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Preparation and properties of dye-sensitized solar cell using chlorophyll derivative immobilized TiO_2 film electrode

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Abstract

A dye-sensitized solar cell using the visible light sensitization of chlorophyll-a derivative, chlorine-e_6 (Chl-e_6) immobilized on TiO_2 film was developed. From fluorescence spectrum of Chl-e_6 immobilized on TiO_2 film, the emission of Chl-e_6 was effectively quenched by TiO_2, indicating that the effective electron injection from the excited singlet state of Chl-e_6 into the conduction band of TiO_2 occurred. The short-circuit photocurrent density (I_{SC}), the open-circuit photovoltage (V_{OC}), and the fill factor (FF) of solar cell consisting of Chl-e_6 immobilized on TiO_2 film electrode and platinum-coated substrate electrode were estimated to be 1.47 mA cm^{-2}, 425 mV, and 57.0%, respectively. IPCE values were reached a maximum around the wavelength of absorption maximum (11.0% at 400 nm, 4.7% at 541 nm and 7.9% at 661 nm), indicating that the dye-sensitized solar cell using visible light sensitization of TiO_2 film by Chl-e_6 was developed.

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Keywords: Photovoltaic conversion device; Chlorine-e_6; Chlorophyll; TiO_2; Visible light sensitization

1. Introduction

Dye-sensitized solar cells have paid much attention as low cost conventional solid-state photovoltaic cells [1]. Many studies on the dye-sensitized solar cell have been reported in recent years [2–18]. The most successful photo-induced electron transfer sensitisers employed so far in these cells are ruthenium(II) polypyridyl complexes. The overall photovoltaic conversion efficiencies was 10% in the dye-sensitized solar cells using organometallic compounds based on the ruthenium(II) polypyridyl complexes such as N3 dye [1–4]. To improve further the performance of the dye-sensitized solar cells using ruthenium(II) polypyridyl complexes, it is imperative to enhance their near-infrared response. Metallophthalocyanines possess intense absorption band in the far-red and near-infrared region and excellent photostability, chemical and thermal stability. The dye-sensitized solar cells using the far-red and near-infrared sensitization of methallophthalocyanines have been reported [17–21]. Chlorophylls, which act as an effective photosensitizer in photosynthesis of green plant, has absorption maximum at 670 nm [22]. Thus, chlorophylls are attractive compound as a photosensitizer in visible region. As the carboxylate groups establish an electronic coupling with the 3d conduction band orbital manifold of Ti, the carboxylate groups substitutents in photosensitizers (dye molecules) are essential for anchoring the dye on the surface of TiO_2. The effective electron injection from the photoexcited state of photosensitizer to the conduction band orbital of Ti is achieved by the electronic coupling between the 3d conduction band orbital manifold of Ti and photosensitizer molecule. Thus, the carboxylate groups in photosensitizer molecule are essential for the dye molecule of dye-sensitized solar cell. As chlorophyll-a does not have the carboxylate group, the effective electron injection from the photoexcited state of chlorophyll to the conduction band orbital of Ti will not be achieved. On the other hand, chlorine-e_6 (Chl-e_6) formed by the hydrolysis of chlorophyll has three carboxylate groups in molecule as shown in Fig. 1. The absorption spectrum of Chl-e_6 is similar to that of chlorophyll, indicating the Chl-e_6 is suitable visible light photosensitizer for the dye-sensitized solar cell. The photosensitization of colloidal TiO_2 with copper chlorophyllin has been investigated by fluorescence quenching, laser flash photolysis, and microwave absorption by Kamat et al. [23]. Moreover, Gratzel et al. reported the mechanism of photosensitization of nanocrystalline TiO_2 solar cells by chlorophyll derivatives Chl-e_6 and copper chlorophyllin [24]. The mechanism of photo-induced electron transfer between the photoexicted state of chlorophyll derivatives and nanocrystalline TiO_2, the photoelectrochemical properties of chlorophyll derivatives immobilized on nanocrystalline

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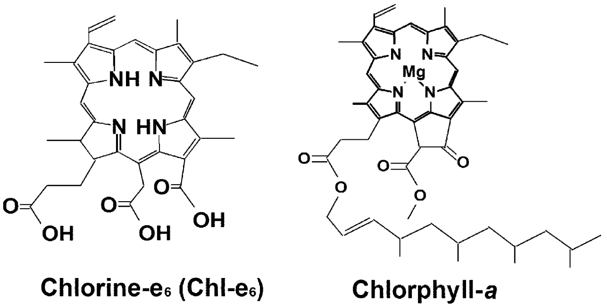

Fig. 1. Chemical structures of Chl-e_6 and chlorophyll-*a*.

TiO_2 and the photocurrent and photovoltage transient were reported. However, the properties of dye-sensitized solar cell using visible light sensitization of TiO_2 film by Chl-e_6 have not been yet clarified. To develop highly photoelectochemical conversion device using dye-sensitized solar cell based on the visible light sensitization of TiO_2 film by Chl-e_6 it is necessary investigate the detailed characteristic of the dye-sensitized cell using Ch-e_6 immobilized on TiO_2 film.

In this work, chlorophyll derivative, Chl-$e_{6,}$ immobilized TiO_2 film electrode was prepared and the photoelectrochemical properties of the dye-sensitized solar cell using visible light sensitization of TiO_2 film by Chl-e_6 were investigated.

2. Experimental

2.1. Materials

Chl-e_6 was purchased from Wako Chemical Co. Ltd. Titanium dioxide powder (P25) was purchased from Degussa. The 0.05 M I_2/0.5 M KI in ethylene glycol/acetonitrile solution was obtained from Sol Ideas Technology Development. The other chemicals were analytical grade or the highest grade available. Optical transparent conductive glass plate (OTE) (10–15 Ω/sq SnO_2: fluorine coated) was obtained from Nihon Sheet Glass Co. Ltd.

2.2. Preparation of TiO_2 film electrode

The TiO_2 film onto an OTE was prepared by a similar procedure to that described in [25,26]. TiO_2 powder was dispersed by grinding conc. HNO_3 in aqueous solution. The viscous suspension was spread onto OTE (5 cm × 5 cm) at room temperature using scotch tape as a spacer. A thin film was obtained by raking off the excess of suspension with a glass rod. After the tape was removed and the plate was dried using a hot plate at 80 °C for 30 min, this plate was annealed at 450 °C for 30 min under ambient condition to form a TiO_2 film electrode. The thickness of the film, determined by using a micron-sensitive caliper, was about 10 μm. The active electrode area was typically 4.0 cm^2.

2.3. Preparation of Chl-e_6 immobilized on TiO_2 film electrode

A Chl-e_6 immobilized TiO_2 electrode was prepared as follows. An OTE glass plate with TiO_2 film was dipped into 0.2 mmol dm^{-3} Chl-e_6 in methanol solution at room temperature for 24 h. After dipping, the plate was washed with methanol several times and then the plate was dried under vacuum overnight.

2.4. Spectroscopic measurements

UV-Vis absorption and emission spectrum of Chl-e_6 immobilized on TiO_2 electrode were recorded using a Multispec-1500 spectrophotometer (Shimadzu) and spectrofluorophotometer with a 150 W xenon lamp as a visible excitation light source (RF-5300PC Shimadzu), respectively. For emission spectrum measurement, excitation and emission bandpasses were 5.0 nm, respectively.

2.5. Characterization of dye-sensitized solar cell using Chl-e_6 immobilized TiO_2 electrode

Photocurrent–photovoltage characteristic of the Chl-e_6 immobilized on TiO_2 electrode was measured with a sandwich type cell. The working electrode with the Chl-e_6 immobilized on TiO_2 film was gently squeezed together with a carbon-coated or platinum-coated OTE glass electrode (counter electrode) using spring and irradiated from the substrate side of working electrode. The carbon-coated electrode was prepared by casting the conducting graphite paste (Okensyoji Co. Ltd.). The platinum-coated electrode was prepared by thermal decomposition of H_2PtCl_6 from isopropanol on an OTE substrate annealed at 380 °C for 30 min under ambient condition [27]. The 0.05 M I_2/0.5 M KI in ethylene glycol/acetonitrile solution was used as the redox electrolyte. A 200 W tungsten lamp was used as light source for the photocurrent and photovoltage characteristics with the two digital multimeters with model 2000-J (Keithley) as a current meter and model 34401A (Agilent) as a voltage meter, respectively. The photocurrent and photovoltage were changed using 500 Ω variable resistor. The distance between lamp and test cell was 4.0 cm. The active electrode area was typically 4.0 cm^2. The light intensity on the surface of cell was 80 mW cm^{-2} measured with laser power meter model AN/2 (Ophir Optronics Inc.). The fill factor (FF) is defined by

$$\mathrm{FF} = \frac{I_{\mathrm{Ph(max)}} V_{\mathrm{Ph(max)}}}{I_{\mathrm{SC}} V_{\mathrm{OC}}} \quad (1)$$

where $I_{\mathrm{Ph(max)}}$ and $V_{\mathrm{Ph(max)}}$ are the photocurrent and photovoltage for maximum power output ($P_{\max}$) and I_{SC} and V_{OC} are the short-circuit photocurrent and open-circuit photovoltage. The overall photoenergy conversion efficiency (η)

is defined by the following equation:

$$\eta = \frac{I_{SC} V_{OC} FF}{P_{in}} \quad (2)$$

Here P_{in} is the power of incident white light.

A 400 W xenon lamp with a monochromator was used as light source for photocurrent action spectra measurements. The cell was operated in the short-circuit mode. The incident photon-to-current conversion efficiency (IPCE) values were determined between 400 and 760 nm. The IPCE was then calculated according to the following equation:

$$\mathrm{IPCE} = \frac{1240 i_{ph}(\mu A)}{P(\mu W)\lambda(nm)} \quad (3)$$

where i_{ph} and P are the photocurrent and power of the incident radiation per unit area and λ is the wavelength of the monochromatic light.

3. Results and discussion

3.1. Spectroscopic characterization of Chl-e_6 immobilized on TiO_2 film

The emission spectra of Chl-e_6 in methanol solution (a) and Chl-e_6 immobilized on TiO_2 film (b) with 600 nm excitation is shown in Fig. 2. For Chl-e_6 in methanol solution, the maximum of the luminescence is located at 675 nm. In contrast, the fluorescence intensity of Chl-e_6 immobilized on TiO_2 film was decreased, indicating that the emission of Chl-e_6 was effectively quenched by TiO_2. In the previously report, the emission quenching processes of aluminum phthalocyanine on TiO_2 film were studied using fluorescence emission quenching and the time-resolved fluorescence spectroscopy [21]. The fluorescence emission intensity of aluminum phthalocyanine on TiO_2 film was smaller than that of aluminum phthalocyanine in solution and the fluorescence lifetime of aluminum phthalocyanine on TiO_2 film was shorter than that of aluminum phthalocyanine in solution. These results indicate that the emission of aluminum phthalocyanine was quenched by the electron injection from the excited singlet state of aluminum phthalocyanine into the conduction band of TiO_2 particles [21]. In our work, the quenching of emission of Chl-e_6 was also found to be due to electron injection from the excited singlet state of Chl-e_6 into the conduction band of TiO_2. Gratzel et al. also reported that the mechanism of photosensitization of nanocrystalline TiO_2 solar cells by Chl-e_6 [23]. The mechanism of photo-induced electron transfer between the photoexcited state of chlorophyll derivatives and nanocrystalline TiO_2, the photoelectrochemical properties of Chl-e_6 immoblized on nanocrystalline TiO_2 and the photocurrent and photovoltage transient were reported. In this report, the flouorescence emission intensity of Chl-e_6 on TiO_2 film was smaller than that of Chl-e_6 in ethanol solution. As the fluorescence emission intensity of Chl-e_6 on TiO_2 film was weak, the peak of fluorescence emission due to Chl-e_6 observed in previous reported. In contrast, no peak of flouorescence emission due to Chl-e_6 observed in our result. This result shows that the effective electron injection from the photoexcited state of Chl-e_6 to the conductive band of TiO_2 was attained.

3.2. Photocurrent–photovoltage characterization of dye-sensitized solar cell using Chl-e_6 immobilized on TiO_2 film electrode

Fig. 3 shows the photocurrent–photovoltage characteristics of a sandwich solar cell based on the Chl-e_6 immobilized on TiO_2 film electrode irradiated with 200 W tungsten lamp with a light intensity of 80 mW cm^{-2} as a light source. For using carbon-coated OTE electrode as a counter electrode, the I_{SC} and values of solar cell using

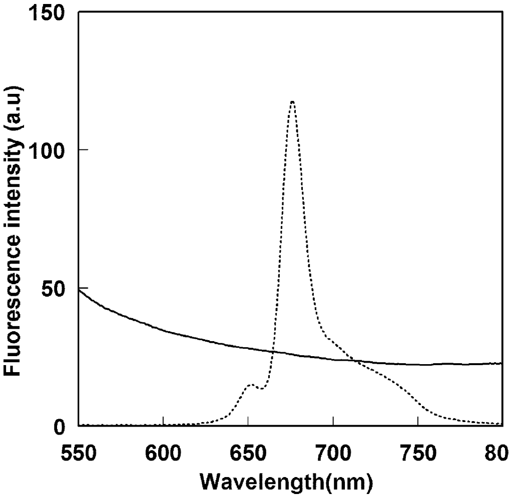

Fig. 2. Fluorescence spectra of Chl-e_6 in methanol solution (dash) and Chl-e_6 adsorbed TiO_2 film (solid). The excitation wavelength was 600 nm.

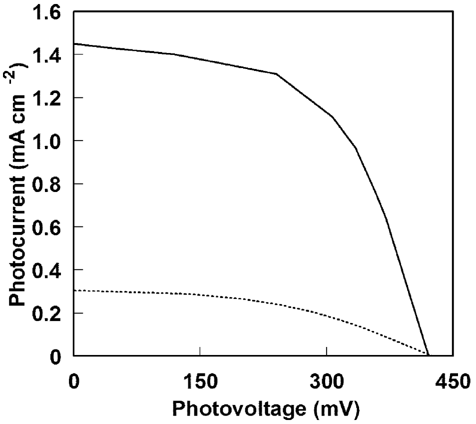

Fig. 3. Photocurrent–photovoltage characterization of dye-sensitised solar cell using Chl-e_6 immobilized on TiO_2 film electrode with 200 W tungsten lamp as a light source. Solid and dash lines are cells using platinum-coated and carbon-coated OTE substrates as counter electrode, respectively. The light intensity was 80 mW cm^{-2}.

Chl-e_6 immobilized on TiO_2 film electrode were estimated to be 0.305 mA cm^{-2} and 426 mV, respectively. The FF value was estimated to be 45.0% using Eq. (1). The η value was estimated to be 0.073%. The P_{max} was 58.6 μW cm^{-2}. In contrast, I_{SC}, V_{OC}, FF and η of Chl-e_6-sensitized solar cell using platinum-coated OTE as a counter electrode were 1.47 mA cm^{-2}, 425 mV, 57.0 and 0.40%, respectively. The maximum power output was 335.9 μW cm^{-2}. We can see that all factors for the cell using platinum-coated OTE as a counter electrode are higher than those of carbon-coated OTE substrate. These results show that the electron transfer from counter electrode to I_3^- is rapid using platinum-coated OTE, compared with that of carbon-coated OTE electrode.

3.3. Photocurrent action spectra of dye-sensitized solar cell using Chl-e_6 immobilized on TiO_2 film electrode

The effect of wavelength of light source on the photocurrent of the solar cell using Chl-e_6 immobilized on TiO_2 film electrode was investigated. Fig. 4 shows the photocurrent action spectrum of dye-sensitized solar cell based on the Chl-e_6 immobilized on TiO_2 film electrode, where the incident photon-to-current conversion efficiency (IPCE) is plotted as a function of wavelength. The photocurrent action spectrum was similar to that of the UV-Vis absorption spectrum of Chl-e_6 in methanol solution as shown in the inset of Fig. 4. IPCE values were reached a maximum around the wavelength of absorption maximum. For using carbon-coated OTE electrode as a counter electrode, IPCE at 400, 541 and 661 nm are 7.40, 1.44 and 2.91%, respectively. In contrast, IPCE of cell using platinum-coated OTE electrode at 400, 541 and 661 nm are 11.0, 4.7 and 7.9%, respectively. IPCE values at all wavelengths for the cell using platinum-coated OTE as a counter electrode are higher than those of carbon-coated OTE substrate. Thus, the dye-sensitized solar cell using visible light sensitisation of TiO_2 film by Chl-e_6 was developed.

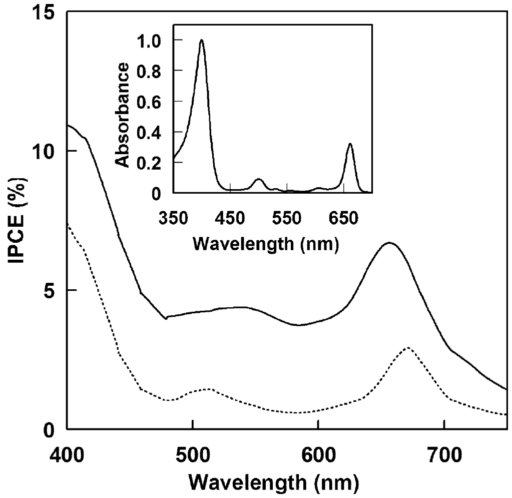

Fig. 4. Photocurrent action spectra of dye-sensitised solar cell using Chl-e_6 immobilized on TiO_2 film electrode. Solid and dash lines are cells using platinum-coated and carbon-coated OTE substrates as counter electrode, respectively. The IPCE is plotted as a function of wavelength. The inset is UV-Vis absorption spectrum of Chl-e_6 in methanol solution.

The resistances of platinum-coated and carbon-coated OTE electrodes were ca. 10 and 70 Ω/sq, respectively. By using platinum-coated OTE electrode as counter electrode, the electron transfer from a counter electrode to redox electrolyte is rapid compared with that of carbon-coated OTE electrode. Thus, the electrical current efficiency is improved using platinum-coated OTE electrode as counter electrode in the photovoltage–photocurrent characterization and photocurrent action spectrum measurement.

Next let us focus on the stability of solar cell using Chl-e_6 immobilized on TiO_2 film electrode against continuous irradiation. Only little photocurrent and photovoltage changes were observed after 24 h irradiation with a 200 W tungsten lamp. These results indicate that Chl-e_6 has a good photostability and solar cell using Chl-e_6 immobilized on TiO_2 film electrode is stable under continuous irradiation.

4. Conclusion

In this work the dye-sensitized solar cell using the Chl-e_6 immobilized TiO_2 film electrode was prepared and its photoelectrochemical properties were studied. All factors for the cell coupling the Chl-e_6 immobilized TiO_2 film electrode and platinum-coated OTE as a counter electrode are higher than those of carbon-coated OTE substrate. I_{SC}, V_{OC}, FF and η of Chl-e_6-sensitized solar cell using platinum-coated OTE as a counter electrode were 1.47 mA cm^{-2}, 425 mV, 57.0 and 0.40%, respectively. The maximum power output was 335.9 μW cm^{-2}. IPCE values at 400, 541 and 661 nm are 11.0, 4.7 and 7.9%, respectively. The photocurrent–photovoltage characteristics of solar cell using Chl-e_6 immobilized on TiO_2 electrode under light intensity of 100 mW cm^{-2} (AM1.5) is being studied in detail.

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