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Short communication

Effects of nanostructures on iron oxide based dye sensitized solar cells fabricated on iron foils

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ABSTRACT

Iron oxide nanowires, nanoflakes and film were successfully synthesized by two-step thermal oxidation process by changing oxidation temperatures. Highly aligned and high quantity nanowires and nanoflakes were obtained at 550 °C and 450 °C respectively. Their structural properties were characterized by SEM, XRD and photovoltaic performance by solar simulator. Results show that different structures of Fe_2O_3 used will influence the photovoltaic performance by the effect of surface area. Fe_2O_3 in nanowires shape gives the highest efficiency of 0.04% with short circuit current, open circuit voltage and fill factor of 0.25 mA/cm^2, 0.42 V and 0.38 respectively. More efficient photoanodes were obtained in Fe_2O_3 nanowires in dye sensitized solar cells (DSSC) as compared to nanoflakes and films due to the high surface area with smaller diameter and high distribution.

1. Introduction

Hematite (α-Fe_2O_3) is one of metal oxides that is extensively studied for many applications because it has attractive optical properties, low cost, is nontoxic and thermodynamically stable. Favourable semiconducting properties of 2.1 eV and antiferromagnetic has been verified in various applications [1–10]. Acting as n-type semiconductor with favourable band gap shows it can be applied in electronic device applications specifically in photo electrochemical and solar cells.

In devices applications, iron oxide nanostructures were prepared on indium doped tin oxide [11,12] and fluorine doped tin oxide (FTO) [3,11,13–16] substrate. Several types of nanostructure were applied in DSSC such as nanoflowers, nanoparticles and nanocluster. Previous research shows several types of α-Fe_2O_3 nanostructure were used in DSSC applications. Agarwala et al., reported hybrid α-Fe_2O_3 flower-like morphology as a working electrode in DSSC which contribute 1.8% power conversion efficiency [3]. A three-dimensional (3D) nanostructure was developed in this study to improve surface area, diffusion coefficient and electron transport of the solar cells. Cavas et al. proved that Fe_2O_3 nanoparticle and nanocluster can be used in ruthenium DSSC and the photocurrent of the sample is increased with light illumination intensity [13]. Niu et al. successfully used flower-shaped hematite as a photoanode in DSSC with energy conversion efficiency of 0.94% [14]. Recently, biohybrid hematite and titanium oxide (TiO_2) nanostructure was used as anodic component in biohybrid DSSC [15]. Solar conversion efficiency of this photovoltaic is below that required for practical use but it has been proposed that it can be used in biohybrid solar-to-fuel nanodevices. However, the performance of α-Fe_2O_3 nanowires and nanoflakes in DSSC have not been reported yet. The synthesis highly aligned and high density α-Fe_2O_3 nanowires and nanoflakes on FTO or ITO glass will be challenging to improve the solar cell performance.

In previous research, α-Fe_2O_3 nanostructures were synthesized on FTO or ITO glass when applied in device applications. Most of the synthesis methods employed to produce good quality nanostructures normally require high temperature. Hiralal et al. were successful in synthesizing nanostructured hematite thin film on FTO glass by thermal oxidation process at low temperature of 255 °C for 24 h [16]. However, α-Fe_2O_3 nanowires produced are not highly aligned and this condition might affect the performance of the nanostructures. Most reported highly aligned and high quantity α-Fe_2O_3 nanostructures are from thermal oxidation directly on the Fe foils [17–19]. However, it was difficult to synthesize the same quality nanostructures on FTO or ITO glass by using the same method. Therefore, it is important to examine the performance of highly aligned and high quantity α-Fe_2O_3 nanostructures prepared on the Fe foils in device applications.

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In this study, we have synthesized α-Fe_2O_3 nanowires, nanoflakes and film on Fe foil by simple air oxidation method by merely changing the temperature. The performance of these nanostructures were examined as photoanodes in DSSC and compared to the film under back-side illumination. To the best of our knowledge, there are no reports on the α-Fe_2O_3 morphology changes at different oxidation temperature. It is crucial to determine the performance of α-Fe_2O_3 nanostructures photoanodes directly prepared on the foils in order to fully utilise their ability.

2. Experimental procedure

Commercial iron foils ($20 \times 20 \times 0.25\,mm^3$) with a purity of 99.99% were used as the initial substrate for Fe_2O_3 nanowire growth. First, iron foils were cleaned in acetone and deionized water for 5 min each. After drying with nitrogen gas, the samples were placed in the centre of a horizontal tube furnace. High purity air (G3) flowed at 0.5 L/min through the tube furnace, and the temperature and time required were fixed. Then, the samples were pre-annealed at 300 °C for 30 min. After that, the samples were continuously heated to 450, 550 and 650 °C for a fixed 6 h. After the oxidation process was completed, the samples were cooled naturally to room temperature. The samples were characterized using a scanning electron microscopy (SEM; Hitachi S-3000H) system, X-ray diffraction (XRD; Rigaku RINT-2100, 40 kV, 30 mA, Cu Kα radiation) system.

For solar cell fabrication, all iron oxide samples were immersed in a ruthenium dye (ruthenium-535 bis TBA, Solaronix) for 12 h. After that, the sample was cleaned in methanol and dried in air for several minutes. Semi-transparent platinum electrode was inserted into the sample and electrolyte (iodide/triiodide redox, Iodolyte AN-50, Solaronix) was dropped in between them. Schematic structure of DSSC layer is shown in Fig. 1. DSSC performance was then measured by using solar simulator ($100\,mW\,cm^{-2}$, AM 1.5 illumination) in air with specific area of $2.0\,cm^2$.

3. Results and discussion

SEM images of iron oxide synthesized at 450, 550 and 650 °C are shown in Fig. 2(A)–(C) respectively. At 450 °C, iron oxide nanoflakes were obtained and have average diameter of 40 nm at the tips and 140 nm at the bottoms with average length of 1.28 μm. These nanoflakes grew in high quantity and covered the entire surface of the substrate. When temperatures increased to 550 °C, aligned iron oxide nanowires were produced with average diameter of 17 nm and average length of 4.8 μm. Smaller diameters, longer average length and high density of nanowires were obtained at this particular temperature. At higher temperatures of 650 °C, no nanostructures were observed and only iron oxide film was present. These results shows oxidation temperatures have a significant effect on the growth of multidimensional and one dimension iron oxide nanostructures.

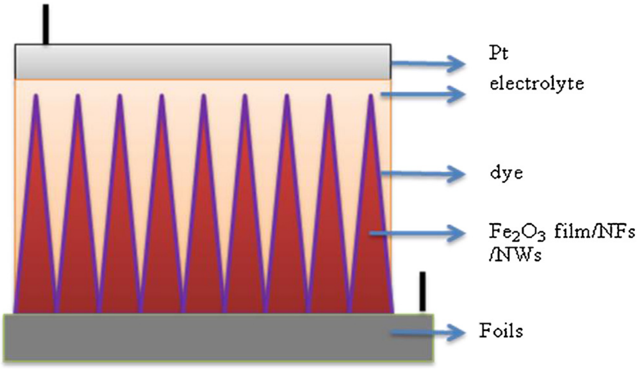

Fig. 1. Dye-sensitized solar cell schematic structure.

Zheng et al. reported that under atmospheric condition, ultra sharp α-Fe_2O_3 nanoflakes can be obtained by oxidation process and successfully applied in electron field emission [20]. In this study, at 450 °C, broader flaky shape iron oxides were obtained whereas during oxidation, α-Fe_2O_3 nanoflake grows on the top of a thin α-Fe_2O_3 layer. With continuous heating, thermal stress is expected to be accumulated on the top of thin α-Fe_2O_3 layer and relaxed by slipping in α-Fe_2O_3 crystal. At the same time screw dislocation might occur at a specific crystal direction causing Fe atom and iron oxide molecules at the surface to move upward and stack in the same plane before finally become a flake. By increasing the oxidation temperature to higher temperature of 550 °C, aligned and high density α-Fe_2O_3 nanowires can be obtained. Fu et al. also obtained highly aligned and high density α-Fe_2O_3 nanowires at 600 °C in atmospheric condition. Within these temperatures, higher stress gradient will accumulate on the top of the α-Fe_2O_3 thin layer surface due to the interfacial reaction, volume changes and thermal expansion mismatch between the iron oxide layer and substrate [18]. This stress gradient acted as a driving force for oxide nanowires growth. At higher oxidation temperatures of 650 °C, no nanowires were observed due to high thermal stress. Grigorescu et al. also found that at oxidation temperature greater than 600 °C, neither flakes nor wire morphology can be observed [19]. In this study, different structures of α-Fe_2O_3 were successfully obtained by changing oxidation temperatures by following the above mentioned mechanism. These morphology transformations might be influenced by the initial nucleation produced after first-step oxidation in addition to the stress-driven formation mechanism at elevated temperatures.

XRD pattern in Fig. 3 shows that Fe_2O_3 and Fe_3O_4 compounds are present in addition to Fe component. The dominant peak of (110) appears at 35.5° in all temperatures which correspond to α-Fe_2O_3 with lattice constants $a = 0.5035$ nm and $c = 1.3749$ nm. At 450 °C at which Fe_2O_3 nanoflakes were formed, combination peak of Fe_2O_3 was observed with the strongest peak of (110). This peak becomes more intense when temperature increased to 550 °C where nanowires were produced. Weak (220) peak of Fe_3O_4 was also detected at 30.15° in both nanoflakes and nanowires samples. More iron oxide groups were detected in iron oxide nanowires and nanoflakes which increases their crystallinity as compared to the film. These results also indicate that Fe_2O_3 nanostructures were grown on the Fe_3O_4 layer by thermal oxidation process [18]. Triple iron and iron oxide layer consisting of $Fe_2O_3/Fe_3O_4/Fe$ were formed after thermal oxidation with Fe_2O_3 nanostructures on the top layer.

Photovoltaic performance of synthesized iron oxide nanowires, nanoflakes and film were examined by applying them as photoanodes in DSSC. *J*–*V* curves in Fig. 4 shows the effects of iron oxide structures on the performances. Short circuit current, open circuit voltage, fill factor and efficiency of iron oxide nanowires, nanoflakes and film are given in Table 1. The performance of the Fe_2O_3 based DSSC increases sharply from films, nanoflakes and finally nanowires. Fe_2O_3 nanowires give the highest photovoltaic performance as compared to others due to the high current density generated in the cells. This value was increased from about 0.01 to $0.08\,mA/cm^2$ when Fe_2O_3 nanoflakes were used as photoanodes. When 1-dimensional nanowires were used, current density is further increased to $0.25\,mA/cm^2$ significantly affecting the efficiency of the solar cells.

In order to discuss the variation of solar performance for different nanostructures, the surface area per unit area of Fe_2O_3 nanostructure was calculated from the SEM images. The surface