Improved Photocurrent of a Poly (3,4-ethylenedioxythiophene)-ClO₄⁻/TiO₂ Thin Film-modified Counter Electrode for Dye-sensitized Solar Cells

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Abstract: We prepared a poly(3,4-ethylenedioxythiophene) (PEDOT)-ClO₄⁻-supported TiO₂ thin-film electrode as a counter electrode on a transparent conductive oxide glass electrode for a dye-sensitized solar cell (DSSC) using a combination of sol-gel and electropolymerization methods. The photocurrent-voltage characteristics indicate that DSSCs with PEDOT-ClO₄⁻/TiO₂ thin-film counter electrodes had a high photovoltaic conversion efficiency similar to that of PEDOT-ClO₄⁻/TiO₂ particle composite-film electrodes. Furthermore, it was found that the photocurrent was increased by attaching a reflector to the opposite side of the transparent counter electrode.

Key words: poly(3,4-ethylenedioxythiophene)-ClO₄⁻/TiO₂ thin-film electrode, photo-current, dye-sensitized solar cell

1 INTRODUCTION

In recent years, solar energy has received considerable attention as a renewable, environmentally friendly energy source. In particular, dye-sensitized solar cells (DSSCs), which are a type of photoelectric conversion devices, have attracted considerable interest because of their inherent advantages including lower production cost as compared to typical crystal silicon-type solar cells and high theoretical conversion efficiencies.

DSSCs operate according to the following principles. First, the photo-excited electrons of a dye are injected into a conduction band of nanocrystalline TiO₂ coated on a fluorine-doped tin oxide (FTO) glass electrode. Second, the electrons are transferred from the nanocrystalline TiO₂ to a counter electrode (CE) through an external circuit and are collected at an FTO glass electrode. The electrons at the CE then react with I₃⁻ ions to form I⁻ ions. Finally, the I⁻ ions diffuse from the CE to the resultant positive holes in the sensitizing dye.

Usually, a Pt-sputtered FTO glass electrode is employed as the CE and acts as a reduction catalyst. However, Pt is a rare metal and is therefore expensive and not abundantly available. Accordingly, a substitute for Pt would enable the development of more practical devices. CE materials require high electronic conductivity, corrosion resistance against iodides, and the ability to act as a reduction catalyst for the I⁻/I₃⁻ redox couple. Recently, it was reported that carbonaceous materials such as carbon black, graphite, and carbon nanotubes, and conductive polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT), polypyrrole, and polyaniline are effective CE catalysts. As an additional consideration, high vacuum processes such as Pt sputtering increase production costs. Therefore, wet processes such as dip coating, spray coating, and plating should be more cost-effective. Among these, electrochemical deposition is an effective method for easy and quick preparation of dense homogeneous films.

In previous papers, we reported that the performance of a CE is significantly improved by using a PEDOT-ClO₄⁻/TiO₂ composite film or a PEDOT-ClO₄⁻/C composite film electrode with increased roughness; however, the photocurrent in these systems was not improved. Therefore, to further improve the photocurrent, the use of reflected light may be effective. Yuh-Lang Lee et al. reported improved photocurrent by using reflected light from an ultrathin platinum CE. However, there are few reports on the improvement of DSSC performance in non-Pt CEs using reflected light.

In this work, we prepared a TiO₂ thin film on an FTO glass electrode by sol-gel processing and subsequently deposited PEDOT-ClO₄⁻ by electropolymerization.
We evaluated the performance of the TiO$_2$(tf)/CE in comparison to a PEDOT-ClO$_4^-$/TiO$_2$ particle film (TiO$_2$(pf)) electrode using cyclic voltammetry and electrochemical impedance measurements and by assessing the performance of a solar cell with a transparent PEDOT-ClO$_4^-$/TiO$_2$(tf) electrode. In addition, we investigated the influence of reflected light on the photocurrent using a modified CE.

2 EXPERIMENTAL PROCEDURES

2.1 Fabrication of a PEDOT-ClO$_4^-$/TiO$_2$(tf) counter electrode

A TiO$_2$(tf) was deposited on a CE using a sol-gel technique. Initially, 0.25, 0.5, and 1.0 M precursor solutions were obtained by dissolving the appropriate equimolar amount of titanium tetraisopropoxide (Tokyo Chemical Industry, Ltd.) and acetic acid (Wako Pure Chemical Industries, Ltd.) in ethanol (Wako Pure Chemical Industries, Ltd.). The TiO$_2$(tf) was obtained by spin-coating these precursor solutions for 30 sec at 3000 rpm and then sintering for 10 min at 500°C. As a reference, a TiO$_2$(pf) was fabricated on a CE by electrophoretic deposition; the procedure is as follows. First, a suspension of TiO$_2$ particles was obtained by supersonically dispersing TiO$_2$ particles (Aeroxide® TiO$_2$ P-25, Nippon Aerosil Co. Ltd.) into an aqueous ethanol solution (50 wt%). Two parallel pieces of FTO conductive glass substrate (Asahi Glass Co. Ltd.) that were the same size as the electrodes were immersed in the TiO$_2$ particle suspension. The TiO$_2$(pf) was then electrochemically deposited on the cathode surface by applying a 10 V DC bias voltage for 5 s and sintered for 30 min at 500°C.

In order to form a PEDOT-ClO$_4^-$/TiO$_2$(tf) layer on the surface of the TiO$_2$(tf), electrochemical polymerization was then performed. For the electrolyte solution of 3,4-ethylenedioxythiophene (EDOT; Sigma-Aldrich Corp.), monomer, an acetonitrile solution containing 10 mM EDOT and 100 mM lithium perchlorate (Wako Pure Chemical Industries, Ltd.) was used. After immersing two parallel pieces of FTO conductive glass into the EDOT solution, PEDOT-ClO$_4^-$ was electrochemically deposited on the cathode by applying a 3.5 V DC voltage for 15 s. The desired PEDOT-ClO$_4^-$/TiO$_2$(tf)/FTO CE was obtained after drying at 100°C for 5 min. For comparison, a PEDOT-ClO$_4^-$/FTO CE was electrochemically prepared.

2.2 Characterization of the as-prepared counter electrode

Small-angle and powder X-ray diffraction patterns were obtained using a Bruker AXS (D8 Discover) and a Bruker AXS (D8 Advance), respectively, to investigate the crystal structure of the as-prepared TiO$_2$ films and commercial TiO$_2$ powders. The surface morphology of an electrode was examined using surface and cross-sectional images obtained using a Hitachi S-400 FESEM system. To observe the reflected light from the electrode surface, diffuse UV-vis spectra were also measured (UV-3100, Shimadzu Corporation).

The photocurrent-voltage (I-V) behavior of the prepared cell was assessed using a potentiostat (versaSTAT3, Princeton Applied Research). To further elucidate the photocurrent behavior of the DSSC, electrochemical impedance spectroscopy (EIS) of the electrochemical cells with PEDOT-ClO$_4^-$/TiO$_2$(tf)/FTO, PEDOT-ClO$_4^-$/TiO$_2$(pf)/FTO, or PEDOT-ClO$_4^-$/FTO glass electrodes was performed over a frequency range of ~10$^{-1}$-10$^6$ Hz. During the EIS measurements, the AC amplitude was adjusted to 150 mV using a potentiostat. A deposited Pt film electrode was used as the CE. The electrolyte solution used for the I-V and EIS measurements consisted of 50 × 10$^{-3}$ mol·dm$^{-3}$ I$_2$ (Wako Pure Chemical Industries, Ltd.), 0.5 mol·dm$^{-3}$ LiI (Wako Pure Chemical Industries, Ltd.), and 0.5 mol·dm$^{-3}$ 4-tert-butylpyridine (Aldrich, USA) in 3-methoxypropionitrile (Tokyo Chemical Industry). The surface area of the electrochemical cell was 50.24 mm$^2$ and the distance between the working electrode (WE) and the CE was maintained at 50 μm, which is similar to that of the samples fabricated for the measurement of the I-V curves.

Cyclic voltammetry (CV) curves were measured in an acetonitrile electrolyte solution containing 1.0 × 10$^{-5}$ mol·dm$^{-3}$ I$_2$, 10 × 10$^{-3}$ mol·dm$^{-3}$ LiI, and 0.1 mol·dm$^{-3}$ LiClO$_4$ at a scan rate of 0.1 V·s$^{-1}$ from −0.5 V to 1.5 V using a potentiostat. The electrochemical cell comprised a PEDOT-ClO$_4^-$/TiO$_2$(tf)/FTO, PEDOT-ClO$_4^-$/TiO$_2$(pf)/FTO, or Pt film WE; a Pt film CE prepared by sputter deposition; and an Ag/AgI reference electrode. The distance between the two electrodes in the electrochemical cell was maintained at 5 mm, and the surface area of the electrode was 64 mm$^2$.

2.3 Fabrication and electrochemical evaluation of solar cells

A WE was fabricated by electrophoretic deposition. Two parallel pieces of FTO conductive glass substrate (Asahi Glass Co. Ltd.) that were the same size as the electrodes were immersed in a TiO$_2$ suspension. By applying a 10 V DC bias voltage for 35 s, TiO$_2$(pf) was electrochemically deposited on the cathode surface followed by the formation of a circular TiO$_2$ film (φ 6 mm) followed by sintering at 500°C for 30 min. The obtained TiO$_2$(pf) was immersed in a 0.3 mM N719 dye (Peccell Technologies Inc.) solution at 40°C for 2 h. The N719 dye solution was prepared by dissolving N719 dye in a 1:1.2 molar ratio mixture of tert-butyl alcohol (Wako Pure Chemical Industries, Ltd.), ethanol, and acetonitrile (Wako Pure Chemical Industries, Ltd.).

Two-electrode sandwich DSSCs were fabricated according to a previously reported procedure$^{20,21}$. The distance between the WE and the CE was maintained at 50 μm, and
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the surface area of the DSSC was 24 mm$^2$.

To investigate the influence of reflected light on performance, DSSCs with either a black paper film with low reflectance or an aluminum foil film with high reflectance attached to the outside of the cathode were prepared. The performance of the prepared DSSCs was measured using a source meter (2400 source meter, Keithley Instruments Inc.) and an AM 1.5 solar simulator (100 mW cm$^{-2}$) with a 500 W Xe lamp light source. The incident photoelectron conversion efficiency (IPCE) spectra were measured using an IPCE spectrometer (Bunkoukeiki Co. Ltd.).

3 RESULTS AND DISCUSSION

3.1 Morphology and crystal structure of the prepared TiO$_2$(tf) electrode

SEM images of the surface and cross-sections of the prepared TiO$_2$(tf) electrode are shown in Fig. 1. The TiO$_2$(tf) films fabricated by spin coating was homogeneously coated for all the precursor concentrations. As can be seen in Figs. 1 (b) and (c), the surfaces of the prepared TiO$_2$(tf) electrodes became smoother, which was due to coating of the uneven sections, than that of a bare FTO glass electrode with unique sub-micron size crystallites. The thicknesses of the as-prepared TiO$_2$(tf) films were determined to be 59.7, 127.1, and 218.1 nm for the 0.25 M, 0.5 M, and 1.0 M precursors, respectively. The TiO$_2$(tf) film prepared from the 1.0 M precursor was confirmed to be a tightly condensed nanoparticle film (not shown), while fuzzy PEDOT-ClO$_4^-$ was formed on the TiO$_2$(tf) electrode prepared by electrochemical polymerization. On the other hand, the FESEM surface images (not shown) of the TiO$_2$(pf) film confirmed that it was porous, had a thickness of 1.2 μm, and had a high surface area. Therefore, Fig. 1 (f) suggests that the PEDOT-ClO$_4^-$ film was embedded within the TiO$_2$ nanoporous particle film.

XRD patterns were measured to clarify the crystal structures of the prepared TiO$_2$ thin films. The XRD patterns of the prepared TiO$_2$(tf), TiO$_2$(pf), and FTO glass substrate are shown in Fig. 2. Characteristic peaks at $2\theta = 25.32^\circ$ and $38.94^\circ$ were observed and can be attributed to the diffraction peaks of the (101) and (112) planes of the TiO$_2$ thin film, respectively; this indicates the formation of an anatase structure. In addition, an anatase peak at $2\theta = 48.02^\circ$, which was assigned to the (200) plane, was observed for the

Fig. 1 SEM images of the electrodes: a) cross-section of a bare FTO glass electrode, b) surface of a bare FTO glass electrode, c) surface of TiO$_2$(tf) (0.5 M) on an FTO glass electrode, d) cross-section of TiO$_2$(tf) (0.5 M) on an FTO glass electrode, e) cross-section of PEDOT-ClO$_4^-$/TiO$_2$(tf) (0.5 M) on an FTO glass electrode, f) cross-section of PEDOT-ClO$_4^-$/TiO$_2$(pf) on an FTO glass electrode.

Fig. 2 X-ray diffraction patterns of TiO$_2$ (tf) grown on FTO glass, TiO$_2$ powder, and FTO glass electrodes obtained using small-angle XRD and powder XRD apparatuses, respectively.
The primary roles of the CE are the reduction of $\Gamma^-/I_3^-$ in the electrolyte and the collection of electrons from the external circuit. Therefore, it is necessary to investigate the electrocatalytic activity of the prepared CEs for the redox reaction. Figure 3 shows cyclic voltammograms of the various electrochemical cells; the parameters are summarized in Table 1. As can be seen in Fig. 3, the oxidation and reduction peaks of $I_3^-/I^-$ on these CEs were similar. Furthermore, two pairs of redox peaks were evident for all the electrodes and were assigned to the following chemical reactions:

\[
I_3^- + 2e^- = 3I^- \tag{1}
\]

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

To assess the performance of the CE in DSSCs, it is very important to evaluate the reduction wave since it indicates the reduction activity towards $I_3^-/I^-$. As can be seen in Fig. 3, the reduction current density was increased by introducing TiO₂(tf) or TiO₂(pf) between the PEDOT-ClO₄⁻ and the bare FTO interface. From Table 1, which summarizes the CV parameters, it can be confirmed that the area of the reduction peak, which corresponds to the quantity of electric charge used for reduction, increased with the exception of the double layer. The observed quantity of electric charge for reduction was found to be $9.49 \, \text{mC cm}^{-2}$ for PEDOT-ClO₄⁻/TiO₂(pf), which was due to the increased particle roughness, as reported previously. On the other hand, for PEDOT-ClO₄⁻/TiO₂(tf), both the reduction current and quantity of electric charge for reduction increased slightly. This may be attributed to the slight increase of roughness irrespective of the density of the packed TiO₂ thin film.

Next, electrochemical impedance experiments were performed to estimate the interfacial resistance between the electrode and the electrolyte. The electrochemical impedance spectra are shown in Fig. 4, and the electrochemical impedance parameters for the interfaces between the electrolyte and various electrodes are summarized in Table 2. The inset in Fig. 4 shows an equivalent circuit of the measurement system. Fig. 4a shows Nyquist plots for the electrochemical cells with PEDOT-ClO₄⁻ film and PEDOT-ClO₄⁻/TiO₂(tf) composite film electrodes in the frequency range of $10^{-1}$ Hz-10⁵ Hz. Figs. 4b and 4c show Bode diagrams of the serial resistance and phase angle differences of the electrochemical cells with various WEs and a Pt-sputtered glass CE, respectively. In the Nyquist plots shown in Fig. 4a, three semicircular arcs are clearly evident, while two semicircular arcs were observed for the Pt electrode. Furthermore, three characteristic frequencies were observed.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Parameters of the cyclic voltammograms for the $\Gamma^-/I_3^-$ redox reaction.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ox. peak pot.</td>
<td>Red. peak pot.</td>
</tr>
<tr>
<td>/ mV</td>
<td>/ mV</td>
</tr>
<tr>
<td>Pt</td>
<td>670.5</td>
</tr>
<tr>
<td>PEDOT-ClO₄⁻</td>
<td>631.0</td>
</tr>
<tr>
<td>PEDOT-ClO₄⁻/TiO₂(pf)</td>
<td>650.7</td>
</tr>
<tr>
<td>PEDOT-ClO₄⁻/TiO₂(tf) (0.25 M)</td>
<td>630.6</td>
</tr>
<tr>
<td>PEDOT-ClO₄⁻/TiO₂(tf) (0.5 M)</td>
<td>630.6</td>
</tr>
<tr>
<td>PEDOT-ClO₄⁻/TiO₂(tf) (1.0 M)</td>
<td>630.3</td>
</tr>
</tbody>
</table>
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Fig. 4  Electrochemical impedance of electrochemical cells with various electrodes:
  a) Nyquist plots of electrochemical cells with various WEs and Pt-sputtered FTO glass electrodes, b) Bode phase plots of the imaginary axis, c) Bode phase plots of the magnitude for impedance. The measurements were carried out at an AC amplitude of 150 mV in the range of $10^{-1}$ to $10^6$ Hz.

in the Bode phase plots (Fig. 4b) for the electrochemical cells with PEDOT-ClO$_4^-$ film, PEDOT-ClO$_4^-$/TiO$_2$ (pf), and PEDOT-ClO$_4^-$/TiO$_2$ (pf) electrodes.

The impedance parameters were obtained by fitting the experimental spectra to that of the equivalent circuit and are summarized in Table 2. In our analyses, the semicircles in the frequency regions above $10^2$ Hz and between $10^{-1}$-10$^6$ Hz were assigned to the impedance ($R_s$) and capacitance (CPE$_1$) for the charge transfer at the Pt film/electrolyte interface and the impedance ($R_1$) and capacitance (CPE$_2$) at the PEDOT-ClO$_4^-$/TiO$_2$ film/electrolyte interface, respectively. Impedance at frequencies below $10^6$ Hz was assigned to resistance caused by the diffusion of $I^-/I_3^-$ ions at a slower charge transfer. In this case, the diffusion resistance of the ions is considered to be a Warburg impedance but with finite diffusion over the narrow distance between electrodes, which results in nonlinear spectra. As can be seen in Fig. 4 and Table 2, the $R_2$ of the electrolyte/TiO$_2$ film interface increased and shifted to a higher frequency. Among the various TiO$_2$ films studied, the interfacial resistance between PEDOT-ClO$_4^-$/TiO$_2$ (pf) and the electrolytes was reduced almost by half. Impedances above $10^6$ Hz could not be measured due to instrumental limitations.

The relaxation time of the TiO$_2$(tf) system was shorter than that of the PEDOT-ClO$_4^-$/bare FTO electrode. Even though FTO and TiO$_2$ do not act against the catalytic reduction of $I^-/I_3^-$, the resistances of the electrolyte/FTO and electrolyte/TiO$_2$ interfaces were above several tens of kilo-ohms. These results, which were obtained by the introduction of TiO$_2$(tf), were considered to result from improved conductivity between PEDOT-ClO$_4^-$ and the bare FTO glass interface. In addition, the frequency increase due to the insertion of TiO$_2$(tf) into the PEDOT-ClO$_4^-$/bare FTO glass interface probably facilitated the movement of electrons. These results suggest that the TiO$_2$ layer not only increases the effective surface area of the catalyst but also improves the performance due to enhanced electron transfer.

Table 2  Electrochemical impedance parameters for the interfaces between the electrolyte and various electrodes.

<table>
<thead>
<tr>
<th></th>
<th>$R_s$ /Ω cm$^2$</th>
<th>$R_1$ /Ω cm$^2$</th>
<th>CPE$_1$ /μF cm$^2$</th>
<th>$n_1$</th>
<th>$T_1$ /μs</th>
<th>$R_2$ /Ω cm$^2$</th>
<th>CPE$_2$ /μF cm$^2$</th>
<th>$n_2$</th>
<th>$T_2$ /ms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>1.02</td>
<td>9.59</td>
<td>5.85</td>
<td>0.898</td>
<td>56.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEDOT-ClO$_4^-$</td>
<td>5.31</td>
<td>4.25</td>
<td>10.09</td>
<td>0.932</td>
<td>42.9</td>
<td>5.94</td>
<td>1529</td>
<td>0.878</td>
<td>9.08</td>
</tr>
<tr>
<td>PEDOT-ClO$_4^-$ / TiO$_2$ (pf)</td>
<td>9.42</td>
<td>4.71</td>
<td>11.39</td>
<td>0.937</td>
<td>53.7</td>
<td>2.82</td>
<td>873</td>
<td>0.815</td>
<td>2.46</td>
</tr>
<tr>
<td>PEDOT-ClO$_4^-$ / TiO$_2$ (tf) (0.25 M)</td>
<td>5.48</td>
<td>3.90</td>
<td>11.21</td>
<td>0.914</td>
<td>43.8</td>
<td>5.70</td>
<td>1300</td>
<td>0.855</td>
<td>7.41</td>
</tr>
<tr>
<td>PEDOT-ClO$_4^-$ / TiO$_2$ (tf) (0.5 M)</td>
<td>5.25</td>
<td>3.66</td>
<td>9.66</td>
<td>0.898</td>
<td>35.3</td>
<td>4.86</td>
<td>605</td>
<td>0.858</td>
<td>2.94</td>
</tr>
<tr>
<td>PEDOT-ClO$_4^-$ / TiO$_2$ (tf) (1.0 M)</td>
<td>6.34</td>
<td>4.15</td>
<td>10.63</td>
<td>0.906</td>
<td>44.1</td>
<td>5.65</td>
<td>615</td>
<td>0.914</td>
<td>3.48</td>
</tr>
</tbody>
</table>

Table 3  Percent ratio of reflected light to incident light at a 530 nm wavelength obtained from the diffuse reflectance UV-vis spectra. BaSO$_4$ powder was used as a reference.

<table>
<thead>
<tr>
<th></th>
<th>Bare FTO</th>
<th>TiO$_2$ (pf)</th>
<th>TiO$_2$ (tf) (0.25 M)</th>
<th>TiO$_2$ (tf) (0.5 M)</th>
<th>TiO$_2$ (tf) (1.0 M)</th>
<th>Pt$_{23}^{(2)}$</th>
<th>Al$_{23}^{(2)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No reflector</td>
<td>4.23</td>
<td>11.06</td>
<td>6.40</td>
<td>5.51</td>
<td>5.69</td>
<td>62.6</td>
<td>92.28</td>
</tr>
<tr>
<td>With Al foil reflector</td>
<td>43.80</td>
<td>44.16</td>
<td>47.57</td>
<td>47.18</td>
<td>46.37</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Unit: %

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3.3 Influence of reflected light on photocatalyst performance
The as-prepared PEDOT-ClO$_4^-$/TiO$_2$ (tf) electrodes were transparent but had a lustrous appearance due to their reflection of light. The Pt-sputtered FTO glass used in this study also had a metallic luster. Therefore, to investigate the influence of light reflected from the surface of the electrode, diffuse UV-vis spectra were measured. The reflectance values obtained from the diffuse UV-vis spectra are shown in Table 3.

A wavelength of ~530 nm corresponds to the maximum absorption of the N719 dye. As can be seen in Table 3, both TiO$_2$ (tf) and TiO$_2$ (pf) had higher reflectance values than bare FTO glass. TiO$_2$ (tf) was apparently transparent, whereas TiO$_2$ (pf) was white and semitransparent. This difference may result from their different reflectance values. When aluminum foil was placed on the opposite side of the CE from the films, the reflectance increased significantly for both films. The iodine electrolyte solution absorbs in the visible light range, i.e., around 660 nm, but the spectrum shape is smooth. Furthermore, since the electrolyte solution was a thin layer of 50 μm, an improvement in the

### Table 4 IPCE parameters.

<table>
<thead>
<tr>
<th></th>
<th>Bare FTO</th>
<th>TiO$_2$ (pf)</th>
<th>TiO$_2$ (tf) (0.25 M)</th>
<th>TiO$_2$ (tf) (0.5 M)</th>
<th>TiO$_2$ (tf) (1.0 M)</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>No reflector</td>
<td>30.79</td>
<td>35.72</td>
<td>34.01</td>
<td>34.45</td>
<td>32.42</td>
<td>41.11</td>
</tr>
<tr>
<td>With Al foil reflector</td>
<td>33.38</td>
<td>36.28</td>
<td>35.28</td>
<td>35.91</td>
<td>35.98</td>
<td>—</td>
</tr>
</tbody>
</table>

Unit: %

### Table 5 Performance of DSSCs with various CEs with and without aluminum foil reflectors. The data in parentheses are the performances of the DSSCs with aluminum foil reflectors.

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$/mA cm$^{-2}$</th>
<th>$V_{oc}$/V</th>
<th>Fill Factor</th>
<th>Efficiency/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>11.89</td>
<td>0.771</td>
<td>0.549</td>
<td>5.03</td>
</tr>
<tr>
<td>PEDOT-ClO$_4^-$</td>
<td>9.25 (10.81)</td>
<td>0.760 (0.741)</td>
<td>0.547 (0.552)</td>
<td>3.85 (4.42)</td>
</tr>
<tr>
<td>PEDOT-ClO$_4^-$ / TiO$_2$ (pf)</td>
<td>10.91 (11.40)</td>
<td>0.750 (0.763)</td>
<td>0.564 (0.552)</td>
<td>4.61 (4.79)</td>
</tr>
<tr>
<td>PEDOT-ClO$_4^-$ / TiO$_2$ (tf) (0.25 M)</td>
<td>10.46 (10.92)</td>
<td>0.771 (0.768)</td>
<td>0.548 (0.545)</td>
<td>4.42 (4.57)</td>
</tr>
<tr>
<td>PEDOT-ClO$_4^-$ / TiO$_2$ (tf) (0.5 M)</td>
<td>10.78 (11.07)</td>
<td>0.746 (0.780)</td>
<td>0.564 (0.537)</td>
<td>4.54 (4.63)</td>
</tr>
<tr>
<td>PEDOT-ClO$_4^-$ / TiO$_2$ (tf) (1.0 M)</td>
<td>10.98 (11.26)</td>
<td>0.743 (0.740)</td>
<td>0.558 (0.548)</td>
<td>4.55 (4.57)</td>
</tr>
</tbody>
</table>
photocurrent due to the increase in reflected light was expected.

Next, IPCE spectra were measured for the DSSCs with different CEs. The obtained IPCE spectra are shown in Fig. 5, and the relevant parameters are summarized in Table 4. As can be seen in Fig. 5 and Table 4, IPCE was particularly improved in the wavelength range of 530 to 730 nm. In addition, photocurrent density-voltage curves (Fig. 6) and their parameters (Table 5) were measured for DSSCs with different CEs.

As can be seen in Fig. 6, the performance of DSSCs with PEDOT-ClO$_4^-$/TiO$_2$(tf) CEs was higher than that of PEDOT-ClO$_4^-$ films alone. Without reflector, the photocurrent density significantly increased from 9.25 mA cm$^{-2}$ for a DSSC with a PEDOT-ClO$_4^-$ film CE to 10.78 mA cm$^{-2}$ for a DSSC with a PEDOT-ClO$_4^-$/TiO$_2$(tf) (0.5 M) CE. In addition, all DSSCs with reflectors had a higher current density ($J_\text{sc}$) than DSSCs without reflectors. The DSSCs with a PEDOT-ClO$_4^-$/TiO$_2$(tf) (0.5 M) CE had a higher conversion efficiency of around 4.63%, which is almost equal to the 4.79% efficiency of the DSSC with a PEDOT-ClO$_4^-$/TiO$_2$(0.5 M) film CE. This increase in $J_\text{sc}$ was probably due to improved adhesion between the TiO$_2$ and PEDOT-ClO$_4^-$ film CE. As can be seen in Table 5, the photocurrent due to the increase in reflected light was expected. The DSSCs with Al foil reflectors had a higher photocurrent density and conversion efficiency of around 4.79% than DSSCs without reflectors. Among the systems with Al reflectors, DSSCs with PEDOT-ClO$_4^-$/TiO$_2$(tf) (1.0 M) CEs had the highest photocurrent (11.26 mA cm$^{-2}$). This value is close to the photocurrent generated by DSSCs with PEDOT-ClO$_4^-$/TiO$_2$(pf) CEs (11.40 mA cm$^{-2}$). These measured photocurrents correspond to about 95% of that achieved by the DSSC with a Pt sputtered CE. These results indicate that DSSCs with reflectors exhibit a higher photocurrent and higher conversion efficiency than DSSCs without reflectors. Therefore, the use of reflected light is necessary for the improvement of $J_\text{sc}$ and, as a result, can improve the conversion efficiency.

4 CONCLUSIONS

The performance of PEDOT-ClO$_4^-$ was improved by the introduction of TiO$_2$(tf). DSSCs with a PEDOT-ClO$_4^-$/TiO$_2$(tf) electrode exhibited a higher photocurrent density and increased conversion efficiency due to improvements in interfacial roughness and electron transfer. The use of reflected light was effective at further improving the performance of DSSCs, which suggests that the use of the reflected light is necessary for the improvement of $J_\text{sc}$ and, as a result, may lead to improved conversion efficiency.

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