

Dye-sensitised Solar Cell Using Chlorophyll Immobilized on TiO₂ Nanocrystalline Film Electrode

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Chlorin e₆ (Chl-e₆) derived from chlorophyll-*a* from *Spirulina* immobilized on TiO₂ nanocrystalline film electrode was prepared and the photoelectrical properties of the dye-sensitised solar cell using visible and near-IR light sensitisation of nanocrystalline TiO₂ film by Chl-e₆ were investigated. To develop the convenient dye-sensitised solar cell, the carbon-coated OTE glass electrode was used as a counter electrode instead of platinum-coated OTE electrode. Photocurrent-photovoltage characteristic and photocurrent action spectrum of Chl-e₆ immobilized on TiO₂ nanocrystalline electrode were measured with sandwich type cell. The working electrode with the Chl-e₆ on TiO₂ film was gently squeezed together with a carbon-coated OTE glass electrode and irradiated from the substrate side of working electrode. The short-circuit photocurrent, the open-circuit photovoltage, and the fill factor of solar cell using Chl-e₆ immobilized on TiO₂ nanocrystalline film electrode were estimated to be 0.305 ± 0.012 mA cm⁻², 426 ± 10 mV, and 0.45, respectively. Photocurrent action spectrum of the solar cell using Chl-e₆ on TiO₂ film electrode was measured. Incident photon-to-current conversion efficiency (IPCE) values were reached a maximum around the wavelength of absorption maximum (7.40% at 400 nm; 1.44% at 514 nm and 2.91% at 670 nm).

Key words: chlorophyll-*a*, dye-sensitised solar cell, TiO₂, chlorin e₆

1. INTRODUCTION

Dye-sensitised nanocrystalline solar cells have attracted much attention as low cost conventional prevailing photovoltaic cells [1]. In recent years, many studies on the dye-sensitised nanocrystalline solar cells have been reported [2-9]. The most successful photoinduced electron transfer sensitizers employed so far in these cells are ruthenium(II) polypyridyl complexes. The overall photovoltaic conversion efficiencies was 10% in the dye-sensitised nanocrystalline solar cells using ruthenium(II) polypyridyl complexes under light intensity of 100mW cm⁻², the equivalent of one sun at AM1.5 [2-4,9]. To improve further the performance of the dye-sensitised nanocrystalline 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-sensitised nanocrystalline solar cells using the IR and near-IR sensitisation of metallo-phthalocyanines have been reported [5-8]. In contrast, chlorophyll-*a*, which acts as an effective visible and near-IR photosensitizer in photosynthesis, has absorption maximum at 670 nm. Thus, chlorophyll-*a* is an attractive compound for dye-sensitised solar cell as a photosensitizer in visible and near-IR region. The carboxylic acid substituents in Ru(II) polypyridyl complexes are essential for anchoring the dye on the surface of TiO₂. The carboxylate groups establish an electronic coupling with the 3d conduction band orbital

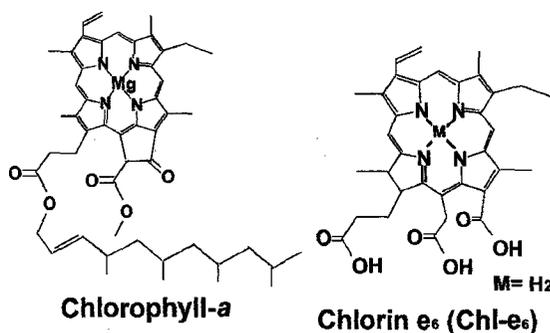


Fig. 1 Chemical structures of chlorin e₆ (Chl-e₆) and chlorophyll-*a*.

manifold of Ti. Chlorin-e₆ (Chl-e₆) as shown in Fig. 1, formed by the hydrolysis of chlorophyll-*a*, was used in this work. The UV-vis absorption spectrum of Chl-e₆ is similar to that of chlorophyll-*a*, indicating the Chl-e₆ is an attractive visible and near-IR photosensitizer for dye-sensitised solar cell. The photosensitization of colloidal TiO₂ with copper chlorophyllin has been investigated by fluorescence quenching, laser flash photolysis, and microwave absorption by Kamat et al [10]. Moreover, Grätzel et al reported the mechanism of photosensitization of nanocrystalline TiO₂ solar cells by chlorophyll derivatives, Chl-e₆ and copper chlorophyllin [11,12]. The mechanism of photoinduced electron transfer between the photoexcited state of chlorophyll derivatives and nanocrystalline TiO₂, the photoelectrochemical properties of chlorophyll

derivatives immobilized on nanocrystalline TiO₂ and the photocurrent and photovoltage transient were reported. However, the properties of dye-sensitised solar cell using visible light sensitisation of TiO₂ film by Chl-e₆ have not been yet clarified. To develop highly photoelectrochemical conversion device using dye-sensitised solar cell based on the visible light sensitisation of TiO₂ film by Chl-e₆, it is necessary to investigate the detailed characteristic of the conventional dye-sensitised solar cell using Chl-e₆ immobilized on TiO₂ film. Moreover, platinum coated ITO electrode with highly catalyst activity of the reduction of I₃⁻ to I⁻ in electrolyte is used for the counter electrode in the dye-sensitised solar cell. However, platinum electrode is expensive. Thus, it is desirable that cheaper electrode such as carbon can be used. If the dye-sensitised solar cell using cheap carbon as a counter electrode instead of platinum electrode is developed, the convenient dye-sensitised solar cell will be accomplished.

In this work, to develop the convenient dye-sensitised solar cell using Chl-e₆ derived from chlorophyll-*a* adsorbed nanocrystalline TiO₂ film electrode, the photoelectrical properties of the solar cell using visible and near-IR sensitisation of nanocrystalline TiO₂ film by Chl-e₆ with the carbon-coated OTE glass electrode as a counter electrode were investigated.

2. MATERIALS AND METHODS

Chl-e₆ trisodium salt was purchased from Wako Chemical Co. Ltd. TiO₂ powder (P25) was purchased from Degussa. The 0.05 mol dm⁻³ I₂ / 0.5 mol dm⁻³ KI in ethylene glycol / acetonitrile solution was obtained from Sol Ideas Technology Development. The other chemicals were analytical grade or the highest grade available. Conductive glass plate (10-15 Ω/square SnO₂: fluorine coated) was obtained from Nihon Sheet Glass Co. Ltd. The nanocrystalline TiO₂ film was prepared by a similar procedure to that described in the literatures [9]. TiO₂ powder was dispersed by grinding in concentrated nitric acid aqueous solution (pH=1.0). The viscous suspension was spread onto transparent conductive glass plate (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 hot plate at 80 °C for 30 min, this plate was annealed at 450 °C for 30 min under ambient condition to form a nanocrystalline TiO₂ film electrode. The thickness of the film, determined by using a micron-sensitive caliper, was about 10 μm. A Chl-e₆ adsorbed nanocrystalline TiO₂ electrode was prepared as follows. An OTE glass plate with a nanocrystalline TiO₂ film was dipped into 0.2 mmol dm⁻³ methanol solution of Chl-e₆ 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. Photocurrent-photovoltage characteristic of Chl-e₆ adsorbed nanocrystalline TiO₂ electrode was measured with sandwich type cell. The working electrode with the Chl-e₆ adsorbed on nanocrystalline TiO₂ film was gently squeezed together with a carbon-coated OTE glass electrode using spring and irradiated from the working electrode side. The 0.05 mol dm⁻³ I₂ / 0.5 mol dm⁻³ 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 multimeter with model 2000-J (Keithley) and model 34401A (Agilent). The distance between the lamp and a test cell was 4.0 cm. The active electrode area was typically 4.0 cm². The light intensity on the surface of a test cell was 80 mW cm⁻² measured with laser power meter model AN/2 (Ophir Optronics, Inc). The fill factor (FF) is defined by

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

where $I_{Ph(max)}$ and $V_{Ph(max)}$ are the photocurrent density and photovoltage for maximum power output and I_{SC} and V_{OC} are the short-circuit photocurrent density and open-circuit photovoltage. The overall photoenergy conversion efficiency (η) is defined by the following equation:

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

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:

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

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

The emission spectra of Chl-e₆ in methanol solution and Chl-e₆ immobilized on TiO₂ film (bold line) with excitation of 500 nm attributed to small absorption peak of Chl-e₆ are shown in Fig. 2. For Chl-e₆ in methanol solution, the maximum of the luminescence is located at 675 nm. In contrast, the fluorescence intensity of Chl-e₆ immobilized on TiO₂ film was decreased, indicating that the emission of Chl-e₆ was effectively quenched by TiO₂. In the previously report, the emission quenching processes of aluminium and zinc phthalocyanine on TiO₂ film were studied using fluorescence emission quenching and the time-resolved

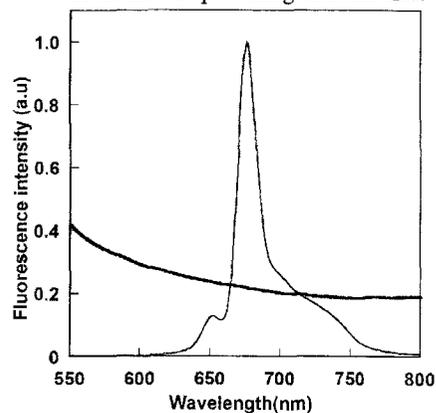


Fig. 2 Fluorescence emission spectra of Chl-e₆ in methanol solution and Chl-e₆ adsorbed TiO₂ film (bold line). The excitation wavelength was 500 nm.

fluorescence spectroscopy [5,6]. The fluorescence

emission intensity of aluminium and zinc phthalocyanine on TiO₂ film was smaller than that of the solution and the fluorescence lifetime of aluminium and zinc phthalocyanine on TiO₂ film was shorter than that of the solution. These results indicate that the emission of aluminium and zinc phthalocyanine was quenched by the electron injection from the excited singlet state of aluminium and zinc phthalocyanine into the conduction band of TiO₂ particles [5,6]. In our work, the quenching of emission of Chl-e₆ was also found to be due to electron injection from the excited singlet state of Chl-e₆ into the conduction band of TiO₂. Grätzel et al also reported that the mechanism of photosensitization of nanocrystalline TiO₂ solar cells by Chl-e₆ [11,12]. The mechanism of photoinduced electron transfer between the photoexcited state of chlorophyll derivatives and nanocrystalline TiO₂, the photoelectrochemical properties of Chl-e₆ immobilized on nanocrystalline TiO₂ and the photocurrent and photovoltage transient were reported. In this report, the fluorescence emission intensity of Chl-e₆ on TiO₂ film was smaller than that of Chl-e₆ in ethanol solution. As the fluorescence emission intensity of Chl-e₆ on TiO₂ film was weak, the peak of fluorescence emission due to Chl-e₆ observed in previous reported. In contrast, no peak of fluorescence emission due to Chl-e₆ observed in our result. This result shows that the effective electron injection from the photoexcited state of Chl-e₆ to the conductive band of TiO₂ was attained.

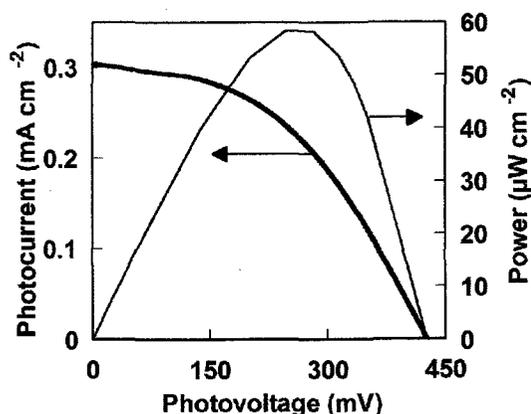


Fig. 3. Photocurrent-photovoltage (bold line) and power-photovoltage characterizations of solar cell using Chl-e₆ adsorbed on nanocrystalline TiO₂ film electrode with 200 W tungsten lamp as a light source. The light intensity was 80 mW cm⁻².

Fig. 3 shows the photocurrent-photovoltage and photovoltage-power output characteristics of a sandwich solar cell based on the Chl-e₆ adsorbed on a nanocrystalline TiO₂ film electrode irradiated with 200 W tungsten lamp with a light intensity of 80 mW cm⁻² as a light source. The I_{SC} and values of solar cell using Chl-e₆ adsorbed on a nanocrystalline TiO₂ film electrode were estimated to be 0.305 ± 0.012 mA cm⁻² and 426 ± 10 mV, respectively. The FF value was estimated to be 0.45 using equation (1). The η value was estimated to be 0.073%. The P_{max} was $58.6 \mu\text{W cm}^{-2}$. The $I_{Ph(max)}$ and $V_{Ph(max)}$, which indicate the photocurrent and photovoltage for P_{max} , are estimated to be 0.240 ± 0.011 mA cm⁻² and 247 ± 10 mV, respectively. In contrast, I_{SC} , V_{OC} , FF and

η of Chl-e₆ sensitised solar cell using platinum-coated OTE electrode as a counter electrode were 1.47 mA cm⁻², 425 mV, 0.57, and 0.40%, respectively. P_{max} was $335.9 \mu\text{W cm}^{-2}$. By using platinum-coated OTE electrode as counter electrode, little change is observed in the V_{OC} value. On the other hand, the I_{SC} increased using platinum-coated OTE electrode, compared with that of carbon-coated OTE electrode. Since the electrical resistance of carbon-coated OTE electrode is larger than that of platinum-coated OTE electrode, the electron transfer from counter electrode to I₃⁻ in electrolyte is rapid using platinum-coated OTE electrode, compared with that of carbon-coated OTE electrode. Moreover, the catalytic activity of platinum for the reduction of I₃⁻ to I⁻ in electrolyte is higher than that of carbon. Thus, the I_{SC} increased using platinum-coated OTE electrode, compared with that of carbon-coated OTE electrode. Next, comparison of the cell performance of a cell using eosin-Y, which is widely used as standard dye molecule and that of Chl-e₆ is discussed. For a solar cell using eosin Y, I_{SC} , V_{OC} , FF and η , were 0.205 ± 0.020 mA cm⁻², 250 ± 11 mV, 0.38, and 0.02%, respectively. P_{max} was $19.0 \mu\text{W cm}^{-2}$. All factors for solar cell using Chl-e₆ adsorbed on a nanocrystalline TiO₂ film electrode are higher than those of the eosin-Y adsorbed electrode. As total of molar coefficient of Chl-e₆ in the visible region between 400 and 700 nm is larger than that of eosin-Y, the light harvesting efficiency of Chl-e₆ is higher than that of eosin-Y. Thus, the cell performance improved using Chl-e₆ adsorbed on a nanocrystalline TiO₂ film electrode.

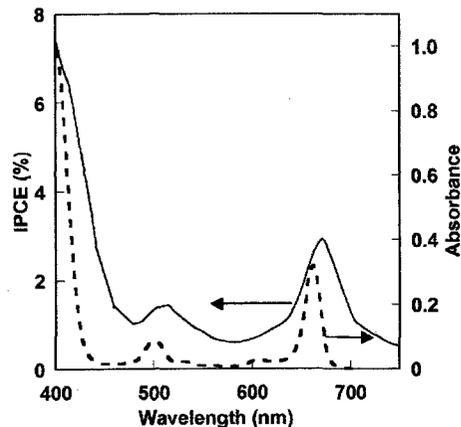


Fig. 4 Photocurrent action spectrum of dye-sensitised solar cell based on the Chl-e₆ adsorbed on a nanocrystalline TiO₂ film electrode. The IPCE is plotted as a function of wavelength. The dash line indicates the UV-vis absorption spectrum of Chl-e₆ in methanol solution.

Next let us focus on the effect of wavelength of light source on the photocurrent of the solar cell using Chl-e₆ adsorbed on a nanocrystalline TiO₂ film electrode was investigated. Fig. 4 shows the photocurrent action spectrum of dye-sensitised solar cell based on the Chl-e₆ adsorbed on a nanocrystalline TiO₂ 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-e₆ in methanol

solution as shown Fig. 4 (dash line). IPCE values were reached a maximum around the wavelength of absorption maximum (7.40% at 400 nm; 1.44% at 514 nm and 2.91% at 661 nm) and IPCE values at 400 and 661 nm are larger than that at 514 nm. Thus, the dye-sensitised solar cell using visible light sensitisation of nanocrystalline TiO₂ film by Chl-e₆ was developed.

Although efficiency is still low compared with that using platinum-coated OTE electrode, the dye-sensitised solar cell using carbon-electrode as a counter electrode can use as a convenient solar cell.

4. CONCLUSION

In this work to develop the convenient dye-sensitised solar cell using Chl-e₆ derived from chlorophyll-*a* adsorbed nanocrystalline TiO₂ film electrode, the photoelectrical properties of the solar cell using visible and near-IR sensitisation of nanocrystalline TiO₂ film by Chl-e₆ with the carbon-coated OTE glass electrode as a counter electrode were studied. J_{SC} , V_{OC} , FF and η for the solar cell coupling the Chl-e₆ immobilized TiO₂ film electrode and carbon-coated OTE as a counter electrode were estimated to be 0.305 ± 0.012 mA cm⁻², 426 ± 10 mV, 0.45, and 0.73%, respectively. The maximum power output was 58.6 μ W cm⁻². IPCE values at 400, 541 and 661 nm are 7.4, 1.4 and 2.9%, respectively. The photocurrent-photovoltage characteristics of solar cell using Chl-e₆ immobilized on TiO₂ electrode under light intensity of 100 mW cm⁻² (A.M.1.5) is being studied in detail.

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