

Influence of TiCl_4 treatment on performance of dye-sensitized solar cell assembled with nano- TiO_2 coating deposited by vacuum cold spraying

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(Received 2006-06-30)

Abstract: Titanium tetrachloride (TiCl_4) treatment was employed to 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 TiO_2 coating was deposited using a composite powder composed of polyethylene glycol (PEG) and 25 nm TiO_2 particles by vacuum cold spraying (VCS) process. A commercial N-719 dye was used to adsorb on the surface of TiO_2 coating to prepare 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 TiO_2 electrode untreated by 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 TiCl_4 treatment to the VCS 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 TiO_2 coating by VCS, after TiCl_4 treatment, the conversion efficiency of the assembled cell reduces slightly due to corrosion of the conducting layer on the ITO glass by TiCl_4 .

Key words: titanium tetrachloride treatment; vacuum cold spraying; dye-sensitized solar cell; nano-crystalline 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 (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- 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 TiO_2 electrode in DSC. Among those methods, doctor blade technique has been more widely employed to prepare nano- 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 TiO_2 electrode, at the interfaces between TiO_2 particles in the coating and at the interface between conducting glass and TiO_2 film was limited due to weak interfaces bonding. It was found that the electrical contiguity was also influenced by TiO_2 coating deposition method and its microstructure. An acceptable conversion yield has been reported for the DSCs employing the electrodes made from TiO_2 nano-wires having high orientation than

TiO₂ nano-particles by doctor blade [8-9]. Using chemical technologies [10] such as mixed template method [11], TiO₂ coating with perfect electrical contiguity could be deposited using common spherical particles. Therefore, a chemical treatment using aqueous TiCl₄ solution was applied to doctor blade TiO₂ coating to improve the photovoltaic performance of the cell [2]. A better electrical contiguity was formed at the interfaces both between particles in TiO₂ coating and between conducting glass and TiO₂ film through TiCl₄ treatment [12-13].

Our previous study demonstrated that vacuum cold spraying (VCS) using an agglomerated powder of polyethylene glycol (PEG) and nano-sized TiO₂ particles is a promising method to deposit nano-structured TiO₂ coating effective to DSC [14]. Dye-sensitized solar cell assembled with VCS TiO₂ 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-TiO₂ particles in the coating by high particle impact during spraying. However, using PEG in the composite powder may limit the contact between TiO₂ particles and subsequently electrical contiguity. It can be considered that the electrical contiguity of VCS nano-TiO₂ coating can be improved by chemical treatment using TiCl₄, which consequently leads to an improved DSC performance.

In this study, a composite powder composed of 25 nm TiO₂ particles (P25) and PEG was used to deposit TiO₂ 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. TiCl₄ treatment was applied to the TiO₂ coating to further improve the electric contiguity of TiO₂ electrode. The photovoltaic performance of a dye-coated VCS TiO₂ electrode was measured by assembling a dye-sensitized solar cell. The influence of TiCl₄ treatment and conducting glass substrate on cell performance was discussed.

2. Experimental

2.1. Preparation of composite TiO₂ powder and TiCl₄ solution

6 g PEG ($M_w = 10000$) was dissolved in alcohol to form solution A. 10 g nano-TiO₂ 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 TiO₂ and PEG. The composite powder was crushed in mortar and filtered to a sub-micrometer size for deposition.

A 0.05 mol · L⁻¹ TiCl₄ solution was prepared using liquid TiCl₄ which was added into water ice kept at -20 °C to make a 2 mol · L⁻¹ TiCl₄ solution. This solution was further diluted to 0.05 mol · L⁻¹.

2.2. Preparation of TiO₂ coating and TiCl₄ treatment

TiO₂ 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 TiO₂ particles was performed by high pressure He gas. Spray parameters are given in Table 1.

TiO₂ 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	2.3×10^2
Pressure of the aerosol room/Pa	1×10^6
He gas flow/(L · min ⁻¹)	2
Distance from nozzle exit to substrate/mm	5
Orifice size of nozzle/(mm × mm)	2.5×0.2
Substrate traverse speed/(mm · s ⁻¹)	1 ~ 5

0.2 cm^2 was sintered at $450 \text{ }^\circ\text{C}$ for 30 min with a heating speed of $3 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. TiO_2 coating deposited on the FTO substrate was dipped in a $0.05 \text{ mol} \cdot \text{L}^{-1}$ aqueous TiCl_4 solution at $70 \text{ }^\circ\text{C}$ for 30 min, while the coating deposited on the ITO substrate was dipped in TiCl_4 solution at $60 \text{ }^\circ\text{C}$ for 10 min. After washed with distilled water, TiCl_4 treated VCS TiO_2 coating was resintered at $500 \text{ }^\circ\text{C}$ for 20 min [2, 13].

2.3. Fabrication of dye-sensitized solar cell

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 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 $40 \text{ }\mu\text{m}$ -thick tape spacer (Zhengtai). The electrolyte was composed of $0.4 \text{ mol} \cdot \text{L}^{-1}$ LiI and $0.04 \text{ mol} \cdot \text{L}^{-1}$ I_2 solution. The solution was made by dissolving LiI and I_2 in acetonitrile.

2.4. Characterization of coating and photoelectrochemical measurements

The Brunauer-Emmett-Teller (BET) surface area and porosity of TiO_2 coating were determined using nitrogen adsorption apparatus (Coulter SA 3100 plus, Beckman Coulter) with all samples degassed at $200 \text{ }^\circ\text{C}$. 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 $1000 \text{ }\Omega$ slide rheostat was used as the load in the outer circuit. The conversion efficiency (η) 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 TiCl_4 treatment on performance of cell using FTO substrate

Fig. 1 shows photocurrent-voltage characteristics of solar cells composed of TiO_2 coating deposited on FTO substrates treated with TiCl_4 in comparison of that without TiCl_4 treatment. It can be seen that the cell without 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 V and an overall conversion efficiency of 4.4% . While after TiCl_4 treatment at $70 \text{ }^\circ\text{C}$ 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 V , respectively which resulted in a higher conversion efficiency of 6.5% . Compared with the cell without TiCl_4 treatment, after applying 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.

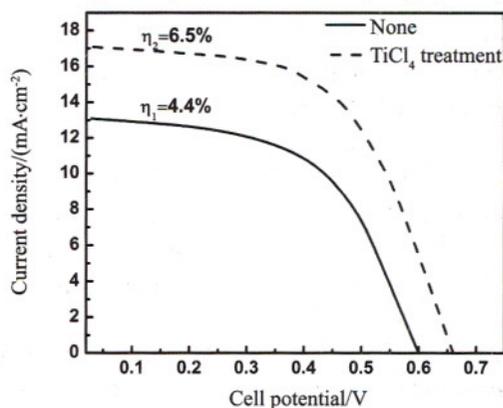


Fig. 1. Photocurrent-voltage characteristics of dye-sensitized solar cells composed of TiO_2 coating deposited on FTO conducting glass by vacuum cold spraying with/without TiCl_4 treatment at $70 \text{ }^\circ\text{C}$ for 30 min.

Electron transport in the mesoporous 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 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 TiO_2 particles promotes photo-injected electron transport in nano-crystalline 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 TiO_2 particles in the coating and between glass substrate and the coating through TiO_2 particle-necking after TiCl_4 treatment. TiCl_4 treatment to VCS TiO_2 coating has enhanced the TiO_2 particle-necking, which leads to a decrease of electron transport path and thus a depression of charge recombination between electron on TiO_2 and oxidant in electrolyte, and consequently an increase in the short circuit current density.

For a VCS 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 TiCl_4 -treated VCS 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 TiCl_4 treatment the weight of a 15 cm^2 VCS TiO_2 coating increased by 14.7%. Hence, the actual surface area of TiO_2 coating, a product of BET surface area and weight of 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 TiO_2 coating prepared by doctor blade using 20 nm TiO_2 powder after 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 TiO_2 actual surface area after 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

TiO_2 coating was treated by 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 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 TiCl_4 treatment. Ito *et al.* [19] also reported that the dark current was reduced after TiCl_4 treatment. The dark current is partially resulted from direct exposure of FTO glass to electrolyte due to incomplete covering of TiO_2 on FTO substrate. On FTO surface where is not covered fully by TiO_2 particles, the exposed part of the FTO to electrolyte may play a role as electrode catalyzing charge recombination reaction of electron and I_3^- . Zhu *et al.* [21] pointed out that recombination occurs predominantly near the FTO substrate. After TiCl_4 treatment, a 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 TiCl_4 treatment on performance of cell using ITO substrate

Fig. 2 shows photocurrent-voltage characteristics of solar cells composed of TiO_2 coating deposited by VCS process using ITO substrates after TiCl_4 treatment. For comparison, the photocurrent-voltage curve of the cell assembled with the as-deposited 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 TiO_2 coating. Those results were slightly lower than using FTO as a substrate. This is attributed to higher electrical resistance

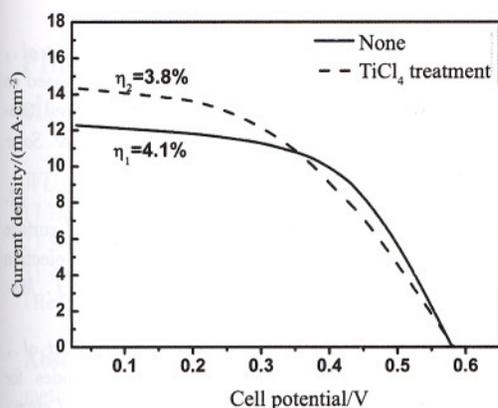


Fig. 2. Photocurrent-voltage characteristics of dye-sensitized solar cells composed of TiO₂ coating deposited on ITO conducting glass by vacuum cold spraying with/without TiCl₄ treatment at 60 °C for 10 min.

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 °C, while the electrical resistance of the FTO glass was not changed after sintering. It can be observed that the influence of TiCl₄ treatment on the performance of the cell using an ITO substrate was different from that using the FTO substrate. After TiCl₄ treatment at 60 °C for 10 min, the short circuit current density was increased to 14.3 mA·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 mmol·L⁻¹ aqueous TiCl₄ solution at 70 °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 TiCl₄ treatment. In₂O₃, the key conducting component in ITO glass, can be dissolved in TiCl₄ 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 In₂O₃, 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 TiCl₄ treatment within 70 min. According to the results shown in Fig. 3, after TiCl₄ treatment at 60 °C for 10 min, the electrical resistance of ITO glass was still lower than that of FTO glass. However, the dissolution of In₂O₃ in ITO glass might destroy the contact of ITO with TiO₂ 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 TiCl₄ treatment for 30 min at 60 °C, VCS TiO₂ coating flaked away from ITO glass.

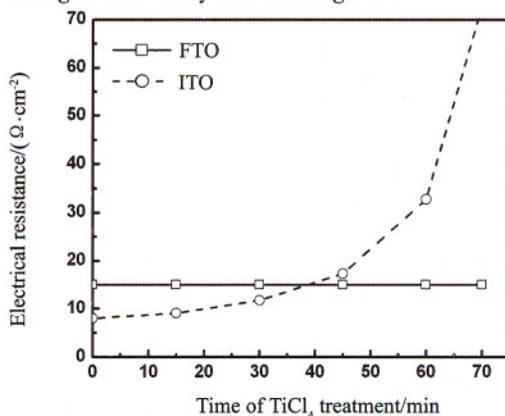


Fig. 3. Influence of TiCl₄ treatment at 70 °C on electrical resistance of FTO and ITO conducting glass, respectively.

4. Conclusions

The performance of the DSC is significantly influenced by TiCl₄ treatment to nano-crystalline TiO₂ coating deposited by vacuum cold spraying using a composite powder of polyethylene glycol (PEG) and 25 nm TiO₂ particles. With an FTO substrate, the TiCl₄ 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-TiO₂ particles in the coating and between TiO₂ coating and conducting glass, an increase of surface area of TiO₂ electrode, and a cover to

the interface between exposed part of FTO conducting glass and electrolyte. With an ITO substrate, TiCl_4 treatment to 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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