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THE EFFECT OF ADDITION OF SnO2 DOPING ON THE ELECTRONIC STRUCTURE OF TiO2 THIN FILM AS PHOTO-ANODE IN DSSC APPLICATIONS

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Abstract
Photoanode is a component of the dye-sensitized solar cell (DSSCc) which is synthesized from metal oxide semiconductor material with nanoparticle size deposited on transparent conductive glass. TiO2 powder was synthesized by mixing 20 mL of Titanium (III) chloride (TiCl3) with 100 mL of the equator and stirred for 1 hour. TiO2-SnO2 thin films have been successfully synthesized using the coprecipitation method and coated on ITO (Indium Tin Oxide) substrate by doctor-blade technique. The structure and morphology of the films were investigated by XRD and SEM respectively. The analysis of optical characteristics shows that the absorbance of TiO2 photoanode is in the wavelength range of 300-600 nm while SnO2 is in the wavelength range of 300-870 nm. The results showed that the synthesized film with SnO2 had a stronger anatase formation than the film with pure TiO2. Finally, incorporating SnO2 into the TiO2 matrix is an effective strategy to improve the overall properties of solar cells in future applications.

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Keywords:
DSSCs; photoanode; solar cells; thin film

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1. Introduction

The need for energy in Indonesia continues to increase. This is due to infrastructure development, regional expansion, road construction, etc[1]. At this time, the need for energy is obtained from energy sources that are conventional and non-renewable, such as coal, gas, and oil[2]. Reserves from these energy sources will decrease, while the need for energy will increase[3]. To overcome these problems, alternative energy sources are needed that can help reduce dependence on non-renewable energy sources[4]. Renewable energy that is growing rapidly in the world today is wind energy and solar energy[5]. Wind and solar energy sources are clean and freely available renewable energy sources.

Dye-sensitized solar cell (DSSCs) is a type of third-generation solar cell that utilizes photoelectrochemical principles[6]. This type of solar cell is believed to be able to provide an alternative energy concept with a more affordable production cost and with a simpler fabrication technology than its predecessor solar cells made from crystalline silicon[7]. A typical DSSC consists of several microns thick nanostructured semiconductor that is deposited on a conductive substrate as a framework of DSSCs photoanode[8]. Titanium dioxide (TiO_2) is one of the most selected and studied extensively photoanodes materials in DSSCs[9]. TiO_2 can be found in its three polymorphs in nature: anatase, brookite, and rutile[10]. However, anatase is mostly used due to its excellent stability and photoactivity. Additionally, TiO_2 has proven as a fascinating material and has been used for many different applications in both gas sensors and DSSCs because of its biological, and chemical inertness, long-term stability against chemical and photo-corrosion

One of the factors that are still a problem in the manufacture of DSSC solar cells is the use of electrolytes, both gels, and solutions, which have an important role in converting light energy into electrical energy in these solar cells[11]. Because the shape is generally in the form of a solution, many problems arise related to the use of electrolytes, such as leakage, evaporation, the possibility of corrosion of the center-electrode, and so on[12]. Most of the problems above are related to the issue of stability of cell performance in the long term[13]. In addition, the selection of the right type of electrolyte solution is also one of the factors that are still widely studied by researchers [14]. In this work, we synthesized TiO_2 and TiO_2-SnO_2 nanocomposites by coprecipitation method, and their structures and morphology were characterized and compared with pure TiO2 photoanodes.

2. Experimental Details

TiO_2 powders were synthesized by mixing 20 mL of Titanium (III) chloride ($TiCl_3$) with 100 mL of equates and were stirred for 1 hour. To this mixture, NH_4OH *solution* was added *dropwise until pH reached* 9. The resultant solution was stirred until the resulting white precipitate. The precipitate was filtered and was then washed several times with distilled water, reaching a value of pH equal to 7. The removal process of residual organics and the stabilization of the materials were carried out by calcination for three hours at 450°C.

The equipment used includes a digital multimeter, hot plate with magnetic stirrer, hair dryer, ultrasonic cleaner, 10 ml and 50 ml beakers, pipettes, 5 ml glass bottles, digital scales, Whatman no.42 filter paper, column chromatography mortar, and spin coater ITO glass substrates were purchased from Mianyang Prochema Commercial Co., Ltd., China. ITO with a size of 1 × 1 cm^2 was thoroughly rinsed with deionized water and anhydrous ethanol and dried on a hot plate. The manufacture of ITO glass layer DSSC which has been coated with TiO2 and has been dipped in the extracted dye solution is called the working electrode. The working electrode is dripped with an electrolyte solution and then covered with a platinum-coated counter electrode called the counter electrode[15]. Then the DSSC device is clamped on both the right and left sides, so it doesn't come off. The DSSC device is shown in Fig. 1. The films were heated at 450°C for one hour and cooled naturally to obtain a nano-porous film. The structure and morphology of the films were characterized by XRD and SEM.

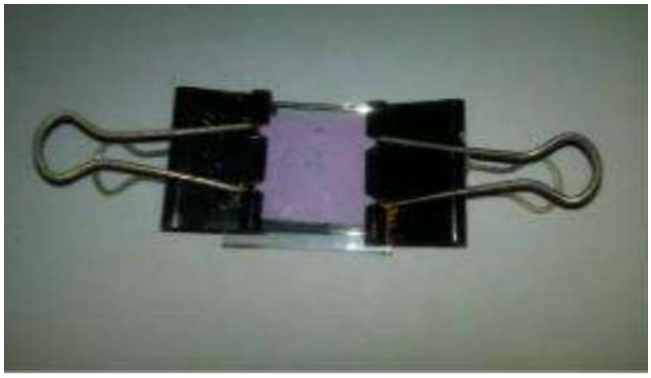

Figure 1. DSSC Device Display

3. Results and Discussion

The crystalline phase of photoanode films was evaluated by XRD analyses, and the result is shown in Fig. 2. It can be seen that the films are polycrystalline, and the diffraction peaks observed around 26 and 49 degrees correspond to the (101) and (200) reflexes of the anatase phase of TiO_2 with the tetragonal crystal structure. The TiO_2 film exhibits a new diffraction peak (222) plane around 31 degrees, which belongs to the ITO peak. These results agree with the analysis of the microstructure of pure TiO_2 film.

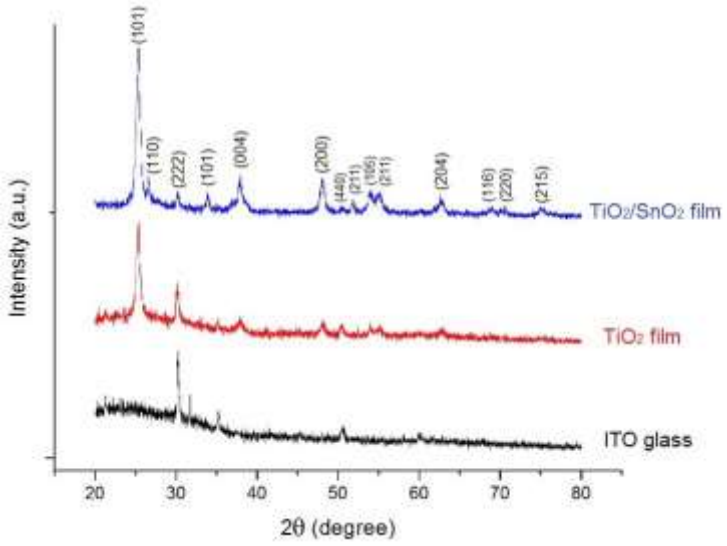

Figure 2. XRD spectra of pure and TiO2-SnO2 photoanodes

Furthermore, the diffraction peaks from rutile phase appear in the X-ray patterns due to the addition of the SnO_2 in the film. The (110), (101), and (211) planes at 2θ values 27, 34.1, and 53 degrees were observed as the characteristic peaks of SnO_2 in the doped TiO_2 film. Similar results have also been reported in previous studies. indicated that the increase of the concentration of dopant in the film has an effect on the transformation anatase to the rutile crystalline phase[16]. Nevertheless, the intensity of the (101) plane is higher than the intensity of pure TiO_2 film because of the electronegativity, and the ionic radius of Sn^{4+} ions is larger than Ti^{4+}[17]. It allowed easily for Sn^{4+} ions to replace and occupy the oxygen position in the TiO_2 lattice Thus, the spectrum shows the intensity of the (101) plane is gradually increased with the decreased ITO peak (222) plane, which indicated that better crystallinity than the pure TiO_2 film was obtained.

This feature gives a more stable chemical bond and permits excellent interconnection and continuity between titania nanoparticles, which in turn enhances electron transfer efficiency in photoanode[18]. This phenomenon showed that the inclusion of SnO_2 in the TiO_2 may stabilize the anatase as the main and strongest phase. The smaller radius of Ti^{4+} (0.68 Å) as compared to Sn^{4+} (0.69 Å) also made the crystallite size of doped TiO_2 film bigger than the pure one[20]. The average crystallite size, which is calculated from XRD data using the Rietveld method, is 34.2 and 10.3 nm for the doped TiO_2 and the pure TiO_2 films respectively.

Fig. 3 show represents the top-view SEM images of the doped and pure TiO_2 films. These images confirm that the microstructure of both samples exhibits spherical-shaped particles with irregular morphology due to the agglomeration of primary particles during the annealing treatment[21]. It can be seen that smaller particles with an average diameter of 10 − 11 nm were measured for pure TiO_2 and around 35 nm for SnO_2 doped TiO_2 film. The enlarging particle size of the doped TiO_2 film results in a larger surface area of the film, thus enabling a high dye loading capacity as well as enhancing the photosensitivity to solar radiation.

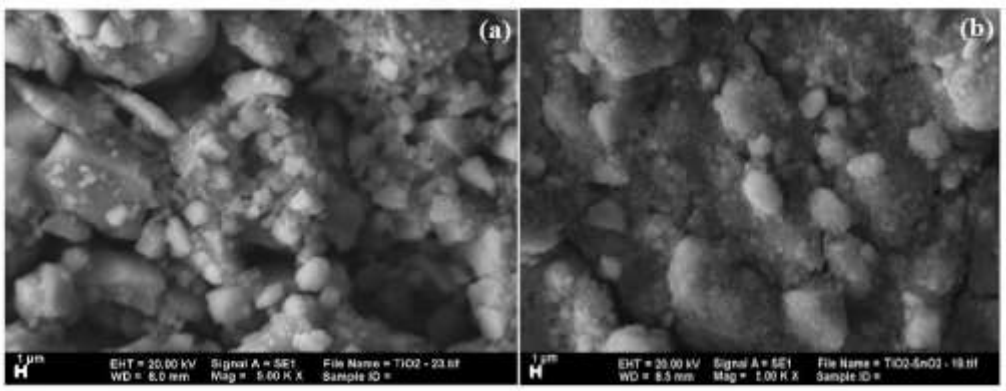

Figure 3. SEM micrographs of (a) pure TiO_2 and (b) TiO_2-SnO_2 films

The porous nature was observed in both films and this structure also plays a role in enhancing the surface area of the film photoanode. A bit rough, large and intense inhomogeneous agglomerations were formed in the pure TiO_2 film. In DSSC's system, these agglomerations decrease electron mobility and result in slow transport and recombination of photoexcited electrons[23]. On the other hand, TiO_2-SnO_2 exhibits smooth and rather well-distinguished uniform aggregates, although also there are a few voids and cracks which may be due to the loss of the binder during the annealing process[24]. These results indicate that the presence of SnO_2 can effectively suppress the grain growth of anatase compared with pure TiO_2.

The results of the analysis of the optical characteristics and band gap of the photoanode are obtained in the form of absorbance and transmittance graphs that describe the optical characteristics of the photoanode. It can be seen that the absorbance of TiO2 photoanode is in the wavelength range of 300-600 nm while SnO2 is in the wavelength range of 300-870 nm.

The photoanode has a wavelength range of 300-870 nm and the highest absorbance value when compared to TiO2 and SnO2 photoanodes. This is because the photoanode is composed of two constituent layers, namely the TiO2 layer which has a high absorbance value and the SnO2 layer which has a wavelength range of 300-870 nm. Fig. 4 shows the absorbance values in a certain wavelength range of TiO2, SnO2, and photoanodes where the absorbance value of photoanodes is lower than that of TiO2 photoanodes in the 300-600 nm wavelength range, but higher than SnO2 photoanodes in the wavelength range. 300-870 nm. This is because the photoanode is composed of one constituent layer, namely the TiO2/SnO2 composite layer so that absorbance is lower than TiO2 photoanode but has the same wavelength range as SnO2 photoanode.

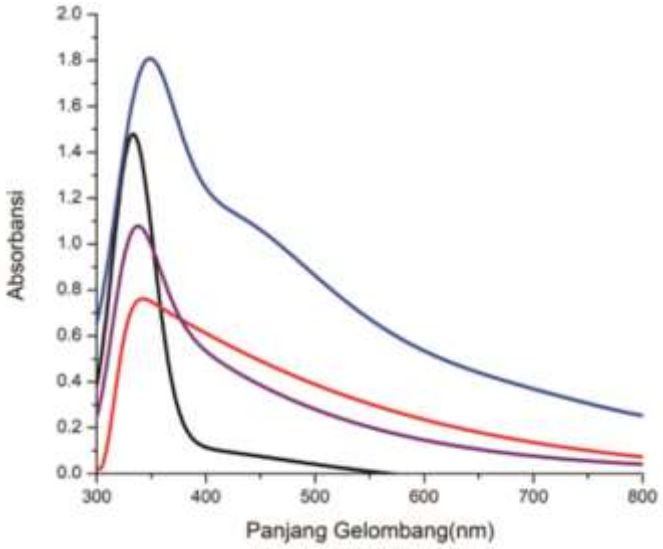

Figure 4. Photoanode absorbance value

In the photoanode the composite structure is layer by layer where there are 2 layers, namely SnO2 and TiO2 layers. SnO2 has a higher density than TiO2 so that the dye only sticks to TiO2. Because the dye only sticks to TiO2, SnO2 only accepts electron injection from TiO2. Meanwhile, in the SL photoanode the composite structure is a mixture of TiO2 and SnO2. So that the dye can stick to the surface of TiO2 and SnO2. This resulted in 2 recombination processes, namely from the TiO2 and SnO2 conduction bands to the HOMO dye level.

4. Conclusion

In summary, the proposed work compared the structural and morphological properties of the TiO2-SnO2 nanocomposite and the synthesized pure TiO2. The XRD pattern of the photoanode of TiO2 anatase with SnO2 shows superior crystallinity and stronger formation compared to the photoanode of pure TiO2 anatase. These results indicated that adding SnO2 could enhance the stability and microstructure of the photoanode. Additionally, the SEM analysis reveals the SnO2 dopants' existence in the TiO2 lattice. The surface of the doped TiO2 film showed a smooth and rather homogeneous aggregate; this explains that SnO2 content can suppress the crystal growth of TiO2 grains. Consequently, incorporating SnO2 into the TiO2 matrix was an effective strategy for enhancing the overall properties of solar cells in future applications.

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