

Properties of Sol-Gel Derived TiO₂ Thin Films Prepared with Different Dip-Coating Layers

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Titanium dioxide (TiO₂) thin films have been prepared on indium doped tin oxide (ITO) glass by sol-gel dip-coating method. Structural, electrochemical and optical properties of the films were studied as a function of dip-coating layers. Films prepared with more coated layers showed better catalyst coverage and more intense crystalline phase. The increases of films thickness promoted the photocurrent and suppressed the dark current. Films transmission was found to decrease with number of dip-coated layers.

Keywords: sol-gel; thin films; heat-treatment; electrochemical properties; dip-coating.

1. INTRODUCTION

Titanium dioxide (TiO₂) is an excellent material which shows most promising prospect in environmental purification, photoelectrochemical solar energy conversion and optical coating applications [1, 2]. This is due to several properties such as remarkable activity, chemical stability, non-toxic, highly oxidative photogenerated holes, high energy conversion, highly transparent and high refractive index [1, 3]. On application as photocatalyst, TiO₂ have been widely investigated either in the suspension or immobilized forms in the treatment of broad range of aqueous pollutants. The later method has become a better option due to TiO₂ in slurry or suspension has to go through separation of dispersed TiO₂ particles after the treatment. Moreover, TiO₂ film supported on a conductive material could exhibit interesting photoelectrochemical properties [4, 5]. In other aspect of coating, TiO₂ films have been widely used as material for optical filter [6], gas sensor [7], ceramic membrane [8] and waveguide [9].

TiO₂ films can be prepared by various deposition methods including sol-gel [10, 11], chemical vapour deposition [12], electrophoretic [13], screen printing [14] and sputtering method [15]. Among all, sol-gel is one of the most preferable techniques due to several advantages such as wide possibility of varying the film properties, low process cost and easier coating on large areas [10]. It is known that the properties of the sol-gel derived films are strongly dependent not only on the composition of the precursor solution, but also the preparation conditions such as solution preparation sequences, ageing temperature and time [11].

In this paper, we prepared the TiO₂ films by sol-gel dip-coating method various dip-coated layers. Their structural, electrochemical and optical properties have been investigated accordingly.

2. EXPERIMENTAL

2.1. Preparation of precursor solutions

The precursor solution for TiO₂ sol was prepared using the system that containing tetraisopropyl-orthotitanate,

polyethelene (glycol) (molecular weight, $M_w = 2000$), diethanolamine, ethanol and water as reported by Kato [16–18]. Modifications were made on chemical molar ratio and adding sequences. The molarity of alkoxide in the ethanol was 0.94 mol/dm³. The molar ratio of diethanolamine to the alkoxide was one. The concentration of polyethelene glycol and water to alkoxide was 6 wt.% and 0.8 wt.%, respectively. The polyethelene glycol solution was dissolved in the ethanol solution before adding other chemicals in the following sequences: diethanolamine, tetraisopropyl orthotitanate and water. The mixture was stirred in a sealed condition for several hours at room temperature. The resulting sol gel was clear and transparent.

2.2 Preparation of TiO₂ thin films

The ITO glasses ($5 \times 2 \text{ cm}^2$, ITO layer = 45.4 nm; $47.54 \Omega \text{ cm}^{-1}$) were used as the conducting supporting materials for TiO₂. The ITO glass was cleaned with acetone in an ultrasonic bath for 15 min. The treated ITO glass was dried in an oven at 100 °C for 15 min and then dip-coated with sol-gel solution and left to dry at room temperature. The coated electrode was heated at 100 °C for 5 min in oven followed by subsequent dip-coating. An area with size of $1.5 \times 2.0 \text{ cm}^2$ at the top was left uncoated to provide the area of the electrical connection. This step was repeated several times depending on the desired dipping times. Finally, the plate was annealed at 400 °C in a Thermolyne 21100 furnace for 2 hours.

2.3 Analytical Measurements

A potentiostat EG & G Princeton Applied Research (PAR) VersaStat driven by model 270 electrochemical Analysis System Software was used in the photoactivity measurements. Standard three-electrode, single compartment cell geometry was employed. The working electrode was TiO₂ coated titanium plate. Other electrodes were Ag/AgCl as reference electrode and platinum as counter electrode. Tungsten halogen projector lamp (Osram, 300 W and 120 V) was used as a light source to test the photoactivity of the films. The light source was chopped manually to differentiate the dark and photocurrent. The electrodes were immersed in 0.1 M Na₂S₂O₄ as electrolytes.

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All the measurements were carried out at room temperature, approximately 298 K.

Optical absorption study was carried out using the Perkin Elmer UV/Vis Lambda 20 Spectrophotometer. The films coated on quartz glass were placed across the sample radiation pathway while an uncoated quartz glass was put across the reference channel. The transmittance and absorbance of films were measured in the wavelength range from 300 nm to 800 nm. Scanning electron microscopy was performed on SEM JSM 6400 JEOL Scanning Microscope to analyse the morphology and surface characteristics of the coated TiO₂ films. X-ray diffractometry (XRD) analysis was employed to identify the crystalline phases on the films. This technique was performed using Shimadzu XRD 6000 Diffractometer for 2θ ranges from 2° to 60° with Ni-Filter and Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$).

3. RESULTS AND DISCUSSION

The SEM micrographs of films prepared at various dip-coating layers are shown in Fig. 1. The result reveals that a thin layer of film was obtained when only one dip-coating was applied to the substrate. The thickness of the layer produced by each dipping is about 2 μm as estimated from the cross sectional analysis from Scanning Electron Microscope. The film with three coated layers appeared thicker with clearer fractured appearance. Generally, all films cracked after heat-treated at 400 °C. The stress and contraction due to thermal gradient together with different pores sizes of the gel contribute to this surface morphology. The film with 5 dip-coated layers shows variation of large cracked size. Film with 6 coated layers exhibited almost similar surface morphology as the film prepared by 5 dips. Closer view by applying higher

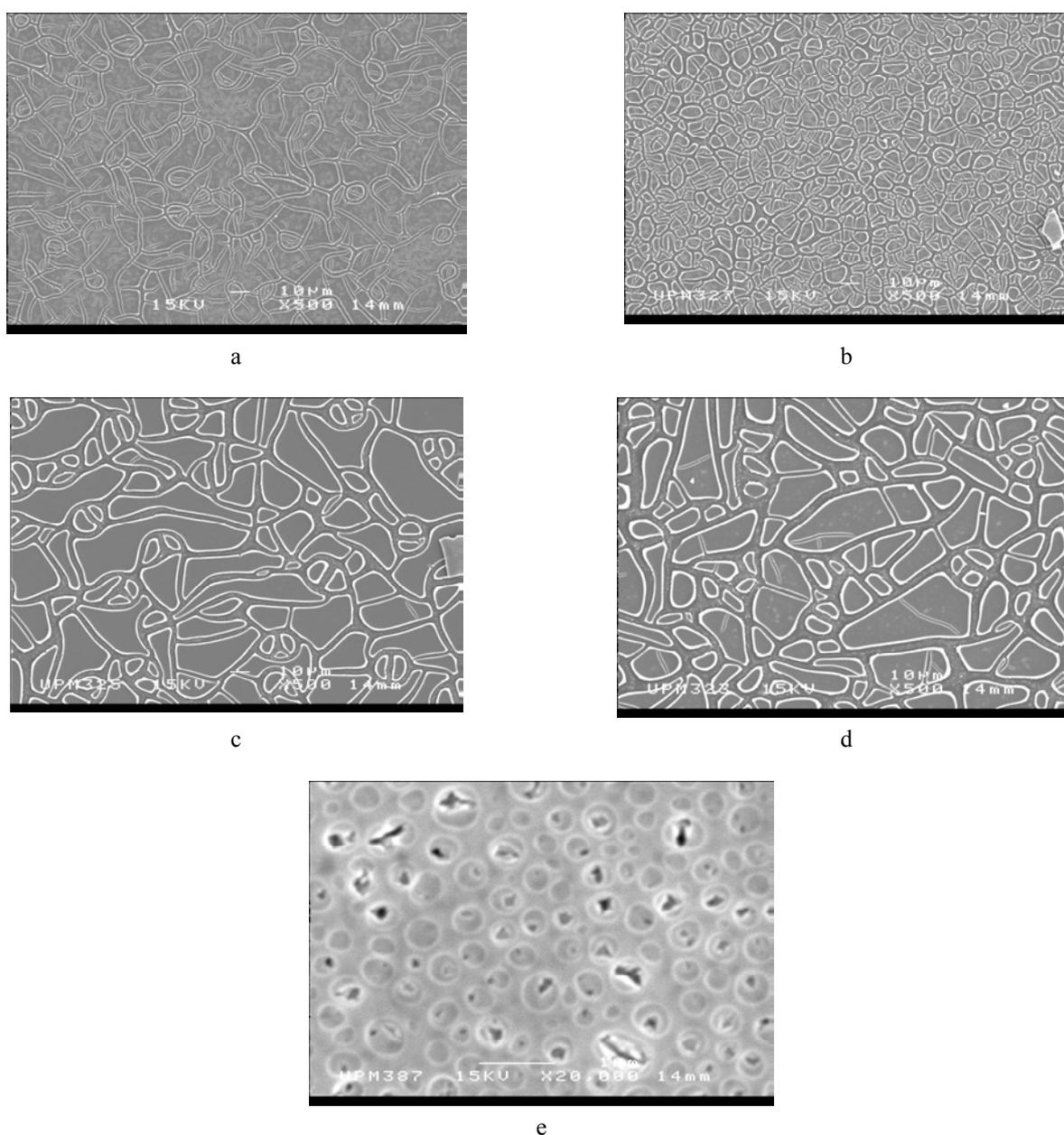


Fig. 1. SEM micrographs of films prepared at different dip-coatings: a – 1 layer; b – 3 layers; c – 5 layers; d – 6 layers (all with magnification of 500 \times); e – 6 layers (with magnification of 20000 \times)

magnification (20000×) shows microscopic structure of film with pores size between 0.1 μm to 0.5 μm. The appearance of pores in the film is due to the lost of polyethylene glycol (PEG) during the heat-treatment [19]. SEM micrograph also indicated that there are other layers in the pores which resulted from the various dip-coating layers.

Fig. 2 shows the XRD patterns of the films prepared by 1 to 6 dip-coatings layers which were heat-treated at 400 °C. The result shows that all films are mostly in anatase phase. The most pronounce peak for all samples occurred at $d = 3.52 \text{ \AA}$ which corresponds to (101) plane of anatase TiO₂. The intensity of this peak increases with increasing number of dip-coated layers. Meanwhile, the other four anatase peaks and one rutile peak which could also be seen on the film did not show clear increase in intensity.



Fig. 2. X-ray diffraction patterns of films prepared with varying dip-coated layers and heat treated at 400 °C

The electrochemical characteristic of the films is investigated in 0.1 M Na₂S₂O₃ solution under illumination and in dark as shown in Fig. 3 (a) and 3 (b), respectively. Meanwhile, Fig. 3 (c) shows the net photocurrent values by measuring the differences between the currents under illumination (I_p) and in dark (I_d). Fig. 3 (a) shows that photocurrent increase gradually with the increase of number of dip-coated layer except for 1 dip-coating. The current show by this particular film is mainly due to the dark current as shown in Fig. 3 (b). The increases of number of dip-coated layer successfully suppressed the dark current which due to the better covered of TiO₂ on titanium plate. The exposure of substrate to the solution will promote the dark current which became more obvious with the increasing of applied potential. This agrees with the report by Sun and Chou [20], which stated that the excellent adhesion of the film could suppress the dark current at high potential.

Fig. 3 (c) shows the net photocurrent increase with the applied of bias potential for all the electrodes but the value decrease when applying potential higher than 0.6 V for electrode coated with 4 layers and below. This is due to the existing of dark current as discussed.

a

b

c

Fig. 3. I – V curves of films prepared with varying dip-coated layers in condition of (a) under illumination, I_p ; (b) in dark, I_d and (c) differences of current between under illumination and in dark, $I_p - I_d$

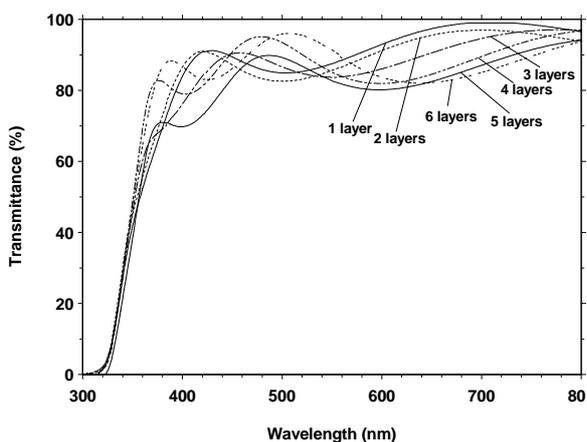


Fig. 4. UV – Vis spectra (in transmittance) of thin films prepared with varying dip-coated layers and heat-treated at 400 °C

Fig. 4 shows the transmission spectra of TiO₂ films deposited on glass in the wavelength range of 300 to 800 nm. All films show high transparency in the visible region. The result shows that all the prepared films are thin and transparent. Beside that, there is no remarkable drop in transmittance because all the films were heat-treated at same temperature. Thus, phase transformation and crystallite size did not change significantly resulting in less light scattering. In this study, the small differences in transmittance values were due to the different in light penetration levels.

4. CONCLUSIONS

Sol-gel derived TiO₂ thin films have been prepared on ITO glass. The effect of number of dip-coatings layers on the structural, electrochemical and optical properties of the films have been studied. The increase of number of dip-coatings layers significantly increased the films photoelectrochemical performance due to better TiO₂ coverage. All the prepared films which coated up to 6 layers show high transmittance.

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