced by a large number of factors which include particle size, surface area, synthesis method and conditions, and crystallinity [11]. DSSCs are composed of four parts as follows: 1) the electrode film layer of TiO₂, covered by a monolayer of dye molecules, that absorbs solar energy; 2) the conductive transparent conductive oxide layer that facilitates charge transfer from the electrode layer; 3) the counter electrode layer made of Pt or C; 4) the redox electrolyte layer for reducing the level of energy supplied from the dye molecules [12, 13]. Thus, research efforts to improve the efficiency of DSSCs have primarily been focused

on improvement of the each DSSCs component [14]. However, due to synergetic effects of its subcomponents, the enhancement of only one component might not be sufficient to improve efficiency of entire cell.

In this present study, we have considered combined strategies to improve the efficiency of DSSCs. We used metal oxide semiconductors in the form of TiO_2 nanowires to improve the electron transport through the film on Ti sheet. In the first step, potentiostatic anodization is applied and subsequently the developed nanoporous TiO_2 is detached from the titanium sheet leaving behind a pattern [15]. Second step, Ti sheet created primarily through the first phase will be used to prepare TiO_2 nanowires by hydrothermal method and to prepare TiO_2 photoanode for DSSCs.

Materials and Methods

In the first step, titanium sheets (Jinshengstd.ASTMB265 Shaanxi company china, 0.2 mm) were used as substrate for anodization. Prior to the anodization, pieces (radius 0.8 cm) of the Ti sheets were sonicated in acetone, 2-propanol, and methanol for 10 min, then washed with water and dried under nitrogen. Anodization was performed in an appropriate electrochemical cell, made of teflon, at ambient temperature [16]. The working electrode area was 10.18 cm^2 and the distance between the anode (Ti sheet) and the cathode (Pt mesh) was set at 1.5 cm. The titanium sheets were anodized at 50 V for 2 h in a fluorinated solution of ethylene glycol (0.25 wt% NH_4F, 10 wt% DI H_2O), followed by a brief cleaning with deionized (DI) water. The titanium nanostructures were further cleaned by dipping the anodes in a beaker with DI water under sonication for 1-3 s. After drying in air, the nanopores were calcined at 450 °C for 2 h in air. In second step, synthesis method of nanowires was basically the same as in previous work [16]. A commercial TiO_2 powder (commercial: a mixture of crystalline rutile and anatase phases) was used as a starting material. In a typical synthesis, 1 g of TiO_2 powder was crushed with 25 mL of 10 M NaOH aqueous solution were put into a teflon-lined stainless autoclave and then heated at 180 °C for 18 h, 20 h, 22 h, and 24 h. The samples were cooled down to room temperature. The treated samples were washed thoroughly with DI water and 0.1 mol L^{-1} HCl aqueous solution until the pH value of the washing solution lower than 7 and dried at 450 °C for 1 h. The structural and chemical natures of the obtained materials were studied using x-ray diffraction (XRD), scanning electron microscopy (SEM). For preparation of dye

sensitized solar cells, TiO_2 nanowire photoelectrode was immersed for 20 h in acetonitrile solution containing 5×10^{-4} M cis-di(thiocyanato)bis(2,2´-bipyridyl-4,4´-dicarboxylate)ruthenium(II) (N-719, Solaronix Inc.) dye. Afterwards, the dye sensitized TiO_2 electrodes were rinsed with ethanol and dried in air. Finally, the working electrodes were dried in an oven at 80 °C for 30 min. A transparent conducting oxide glass (TCO) is used as counter electrode. After, TCO glass was cleaned with alcohol solution in an ultrasonic bath for 10 min and rinsed with DI water, a platinum catalyst was deposited on the TCO glass by coating with drops of platinum solution (H_2PtCl_6). The TCO glasses were heated for 30 min at 80 °C. Then, TiO_2 nanowires photoelectrode and Pt coated glass electrode were assembled into a sandwich structure. An electrolyte (KI/Iodine electrolyte) was injected in to the cell. The Pt coated glass electrode was pressed on top of the working electrode to form a dye-sensitized solar cell. The cell has active area of 2.01 cm^2. The current-voltage characteristic curves were measured with Keithley 2400 source meter. The xenon arc lamp was used as an irradiation source and the intensity of the incident light was 70 mW cm^{-2}. Finally, the efficiency of dye sensitized solar cells was calculated.

Results and Discussion

The synthesis of the porous TiO_2 nanowires was divided into two steps. Firstly, TiO_2 nanopores were fabricated by anodizing the pure Ti sheet as described previously. The samples were synthesized at the same temperature of 180 °C but for different periods of time, defined as 18 h, 20 h, and 24 h. Ti- anodization (substrate for the anodization and calcined at 450 °C for 2 h) and TiO_2 crystal structure were used for the comparison purpose.
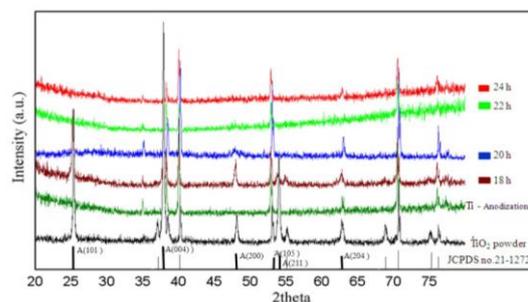

Fig. 1 XRD patterns of the samples were synthesized at the same temperature of 180 °C but for different periods of time, defined as 18 h, 20 h, and 24 h. Ti- anodization (substrate for the anodization and calcined at 450 °C for 2 h) and TiO_2 powder.

As seen in Fig. 1, all diffracted peaks are sharp and strong in intensity indicating the highly crystalline in nature of the products. TiO_2 anatase phase was observed in the XRD patterns and diffraction data was in good agreement with JCPDS card of TiO_2 (JCPDS No. 21-1272). The data indicates that the samples on the substrates are TiO_2 and partially crystalline of Ti-anodization substrates. The peaks located at 25.4°, 37.8°, 48.0°, 53.84°, 54.5° correspond to the (101), (004), (200), (105 and 211) planes of the anatase phase (JCPDS 21-1272), respectively. The experimental XRD pattern agrees with the JCPDS card no. 21-1272 (anatase TiO_2) and the XRD pattern of TiO_2 nanostructures reported by other literatures [17]. The 2θ at peak 25.4° confirms the TiO_2 anatase structure [18]. Strong diffraction peaks at 25.4°, 37.8° and 48.0° indicating TiO_2 in the anatase phase [19]. There is no any spurious diffraction peak found in the sample. It is found that the phase The crystal structure of TiO_2 remains the same at 25.4°, 37.8°, 48.0°, 53.84°, 54.5° when the samples were prepared by anodization and calcined at 450 °C for 2 h. The noticeable peak at 48° is clearly visible when the sample was annealed for 18 h. The intensity of the noticeable peak at 48° will begin to decline when a period of heating time was extended longer than 18 h (20 h, 22 h, and 24 h).

Considering the report of John A. Stride and Nam T. Tuon about [20] a reaction time and temperature, a range of reaction times (3 − 48 h.) and temperatures (150 − 230 °C) have been investigated and found to have significant effects on the extent of crystallite growth and particle size. As more energy is applied to the hydrothermal reaction, either through higher temperatures and/or longer reaction times, particle growth is favoured as it acts to reduce the integrated surface interfacial energy, which thermodynamically offsets the decrease in entropy on moving to larger crystallites. This observation is found in Fig. 1. It does not correspond to the crystalline growth pattern at the 2θ at peak 48.0°.
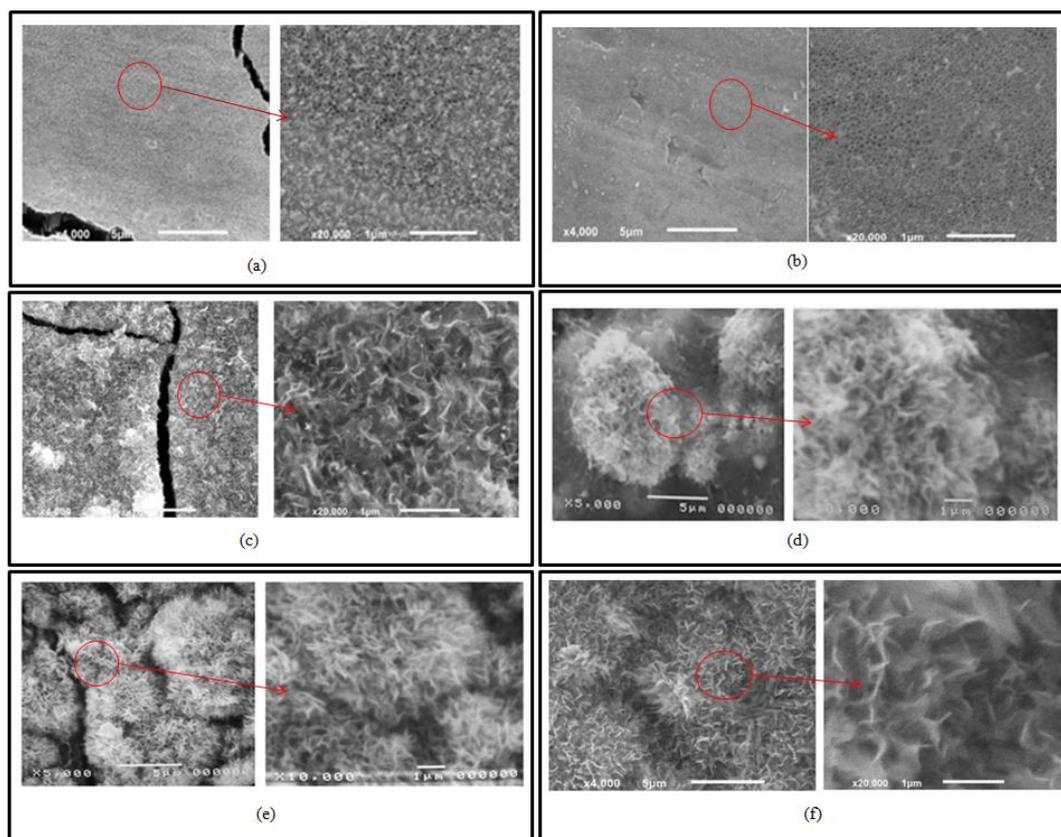
Fig. 2 SEM images of TiO_2 nanopores top-view: (a) for anodization on Ti sheet before calcination (b) for anodization on Ti sheet calcined at 450 °C for 2 h and TiO_2 nanowires top-view: The samples were prepared by hydrothermal at 180 °C (c) for 18 h, (d) for 20 h, (e) for 22 h, and (f) for 24 h

SEM analysis shows that anodized TiO_2 on Ti sheet has nanoporous structure that is small enough to diffuse in and out of nanosized pores. The SEM image of TiO_2 on Ti sheet ($U_{growth} = 50$ V for 2 h) before and after annealing are shown in Fig. 2 (a and b) respectively. Comparative nanowire grown on Ti sheet after annealing for 18, 20, 22, and 24 h is shown in Fig. 2(c), 2(d), 2(e) and 2(f), respectively. A dense of samples with dispersive nanostructure and sparse nanowires growth is resulted from the 10 M NaOH aqueous solution alone treated at 180 °C. Fig. 2(c) shows some nanowires, formed under condition of annealing for 18 h, with an average length range approximately 100 nm. Fig. 2(d) shows entangled nanowires with less than 100 of nanometers in length, formed under a condition of annealing for 20 h. Fig. 2(e) show the surface morphology of TiO_2 on Ti sheet prepared by hydrothermal at 180 °C for 22 h. Clearly, a nanowires surface in the sample were randomly oriented with diameters of 50 – 100 nm, and lengths in length on average less than 1 micrometer. Fig. 2(f) shows morphology that is fully distributed nanothorn on the surface. We found that the number of nanowires density and diameter increases with time. A compare surface samples of nanoporous and nanowires on the efficiencies of dye-sensitized solar cells. The samples were selected for nanowires and nanoporous for dye-sensitized solar cells fabricated. We were interested to take samples prepared under conditions of anodizing then calcined at 450 °C for 2 h, labeled (a) in Fig.3 and prepared with hydrothermal method at 22 h, labeled (b) in Fig.3 for the preparation of dye sensitized cells. The efficiencies of dye-sensitized solar cells were measured by current voltage curves. The current-voltage curves were showed in Fig. 3.
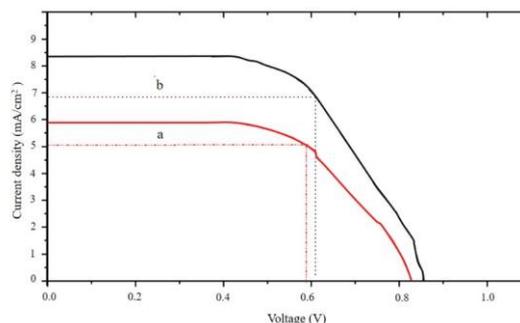
Fig. 3 J-V curves of the dye-sensitized solar cells (a) with the TiO_2 nanoporous structures (b) with the TiO_2 nanowires structures.

The efficiencies of dye-sensitized solar cells were measured by current voltage curves (Fig. 3). The efficiencies of dye-sensitized solar cells increase when nanostructure increasingly forms and continually increase when nanoporous TiO_2 changes to nanowires. The efficiencies of dye-sensitized solar cells of nanoporous TiO_2 structure and nanowire are 4.2% and 5.8%, respectively (Table 1). The reasons of the efficiency of dye-sensitized solar cell of nanowire is higher than that of dye-sensitized solar cell of nanoporous TiO_2 are: the surface area of nanowires is higher than nanoporous structure as shown in the Fig. 2 (SEM); the electrons transfer to nanowires is better than nanoporous [2];electron transfer in wires is faster than in porous structure. The electrons are excited by the incident light and then injected into the conduction band of the TiO_2. The electrons will diffuse rather than drift that dominates the transport of the electrons from the TiO_2 surface to the transparent electrode in dye-sensitized solar cells [22].

Table1 The efficiencies of dye-sensitized solar cells.

Sample	Power in (mW cm^{-2})	Power outmaximum (mW cm^{-2})	FF	Efficiency (%)
b	70	4.11	0.57	5.8
a	70	2.96	0.60	4.2

Conclusion

TiO_2 nanowires for dye sensitized solar cell were successfully prepared by using two-step depositions of nanoporous TiO_2 on Ti film layer. Anodization was the first step and the second step was the hydrothermal method and the optimal condition of the hydrothermal method is under annealing at 180 °C with 10 M NaOH aqueous solution for 22 h. The efficiencies of the nanoporous TiO_2 and TiO_2 nanowires on the Ti sheet for dye-sensitize solar cell are 4.2% (ff: 0.60, Voc: 0.82 V, Jsc: 5.9 mA cm^{-2}) and 5.8% (ff: 0.57, Voc: 0.85 V, Jsc: 8.4 mA cm^{-2}) respectively. In this

report, we found that the change of the structure of the sample from nanoporous TiO$_2$ to nanowire form increases the efficiency of dye sensitized cells to 1.6%. In this report, interesting issue there was a significant reduction in crystal growth at the 2θ as 48°, when the time for the hydrothermal preparation was increased.

Acknowledgements

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