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Single-step hydrothermal fabrication of nanorice-shaped fluorine-doped tin oxide for enhanced dye-sensitized solar cells

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ABSTRACT

A one-step method to synthesize nanorice fluorine-doped tin oxide (nr-FTO) was successfully applied to a bare FTO substrate via a hydrothermal process. This technique successfully creates uniform films of nr-FTO with spherical morphology. According to FESEM analysis, FTO nanorice has an average grain size of 54.8 nm in length and 21.0 nm in diameter. This technique provides a simple fabrication procedure to create nanorice FTO thin films without requiring an extra seed layer. The data from XRD analysis and the d-spacing values obtained from TEM imaging are in good agreement, further demonstrating the crystalline character of the synthesized nr-FTO. The chemical analysis provided by the EDS results further indicates the excellent purity of the nanorice FTO thin film. The one-step hydrothermal synthesis method described here offers a quick and effective way to create high-quality nr-FTO thin films for various uses.

Keywords: *Fluorine, doped, hydrothermal, nanorice, dye-sensitized solar cell*

1. INTRODUCTION

In recent years, there has been a significant increase in worldwide reliance on fossil fuel resources, attributable to the rapid progression of technology and the transition to a modern lifestyle. This trend has raised concerns about the sustainability of the current energy system and the need for a shift toward alternative, renewable energy sources. As our reliance on traditional fossil fuels continues negatively impacting the environment, we must prioritize research activities to explore and develop alternative energy sources.

Due to the hot climate throughout the year, Malaysia has abundant solar energy, making it a primary option among other alternative energy sources. Solar energy conversion technology in photovoltaic cells has gained significant attention from researchers trying to create highly efficient dye-sensitized solar cells (DSSCs). Dye-sensitized solar cells, also known as Grätzel cells, offer several advantages over traditional silicon solar cells. DSSCs use economically affordable components, have minimal environmental impact, are easy to construct, have a long lifespan, are highly flexible, and offer transparency [1]. Utilizing metal oxide semiconductors for non-polluting energy generation and environmental remediation via solar power has gained significant attention in photovoltaic and photocatalytic fields [2]. Transparent conducting oxides (TCOs), when applied to optically transparent substrates, create a substrate with unique advantageous properties, including: i) high optical transparency, ii) high electrical conductivity, iii) a tunable energy bandgap (2.8–4.2 eV) and iv) remarkable chemical and mechanical stability [3]. The most widely studied among TCOs is indium-tin-oxide (ITO), which has been experiencing production growth. It has low electrical resistivity (approximately 1×10^{-4} Ω cm) [4]. However, ITO has limitations regarding temperature and chemical stability, and indium, one of its components, is a scarce and toxic element [5]. Tin dioxide (SnO_2) is widely used in gas sensing devices and as a photoelectrode material in DSSCs. Compared to TiO_2, SnO_2 has a more significant band gap and generates fewer oxidative holes under UV illumination, which minimizes dye degradation and improves DSSCs' long-term stability [6].

SnO_2 semiconductor has a 3.6 eV band-gap energy [7]. It reflects mainly in the higher infrared region while being transparent in the visible region. [8]. The material's conductivity is due to the oxygen vacancies in the lattice. The lattice structure is tetragonal and similar to rutile [9]. The doping process can further increase the conductivity of SnO_2. To improve the conductivity of SnO_2, doped with elements from the periodic table's III, V, VI, and VII groups contribute to the significant improvement. Thallium (Tl), antimony (Sb), tellurium (Te), and fluorine (F) are some of the commonly used dopants [10]. Fluorine is the most widely used dopant, and its addition results in a chemically and thermally stable film called fluorine-doped tin oxide (FTO) [11].

Using one-dimensional nanoparticles in the FTO film can significantly enhance the film's surface area, leading to improved electron mobility and reduced recombination. This approach can be a promising strategy to enhance the performance of FTO films in various applications [12]. These one-dimensional nanostructures' physical and chemical properties differ from those of crystalline solids when their diameter is small. The nanostructures depend on the precursor material and the thermodynamics of the synthesis method used in the fabrication process [13]. Various types of nanostructures can be grown, such as nanoparticles [14], nanorods [15], nanoflowers [16] and nanowires [17] and nanorice [18]. However, nanorice structures have advantages over other structures due to their efficient surface area, which could prove to be a more active site for dye adsorption [19].

There are many methods to prepare the FTO film, such as spray pyrolysis [20], chemical vapor deposition [21], and hydrothermal methods [22]. Based on our knowledge, hydrothermal is considered one of the most promising low-cost nanostructure production methods. The hydrothermal method is a widely used liquid deposition process that involves the use of liquid chemicals. This approach is known as the "bottom-up approach" and is highly effective in creating a homogeneous thin film that is assisted with stable temperature and pressure. As a result, this method is commonly used in various industries that require the production of high-quality thin films [13]. This method can produce nanoparticles with uniform size and shape, and it's highly controllable.

Additionally, it has excellent potential for growing new thin film nanostructures. FTO thin films are widely used in various technologies for making devices, such as solar cells, gas sensor devices, electro-deposition substrates, and optoelectronic transparent electrodes. The fabrication of nanostructure FTO films was first synthesized by Wang et al. [23]. They have prepared a SnO2 microsphere film consisting of nanosheets and nanoparticles. Hong Kang et al. developed a new type of FTO nanostructure composed of double layers of SnO_2 films [24]. These layers comprised SnO_2 nanoflowers and SnO_2 nanosheet films and were synthesized using $SnCl_2$, NaF, and water as precursors. The FTO seed layer was first applied to conventional FTO-coated glass, and then the hydrothermal method was used to fabricate both FTO nanostructures. The first layer comprised SnO_2 nanosheet films with a thickness of 1 μm, and the second layer consisted of SnO_2 hierarchical microspheres attached to the first SnO_2 nanosheet layer. The first layer of FTO was applied as a seed layer. In our work, we have successfully synthesized aligned nr-FTO film and spherical nr-FTO without using any seed layer. The growth of the nanostructure was performed by using a constant concentration of precursor comprised of tin (IV) chloride ($SnCl_4$) and ammonium fluoride (NH_4F). This process allowed for a significant reduction in fabrication steps and time without requiring a seed layer to produce the nanostructure FTO film. Our investigation into the film's surface morphology, structural properties, and growth mechanism has demonstrated its potential as a highly efficient and reliable conducting electrode for dye-sensitized solar cells.

2. EXPERIMENTAL

The procedure involved utilizing a 10 mm x 25 mm glass substrate coated with FTO procured from Sigma-Aldrich. The glass was meticulously cleaned to ensure that no impurities remained on its surface. The cleaning process involved immersing the glass in equal parts of acetone, ethanol, and deionized water. The mixture was sonicated for 30 minutes to remove any residual impurities on the glass surface, followed by air drying.

A solution of 0.1M $SnCl_4$ and 0.3M NH_4F in 50 ml of deionized water was prepared to create nr-FTO. The solution was mixed with hydrochloric acid (10 ml) and acetone (4 ml) before being stirred for 30 minutes. The resulting mixture was then poured into a Teflon autoclave of 300 ml capacity, containing the FTO-coated glass with its surface facing upwards. The autoclave was then put in an oven for the hydrothermal process, which was carried out at a temperature of 150 °C for 10 hours.

After hydrothermal, the samples were thoroughly washed with deionized water and dried in an oven at 60 °C for 30 minutes. The samples were then subjected to further analysis to study their properties. Field emission scanning electron microscopy (FESEM-JOEL-JSM-7600F) and transmission electron microscopy (JOEL TEM 2100) were used to study the surface morphology, while X-ray diffraction (XRD Pananlytical) was utilized to study the structural properties. Energy dispersive spectroscopy (EDS) was used to analyze the chemical composition.

The photoanodes were expertly prepared and sensitized with N719 dye to enhance their light-harvesting capabilities. Afterward, the photoelectrode films were submerged in dye solution for 24 hours to ensure optimal adsorption of the dye molecules. A platinum-coated FTO electrode was carefully created under moderate vacuum conditions using a sputtering method with platinum target material. The electrolyte solution sourced from Aldrich was iodine/iodide.

A sandwiched-type structure was used to construct the solar cell by clamping the dye-sensitized SnO_2 photoanode with the Pt-FTO counter electrode. Then, the electrolyte solution was injected into the interspace between the photoanode and the counter electrode. The solution was wicked up between the electrodes using capillary action. The performance of the DSSC was examined under illumination from the photoanode side. The power conversion efficiency of the DSSC was measured using a solar simulator (ORIEL Sol1A).

3. RESULTS AND DISCUSSION

The surface morphologies of the FTO nanorice have been analyzed and presented in Figures 1(a) and (b). It is evident from the images that the prepared FTO layer is dense and comprises nanorice The images further depict FTO nanorice films having an average length of 54.8 nm and a width size of 21.0 nm. The growth of FTO nanorice is followed by the spherical formation of FTO nanorice, which only requires low tension energy and is very stable in formation [24]. The development of a spherical nanostructure, as described by Hyung *et al*., presented benefits in enhancing the light

scattering effect [25]. The transition of the nanorice structure to a spherical form trapped the incoming light, leading to prolonged light interaction within the cells. This improved the likelihood of the sunlight engaging with the dye, thereby enhancing the efficiency of the DSSC. It was also observed that the nano rice is well-aligned and uniformly deposited on the FTO substrate, as shown in the cross-sectional image of Figure 1(c) and (d), with a thickness of 210 nm. The FTO substrate helps minimize the surface energy required to grow the FTO nanorice, making it easier to align on the surface of FTO substrates. Notably, the absence of a seed layer helps in the growth of FTO nanorice in solution form. However, it will not anchor and distribute well on the surface of the glass substrate during the process of surface diffusion, as reported by Wu *et al.* [26]. Therefore, the FTO substrate has been used, which ensures that the nanorice is aligned easily on the surface of FTO substrates, as shown in Figure 1(c). According to the study conducted by Wang Q *et al*., they have successfully synthesized SnO_2 nanoflowers with a unique structure [27]. These nanoflowers comprise numerous SnO_2 nanorods, each measuring about 25 nm in diameter. The entire nanoflower has an average size of approximately 200 nm. However, to enhance the crystallinity of the samples, they were subjected to annealing at 450 °C for 2 hours. For this study, no annealing process is required that can shorten the sample preparation. Lexi Zhang *et al*. reported on mesoporous SnO_2 nanosheets using hydrothermal methods [28]. The post-heat treatment was also applied in this study to increase the crystallinity of the sample.

Further, the TEM images of the FTO nanorice films prepared at 10 hours of reaction time using the hydrothermal method are presented in Figure 1(e). The image depicts that fluorine is amorphously covered on the surface of crystalline SnO_2. The spacing between the lattices of FTO nanorice films at the preferred orientation plane (110) is 0.33 nm, as shown in Figure 1(f). The nanorice agglomeration in this image is similar to FESEM images and is visible in nanosize.

Hence, the analysis of the surface morphology of FTO nanorice films provides crucial insights into their growth mechanism and helps optimize the process parameters to achieve the desired morphology and alignment.

The present study proposes a novel approach for forming nanorice and spherical nanorice in FTO films. The plausible structure is illustrated in Figure 2(a). During the initial stages of the hydrothermal process, the bare FTO substrate was placed on a stage in an autoclave containing precursor solution. Stage 2 demonstrates two simultaneous growth points of FTO nanorice. Primarily, the nuclei from a solution near the surface of the bare FTO substrates would attach to the substrate through a surface diffusion mechanism. The following equation can describe the possible formation of SnO_2 nanorice [24].

$$SnCl_4 + 4H_2O \longrightarrow Sn(OH)_4 + 4HCl \quad (1)$$

$$Sn(OH)_4 + NH_4F \longrightarrow SnO_2{:}F \quad (2)$$

$$HCl + NH_4F \longrightarrow NH_4Cl + HF \quad (3)$$

Tin(IV) chloride tends to react with water (H_2O) and form $Sn(OH)_4$, a process known as hydrolysis (equation 1). The decomposition and polymerization of $Sn(OH)_4$ lead to the formation of SnO_2 crystallites, which is achieved through dehydration. This process is regulated by forming Sn–F bonds with NH_4F as the fluorine donor (equation 2). When NH_4F is added in excessive amounts, it can negatively affect the formation of a hierarchical structure in the end product (equation 3). In Stage 3 of the process, the FTO nanorice is formed on the surface of the bare FTO substrate. The growth process occurs in a solution through cluster coalescence. The nuclei in the solution randomly move and attach to a large cluster and undergo surface diffusion, resulting in the nuclei's permanent alignment at a location. These aligned nuclei eventually grow into spherical nanorices, as observed in Stage 3. As the size of the spherical nanorice of FTO increases and gains weight, it falls on the surface of nanorice arrays and no longer moves in the solution [22].

Figure 2(b) depicts the XRD spectrum of the FTO nanorice films. The XRD pattern displays peaks at (110), (101), (200), (211), (220), (310), and (301) that are indexed to the cassiterite type with the tetragonal structure of SnO_2 phase, based on the standard JCPD data number (98-003-9178). From the XRD spectra, we observed that the peaks only showed the presence of the SnO_2 phase without the fluorine phase, due to overlapping with the SnO_2 peaks. A high crystallinity sample was obtained without annealing treatment. This finding is parallel with the previous study [24].

The preferential orientation (PO) for FTO nanorices is at the (110) plane with 3.4 Å of d-spacing, indicating that the growth of FTO nanorices occurs along the [110] direction. These results are in good agreement with those obtained from TEM analysis. Furthermore, the PO depends on the nature of the used tin precursor, while the film thickness is caused by substituting fluorine ions with oxygen ions [16].

It is worth noting that for the tetragonal structure of SnO_2 nanorice crystallinity, the (110) plane is the most stable due to the lowest surface energy compared to other planes. Understanding this fundamental aspect of the growth process is important for developing FTO nanorices with desirable properties.

The EDX spectrum of the FTO nanorice, as shown in Figure 3(c), reveals that the sample consists of only three elementary species: fluorine (F), tin (Sn), and oxygen (O). The presence of fluorine was successfully determined. The absence of other elements indicates a high degree of purity in the final product, which was successfully doped with fluorine.

The power conversion efficiency of the DSSC using nr-FTO films was measured under simulated full sunlight of 100 mW/cm^2, as shown in Figure 3. The configuration of the DSSC is nr-FTO/TiO_2/dye/electrolyte/Pt by using the sandwich method. Table 1 provides an overview of the photovoltaic characteristics, including open-circuit voltage (V_{OC}), fill factor (FF), short-circuit photocurrent density (J_{SC}), and photovoltaic efficiency. The V_{OC} value for the FTO commercial with the nanorice (750 mV) exceeds that of the FTO commercial (730 mV). The J_{SC} value for FTO commercial with nanorice (0.47 mA/cm^2) is also higher

than that for FTO commercial (0.38 mA/cm^2). It was found that the short-circuit current density and the open-circuit voltage significantly increased with nr-FTO film due to the improvement in the surface area from nr-FTO. The power conversion efficiency of DSSC using the nr-FTO was about 2.77%, which is higher than conventional FTO (1.93%). This improvement in efficiency is attributed to the enhanced surface area of the nr-FTO film. This phenomenon significantly contributes to the light-harvesting efficiency under illumination, causing more dyes in photoelectrons to the SnO_2 conduction, which in turn causes the photocurrent to rise [19].

Overall, these findings demonstrate that using nr-FTO films can significantly enhance the efficiency of DSSCs and pave the way for future advancements in the field of solar energy.

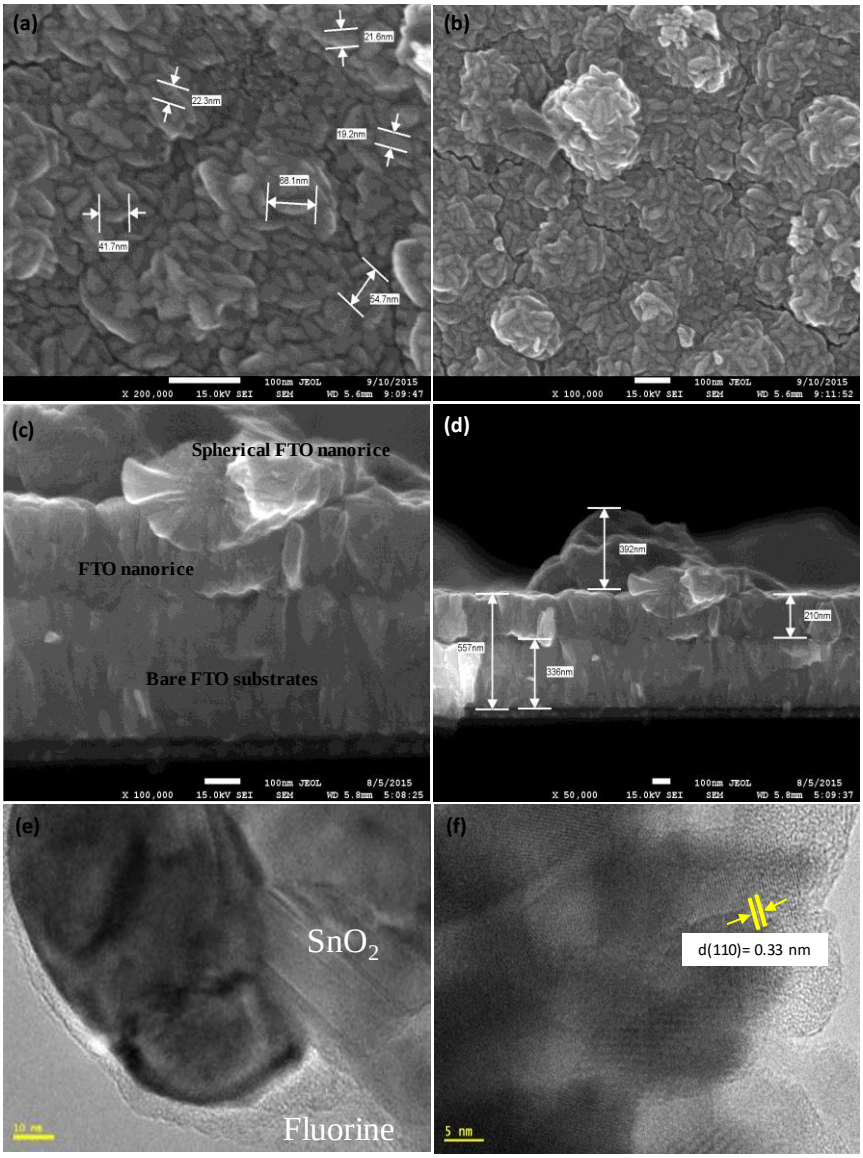

Figure 1 (a) and (b) FESEM images of nr-FTO, (c) and (d) cross-sectional view of nr-FTO, (d) and (e) TEM images of nr-FTO

Table 1 The V_{OC}, J_{SC}, FF(fill factor), and efficiency between FTO commercial and FTO commercial with FTO

Sample	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF	Efficiency (%)
FTO commercial + nanorice	750	7.01	0.47	2.77
FTO commercial	730	3.98	0.59	1.93

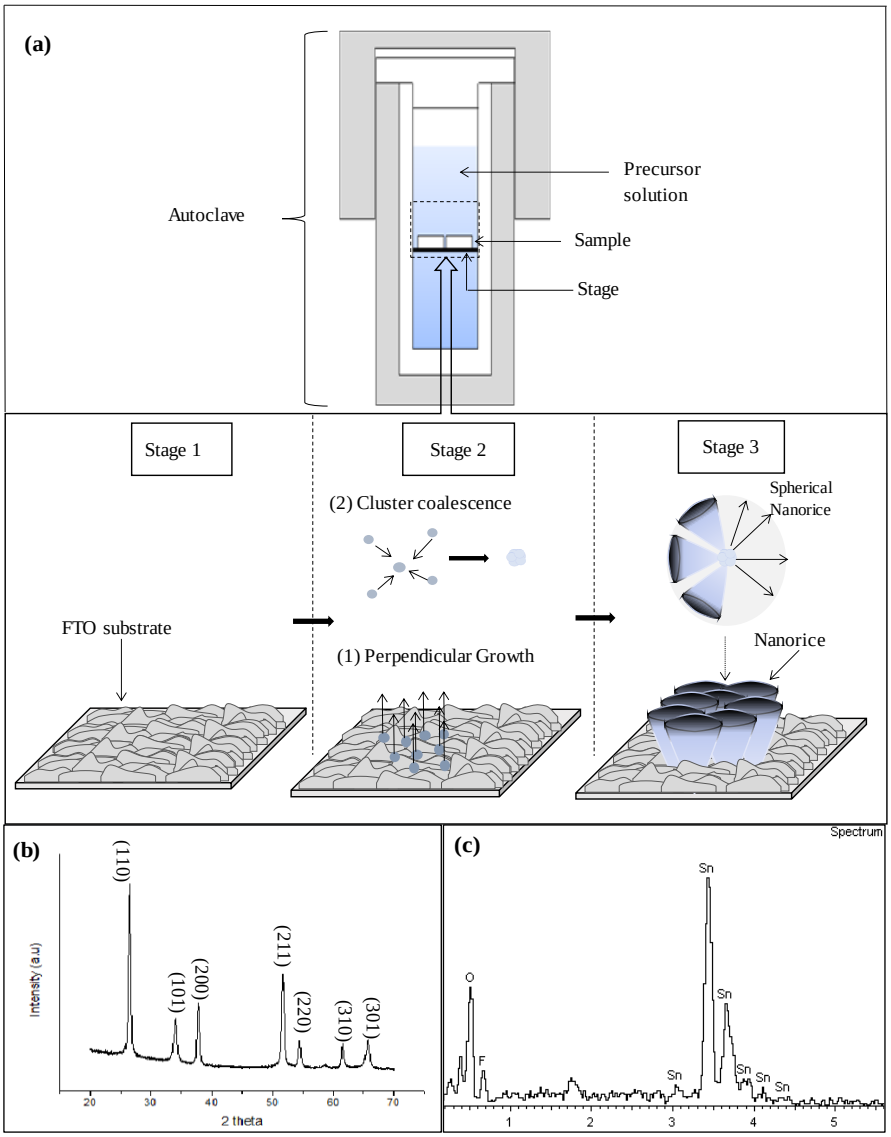

Figure 2 (a) Growth mechanism of nr-FTO film, (b) XRD spectrum, and (c) EDX spectrum of nr-FTO film

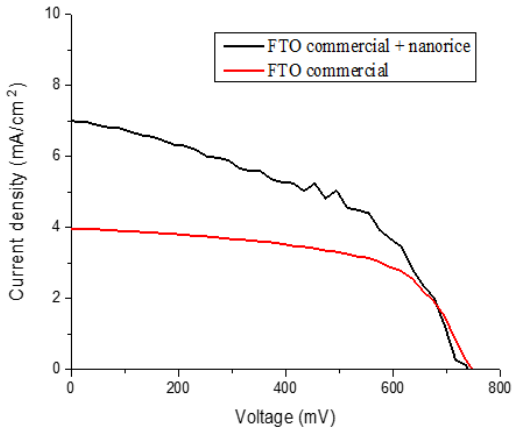

Figure 3 JV curve of DSSC using conventional FTO and nanorice FTO film

4. CONCLUSION

In summary, FTO nanorices were successfully fabricated using the hydrothermal technique at 150 °C in 10-hour reaction time. The hydrothermal method creates nanorice-shaped FTO for DSSCs in just one step. The surface morphology shows that the grain size of FTO nanorices was 54.8nm in length and 21.0 nm in width. XRD analysis of the prepared films shows cassiterite types and tetragonal structures with 3.3658Å of d-spacing. This value was matched with the TEM result. Based on the EDX analysis, pure FTO thin film was successfully synthesized without impurities. The prepared nr-FTO and spherical FTO were used as DSSC electrodes, contributing 2.77% of power conversion efficiency. This simplifies production, reduces costs, and is environmentally friendly. The unique nanorice shape increases the performance of DSSCs by making them more competitive with traditional silicon-based options. FTO's versatility in other technologies, such as sensors and displays, also contributes to economic growth and innovation in the renewable energy sector.

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