Preparation of TiO\textsubscript{2} Photoelectric Thin Films by Sol-gel Dip-coating Method

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ABSTRACT: TiO\textsubscript{2} thin films were fabricated by a sol-gel dip-coating method. The surface morphology, crystal, light transmittance and photoelectric properties of the films were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), film transmittance tester and solar cell IV test system. It shows from the results that the sol-gel derived TiO\textsubscript{2} film is transparent and smooth. After sintered at 550\textdegree C, strong crystal anatase phase is formed in TiO\textsubscript{2} film, and when used as photo anode, it can improve the photoelectric properties of the Dye sensitized solar cells.

1 INTRODUCTION

Titanium dioxide (TiO\textsubscript{2}) is a semiconductor with wide band gap (3.2eV), which is transparent in visible light. It notably possesses some excellent advantages such as non-toxicity, high thermal stability, low cost and easy preparation, has been most widely used in photoelectric and Photocatalysis application. TiO\textsubscript{2} thin films, used as photo anodes in dye-sensitized solar cells (DSSC), have attracted much attention in recent years. To obtain better performance of the solar cells, highly crystalline pure anatase phase thicker TiO\textsubscript{2} films (8-7µm) are preferable. Thicker film can support the large amount of dye for good solar light harvesting, lower ionic resistance within the TiO\textsubscript{2} electrode and good interconnected crystalline network for effective electron transfer from dye molecules. However, when the film thickness is increased, it tends to have cracks because of considerable stress in the TiO\textsubscript{2} film due to the film shrinkage in heat treating process. Which causes considerable challenges in adhesion properties between TiO\textsubscript{2} film and its various substrates. The sol-gel method is generally recognized as one of the most important techniques for fabrication of ceramic thin films. Most commonly applied sol gel method for TiO\textsubscript{2} solar cell is to prepare titania sol (Ti-sol) or modified with P25 powders to make TiO\textsubscript{2} paste and followed with screen printing. Some researchers directly use sol-gel dip-coating method to prepare TiO\textsubscript{2} film because it possesses several advantages, such as low temperature processing, easy coating of large area, and being suitable for improving the bonding strength.
However, the TiO$_2$ sol is commonly used to prepare TiO$_2$ nanopowder, but for film preparation process, TiO$_2$ sol is easy condensation and unstable. This property has apparent effect on the film fabrication in real application. In this study, TiO$_2$ sol was prepared and thin film was fabricated by dip-coating method, the effects of chemical ratios and film characteristic are studied in detail.

2 EXPERIMENTAL PROCEDURE

2.1 TiO$_2$ sol preparation

Analytical reagent grade chemicals were used throughout this study. TiO$_2$ sol was prepared at room temperature in the following way: 10 ml Tetrabutyl titanate, (AR, Kermel, Tianjin) was dissolved in the mixture solution of 20 ml ethanol and 0.5 ml acetylacetone as A solution. 0.5 ml nitric acid was drop wised into the mixed 10 ml ethanol and 2.0 ml deionized water as B solution. To prepare TiO$_2$ sol, B solution was dropwised into A solution and acquired designed pH value. Then, the mixed solution was magnetic stirred for 3 h. At last, the sols were aged in a sealed beaker kept in 40°C water bath for 2 h.

2.2 Coating preparation

Fluorine doped tin oxide(FTO) transparent conducting glass substrate, 20mm×30mm, was first cleaned with deionized(DI) water, followed by ultrasonic cleaning with anhydrous alcohol for 30min, and then heated under vacuum at 80 °C for 1 h to bake out solvents and other impurities. During coating process, FTO substrate was dipped vertically into the sol and withdrawn at a speed of 10 mm/min to allow formation of a thin but good bond layer. The sol-coated substrate was then immediately transferred to an oven at 150 °C to dry for 10 min. To study the influence of coating thickness on the photo-electric property of the films, the dipping-drawing drying process was repeated 1-4 times to fabricate thicker film. The sol-gel derived films were followed by calcinations at designed temperature for 0.5 h.

2.3 Assembly of dye-sensitized solar cell

TiO$_2$ film was used as the photo-anode. It was stained in N719 dye for half an hour, and dried at room temperature before cell assembly. Another graphite coated conductive glass, was used as the cathode. Then the cathode and the anode were pressed on both sides, and electrolyte was added in the middle of the cell.
2.4 Characterization of thin films

The surface morphology of the TiO₂ film was examined with S-3000N scanning electron microscope (SEM, HITACHI). The phase characterization was conducted by X-ray diffraction analysis (XRD, Philips, PW1830) using monochromatic CuKα radiation. The transmissivity of the film was measured with a film transmittance tester (LH-1013). Photovoltaic measurements were carried out with an AM 1.5 solar simulator equipped with a 450 W xenon lamp. I-V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a digital source meter.

3 RESULTS AND DISCUSSION

3.1 Characterization of sol-gel derived TiO₂ thin films

3.1.1 Surface morphology

The typical surface morphology of sol–gel derived TiO₂ thin film is shown in Figure 1. It shows from Figure 1 that the coating surface is fully dense, no apparent pores or voids are observable. The surface morphology shows that sol-gel dip-coating method is suitable for TiO₂ thin film fabrication.

![Figure 1](image1.png)

3.1.2 XRD analysis

Figure 2 shows the XRD patterns of TiO₂ films after dip-coating process and sintered at 350°C-550°C. It shows from Figure 2 that two crystal phases of TiO₂ can be observed. After sintering process, anatase and rutile phase. It is reported that 350°C-550°C is the range of amorphous TiO₂ change to anatase phase. At higher temperature rutile phase begin to appear. It shows from XRD patterns that at 350°C and 450°C, only anatase crystal peaks can be observed.
As the temperature increased to 550℃, small crystal peaks from rutile phase appear. The intensity of TiO₂ peaks also show that sintering temperature has apparent effect on the crystallization of TiO₂. As the temperature increase, the crystal peaks are intensified accordingly.

![XRD analysis of TiO₂ thin film](image)

Figure 2. Typical XRD analysis of TiO₂ thin film by the sol–gel dip-coating method after sintering.

3.2 Light transmittance of the TiO₂ film

In DSSC, TiO₂ film plays important role in charge separation and transport of the carrier. The transmittance property of TiO₂ film has effect on the incident light absorption rate. Figure 3 shows the transmittance property of TiO₂ films with different coating layers. It shows from Figure 3 that, the transmissivity of infrared and visible rays are decreased as the coating layer increase accordingly. But for ultraviolet ray, only one layer of TiO₂ film can decrease the transmissivity to 50%, far lower than that for infrared and visible rays (about 70%). The decrease of transmissivity of ultraviolet ray is generally induced by TiO₂ band gap excitation. It is reported that the strong absorption below 380 nm arises from the band gap transition of TiO₂.

![Light transmittance properties](image)

Figure 3. Typical Light transmittance properties of TiO₂ thin film.
3.3 The effect of sintering temperature on DSSC photoelectric properties

A series of DSSC were assembled with the sol-gel derived TiO$_2$ film as photo anodes. The effects of sintering temperature on open circuit voltage and short current of the DSSC are shown in Figure 4.

![Figure 4. The effect of sintering temperature on open circuit voltage and short current of the DSSC.](image)

It shows from Figure 4 that the sol-gel derived TiO$_2$ film have photoelectric properties in DSSC. As sintering temperature increase from 350°C to 550°C, both the open circuit voltage and short circuit current of the DSSC increases accordingly. But as the sintering temperature further increase to 600°C, the open circuit voltage and short circuit current began to decrease. The test results show that sintering temperature at 550°C has significant effect in promoting photoelectric properties. The improvement of electric properties is from the crystallization of TiO$_2$. As shown in Figure 5, after sintering from 350°C to 550°C, anatase crystal phase is formed in TiO$_2$ film which is beneficial to the photoelectric properties. As the sintering temperature increase, the intensity of the anatase crystal peaks becomes stronger, the open circuit voltage and short current increase accordingly. The result shows that the crystallization of anatase phase plays important role in DSSC photoelectric properties.

4 CONCLUSION

TiO$_2$ films are successfully fabricated by sol-gel dip-coating method on conducting glass substrate. It shows from X-ray diffraction patterns, in the range of 350°C- 550°C, anatase is the main crystal phase after sintering process. Only as the temperature increased to 550°C, small crystal peaks from rutile phase appear. The transmittance property tests show that the TiO$_2$ films
can transmit infrared, visible and ultraviolet light, the transmissivity of TiO₂ films are decreased as the coating layer increase. The TiO₂ films as photo anodes in dye sensitized solar cell, after sintering at 550°C, can get max open circuit voltage and short circuit current.

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REFERENCE


