

## Influence of $\text{TiCl}_4$ treatment on performance of dye-sensitized solar cell assembled with nano- $\text{TiO}_2$ coating deposited by vacuum cold spraying

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**Abstract:** Titanium tetrachloride ( $\text{TiCl}_4$ ) treatment was employed to  $\text{TiO}_2$  coating deposited on fluoride-doped tin oxide (FTO) conducting glass and indium oxide doped tin oxide (ITO) conducting glass, respectively. The nano-crystalline  $\text{TiO}_2$  coating was deposited using a composite powder composed of polyethylene glycol (PEG) and 25 nm  $\text{TiO}_2$  particles by vacuum cold spraying (VCS) process. A commercial N-719 dye was used to adsorb on the surface of  $\text{TiO}_2$  coating to prepare  $\text{TiO}_2$  electrode, which was applied to assemble dye-sensitized solar cell (DSC). The cell performance was measured under simulated solar light at an intensity of  $100 \text{ mW} \cdot \text{cm}^{-2}$ . Results show that with an FTO substrate the DSC composed of a VCS  $\text{TiO}_2$  electrode untreated by  $\text{TiCl}_4$  gives a short-circuit current density of  $13.1 \text{ mA} \cdot \text{cm}^{-2}$  and an open circuit voltage of 0.60 V corresponding to an overall conversion efficiency of 4.4%. It is found that after  $\text{TiCl}_4$  treatment to the VCS  $\text{TiO}_2$  electrode with an FTO substrate, the short circuit current density of the cell increases by 31%, the open-circuit voltage increases by 60 mV and a higher conversion yield of 6.5% was obtained. However, when an ITO substrate is used to deposit  $\text{TiO}_2$  coating by VCS, after  $\text{TiCl}_4$  treatment, the conversion efficiency of the assembled cell reduces slightly due to corrosion of the conducting layer on the ITO glass by  $\text{TiCl}_4$ .

**Key words:** titanium tetrachloride treatment; vacuum cold spraying; dye-sensitized solar cell; nano-crystalline  $\text{TiO}_2$  coating

### 1. Introduction

Since a highly efficient dye-sensitized solar cell (DSC) was reported by Grätzel *et al.* [1], DSC has become the most promising alternative to conventional silicon solar cell and has been currently investigated extensively [2-3]. Titanium dioxide ( $\text{TiO}_2$ ) is one of the key components influencing the performance of DSC. A high surface area of DSC electrode can be achieved using nano- $\text{TiO}_2$  coating, which leads to high light harvesting by a monolayer of sufficiently adsorbed dye [4].

Many methods including doctor blade [2], mechanical compression [5], electrophoretic deposition [6] and hydrothermal crystallization

[7] have been employed to deposit nano-crystalline  $\text{TiO}_2$  electrode in DSC. Among those methods, doctor blade technique has been more widely employed to prepare nano- $\text{TiO}_2$  coating from colloids [2]. This approach can deposit a porous electrode with high surface area. However, the electrical contiguity, which influences electron transfer in  $\text{TiO}_2$  electrode, at the interfaces between  $\text{TiO}_2$  particles in the coating and at the interface between conducting glass and  $\text{TiO}_2$  film was limited due to weak interfaces bonding. It was found that the electrical contiguity was also influenced by  $\text{TiO}_2$  coating deposition method and its microstructure. An acceptable conversion yield has been reported for the DSCs employing the electrodes made from  $\text{TiO}_2$  nano-wires having high orientation than

TiO<sub>2</sub> nano-particles by doctor blade [8-9]. Using chemical technologies [10] such as mixed template method [11], TiO<sub>2</sub> coating with perfect electrical contiguity could be deposited using common spherical particles. Therefore, a chemical treatment using aqueous TiCl<sub>4</sub> solution was applied to doctor blade TiO<sub>2</sub> coating to improve the photovoltaic performance of the cell [2]. A better electrical contiguity was formed at the interfaces both between particles in TiO<sub>2</sub> coating and between conducting glass and TiO<sub>2</sub> film through TiCl<sub>4</sub> treatment [12-13].

Our previous study demonstrated that vacuum cold spraying (VCS) using an agglomerated powder of polyethylene glycol (PEG) and nano-sized TiO<sub>2</sub> particles is a promising method to deposit nano-structured TiO<sub>2</sub> coating effective to DSC [14]. Dye-sensitized solar cell assembled with VCS TiO<sub>2</sub> coating presented a promising performance when a composite powder containing PEG of 40% - 60% was used [14]. This fact suggests that a good electrical contiguity is achieved at the interfaces between nano-TiO<sub>2</sub> particles in the coating by high particle impact during spraying. However, using PEG in the composite powder may limit the contact between TiO<sub>2</sub> particles and subsequently electrical contiguity. It can be considered that the electrical contiguity of VCS nano-TiO<sub>2</sub> coating can be improved by chemical treatment using TiCl<sub>4</sub>, which consequently leads to an improved DSC performance.

In this study, a composite powder composed of 25 nm TiO<sub>2</sub> particles (P25) and PEG was used to deposit TiO<sub>2</sub> coatings on both fluoride-doped tin oxide (FTO) conducting glass and indium oxide doped tin oxide (ITO) conducting glass by vacuum cold spraying (VCS) process. TiCl<sub>4</sub> treatment was applied to the TiO<sub>2</sub> coating to further improve the electric contiguity of TiO<sub>2</sub> electrode. The photovoltaic performance of a dye-coated VCS TiO<sub>2</sub> electrode was measured by assembling a dye-sensitized solar cell. The influence of TiCl<sub>4</sub> treatment and conducting glass substrate on cell performance was discussed.

## 2. Experimental

### 2.1. Preparation of composite TiO<sub>2</sub> powder and TiCl<sub>4</sub> solution

6 g PEG ( $M_w = 10000$ ) was dissolved in alcohol to form solution A. 10 g nano-TiO<sub>2</sub> powder (P25, Degussa) was dispersed in 250 ml alcohol to form suspension B under ultrasonic stirring for 1 h. The solution A was added to suspension B drop by drop to prepare a colloid C which was ultrasonically stirred for another 1 h. The colloid C was distilled in a rotatory evaporator for an hour, resulting in dry composite powder of TiO<sub>2</sub> and PEG. The composite powder was crushed in mortar and filtered to a sub-micrometer size for deposition.

A 0.05 mol · L<sup>-1</sup> TiCl<sub>4</sub> solution was prepared using liquid TiCl<sub>4</sub> which was added into water ice kept at -20 °C to make a 2 mol · L<sup>-1</sup> TiCl<sub>4</sub> solution. This solution was further diluted to 0.05 mol · L<sup>-1</sup>.

### 2.2. Preparation of TiO<sub>2</sub> coating and TiCl<sub>4</sub> treatment

TiO<sub>2</sub> coating was deposited on both FTO (15 Ω/□, TEC-15, LOF) and ITO (8 Ω/□, STN-180, Nanbo) conducting glass substrates using vacuum cold spraying system developed in our laboratory. The system constituted of a vacuum chamber, a vacuum pump, an accelerating gas feeding unit, a particle accelerating nozzle, a two dimensional worktable and a control unit. The acceleration of TiO<sub>2</sub> particles was performed by high pressure He gas. Spray parameters are given in Table 1.

TiO<sub>2</sub> coating of a thickness of 15 μm prepared by VCS process, with an effective area of

Table 1. Vacuum cold spraying parameters

Chamber pressure/Pa	$2.3 \times 10^2$
Pressure of the aerosol room/Pa	$1 \times 10^6$
He gas flow/(L · min <sup>-1</sup> )	2
Distance from nozzle exit to substrate/mm	5
Orifice size of nozzle/(mm × mm)	$2.5 \times 0.2$
Substrate traverse speed/(mm · s <sup>-1</sup> )	1 ~ 5

$0.2 \text{ cm}^2$  was sintered at  $450^\circ\text{C}$  for 30 min with a heating speed of  $3^\circ\text{C} \cdot \text{min}^{-1}$ .  $\text{TiO}_2$  coating deposited on the FTO substrate was dipped in a  $0.05 \text{ mol} \cdot \text{L}^{-1}$  aqueous  $\text{TiCl}_4$  solution at  $70^\circ\text{C}$  for 30 min, while the coating deposited on the ITO substrate was dipped in  $\text{TiCl}_4$  solution at  $60^\circ\text{C}$  for 10 min. After washed with distilled water,  $\text{TiCl}_4$  treated VCS  $\text{TiO}_2$  coating was resintered at  $500^\circ\text{C}$  for 20 min [2, 13].

### 2.3. Fabrication of dye-sensitized solar cell

$\text{TiO}_2$  coating was immersed in a  $3 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$  alcohol solution of dye (N719, Solaronix) for 24 h at room temperature for dye adsorption. After it was rinsed with absolute alcohol and dried, dye-coated  $\text{TiO}_2$  electrode was soaked in  $0.3 \text{ mol} \cdot \text{L}^{-1}$  4-tertButylPyridine (4-tBP) solution in acetonitrile for 45 min. Then, it was dried and assembled to a sandwich-type solar cell with a Pt counter electrode and a  $40 \mu\text{m}$ -thick tape spacer (Zhengtai). The electrolyte was composed of  $0.4 \text{ mol} \cdot \text{L}^{-1}$  LiI and  $0.04 \text{ mol} \cdot \text{L}^{-1}$   $\text{I}_2$  solution. The solution was made by dissolving LiI and  $\text{I}_2$  in acetonitrile.

### 2.4. Characterization of coating and photoelectrochemical measurements

The Brunauer-Emmett-Teller (BET) surface area and porosity of  $\text{TiO}_2$  coating were determined using nitrogen adsorption apparatus (Coulter SA 3100 plus, Beckman Coulter) with all samples degassed at  $200^\circ\text{C}$ . The thickness of the coating was measured by scanning electron microscopy (SEM) (Quanta 200).

The performance of the dye-sensitized solar cell was examined using a 500 W Xeon light source (CHF-500W, Chuangtuo) equipped with a Chuangtuo RGB-3 filter at an intensity of  $100 \text{ mW} \cdot \text{cm}^{-2}$  (A.M. 1.5). The photocurrent-voltage characteristics were tested through the approach reported in the reference [15]. A  $1000 \Omega$  slide rheostat was used as the load in the outer circuit. The conversion efficiency ( $\eta$ ) of the cell was characterized by the short-circuit photocurrent density, the open-circuit voltage, the fill factor of the cell and the intensity of the

incident light.

## 3. Results and discussion

### 3.1. Influence of $\text{TiCl}_4$ treatment on performance of cell using FTO substrate

Fig. 1 shows photocurrent-voltage characteristics of solar cells composed of  $\text{TiO}_2$  coating deposited on FTO substrates treated with  $\text{TiCl}_4$  in comparison of that without  $\text{TiCl}_4$  treatment. It can be seen that the cell without  $\text{TiCl}_4$  treatment presented a short-circuit current density of  $13.1 \text{ mA} \cdot \text{cm}^{-2}$ , an open circuit voltage of  $0.60 \text{ V}$  and an overall conversion efficiency of  $4.4\%$ . While after  $\text{TiCl}_4$  treatment at  $70^\circ\text{C}$  for 30 min, the short circuit current density and open circuit voltage of the solar cell were increased to  $17.1 \text{ mA} \cdot \text{cm}^{-2}$  and  $0.66 \text{ V}$ , respectively which resulted in a higher conversion efficiency of  $6.5\%$ . Compared with the cell without  $\text{TiCl}_4$  treatment, after applying  $\text{TiCl}_4$  treatment, the short circuit current density, open circuit voltage and conversion efficiency of the cell were increased by  $31\%$ ,  $10\%$  and  $48\%$ , respectively.

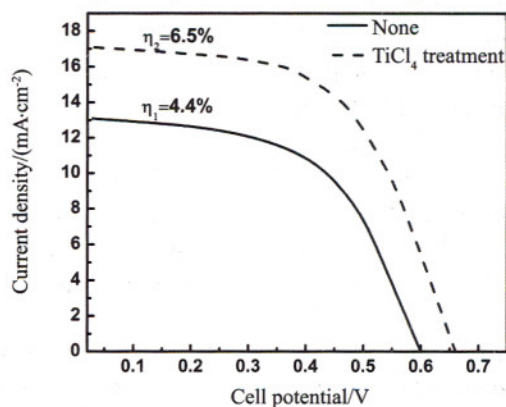


Fig. 1. Photocurrent-voltage characteristics of dye-sensitized solar cells composed of  $\text{TiO}_2$  coating deposited on FTO conducting glass by vacuum cold spraying with/without  $\text{TiCl}_4$  treatment at  $70^\circ\text{C}$  for 30 min.

Electron transport in the mesoporous  $\text{TiO}_2$  electrode is assumed to proceed by diffusion because of the absence of a significant electrical potential gradient in the film [16-17]. Necks between  $\text{TiO}_2$  particles, as the electron diffusion

path, significantly influence the electron transport properties which could be characterized by effective diffusion coefficient,  $D_e$  [18]. Effective connection between  $\text{TiO}_2$  particles promotes photo-injected electron transport in nano-crystalline  $\text{TiO}_2$  coating. It can be considered that the increase of short circuit current density resulted from improvement of the electrical continuity at the interfaces between  $\text{TiO}_2$  particles in the coating and between glass substrate and the coating through  $\text{TiO}_2$  particle-necking after  $\text{TiCl}_4$  treatment.  $\text{TiCl}_4$  treatment to VCS  $\text{TiO}_2$  coating has enhanced the  $\text{TiO}_2$  particle-necking, which leads to a decrease of electron transport path and thus a depression of charge recombination between electron on  $\text{TiO}_2$  and oxidant in electrolyte, and consequently an increase in the short circuit current density.

For a VCS  $\text{TiO}_2$  coating, the porosity measured by BET approach was 57%, the mean pore size was 33 nm, and the BET special surface area was  $55 \text{ m}^2 \cdot \text{g}^{-1}$ . For a  $\text{TiCl}_4$ -treated VCS  $\text{TiO}_2$  coating, the porosity decreased to 51% with a mean pore size of 31 nm, and the BET special surface area decreased to  $51 \text{ m}^2 \cdot \text{g}^{-1}$ . On the other hand, it was found that after  $\text{TiCl}_4$  treatment the weight of a  $15 \text{ cm}^2$  VCS  $\text{TiO}_2$  coating increased by 14.7%. Hence, the actual surface area of  $\text{TiO}_2$  coating, a product of BET surface area and weight of  $\text{TiO}_2$  coating, increased by 6.4%. This could lead to an improvement of dye uptake density and thus an increase in cell's short circuit current density. Ito *et al.* [19] reported a 19% enhancement in actual surface area of  $\text{TiO}_2$  coating prepared by doctor blade using 20 nm  $\text{TiO}_2$  powder after  $\text{TiCl}_4$  treatment and a resulting increase of the short circuit current density by 10% calculated from the reported data. The present result above is consistent with that reported by Ito *et al.* Therefore, the increase in  $\text{TiO}_2$  actual surface area after  $\text{TiCl}_4$  treatment is also one factor contributing improvement of cell performance.

It was also found that the open circuit voltage of the cell was increased by 60 mV after the

$\text{TiO}_2$  coating was treated by  $\text{TiCl}_4$ . Open circuit voltage can be calculated from the diode equation [20],

$$V_{oc} = (nRT/F) \ln[(i_{sc}/i_0) - 1] \quad (1)$$

where  $n$  is the ideality factor, whose value is between 1 and 2;  $i_{sc}$  is short circuit current,  $i_0$  is the reverse saturation dark current and  $R$  and  $F$  are the ideal gas constant and Faraday's constant, respectively. Supposing that dark current was not changed by  $\text{TiCl}_4$  treatment, using 2 as a value for the ideality factor in a DSC, a voltage increase by 60 mV meant at least a three-fold increase in  $i_{sc}$  according to equation 1. However, only 31% increase in  $i_{sc}$  was observed. This fact suggests that the dark current must be suppressed after  $\text{TiCl}_4$  treatment. Ito *et al.* [19] also reported that the dark current was reduced after  $\text{TiCl}_4$  treatment. The dark current is partially resulted from direct exposure of FTO glass to electrolyte due to incomplete covering of  $\text{TiO}_2$  on FTO substrate. On FTO surface where is not covered fully by  $\text{TiO}_2$  particles, the exposed part of the FTO to electrolyte may play a role as electrode catalyzing charge recombination reaction of electron and  $\text{I}_3^-$ . Zhu *et al.* [21] pointed out that recombination occurs predominantly near the FTO substrate. After  $\text{TiCl}_4$  treatment, a  $\text{TiO}_2$  thin layer could be deposited on exposed part of FTO and the charge recombination is limited, which contributes to the increase in the open circuit voltage.

### 3.2. Influence of $\text{TiCl}_4$ treatment on performance of cell using ITO substrate

Fig. 2 shows photocurrent-voltage characteristics of solar cells composed of  $\text{TiO}_2$  coating deposited by VCS process using ITO substrates after  $\text{TiCl}_4$  treatment. For comparison, the photocurrent-voltage curve of the cell assembled with the as-deposited  $\text{TiO}_2$  coating is also presented in Fig. 1. A short-circuit current density of  $12.3 \text{ mA} \cdot \text{cm}^{-2}$  and a conversion efficiency of 4.1% were obtained for the cell using the as-deposited  $\text{TiO}_2$  coating. Those results were slightly lower than using FTO as a substrate. This is attributed to higher electrical resistance

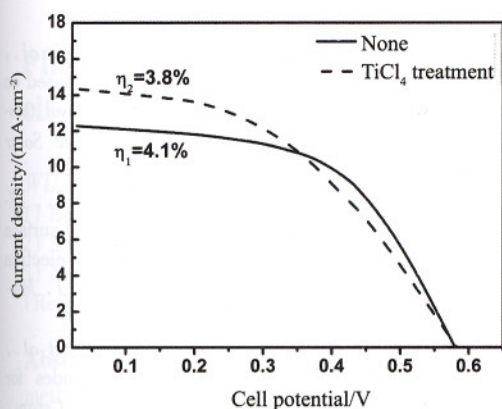


Fig. 2. Photocurrent-voltage characteristics of dye-sensitized solar cells composed of  $\text{TiO}_2$  coating deposited on ITO conducting glass by vacuum cold spraying with/without  $\text{TiCl}_4$  treatment at  $60^\circ\text{C}$  for 10 min.

of ITO conducting glass than FTO glass. It was observed that the electrical resistance of the ITO glass was increased by three folds after sintering at  $450^\circ\text{C}$ , while the electrical resistance of the FTO glass was not changed after sintering. It can be observed that the influence of  $\text{TiCl}_4$  treatment on the performance of the cell using an ITO substrate was different from that using the FTO substrate. After  $\text{TiCl}_4$  treatment at  $60^\circ\text{C}$  for 10 min, the short circuit current density was increased to  $14.3\text{ mA}\cdot\text{cm}^{-2}$ , while VOC almost retained the same level. Moreover, the conversion efficiency was decreased slightly to 3.8% due to a relatively low fill factor of 0.455. When ITO glass was immersed in  $50\text{ mmol}\cdot\text{L}^{-1}$  aqueous  $\text{TiCl}_4$  solution at  $70^\circ\text{C}$ , it was found that ITO electrical resistance increased with immersing time and became infinite after 70 min (Fig. 3). Therefore, the change of the cell's performance is associated with destruction of ITO conducting layer during  $\text{TiCl}_4$  treatment.  $\text{In}_2\text{O}_3$ , the key conducting component in ITO glass, can be dissolved in  $\text{TiCl}_4$  by the following reaction [22],

$$\text{TiCl}_4 + \text{H}_2\text{O} = \text{Ti}(\text{OH})\text{Cl}_3 + \text{H}^+$$

$$\text{In}_2\text{O}_3 + 6\text{H}^+ = 2\text{In}^{3+} + 3\text{H}_2\text{O} \quad (2)$$

The conducting layer in ITO glass becomes thin due to corrosion of  $\text{In}_2\text{O}_3$ , resulting in the decrease of conductivity. From Fig. 3 it can al-

so be observed that the conductivity of FTO glass was not influenced by  $\text{TiCl}_4$  treatment within 70 min. According to the results shown in Fig. 3, after  $\text{TiCl}_4$  treatment at  $60^\circ\text{C}$  for 10 min, the electrical resistance of ITO glass was still lower than that of FTO glass. However, the dissolution of  $\text{In}_2\text{O}_3$  in ITO glass might destroy the contact of ITO with  $\text{TiO}_2$  coating, and hence increase the contact electrical resistance, which degraded the fill factor and thus conversion efficiency of the cell. A further evidence for dissolution of conducting layer on ITO was that after  $\text{TiCl}_4$  treatment for 30 min at  $60^\circ\text{C}$ , VCS  $\text{TiO}_2$  coating flaked away from ITO glass.

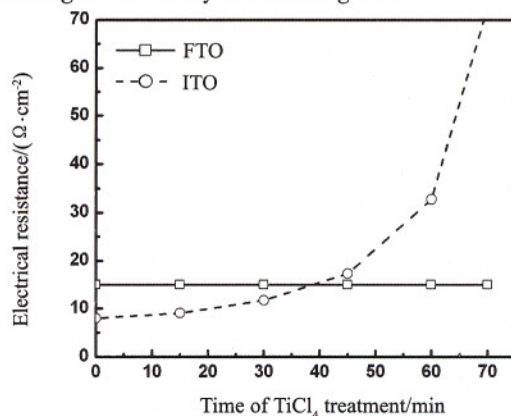


Fig. 3. Influence of  $\text{TiCl}_4$  treatment at  $70^\circ\text{C}$  on electrical resistance of FTO and ITO conducting glass, respectively.

#### 4. Conclusions

The performance of the DSC is significantly influenced by  $\text{TiCl}_4$  treatment to nano-crystalline  $\text{TiO}_2$  coating deposited by vacuum cold spraying using a composite powder of polyethylene glycol (PEG) and 25 nm  $\text{TiO}_2$  particles. With an FTO substrate, the  $\text{TiCl}_4$  treatment increases the short-circuit current density by 31% and the open-circuit voltage by 60 mV. The conversion yield is increased from 4.4% to 6.5%. The improvement in cell's photovoltaic performance is attributed to the enhancement of electrical contiguity at the interfaces between nano- $\text{TiO}_2$  particles in the coating and between  $\text{TiO}_2$  coating and conducting glass, an increase of surface area of  $\text{TiO}_2$  electrode, and a cover to

the interface between exposed part of FTO conducting glass and electrolyte. With an ITO substrate,  $\text{TiCl}_4$  treatment to  $\text{VCS TiO}_2$  coating causes the corrosion of the conducting layer on glass surface and reduces the cell's conversion efficiency.

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