Experimental Study of Acid Treatment Toward Characterization of Structural, Optical, and Morphological Properties of TiO$_2$-SnO$_2$ Composite Thin Film

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Abstract. The TiO$_2$-SnO$_2$ thin film with single and double-layer structure has successfully synthesized on FTO (Fluorine-doped Tin Oxide) substrate using the screen printing technique. The structural, optical, and morphological properties of the film were investigated by XRD, UV-Vis, and SEM, respectively. The results showed that the single and double-layer structure of TiO$_2$-SnO$_2$ thin film has mixed phase with a strong formation of casserite phase. The acid treatment effect on TiO$_2$-SnO$_2$ thin film decreases the peak intensity of anatase phase formation and thin film’s absorbance values. The morphological study is also revealed that the single layer TiO$_2$-SnO$_2$ thin film had a more porous nature and decreased particle size distribution after acid treatment, while the double-layer TiO$_2$-SnO$_2$ thin film Eroded due to acid treatment.

1. Introduction

Recently, DSSC has gained extensive attention due to their environment-friendliness, simple fabricating procedure and low-cost alternative to conventional Si solar cells [1-2]. A typical DSSC is composed of a nanoporous TiO$_2$ photoanode and a Pt counter electrode separated by an iodide/triiodide electrolyte [3]. The photoanode is usually prepared from TiO$_2$ nanoparticles on a transparent conducting oxide (TCO), while the counter electrode is a thin layer of Pt deposited on another TCO substrate [2].

Titanium dioxide (TiO$_2$) is one of the most studied extensively as photoanodes materials in DSSCs specially anatase phase due to its excellent stability and photoactivity. As the main material of the photoanode, characteristic of TiO$_2$ such as structure and morphology will undoubtedly affect the performance of DSSC [4]. Photoanode in DSSCs must have some characteristic of the porous structure, a large surface area which can increased molecules dye-loading capacity in photoanode. Some strategy to got the criteria are TiO$_2$ composite with SnO$_2$ and acid treatment on its surface.

Tin(IV) oxide, SnO$_2$, has seen considerable usage in composites with TiO$_2$ for photocatalysis, and battery applications. (Composite TiO$_2$ nanomaterial). Tin oxide has some advantages over TiO$_2$
because of higher diffusion rates of electrons in bulk SnO$_2$ [5]. Some research obtains that the acid treatment of photoanode surface can be enhanced the porosity characteristic and the performance of DSSC [6-7]. However, Hao [8] reported the decreased performance of acid-treated DSSCs, so this inconsistent result needs further clarification. To better understand those effect, acid treatment on surface photoanode should be investigated.

In this article, composite film TiO$_2$/SnO$_2$ was synthesized by double and single-layer screen printing method on FTO glass with TiO$_2$ and SnO$_2$. The influence of the acid treatment on Structural, Optical, and Morphological photoanode is investigated by X-ray Diffraction (XRD), UV-Vis, and Scanning Electron Microscopy (SEM). It is found that results of acid treatment was different for each type of composite structure (single and double layer composite) and also can change the optical, and morphological thin film.

2. Experimental

2.1. Deposition of Blocking Layer

Blocking layer TiO$_2$ was made by depositing a solution of TiO$_2$ blocking layer in FTO glass using spin coating method. Spin coating speed is 5000 rpm for 30 s. Finally, blocking layer with substrate was heated periodically at 100 °C for 15 min, 300 °C for 15 min, and 450 °C for 30 min.

2.2. Preparation of SnO$_2$ paste

The preparation of SnO$_2$ paste begins by dissolving 0.13 g of ethylcellulose was added into 3 mL of isopropanol solution and stirring for 1.5 h. Further 0.25 g of SnO$_2$ powder was added to the solution and continued stirring for 2 h.

2.3. Preparation of composite TiO$_2$/SnO$_2$ paste

0.05 g of ethylcellulose was added to mixing solution of 0.25 mL terpineol, and 0.25 mL of ethanol then stirred with a temperature of 80 °C for 10 min. 0.09 g of TiO$_2$ paste and 0.09 g of SnO$_2$ paste dissolved into ethylcellulose solution then stirred at 60 °C for 30 min.

2.4. Preparation of thin film

Each paste was deposited on the FTO glass using screen printing method. An active area of 0.5 × 0.5 cm$^2$ was formed in the FTO glass conductive part. Four types of thin film samples are TiO$_2$, SnO$_2$, single layer TiO$_2$ / SnO$_2$ composite, and a double-layer TiO$_2$ / SnO$_2$ composite. For a double-layer composite TiO$_2$ / SnO$_2$, SnO$_2$ and TiO$_2$ paste was deposited with TiO$_2$ above SnO$_2$. After the deposition process, the samples were gradually heated from 100 °C for 15 minutes, 300 °C for 15 min and 450 °C for 30 min.

2.5. Acid treatment

All thin film samples were immersed in the 2M HNO$_3$ solution for 20 min. All samples were cleaned with distilled water to remove the remaining HNO$_3$ from the immersion process. The use of nitric acid is expected to improve the photoanode performance for DSSC as some previous studies [6,12]

3. Result and Discussion

3.1. Thin film XRD analysis

The diffraction pattern in the form of an amorphous solid is obtained from the glass substrate diffraction pattern. With qualitative analysis using software match! It is shown in Figure 1 that the TiO$_2$ has anatase phase. The crystal plane 101 at ° 2Theta around 25.3 ° is the dominant crystal plane with the highest intensity in the TiO$_2$ thin film. While on other semiconductor materials, it was found that SnO$_2$ has cassiterite phase with the highest intensity in the (110), (101) and (211) planes.

The diffraction patterns formed from CDL (thin film double-layer TiO$_2$/SnO$_2$ composite) and CSL (thin film single-layer TiO$_2$/SnO$_2$ composite) are a combination of the peaks from TiO$_2$ and SnO$_2$ in a particular crystal plane. The CDL diffraction pattern is dominated by the crystalline planes of the SnO$_2$
cassiterite phase while the CSL diffraction pattern shows the crystal plane 101 derived from the anatase phase TiO₂ and the crystal plane (110) from the SnO₂ cassiterite phase. Li et al. [9] also obtained the same diffraction pattern on the TiO₂ / SnO₂ composite film. The addition of SnO₂ to the composite was also able to reduce the peak (101) of TiO₂, a similar result obtained by Arunachalam [10] in his study of the effect of the addition of Sn for the fabrication of composite TiO₂/SnO₂ thin films.

3.2. Morphological study
The morphology of the thin layer of CDL (Figure 3a) shows more pore than the thin layer of CSL (Figure 3e) on its surface. After immersion with an HNO₃ solution in thin film, it was found that there was an erosion of the coating and the reduction of TiO₂ particles in CDLA thin film (Figure 3d) and more pore formation on CSLA thin film (Figure 3c). This is due to the difference of thin film structure at the time of immersion with an HNO₃ solution.

Figure 2 shows the diffraction pattern of CDL and CSL thin film after the immersed process in HNO₃ (CDLA and CSLA). It can be seen that there is an intensity reduction at anatase phase in all the diffraction peaks in CDL and CSL thin film due to the reduced number of particles in the thin film. This effect also indicates a decrease in the degree of crystallinity in the thin film [11-12].

The SEM analysis also provides particle size distribution information from the thin film. Figure 4 shows the average particle size of the CDL thin film is between 0-150 nm with the dominance of the most particle size being approximately 40 nm. In the average CSL shows the particle size is in the
range 0-250 nm with an almost equal distribution of particle size with the dominance of the most particle size being approximately 50 nm. The acid treatment also gives effect to the particle size distribution. In CDLA thin film, the particle size becomes larger while decreased particle size of CSLA.

![Figure 4](image-url)  
**Figure 4.** The average particle size of CDL, CDLA, CSL, and CSLA thin film obtained from SEM micrograph.

### 3.3. Optical characteristic study

We obtained results in the graph of absorbance which illustrates how the optical characteristics of the thin film using UV-Vis. Figure 5 shows that the absorbance wavelength of the TiO$_2$ thin film in the 300-600 nm while SnO$_2$ is in the 300-870 nm wavelength (Figure 5a). CDL thin film has a wavelength range of 300-870 nm and the highest absorbance value when compared with the TiO$_2$ and SnO$_2$ thin films. This is due to CDL thin film is consist of two layers TiO$_2$ layer which has a high absorbance value and a SnO$_2$ layer which has a wavelength range 300-870 nm. Figure 5b shows absorbance values over a specified wavelength range of the TiO$_2$, SnO$_2$, and CSL thin films where the CSL thin film absorbance is lower than TiO$_2$ thin film in the range wavelength 300-600 nm but higher than SnO$_2$ thin film in the range wavelength 300-870. This is due to CSL thin film was a composite layer of TiO$_2$/SnO$_2$ so that the absorbance is lower than the TiO$_2$ thin film but has the same wavelength range as the SnO$_2$ thin film. Batmunkh et al. also obtained similar results [13].

Acid treatment gives affect decreased absorbance for each thin film (figure 5c and d). Decreased in absorbance of CDLA shows indicates the erosion of TiO$_2$ layer after immersed in the HNO$_3$ solution, this result also obtained by Wen et al.[14] where the decreased due to the increased molar acid solution in thin film immersion. Decreased in absorbance of CSLA indicates of increased porosity on TiO$_2$ thin film after immersed in the HNO$_3$ solution, this result is also obtained by Watson et al.[6]. Both the erosion and increased porosity of TiO$_2$ give effect to the decreased in the absorbance due to the amount of light passed through the thin film.

![Figure 5](image-url)  
**Figure 5.** UV-Vis shows the absorbance graphs of (a) TiO$_2$, SnO$_2$, and CDL; (b) TiO$_2$, SnO$_2$, and CSL; (c) CSL and CSLA; (d) CDL and CDLA.
4. Conclusion
In summary, the single and double-layer structure of TiO$_2$-SnO$_2$ thin film has mixed phase with a strong formation of cassiterite phase. The acid treatment effect on TiO$_2$-SnO$_2$ thin film decreases the peak intensity of anatase phase formation and thin film’s absorbance. The decreased absorbance on thin film due to morphological study which also revealed that the single layer TiO$_2$-SnO$_2$ thin film had a more porous nature and decreased particle size distribution after acid treatment, while the double-layer TiO$_2$-SnO$_2$ thin film eroded due to acid treatment.

Acknowledgments
All authors would like to thank the Ministry of Research, Technology and Higher Education of the Republic of Indonesia, and LPPM-Institut Teknologi Sepuluh Nopember for providing Laboratory Grant 2017 with contract number: 697/PKS/ITS/2017 and the Physics of Magnetism and Photonics Research Division, FMIPA-Institut Teknologi Bandung over all their facilities during this study.

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