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Improvement in performance of dye-sensitized solar cells with porous TiO$_2$ electrodes using squid ink particles

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Received November 26, 2015; accepted December 28, 2015; published online April 8, 2016

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted considerable attention as an ecofriendly and low-cost alternative to the silicon-based solar cells currently in use.$^{1-3}$ DSSCs have a porous TiO$_2$ film photoelectrode that is fabricated by sintering TiO$_2$ paste applied to a transparent conductive oxide (TCO) glass substrate. Several manufacturing techniques for TiO$_2$ film electrodes have been studied to improve the performance of DSSCs.$^{4-12}$ Many researchers have tested composite pastes in which TiO$_2$ nanoparticles are mixed with other materials, such as graphene,$^{13,14}$ carbon nanotubes,$^{15,16}$ and polystyrene spheres.$^{17}$

Our previous study demonstrated that size-controlled ink particles (SIPs) isolated from the squid enhance the fabrication of porous TiO$_2$ film electrodes.$^{18}$ Composite pastes prepared by incorporating SIPs into commercially available TiO$_2$ pastes were deposited on TCO substrates through the screen-printing method. When the paste-coated substrates were sintered at 450°C, the SIPs decomposed, leaving abundant cavities in the TiO$_2$ films. The increase in the mixture ratio of SIPs in the paste formulations was found to markedly enhance the porosity of the TiO$_2$ film electrodes. However, a potential disadvantage of the addition of SIPs was that a huge crack appeared in the TiO$_2$ films. In fact, the use of composite paste consisting of 30% SIPs increased the TiO$_2$ film porosity but decreased the photoelectric conversion efficiency (PCE). This is likely because the huge crack outbreak from the decomposition of SIPs caused a break in the network of TiO$_2$ grains in the films, interrupting electron transport in the electrodes. Therefore, a new method of preventing these huge cracks from occurring is necessary for TiO$_2$ film fabrication utilizing a unique feature of SIPs.

In the present study, we propose an improved method of manufacturing highly porous TiO$_2$ film electrodes by using a water-soluble TiO$_2$–SIP composite paste. We planned considerable improvements of the paste properties as well as the structures of the TiO$_2$ film electrodes. The former is characterized by water solubility and large particle size to increase affinity to SIPs. Water solubility should facilitate a uniform dispersion of SIPs in TiO$_2$ aqueous suspensions, unlike the commercially available TiO$_2$ paste used in the previous study.$^{18}$ It is also expected that the excess restructuring of TiO$_2$ particles in the film will be inhibited after the decomposition of SIPs by the sintering process, when the TiO$_2$ particle used in the paste is about the same size as the SIP. The point of the latter improvement is that the TiO$_2$ film electrodes possess two laminar structures consisting of a thin adhesion layer and a porous active layer to guarantee high conductivity and promote dye adsorption. The aim of preparing the thin adhesion layer is to achieve better adhesion of the porous active layer to the TCO substrate, inherently showing good electron-transport characteristics. The porous active layer for adsorbing dye was deposited on the thin adhesion layer by the screen printing of the TiO$_2$–SIP composite paste, and was then completed after sintering at 450°C. This method successfully enabled us to manufacture highly porous TiO$_2$ films without huge cracks. The utilization of SIPs in the fabrication of TiO$_2$ film electrodes consequently led to the very promising performance of DSSCs.

2. Experimental procedure

Figure 1 shows a schematic diagram of the process of fabricating porous TiO$_2$ film electrodes consisting of a thin adhesion layer and a porous active layer. Fluorine-doped tin oxide (FTO)-layered glass (AGC Fabritech A110U80) was used as a TCO substrate. The process starts with the preparation of a thin adhesion layer by screen printing. A commercially available TiO$_2$ paste (Solaronix Ti-Nanoxide HT/SP) containing TiO$_2$ nanoparticles with an average diameter of 9 nm was deposited on the FTO substrate using a screen printer (Newlong HP-320).

The water-soluble TiO$_2$–SIP composite paste for the porous active layer was prepared as follows. A TiO$_2$ aqueous suspension was prepared by mixing a commercially available TiO$_2$ particle (Ishihara Sangyo ST41, 100% anatase, approximately 160 nm in diameter) with a 30 wt % aqueous solution of poly(ethylene glycol) (PEG; Wako PEG20,000). SIPs are composed mainly of natural eumelanins, and are biological particles with a diameter of a few hundred nanometers.$^{21-24}$ The thermal decomposition of SIPs occurs at 450°C.$^{18}$ In the present study, SIPs with distribution peaks of approximately 300 nm were isolated from the ink sacs of the Humboldt squid (Dosidicus gigas) by...
ultrafiltration (Millipore Labscale TFF System) in accordance with the procedures described in the literature. The obtained SIPs were dispersed with ultrapure water. The TiO₂–SIP composite paste was prepared by incorporating SIPs into a TiO₂ aqueous suspension containing PEG. The composite pastes were thoroughly mixed with a pestle to break up any aggregates of nanoparticles. The weight ratios between TiO₂ suspensions and SIPs were adjusted to 10 : 0, 9 : 1, 8 : 2, and 7 : 3 (summarized in Table I). To fabricate the active layer, the TiO₂–SIP composite paste was deposited on the thin adhesion layer by screen printing. The screen-printing procedure was repeated to adjust the thickness of the TiO₂ films to approximately 12 µm. The area of the films was 0.5 × 0.5 cm². The screen-printed TiO₂ film electrodes were then sintered at 450 °C for 90 min in air in an electric furnace (As-one MMF-1). The heating rate was 1.8 °C/min.

To analyze the surface morphology and roughness of the sintered TiO₂ film electrodes, atomic force microscopy (AFM) observation was conducted under an ambient atmosphere (50 ± 10% relative humidity) using a scanning probe microscope (Shimadzu SPM-9500J3) in a dynamic mode. The sample substrate was cut into pieces of 1 × 1 cm² using a glass knife, and then was glued to steel discs with a double-coated tape. The cantilever used was a medium stiffness cantilever (Olympus OMCL-AC200TN) with a nominal spring constant of ca. 9 N/m and a curvature radius of ca. 7 nm. The scanning rate was between 0.5 and 1 Hz at 512 lines per frame. All the AFM measurements were performed at room temperature. The surface roughness was analyzed using the supplied software (Shimadzu SPM manager 2.11).

DSSCs using the sintered TiO₂ film electrodes were assembled to evaluate their photoelectrochemical parameters. The sintered TiO₂ film electrodes were immersed in a 0.3 mM ruthenium complex dye (Solaronix Ruthenizer 535-bisTBA abbreviated as N719) solution in a mixture of tert-butanol and acetonitrile (volume ratio = 1 : 1) at room temperature for 24 h. For a counter electrode, a thin layer of platinum was coated onto the FTO substrate. The gap between electrodes was filled with an electrolyte (Solaronix Iodolyte AN-50). The current density–voltage (J–V) characteristics of the assembled DSSCs were measured using a digital source meter (Keithley 2400) under a standard air mass (AM1.5) with a simulated solar illumination at 100 mW/cm². It is well known that the photoelectric conversion efficiency (η) of DSSCs can be represented as

\[
\eta = \frac{J_{sc} \times V_{oc} \times FF \times P_{in}}{100},
\]

where \(J_{sc}\), \(V_{oc}\), \(P_{in}\), and \(FF\) are the short-circuit current density, open-circuit voltage, power density of incident light, and fill factor, respectively. The photoelectrochemical parameters of the DSSCs were evaluated using commercial software (Pecell J-V curve analyzer).

3. Results and discussion

3.1 Morphology of TiO₂ film electrodes fabricated from the TiO₂–SIP composite pastes

Figure 2(a) shows digital photographs of the TiO₂–SIP composite pastes at various mixture ratios. The TiO₂ film electrodes (b) before and (c) after sintering at 450 °C are also shown, which were fabricated from the TiO₂–SIP composite pastes at various mixture ratios.

Table I. Mixture ratios between TiO₂ aqueous suspension and SIPs in the paste formulation.

<table>
<thead>
<tr>
<th>TiO₂ : SIP</th>
<th>TiO₂ suspension (g)</th>
<th>SIP (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 : 0</td>
<td>13.5 (= 30 wt % PEG 10 g + ST41 3.5 g)</td>
<td>0.0</td>
</tr>
<tr>
<td>9 : 1</td>
<td>13.5 (= 30 wt % PEG 10 g + ST41 3.5 g)</td>
<td>1.5</td>
</tr>
<tr>
<td>8 : 2</td>
<td>12.0 (= 30 wt % PEG 8.9 g + ST41 3.1 g)</td>
<td>3.0</td>
</tr>
<tr>
<td>7 : 3</td>
<td>10.5 (= 30 wt % PEG 7.8 g + ST41 2.7 g)</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Fig. 1. (Color online) Process of fabricating porous TiO₂ film electrodes.

Fig. 2. (Color online) (a) Digital photographs of the water-soluble TiO₂–SIP composite pastes at various mixture ratios (TiO₂ : SIP = 10 : 0, 9 : 1, 8 : 2, 7 : 3). The TiO₂ film electrodes (b) before and (c) after sintering at 450 °C are also shown, which were fabricated from the TiO₂–SIP composite pastes at various mixture ratios.
between TiO2 suspensions and SIPs were adjusted to 10 : 0, 9 : 1, 8 : 2, and 7 : 3. The pastes changed in color from white to sepia as the mixture ratio of SIPs increased in the paste formulation. The color of the SIPs remained in all the TiO2 films prior to sintering (except for the control), as shown in Fig. 2(b). After sintering, all films became an opaque white regardless of the mixture ratio, as shown in Fig. 2(c). Thus, it is clear that the sintering procedure at 450 °C decomposed SIPs in the paste formulation. All SIPs in the paste evaporate, leaving submicrometer cavities that are randomly distributed in the active layer. This phenomenon causes the high porosity of TiO2 film electrodes. However, in the previous paper, an undesirable result, which is the inhomogeneous formation of huge cracks, was reported to interrupt the electron transport between TiO2 grains on the electrodes.18) The same problem occurred in the case of the TiO2 pastes mixed with polystyrene spheres.17) In the present study, huge cracks were not observed. This is likely attributable to the fact that the excess restructuring of TiO2 particles in the film did not occur after the decomposition of SIPs, since the SIPs and TiO2 particles are almost of the same size. In addition, it is difficult to generate such cracks throughout an entire TiO2 film electrode consisting of adhesion and active layers, because there are no SIPs in the adhesion layer. Even if huge cracks did occur, they might be limited to a portion of the active layer, which would hardly affect the electron transport because the adhesion layer is present between FTO and the active layer. It is entirely reasonable to suppose that the SIPs decompose from the active layer so that the sintered TiO2 films do not crack. Thus, the improved method in the present study enabled us to prevent the huge cracks from occurring in the fabrication of the TiO2 film electrodes.

The effects of the mixture ratio between TiO2 suspension and SIPs on the film morphology were analyzed from the standpoint of surface roughness. Figure 4 shows the root-mean-square surface roughness ($R_{\text{rms}}$) of the sintered TiO2 film electrodes plotted as a function of the mixture ratio of SIPs in the paste formulation. All $R_{\text{rms}}$ values denoted by open circles with an error bar were approximately 100, considerably larger than those (approximately 30 to 80) in the previous report.18) This is due to the fact that the diameter of the TiO2 particles (ST41) used in the present study was eight times larger than that (~20 nm, Solaronix Ti-Nanoxide D/SP) used in the previous report. On the other hand, the proportion of SIPs in the paste did not conspicuously affect the surface roughness of the film electrodes, since the obtained $R_{\text{rms}}$ had almost the same value regardless of the mixture ratio of SIPs. Although the surface roughness might not be critical evidence with which to demonstrate the internal structures of the film electrodes, it is noteworthy that...
3.2 Characteristics of DSSCs

We evaluated the photoelectrochemical parameters of DSSCs using the electrodes fabricated from the TiO\textsubscript{2}–SIP composite pastes. Figure 5 shows the J–V characteristics of DSSCs at various mixture ratios of SIPs in the paste formulations. The mean values of $J_{sc}$, $V_{oc}$, $FF$, and PCE ($\eta$) are summarized in Table II. The PCEs of all the electrodes fabricated from the composite pastes rose versus that of the electrode without SIP addition, as shown in Fig. 6. The highest PCE was recorded when the mixture ratio between TiO\textsubscript{2} suspension and SIPs in the paste was adjusted to 8 : 2, yielding a 35% increase in PCE compared with that in DSSCs without SIP addition. Without huge cracks, the attainable $V_{oc}$ values (0.7 to 0.8 V) in the TiO\textsubscript{2} film electrodes were obtained, which means that these electrodes are sophisticated. This proved clearly that the SIPs are superior in quality as organic binders for enhancing the porosity of the film electrodes. However, the PCE decreased when the mixture ratio of SIPs was further increased to 30%. It is deduced that this decrease arose from an outbreak of excessive numbers of pores by the decomposition of binders such as SIPs, interrupting the intragranular electron transport.\textsuperscript{28} Thus, it is concluded that the use of the composite paste consisting of 20% SIPs is most suitable to the manufacture of highly porous TiO\textsubscript{2} films without huge cracks.

The PCEs in the present study were lower than those in the previous report.\textsuperscript{18} In the present study, the TiO\textsubscript{2} particle with almost the same size as the SIP was used in the paste to inhibit the excess restructuring of TiO\textsubscript{2} particles in the film after the decomposition of SIPs by the sintering process. This purpose was achieved. However, the use of a large TiO\textsubscript{2} particle did not improve the performance of DSSCs. TiO\textsubscript{2} particles such as ST41, used in the present study, are rarely used for active layers. TiO\textsubscript{2} particles with a diameter of a few hundred nanometers have been continually used for scattering layers, because such large particles can diffuse visible light.\textsuperscript{29–31} In the TiO\textsubscript{2} film electrodes using large particles, dye aggregation occurred on intragranular pores owing to the physical adsorption of the dye molecule, which was responsible for the low electron injection yield.\textsuperscript{32} If one fabricated an active layer consisting of TiO\textsubscript{2} particles with a diameter of approximately 30 nm, further enhancement of the PCE would be expected. In addition, a decrease in series internal resistance in DSSCs is an important approach to elevating PCE. It has been found that series internal resistance generally decreases through a decrease in the thickness of the electrolyte layer (defined as the distance between the TiO\textsubscript{2} electrode and the platinum counter electrode), and through an increase in the roughness factor of the platinum counter electrode.\textsuperscript{33} To enhance the performance of DSSCs in the future, we will attempt to decrease the series internal resistance as well as to improve the TiO\textsubscript{2} electrodes.

### Table II. Photoelectrochemical parameters of DSSCs with the sintered TiO\textsubscript{2} film electrodes prepared using the TiO\textsubscript{2}–SIP composite pastes at various mixture ratios.

<table>
<thead>
<tr>
<th>TiO\textsubscript{2} : SIP</th>
<th>$J_{sc}$ (mA cm\textsuperscript{-2})</th>
<th>$V_{oc}$ (V)</th>
<th>$FF$</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 : 0</td>
<td>6.1 ± 0.1</td>
<td>0.71 ± 0.01</td>
<td>0.55 ± 0.02</td>
<td>2.4 ± 0.1</td>
</tr>
<tr>
<td>9 : 1</td>
<td>5.7 ± 0.5</td>
<td>0.71 ± 0.01</td>
<td>0.62 ± 0.01</td>
<td>2.5 ± 0.2</td>
</tr>
<tr>
<td>8 : 2</td>
<td>7.3 ± 0.2</td>
<td>0.75 ± 0.00</td>
<td>0.58 ± 0.02</td>
<td>3.2 ± 0.2</td>
</tr>
<tr>
<td>7 : 3</td>
<td>6.3 ± 0.5</td>
<td>0.73 ± 0.01</td>
<td>0.63 ± 0.00</td>
<td>2.9 ± 0.3</td>
</tr>
</tbody>
</table>

PCE compared with that in DSSCs without SIP addition. Without huge cracks, the attainable $V_{oc}$ values (0.7 to 0.8 V) in the TiO\textsubscript{2} film electrodes were obtained, which means that these electrodes are sophisticated. This proved clearly that the SIPs are superior in quality as organic binders for enhancing the porosity of the film electrodes. However, the PCE decreased when the mixture ratio of SIPs was further increased to 30%. It is deduced that this decrease arose from an outbreak of excessive numbers of pores by the decomposition of binders such as SIPs, interrupting the intragranular electron transport.\textsuperscript{28} Thus, it is concluded that the use of the composite paste consisting of 20% SIPs is most suitable to the manufacture of highly porous TiO\textsubscript{2} films without huge cracks.

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4. Conclusions

A series of water-soluble TiO\textsubscript{2}–SIP composite pastes with
different mixture ratios were examined for the manufacture of highly porous TiO₂ films without huge cracks. The improvement of the paste properties and film structures enabled us to prevent huge cracks from occurring in the fabrication of TiO₂ film electrodes. The proportion of SIPs in the paste correlated with the PCE of DSSCs using the electrodes. The highest PCE was achieved when the mixture ratio of SIPs was increased to 20%. This process is highly reproducible and leads to a 35% increase in PCE compared with that in DSSCs without SIP addition. Although further investigation is required to improve the performance of DSSCs utilizing TiO₂–SIP composite pastes, we revealed that the utilization of SIPs in the fabrication of TiO₂ film electrodes enhances the performance of DSSCs.

Acknowledgments

This work was supported in part by the Adaptable and Seamless Technology Transfer Program through the Target-driven R&D (A-STEP) from the Japan Science and Technology Agency (JST), and by a research grant from the Northern Advancement Center for Science and Technology (NOAICTE).

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