JOURNALOF

Ceramic Processing Research

# The effect of different TiO<sub>2</sub> passivating layers on the photovoltaic performance of dye-sensitized solar cells

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The aim of this study is to prevent back transfer of electrons due to direct contact between the electrolyte and the FTO glass substrate using a  $TiO_2$  passivating layer. The  $TiO_2$  sol was prepared by a sol-gel method, and the  $TiO_2$  was coated on the FTO glass by spin coating method. The crystalline structure was adjusted by various catalyst concentrations: 0.1 mol, 0.5 mol. As With an increase in the catalyst concentration, the crystalline structure of the  $TiO_2$  passivating layer become the rutile phase. A nanoporous  $TiO_2$  upper layer was deposited by a screen printing method on the  $TiO_2$  passivating layer. The optical transmittance and particle size of the  $TiO_2$  passivating layer depend on the crystalline structure of the  $TiO_2$  passivating layer. The dye-sensitized solar cell was influenced by the crystalline structure of the  $TiO_2$  passivating layer. The dye-sensitized solar cell was influenced by the crystalline structure of the  $TiO_2$  passivating layer. The dye-sensitized solar cell was influenced by the crystalline structure of the  $TiO_2$  passivating layer. The dye-sensitized solar cell was influenced by the crystalline structure of the TiO\_2 passivating layer. Solar cell using a  $TiO_2$  passivating layer of the rutile phase was measured to have a maximum conversion efficiency of 3.98 % due to the effective prevention of an electron recombination to the electrolyte.

Key words: DSSCs, Passivating layer, TiO<sub>2</sub>, Spin coating

## Introduction

Dye-sensitized solar cells (DSSCs) have been intensively studied since the discovery of them in 1991 [1]. There is currently considerable interest in DSSCs for use in a new generation of energy harvesting devices due to the simple structure and process, low cost fabrication, transparency, color control, and applicability in flexible DSSCs [2-4]. DSSCs consist of a wide bandgap nanoporous metal oxide film such as TiO<sub>2</sub> deposited on a conductive oxide layer as an electron transport layer. Nanoporous TiO<sub>2</sub> is commonly used in DSSCs to embed a high density of dye molecules onto the TiO<sub>2</sub> surface to hence enhance the photo-absorption process. However, the highly porous structure of the TiO<sub>2</sub> layer may cause an electrical short circuit between the electrolyte and the transparent conducting oxide (TCO). To avoid this problem, sol-gel processed TiO<sub>2</sub> is used as a compact layer in DSSCs [5]. During the last decade, many studies have been reported on the electrode modification of TiO<sub>2</sub>. The purpose of electrode modification is to decrease the number of electron recombinations at the interface between the TCO and electrolyte [6-8]. Electron transport was therefore found to be slower in more porous films. Also the  $TiO_2$ particle the size has been investigated; increasing size was found to lead to faster electron transport and

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slower recombination [9].

In this study, we have prepared  $TiO_2$  passivating layers using a spin coating method. We will show the efficiency of a DSSC can be improved by introduction of  $TiO_2$  thin films as an electron recombination blocking layer.

# **Experimental**

# Preparation of the TiO<sub>2</sub> Passivating Layers

TiO<sub>2</sub> passivating layers were prepared by a spin coating method of the TiO<sub>2</sub> sol on a SnO<sub>2</sub> : F glass (denoted FTO). The TiO<sub>2</sub> sol was prepared by a sol gel method with various catalyst concentrations. TiO<sub>2</sub> sol was prepared based on a previous report [10]. The spinning rate of the substrate was 3000 rpm. The films were annealed at various temperatures for 1hour to obtain the desired crystallinity of the TiO<sub>2</sub>. Table 1 shows the manufacturing conditions of TiO<sub>2</sub> passivating

**Table 1.** Conditions of  $TiO_2$  passivating layers with different catalyst concentrations and annealing temperatures

	Catalyst concentrations	Annealing temperatures
A type	0.1 mol	500 °C
B type	0.1 mol	550 °C
C type	0.1 mol	600 °C
D type	0.1 mol	650 °C
E type	0.5 mol	500 °C
F type	0.5 mol	550 °C
G type	0.5 mol	600 °C
H type	0.5 mol	650 °C

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layers.

At above 0.5 mol of catalyst concentration, the  $TiO_2$  passivating layers was collapsed and could not be used as passivating layers. This would increase the possibility of the electron recombination between the FTO and the electrolyte.

# Preparation of Nanoporous TiO<sub>2</sub> Upper Layer

Tetra titanium isopropoxide (TTIP, Aldrich Chemical), ethyl alcohol, nitric acid, and DI water were used as the starting materials.

The TiO<sub>2</sub> powders were manufactured by a sol gel method, and TiO<sub>2</sub> pastes were prepared as a reference [11]. Nanoporous TiO<sub>2</sub> upper layers 5  $\mu$ m thick were coated on the TiO<sub>2</sub> passivating layer-coated FTO glass using a screen printing method. The prepared TiO<sub>2</sub> electrode was sintered at 450 °C for 1 hour in air.

#### **Fabrication of DSSC**

The TiO<sub>2</sub> working electrodes were allowed to cool to 100 °C before immersion into the 0.5 mM dye complex of ruthenium (II), commonly referred to as N719 in an ethanol solution for 24 hours. Excess dye was removed by rinsing with ethanol. The counter electrodes were prepared by dropping a 5 mM H<sub>2</sub>PtCl<sub>6</sub> solution onto FTO glass and heating at 450 °C for 30 minutes.

The dye-adsorbed  $TiO_2$  electrodes and the Pt-counter electrodes were assembled into a sandwich type cell using hot-melt sealant and were laminated for 10 minutes at 100 °C. The electrolyte was introduced through a hole in the counter electrode that was sealed afterwards. The active area of the solar cells was 1.0 cm<sup>2</sup>.

#### Characterization

The phase identification of the prepared  $TiO_2$  thin film was performed by means of X-ray diffraction (XRD, Rigaku D/MAX-2200). The morphology and particle size of the  $TiO_2$  thin film were investigated with field-emission scanning electron microscopy (FE-SEM, HITACHI S-4700). The transmittance of the passivating layer was measured using a UV spectrometer (Agilent, UV-vis 8453).

Photocurrent-voltage measurements was performed using an I-V solar simulator (Oriel, Soalr simulator). A solar simulator equipped with a 450 W Xenon lamp was used as a light source.

#### **Results and Discussion**

Fig. 1. and Fig. 2. show the XRD patterns of the  $TiO_2$  passivating layers annealed at the various temperatures. The observed X-ray peaks are due to the FTO back contact and other phase on labelled.

Fig. 1 shows XRD patterns of the passivating layers prepared at a 0.1 mol of catalyst concentration. The XRD pattern of the TiO<sub>2</sub> passivating layer annealed at 500 °C shows prominent anatase peaks  $25.4^{\circ}$  (101), and



**Fig. 1.** XRD patterns of  $\text{TiO}_2$  passivating layers prepared at 0.1 mol catalyst concentration with different annealing temperatures. (a) 500 °C (b) 550 °C, (c) 600 °C, (d) 650 °C ( $\bigoplus$  : anatase phase,  $\blacktriangle$  : rutile phase  $\blacksquare$  : FTO phase).



**Fig. 2.** XRD patterns of TiO<sub>2</sub> passivating layers prepared at 0.5 mol catalyst concentration with different annealing temperatures. (a) 500 °C (b) 550 °C, (c) 600 °C, (d) 650 °C (●: anatase phase,  $\blacktriangle$ : rutile phase  $\blacksquare$ : FTO phase).

48° (200). The XRD pattern of the film annealed at 650 °C shows that all the peaks, at 27.4° (110), 36.1° (101), and 56.6° (220), can be assigned to the rutile phase [12]. A mixture of the anatase phase and rutile phase was revealed when the TiO<sub>2</sub> passivating layer was annealed at 550 °C and 600 °C.

Fig. 2 shows XRD patterns of the passivating layers prepared at a 0.5 mol of catalyst concentration. The XRD pattern of the TiO<sub>2</sub> passivating layer annealed at 500 °C shows evidence only of the anatase phase of TiO<sub>2</sub>. The passivating layer at 550 °C, exhibits good crystallinity with both anatase and rutile peaks. The passivating layers at 600 °C and 650 °C show rutile peaks (110). It is clearly evident that the rutile characteristic peaks become stronger than the anatase characteristic peaks with an increase of the annealing temperature. When compareing with 0.1 mol and 0.5 mol, catalyst concentraties at 0.5 mol the shift to rutile was easier than at 0.1 mol as the with an increase in the annealing temperature.



Fig. 3. FE-SEM images showing cross sectional views of TiO<sub>2</sub> passivating layers annealed at 500 °C: (a) 0.1 mol, (b) 0.5 mol.

Field-emission scanning electron microscopy (SEM) was used to study the morphology of the TiO<sub>2</sub> films. Fig. 3 shows surface SEM images of TiO<sub>2</sub> passivating layer-deposited FTO glasses. From the surface SEM images, the TiO<sub>2</sub> particles exhibit spherical shpes. With an increasing in the temperature, the grain size became large with agglomeration. At 0.1 mol, the grain size has increased to 50 nm at 650 °C. At 0.5 mol, the grain size has increased to 75 nm at 650 °C. The grain size of the TiO<sub>2</sub> passivating layer prepared at 0.5 mol is generally larges compared with the passivating layer of 0.1 mol. It was observed that the TiO<sub>2</sub> films transformed into the rutile phase, which has a more stable structure, as

the catalyst concentration increases, and it shows the fact that it influences the size of the first particle.

Cross sectional views of the passivating layers prepared with different catalyst concentrations on FTO glass are shown in Fig. 4. The FE-SEM images clearly indicate that they are comprised of three parts. The top one is the TiO<sub>2</sub> passivating layer and lowest one is the FTO substrate. The SEM images reveal that the films were uniform, smooth and crack-free on the surface. According to the SEM results, the thicknesses of the TiO<sub>2</sub> passivating layers were estimated to be each 480 nm, and 410 nm at 0.1 mol, and 0.5 mol. It seems that the thickness of the TiO<sub>2</sub> passivating layer prepared with



Fig. 4. FE-SEM images of  $TiO_2$  passivating layers prepared at 0.1 mol and 0.5 mol catalyst concentration with different annealing temperatures.



Fig. 5. Optical transmittance spectra of the  $TiO_2$  passivating layers with 0.1 mol catalyst concentration.

different catalyst concentrations does not change much.

Fig. 5 shows the optical transmittance spectra of the FTO glass substrate coated by the TiO<sub>2</sub> passivating layer at different annealing temperatures. At 550 nm wavelength, the TiO<sub>2</sub> passivating layer annealed at 500 °C showed an identical transmittance of 89 % to that of the bare FTO glass sample. An Increase in the annealing temperature leads to a decrease in the transmittance. In the case of the TiO<sub>2</sub> passivating layer annealed at 650 °C, it shows a decreased optical transmittance of



Fig. 6. Optical transmittance spectra of the  $TiO_2$  passivating layers with 0.5 mol catalyst concentration.



**Fig.** 7. I-V characteristics of DSSCs using  $TiO_2$  passivating layers prepared at 0.1 mol catalyst concentration.

#### 76 % at 550nm wavelength.

Fig. 6 shows the transmittance of the passivating layers with 0.5 mol catalyst concentration. The transmittance of the films is decreased by an increase of the annealing temperature. At 550 nm wavelength, the passivating layer annealed at 500 °C showed an identical transmittance of 67 %. The optical transmittance of the passivating layer annealed at 650 °C showed 50 % at 550 nm wavelength. The transmittance of the TiO<sub>2</sub> films prepared at 0.5 mol is considerably reduced in the visible region of 400-800 nm compared with TiO<sub>2</sub> films prepared at 0.1 mol. The films turn out to be translucent when annealed at these higher temperatures. This is due to the adsorption resulting from the phase transformation from the anatase-to-the rutile phase, and the light scattering increases with the crystallite size of the thin films and the grain agglomeration.

Fig. 7 and Fig. 8 show current-voltage curves of DSSCs obtained under 100 mW/cm<sup>2</sup> illumination with the AM 1.5G condition of the DSSCs fabricated using  $TiO_2$  passivating layers prepared with various conditions. One of the most important parameters for a solar cell is



Fig. 8. I-V characteristics of DSSCs using  $TiO_2$  passivating layers prepared at 0.5 mol catalyst concentration.

its photoelectric conversion efficiency, i.e. the ratio of the output power to the incident power. The energy conversion efficiency  $\eta$  is estimated as:

$$\eta = \frac{VocJscFF}{Ps} \tag{1}$$

Where Voc is the open circuit voltage, Jsc is the integral photocurrent density, FF is the fill factor:

$$FF = \frac{VmJm}{VocJsc},\tag{2}$$

and Ps is the intensity of the incident light [13].

The efficiency, fill factor, open circuit voltage, and integral photocurrent for the solar cells are summarized in Table 2.

From the Fig. 7, the DSSC using a passivating layer annealed at 600 °C was observed to have a higher conversion efficiency, with a photocurrent density (Jsc) of 9.89 A/cm<sup>2</sup>, an open circuit potential (Voc) of 0.766 V and a cell conversion efficiency of 3.83 %. From the Fig. 8, the DSSC using a 0.5 mol TiO<sub>2</sub> passivating layer annealed at 600 °C was observed to have the highest efficiency, with a photocurrent density (Jsc) of 11.80 A/cm<sup>2</sup>, an open circuit potential (Voc) of 0.758 V and a cell conversion efficiency of 3.98 %. This indicates that a TiO<sub>2</sub> passivating layer of the rutile phase can act

**Table 2.** The effect of  $TiO_2$  passivating layers on the performance of DSSC

Sample		Voc (V)	Jsc (A/cm <sup>2</sup> )	FF (%)	η (%)
0.1 mol	500 °C	0.766	9.13	47.38	3.54
	550 °C	0.782	9.71	47.38	3.59
	600 °C	0.766	9.89	50.61	3.83
	650 °C	0.764	9.47	43.86	3.17
0.5 mol	500 °C	0.764	10.1	45.48	3.51
	550 °C	0.792	10.8	44.19	3.76
	600 °C	0.758	11.8	44.5	3.98
	650 °C	0.802	8.7	43.22	3.01

as a high quality electron recombination blocking layer.

However, a further increase in the annealing temperature of the TiO<sub>2</sub> film up to 650 °C resulted in a decrease of Jsc  $(8.7 \text{ A/cm}^2)$  due to a decreased conductivity for electron transfer from the nanoporous TiO<sub>2</sub> layer to the FTO. Comparing the 0.1 mol and 0.5 mol, revealed that fill factors were lowered with an increase of the particle size. It seems that the FF was related to the optical transmittance of the TiO<sub>2</sub> passivating layer. However, the behavior observed oh the photo current density (Jsc) was opposite. It was found that particle size of the TiO<sub>2</sub> passivating layer influenced the photocurrent density. An increase of Jsc is generally related to an enhancement of the number of photogenerated electrons which are efficiently transferred to the TiO<sub>2</sub> electrode [14]. From this it is deduced that as the catalyst concentrations is increased, the grain size and crystalline structure of the TiO<sub>2</sub> passivating layer highly affects the conversion efficiency of the DSSC.

## Conclusion

In this study, different TiO<sub>2</sub> passivating layers, coated by a spin coating method, were introduced between transparent conducting substrates and nanoporous TiO<sub>2</sub> films. The optical transmittance and particle size of the passivating layer depend on its crystalline structure. The passivating layer, coated with 0.5 mol catalyst concentration and annealed at 550 °C, shows the highest efficiency (3.98%). It can be said that the improved fill factor after the passivating layer formation could be associated with the an improved optical transmittance. The photocurrent density enhancement could be ascribed to the formation of a passivating layer on the surface of the FTO, which suppresses the recombination at the FTO/electrolyte interface. This revealed that the crystallinity of the passivating layer has an important effect on smooth electron movement due to the suitable energy band potentials.

# Acknowledgment

This work was supported by the Human Resources Development of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Knowledge Economy (No. 20104010100510).

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