

Structural and morphological characterization of TiO₂-SnO₂ thin film prepared by combining doctor-blade and sol-gel techniques

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Abstract. The TiO₂-SnO₂ thin film has successfully been synthesized using the co-precipitation method and was coated on ITO (Indium Tin Oxide) substrate by doctor-blade technique. The structure and morphology of the film were investigated by XRD and SEM, respectively. The results showed that the film with SnO₂ has a stronger formation of anatase phase compared to TiO₂ film. The morphological study is also revealed that the TiO₂-SnO₂ film has a more porous nature and uniform particle aggregates, and the presence of SnO₂ has been confirmed with EDX spectra.

Keywords: co-precipitation, doctor blade, TiO₂-SnO₂ thin film, microstructure, nanoporous

1. Introduction

Titanium dioxide (TiO₂) is one of the most selected and studied extensively as photoanodes materials in DSSCs [1-2]. TiO₂ can be found in its three polymorphs in nature: anatase, brookite, and rutile. However, anatase is mostly used due to its excellent stability and photoactivity. As the main material of the photoanode, characteristics of TiO₂ such as structure and morphology will certainly affect the whole characteristics of DSSC.

The photoanode in DSSC should possess stable and porous structure, enormous surface area, high molecules dye-loading capacity and solid structure of the surface film [2-4]. The physical and chemical properties of TiO₂ can be modified by incorporating metals and nonmetals element to tailor the properties of TiO₂ for enhancing the photovoltaic application especially in DSSCs [1]. Doping with SnO₂ can improve the stability of crystallinity of TiO₂ because it has porous nature, fast rate of electron transport, higher electric mobility, long-term stability under UV-illumination and excellent performance in an acidic condition [2, 5, 6].

Many methods have been employed to synthesize TiO₂ nanoparticles, such as Stöber [7], hydrothermal [8] and sol-gel [9]. Recently, the co-precipitation method has been extensively investigated to synthesized TiO₂ nanoparticles due to low processing temperature, ease of composition control, high purity and good chemical homogeneity [10]. In this work, we synthesized TiO₂ and TiO₂-SnO₂ nanocomposites by a co-precipitation method, then coated on ITO film. The structure and morphology of TiO₂-SnO₂ film were characterized and compared to TiO₂ film.



2. Materials and methods

2.1. TiO_2 synthesis

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

2.2. TiO_2-SnO_2 synthesis

SnO_2 nanopowders was purchased from Sigma Aldrich. SnO_2 powders were mixed with TiO_2 nanopowders. The powders mixture was grinded with a grinding bowl and then annealed at $450^\circ C$ for 30 min. To the mixture aquades, ethylcellulose, terpineol and ethanol were added and kept stirring for 10 min. The mixed oxide pastes were obtained from 0.7 mL of acetic acid, 0.3 g of PEG, and 0.7 mL of Triton X-100. The TiO_2 pastes were prepared in the same way.

2.3. TiO_2-SnO_2 thin films

ITO glass substrates were purchased from Mianyang Prochema Commercial Co., Ltd., China. ITO with a size of $1 \times 1 \text{ cm}^2$ were thoroughly rinsed with deionized water and anhydrous ethanol and dried on a hot plate. TiO_2 and TiO_2-SnO_2 pastes were deposited onto a conductive glass substrates-ITO glass using doctor blade technique. The films were heated at $450^\circ C$ for one hour and cooled naturally to obtain a nanoporous film. The structure and morphology of the films were characterized by XRD and SEM-EDX.

3. Results and discussion

3.1. Structural study

The crystalline phase of photoanodes films was evaluated by XRD analyses, and the result is shown in figure 1. 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) of the anatase phase of TiO_2 with the tetragonal crystal structure (PDF no. 00-078-2486, ICDD) [11]. The TiO_2 film exhibits a new diffraction peak (222) plane around 31 degree, which belongs to the ITO peak. These results agree with the analysis of the microstructure of pure TiO_2 film by Arunachalam *et al.* [5].

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. The similar results have also been reported in the previous studies [11-13].

Nevertheless, the intensity of (101) plane is higher than the intensity of TiO_2 film because of the electronegativity, and the ionic radius of Sn^{4+} ions are larger than Ti^{4+} . It allowed easily for Sn^{4+} ions to replace and occupy the oxygen position in the TiO_2 lattice [3, 5] Thus, the spectrum shows the intensity of (101) plane is increased with the decrease ITO peak (222) plane, which indicated the better crystallinity than the TiO_2 film was obtained. This feature gives a more stable chemical bond and permits excellent interconnection and continuity between titania nanoparticle, which in turn enhances electron transfer efficiency in photoanode [3-4]. This phenomenon showed that the inclusion of SnO_2 in the TiO_2 may stabilize the anatase as the main and strongest phase [5, 13]. The smaller radius of Ti^{4+} (0.68 Å) as compared to Sn^{4+} (0.69 Å) [5] also made the crystallite size of doped TiO_2 film is bigger than the undoped one. The average crystallite size, which is calculated from XRD data using Rietveld method, is 34.2 and 10.3 nm for the doped TiO_2 and the undoped TiO_2 films respectively.

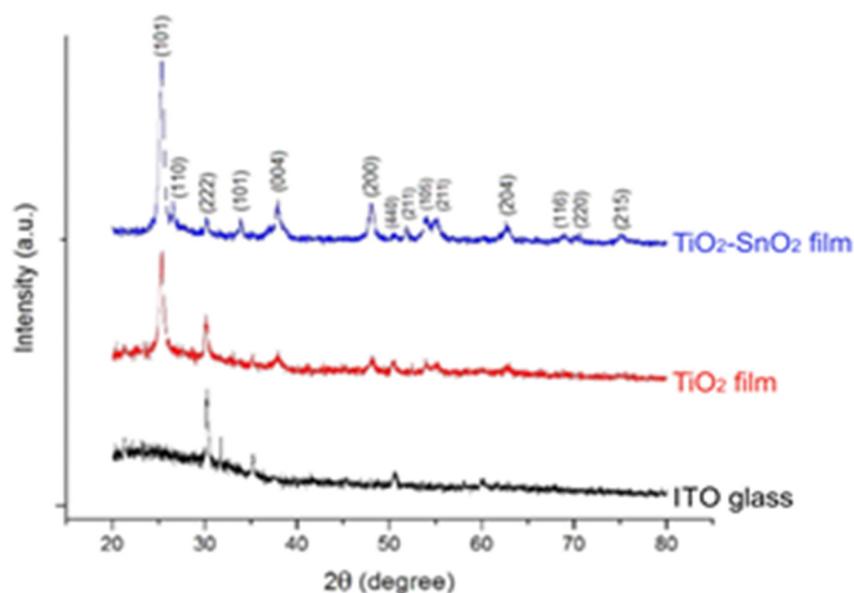


Figure 1. XRD spectra of ITO, TiO_2 and $\text{TiO}_2\text{-SnO}_2$ films.

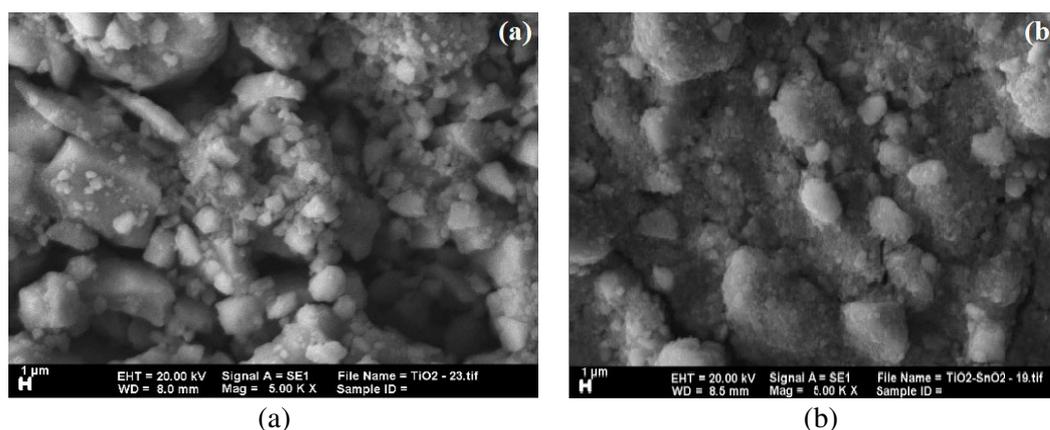


Figure 2. SEM micrographs of (a) TiO_2 and (b) $\text{TiO}_2\text{-SnO}_2$ films

3.2 Morphological study

Figure 2 represents the top-view SEM images of the $\text{TiO}_2\text{-SnO}_2$ and TiO_2 films. These images confirm that the microstructure of both samples exhibits spherical shaped particle with irregular morphology due to the agglomeration of primary particles during the anneal treatment. It can be seen that smaller particles with an average diameter of 10-11 nm were observed for TiO_2 film and around 35 nm for SnO_2 doped TiO_2 film. The enlarging particle size of the doped TiO_2 film results in the larger surface area of the film [9], thus enabling a high dye loading capacity [14] as well as enhancing the photosensitivity to solar radiation [15]. The porous nature was observed in both films and this structure also plays a role in enhancing the surface area of the film photoanode [5, 9, 16]. A bit rough, large and intense inhomogeneous agglomerations were formed in the pure TiO_2 film. On the other hand, $\text{TiO}_2\text{-SnO}_2$ film exhibits smooth and rather well-distinguished uniform aggregates, although also there are few voids and cracks which may be due to losing of the binder during the annealing process [16]. These results indicate that the presence of SnO_2 can effectively suppress the grain growth of anatase compare with the pure TiO_2 [5].

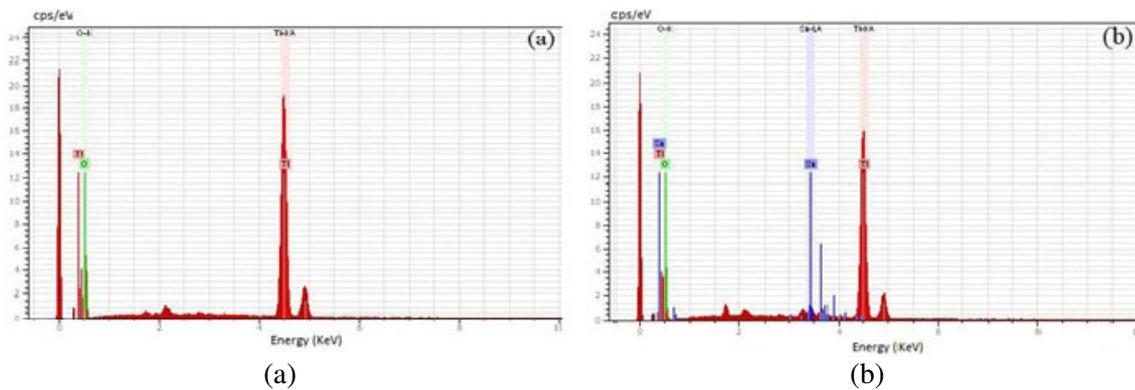


Figure 3. The EDX spectra of (a) TiO₂ and (b) TiO₂-SnO₂ films

Table 1. The element compositions of the samples which are obtained from the EDX spectra

Ingredient number (at%)	TiO ₂ film	TiO ₂ -SnO ₂ film
Ti	67.24	71.06
O	32.76	27.66
Sn	0	1.28

The EDX spectra represents the element analysis of TiO₂ film and SnO₂ doped TiO₂ film. The EDX analysis of the TiO₂ film (figure 3a) confirms the presence of Ti and O. Figure 3b shows the existence of the SnO₂ dopants into TiO₂ lattice. From table 1 can be deduced that the Sn was presented around 1.28% in the TiO₂-SnO₂ film, and the percentage of O in the composites was decreased compared to TiO₂ film. The condition proved that the doping of SnO₂ has been successful.

4. Conclusions

In summary, the proposed work was a comparison the structural and morphological of the TiO₂-SnO₂ nanocomposite and the synthesized of TiO₂. The XRD pattern of TiO₂ anatase with SnO₂ besides showing the better crystallinity is also showing the stronger formation when compared to the anatase TiO₂. Additionally, the EDX analysis reveals the existence of the SnO₂ dopants into the TiO₂ lattice. The surface of the doped TiO₂ film showed smooth and rather homogeneous aggregate.

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