Preliminary Study of Performance of Dye-Sensitized Solar Cell of Nano-TiO$_2$ Coating Deposited by Vacuum Cold Spraying

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The control of nanoporous microstructure of TiO$_2$ coating in the dye-sensitized solar cells (DSC) through preparation methods influences significantly the performance of the cells. To investigate the effect of microstructure of TiO$_2$ deposit on the cell’s performance, in present study, vacuum cold spray (VCS) process is employed to deposit nanocrystalline TiO$_2$ coatings on an ITO conductive glass substrate. TiO$_2$ deposits were produced using nanosized particles of 25 nm in the diameter and composite powder composed of polyethylene glycol (PEG) and 25 nm TiO$_2$ particles. The deposition characteristics and the microstructure of the coating are characterized by scanning electron microscopy, x-ray diffraction analysis. The performance of the cell is tested under illumination of a metal halide lamp with a radiation intensity of 600 W m$^{-2}$. It was found that a dense TiO$_2$ coating with retention of crystal structure of powder can be deposited by vacuum cold spraying directly using nanosized TiO$_2$ powder. A cell with TiO$_2$ coating of 3.8 $\mu$m thick deposited directly by 25 nm powders yielded a short current density of 90.0 A m$^{-2}$ and conversion efficiency of 5.1% which is comparable with that of the wet doctor blading TiO$_2$ coating. Using a composite powder of TiO$_2$ with PEG, a porous TiO$_2$ coating with a thickness up to several tens of micrometers can be deposited by vacuum cold spraying. A DSC cell of TiO$_2$ coating deposited using a composite powder containing 41.2% PEG presented a higher short current density of 145.0 A m$^{-2}$, and conversion efficiency of 7.1%. [doi:10.2320/matertrans.47.1703]

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1. Introduction

Since a highly efficient (\textasciitilde 10\%) dye-sensitized solar cells (DSC) was reported by Regan 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. Nanoporous TiO$_2$ coating of high porosity has been fabricated as DSC’s electrode to increase surface area and to provide high light harvesting by a monolayer of sufficiently adsorbed dye.$^4$ High porosity is also beneficial for diffusion of reversible redox couples through TiO$_2$ membranes.$^5$

Several processing methods, including doctor blading,$^2$ spin coating,$^6$ screen printing$^7,8$ and layer by layer deposition,$^9$ have been employed to deposit nanocrystalline TiO$_2$ coatings applied to DSC. With all those processes, TiO$_2$ films are prepared from TiO$_2$ slurry or suspension in water with other additives such as detergent$^9$ and composite polyanion.$^8$ The film is formed through evaporation of water in the ambient atmosphere, which leads to the agglomeration TiO$_2$ particles in nanometer. Although DSC of a reasonable efficiency has been prepared using TiO$_2$ coatings through those processes, it is still necessary to develop a more efficient coating deposition process for TiO$_2$ coating used in DSC.

Thermal spraying process has been widely employed to deposit TiO$_2$ coatings owing to its flexibility and high deposition efficiency. However, the usage of powders in a size of several tens micrometers makes it difficult to deposit thin coating in about 10 micrometer. Moreover, the necessity of fully or partially melting of powder results in additional difficulty to control microstructure of coating. With metallic alloy, a dense coating can be deposited by cold spraying with solid particles in a size from several micrometers to several tens micrometers at ambient atmosphere.$^{10}$ It has been demonstrated that nanostructured TiO$_2$ coating with active photocatalytic performance can be deposited by cold spraying using an agglomerated nanosized TiO$_2$ particles.$^{11}$ A recent study revealed that a ceramic coating can be directly deposited using solid ceramic particles in a size of submicrometers under a reduced atmosphere at a room temperature.$^{12}$ Through this process, the microstructure of ceramic coating can be easily controlled. In terms of cold spraying using solid particles, here the deposition of ceramic coating using submicrometer particles under a reduced atmosphere is referred to as vacuum cold spraying. In this study, a vacuum cold spray (VCS) system was developed to deposit TiO$_2$ coating using a nanocrystalline TiO$_2$ powder applied to DSC. The controlling of microstructure of coating was attempted through using a TiO$_2$ powder mixed with polyethylene glycol (PEG) in different contents. The effect of microstructure of TiO$_2$ coating on the performance of the cell was examined.

2. Experimental Procedures

2.1 Materials

TiO$_2$ powder of 25 nm (P25, Degussa) in diameter was used as primary feedstocks for coating deposition by vacuum cold spraying and doctor blading, which is referred to as Type-A powder. A mixture of Type-A powder with polyethylene glycol (PEG) at different PEG contents was prepared by following process to control porosity of TiO$_2$ coating. A certain mass of PEG ($M_W = 10000$) was dissolved in alcohol to form solution A with different PEG concentration. 10 g Type-A TiO$_2$ powder was dispersed in 250 mL
alcohol to form suspension B under ultrasonic stirring condition for an hour. The solution A was added to suspension B drop by drop to prepare a colloid C which was in continuously ultrasonic stirring for another one hour. Finally the colloid C was distilled in a rotatory evaporator for an hour resulting in dry composite powder of TiO$_2$ and PEG with different PEG content of 9.1%, 23.1%, 37.5%, 41.2% in weight. The composite powder was crushed in mortar to a submicrometer size for deposition. The composite powder was referred to as Type-B powder and only used for vacuum cold spraying in this study.

A transparent indium oxide doped tin oxide (ITO) conducting glass (STN-180, Nanbo) was employed as a substrate for coating deposition with a dimension of 1.5 cm × 2 cm. Prior to spraying, the substrate was cleaned in an ultrasonic acetone bath. Detergent (OP-10, Xi’an Liangshan) was prepared through sintering Pt slurry on an insulated slide rheostat was used as the load

### 2.2 Preparation of TiO$_2$ coating

TiO$_2$ coating was deposited using a home-developed vacuum cold spray system. The system consisted of a vacuum chamber, vacuum pump, aerosol room, accelerating gas feeding unit, particle accelerating nozzle, two dimensional worktable and control unit. The acceleration of TiO$_2$ particles was performed by high pressure He gas. Spray parameters are given in Table 1.

For a comparison, the doctor blading method was also used to deposit TiO$_2$ coating. Type-A TiO$_2$ powder was ground in distilled water followed by addition of a little amount of OP-10 to form a colloid suspension. Then this colloid was coated with a rubber rod on the glass substrate and dried to form the coating.

### 2.3 Characterization of the coating

The topographic morphology and microstructure of the coating were examined by scanning electron microscopy (SEM) (Quanta 200). The thickness of the coating was measured using SEM. The crystalline structure of both the deposited coating and powder was characterized through X-ray diffraction (XRD) analysis (Shimazu XRD-6000) by Cu Kα radiation.

### 2.4 Fabrication of Dye-sensitized Solar Cell

TiO$_2$ electrode with an effective area of 0.2 cm$^2$ prepared by VCS process or doctor blading on ITO glass substrate was sintered at a temperature of 450°C for 30 min with a heating speed of 1.5°C/min. When TiO$_2$ coating was cooled to a temperature of ca. 80°C, it was soaked in a 3 × 10$^{-4}$ kmol/m$^3$ alcohol solution of dye and held in the solution for 24 hours at room temperature. A porous counter electrode was prepared through sintering Pt slurry on an insulated ceramic substrate at 800°C for an hour with a heating speed of 3°C/min. The surface morphology of counter electrode is shown in Fig. 1. The counter electrode was placed on the top of the dye-coated TiO$_2$ electrode separated by a 40-μm-thick tape (Zhengtai) as a spacer to assemble a sandwich-type solar cell. An electrolyte with 0.3 kmol/m$^3$ LiI and 0.03 kmol/m$^3$ I$_3$ in acetonitrile was filled into the inter-electrode space by capillary forces.

### 2.5 Photovoltaic measurement

The performance of the dye-sensitized solar cell was examined under the illumination of a metal halide lamp (Philips, MHN-TD 150W) with a radiation intensity of 600 W·m$^{-2}$ determined by a radiometer (FZ-A). The spectrum of the lamp is shown in Fig. 2. The current-voltage characteristics were tested through the approach reported in the reference.$^{13}$ A 1000 Ω slide rheostat was used as the load in the outer circuit. The conversion efficiency (η) of the cell was calculated by the short-circuit photocurrent density ($I_{SC}$), the open-circuit voltage ($V_{OC}$), the filling factor of the cell ($ff$) and the intensity of the incident light ($I_{0} = 600$ W·m$^{-2}$),

$$
\eta = I_{SC} \times V_{OC} \times ff / I_{0}
$$

### 3 Results

#### 3.1 Microstructure of TiO$_2$ coating

Figure 3 shows a typical morphology of coatings prepared by VCS using Type-A powder. In comparison of surface morphology of the coating deposited through doctor blading method (Fig. 4), the surface morphology of the coating deposited by VCS directly using Type-A 25 nm powder suggests the formation of a more compact coating (Fig. 3(a)) than by doctor blading. A detailed examination (Fig. 3(b))

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**Table 1** Vacuum cold spray parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chamber pressure, $P$/Pa</td>
<td>$2 \times 10^3$ Pa</td>
</tr>
<tr>
<td>Pressure of the aerosol room, $P$/Pa</td>
<td>$1 \times 10^6$ Pa</td>
</tr>
<tr>
<td>Atomization He gas flow, $F$/L·min$^{-1}$</td>
<td>0.5–1.5 L/min</td>
</tr>
<tr>
<td>Total He gas flow, $F$/L·min$^{-1}$</td>
<td>3</td>
</tr>
<tr>
<td>Distance from nozzle exit to substrate, $d$/mm</td>
<td>5</td>
</tr>
<tr>
<td>Orifice size of nozzle, $d \times d$/mm × mm</td>
<td>2.5 × 0.2 mm</td>
</tr>
<tr>
<td>Substrate traverse speed, $v$/mm·s$^{-1}$</td>
<td>5</td>
</tr>
</tbody>
</table>

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**Fig. 1** Morphology of Pt coating sintered at 800°C for an hour using Pt slurry.
suggests that the VCS coating was stacked of particles of about one hundred nanometers in agglomerate. The deposition of Ti coating by cold spraying in our previous study revealed that the tamping effect resulting from successive impacting of spray particles on the deposited coating is one possible mechanism to densification of a cold spray coating. Although it is difficult for ceramic particles to deform under impact of spray particles, the tamping effect will compact the coating through slipping of nanoparticles in the coating under a high impact pressure. As a result, an apparent dense coating is formed with successive deposition of spray particles. Owing to insufficient compaction and lack of dense aggregation between nanoparticles, it can be considered that the coating formed in the present study has a mesoporous microstructure. A relatively flat surface shown in Fig. 3 suggests that VCS TiO$_2$ coating was deposited by small particles.

Figure 5 shows the typical cross-sectional morphologies of fractured nanocrystalline TiO$_2$ coatings deposited by vacuum cold spraying using 25 nm Type-A TiO$_2$ powder to two different thicknesses. The coatings were deposited on ITO glass surface and fractured after deposition. Fig. 5(b) showed that the coating with a thickness of several micrometers was deposited using Type-A powder. In fact, a coating with a thickness up to several tens of micrometers could also be
prepared through changing spray parameters such as increasing atomization gas flow and spray pass, lowering substrate traverse speed. Moreover, a relatively rough morphology was present in the fractured cross section. Compared with the relatively flat surface morphology, such rough morphology of the fractured coating suggests that spalling of the agglomerates of nanosized TiO$_2$ particles occurred during fracturing. This fact implies that the bonding between the agglomerates in the coating was relatively weak. The spalling of a thick coating during deposition evidently indicated the formation of weak bonding using nanosized particles under the present conditions.

With using Type-B powders it was found that over several tens micrometer thick TiO$_2$ coatings with an improved adhesion could be deposited by VCS more easily, as shown in Fig. 6. It can also be recognized from Fig. 6 that the fractured coatings presented a uniform thickness. Those facts indicate that powder type especially particle size has a significant effect on coating formation.

Figure 7 shows a surface morphology of TiO$_2$ coating deposited by VCS using Type-B powder. It was clear that a rougher surface was present compared with the coating deposited using Type-A TiO$_2$ powder though the size of the primary TiO$_2$ particles in two powders was the same. Possibly, this difference is attributed to the particle size distribution and particle features of spray powders.

With the coating deposited by Type-B powder, after sintering at 450°C, the surface morphology (Fig. 7(b)) showed no significant difference in microsize from the as-coating state (Fig. 7(a)), which implies that PEG particles mixed with TiO$_2$ powder was in a small size.

Figure 8 shows the XRD patterns of TiO$_2$ coatings deposited by vacuum cold spray in comparison of that of the starting powder. The crystalline structure of Type-A TiO$_2$ coating (Fig. 8(b)) was the same as that of the starting powder (Fig. 8(a)). This means that the coating was formed with a full retention of the original crystal structure of powder. A peak at a $2\theta$ of 23.5° was present in XRD pattern of Type-B coating (Fig. 8(c)). This peak was resulted from PEG in the coating. It was found that this peak disappeared as the coating was annealed at a temperature of 450°C. XRD result shown in Fig. 8(d) indicated that the coating after annealing treatment at 450°C still retained the crystal structure of the starting TiO$_2$ powder. This result means that using vacuum cold spray process the original crystalline structure of powder can be completely transferred into deposit. Therefore, the deposit crystalline structure can be controlled through design of starting powder structure for its application to DSC.

Moreover, it is clear from XRD analysis that after annealing at 450°C, PEG included in the coating was
The removal of PEG leads to the creation of an additional porosity in the coating. The porosity in the coating depends on the content of PEG included in the coating. Therefore, through controlling of the PEG content in the original Type-B powder, the porosity in the nanostructured TiO$_2$ coating can be changed.

### 3.2 Current-voltage characteristics and conversion yields of dye-sensitized solar cell

#### 3.2.1 Effect of coating thickness on the performance of DSC cell

Figure 9 shows the typical output performance of the cell of TiO$_2$ coating deposited using Type-B powder containing 41.2% PEG. The mean thickness of TiO$_2$ coating was 11.2 μm. The cell presented a short circuit current density of 145.0 A·m$^{-2}$ and an open circuit voltage of 0.68 V. It was found that the thickness of TiO$_2$ coating has a significant influence on the performance of the cell as shown in Fig. 10. Clearly, with increasing TiO$_2$ coating thickness up to about 11 μm, the short-circuit current density and conversion yield were increased. However, with a further increase in TiO$_2$ coating thickness, both the short-circuit current density and conversion yield were decreased. Therefore, a DSC cell of TiO$_2$ coating in a thickness about 11 μm will achieve better performance. This result is consistent with that reported for TiO$_2$ coating formed by doctor blading method.

#### 3.2.2 Effect of PEG content in the composite powder on the performance of DSC cells

The characteristic values of two DSC cells composed of nanocrystalline TiO$_2$ coatings deposited using Type-A powders are shown in Table 3. The mean thickness of TiO$_2$ coatings in two cells was about 2 μm and 3.8 μm. It was also

### Table 2 Performance characteristics of dye-sensitized solar cell based on TiO$_2$ coating prepared by VCS using Type-B powders containing different PEG.

<table>
<thead>
<tr>
<th>PEG content (%)</th>
<th>Coating thickness, $d$/μm</th>
<th>Short-circuit current density, $I_{SC}$/A·m$^{-2}$</th>
<th>Open-circuit voltage, $V_{OC}$/V</th>
<th>Conversion yield, $\eta$/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.1</td>
<td>12.3</td>
<td>105.0</td>
<td>0.58</td>
<td>4.1</td>
</tr>
<tr>
<td>23.1</td>
<td>11.5</td>
<td>116.5</td>
<td>0.61</td>
<td>4.1</td>
</tr>
<tr>
<td>37.5</td>
<td>12.0</td>
<td>120.5</td>
<td>0.62</td>
<td>5.7</td>
</tr>
<tr>
<td>41.2</td>
<td>11.2</td>
<td>145.0</td>
<td>0.68</td>
<td>7.1</td>
</tr>
</tbody>
</table>
confirmed that the thickness of TiO₂ coating has a significant effect on DSC performance. Compared with a short-circuit current density of 45.0 A m⁻² with the cell of 2 μm TiO₂ coating, a short circuit current density of 90.0 A m⁻² was obtained with the cell of 3.8 μm TiO₂ coating. With using Type-A powder, although a thick coating could also be deposited, it was found that the dye adsorption on TiO₂ particles in the coating near ITO substrate was much difficult owing to dense microstructure. This had been proved by the fact that the dye adsorption to an equilibrium condition on a coating over 10 μm thick needed several days or longer through simple color-change observation from ITO substrate side. Theoretically, infiltration of the dye with a diameter of ca. 1.4 nm needs at least 4.2 nm pores. With Type-A powder, the coating was deposited by agglomerates of nanosized TiO₂ particles in 25 nm. With increasing coating thickness, the tamping effect leads to densification of coating which makes dye infiltration through coating more difficult.

Table 3 Performance characteristics of dye-sensitized solar cell based on TiO₂ coating prepared by VCS and doctor blading using Type-A powders.

<table>
<thead>
<tr>
<th>Coating preparation methods</th>
<th>Coating thickness, d/μm</th>
<th>Short-circuit current density, JSC/A m⁻²</th>
<th>Open-circuit voltage, VOC/V</th>
<th>Conversion yield, η/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>VCS</td>
<td>2.0</td>
<td>45.0</td>
<td>0.69</td>
<td>3.1</td>
</tr>
<tr>
<td>VCS</td>
<td>3.8</td>
<td>90.0</td>
<td>0.68</td>
<td>5.1</td>
</tr>
<tr>
<td>Doctor blading</td>
<td>8.0</td>
<td>101.5</td>
<td>0.7</td>
<td>6.6</td>
</tr>
</tbody>
</table>

4. Discussion

The short circuit current density, open circuit voltage and filling factor are three essential parameters which determine the conversion yield for a solar cell. Those parameters of a DSC cell are influenced by a number of factors including primary TiO₂ grain size, contact condition of TiO₂ grains, porous structure of TiO₂ coating, features of dye, adsorption state of dye on TiO₂ grains, electrolyte and counter electrode. The present results clearly showed that the TiO₂ coating deposited by VCS can be effectively used as an electrode in DSC cell. The cell achieved a short circuit current density up to 145.0 A m⁻². For comparison, a cell employed TiO₂ coating prepared by doctor blading method was also assembled using starting TiO₂ powder of the same particle size as VCS. TiO₂ coating was about 8 μm in thickness. The output performance of the cell was shown in Fig. 9 along with two cell using VCS TiO₂ coating as the electrode for comparison. It can be found that the cell yielded a short current density of 102.0 A m⁻². This result is comparable to that of the cell employing VCS TiO₂ coating by Type-B powder.

It was also confirmed in the present study that an optimal coating thickness is necessary to achieve a high short-circuit current density. The optimal TiO₂ coating thickness is about 11 μm. This result is consistent with that reported by Nazeeruddin et al.²)

The present results revealed that the JSC, VOC, and η of the cells increased with increasing the PEG content in the composite powder. This could be attributed to the increase of porosity in the coating with increasing PEG content in composite powder. Larger pores were acquired to promote the transfer of ions in electrolyte through diffusion. Increasing PEG content means raising total porosity of the coating, which resulted in increasing adsorption amount of dye per volume of the TiO₂ coating. Moreover, the uniform adsorption of dye to the TiO₂ near interface with ITO glass can be more easily achieved. As a result, more photoelectrons could be produced from the dye excitation and injected to TiO₂ particles and accumulated on the ITO substrate to form a high JSC and high VOC as well according to the following diode equation,¹⁶)

\[ V_{OC} = \left( \frac{nRT}{F} \right) \ln \left( \frac{J_{SC}}{i_0} \right) - 1 \]  

where \( n \) is the ideality factor whose value is between 1 and 2 for the DSC, \( i_0 \) is the reverse saturation current, \( R \) and \( F \) are the ideal gas constant and Faraday’s constant, respectively.

The results in Table 2 showed that a maximum output efficiency of 7.1% was obtained when the cell was composed of VCS coating using powders with the 41.2% PEG content. This result is a litter higher than the cell assembled with TiO₂ by conventional doctor blading method. Based on those result, a composite powder containing more PEG would be preferable to improve further the performance. However, a higher PEG content results in a high elasticity of the composite powder, which makes composite powder not to be able to crushed to produce submicrometer particles for vacuum cold spraying under ambient condition.

From the results shown in Fig. 9, it can be found that the filling factor (\( ff = 0.43 \)) of DSC of Type-B-41.2% TiO₂ VCS coating was lower than those cells of both type-A TiO₂ VCS coating and doctor blading coating. The factors influencing the cell’s \( ff \) include the dark current (\( I_D \)), and cell’s inverse resistance derived from ITO resistance, redox ions transfer through electrolyte, charge transfer on Pt counter electrode. The dark current was generated mainly on the uncovered ITO substrate and TiO₂/electrolyte junctions without adsorption of dye owing to the direct reduction of \( I_3^- \) by the following reaction,¹⁷)

\[ I_3^- + 2e = 3I^- \]  

A high dark current will lead to disappearing of platform in the current-voltage curve, which was evidently observed in Fig. 9(a). The lower filling factor of the DSC cell by 41.2% PEG composite powder is possibly due to direct exposure of ITO substrate surface to electrolyte owing to a high porosity in the coating near the substrate.¹⁷) On the hand, with the DSC cell of a low short current density, it was found that the filling factor was improved. This means that the total internal electric resistance within the cell also significantly influence filling factor. Resistance of the present ITO glass after annealed at 450°C was increased up to three times larger than the untreated one. The high resistance of conducting ITO glass results in a high ohmic loss under high current output. Therefore, in order to improve the performance of DSC cell, reduction of internal ohmic resistance and controlling of coating microstructure are necessary. The later will lead to the improvement of reduction of dark current, uniform and high amount of dye adsorption over TiO₂ surface, and fast transportation of redox ions within TiO₂ electrolyte.
5. Conclusions

The nanocrystalline TiO$_2$ coatings was successfully deposited on ITO conducting glass using nanocrystalline TiO$_2$ powder of 25 nm in the diameter and a composite powder of 25 nm TiO$_2$ with PEG by vacuum cold spray process. A TiO$_2$ coating of a uniform thickness up to several tens of micrometers was achieved using the composite powder. The results showed that the crystalline structure of the starting powder was fully retained in the coating. The PEG in the composite coating can be removed under annealing treatment at a temperature of 450°C. The annealing under this temperature influenced little the crystalline structure. The removal of the PEG modified total porosity and porous structure in the coating. The dye-sensitized solar cell assembled using VCS TiO$_2$ coating presented a high output efficiency which was comparable to that of the conventional wet doctor blading method.

REFERENCES