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Dye-sensitized Solar Cell with the Electrode of Chlorophyll Derivative Adsorbed on Titanium Dioxide Film

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A dye-sensitized solar cell using a chlorine- e_6 (Chl- e_6) derived from chlorophyll- α , as visible and near-infrared sensitizer for nanocrystalline TiO_2 films was developed. The short-circuit photocurrent density (I_{sc}), the open-circuit photovoltage (V_{oc}), and the fill factor (FF) of solar cell using Chl- e_6 adsorbed on nanocrystalline TiO_2 film electrode were estimated to be $0.305 \pm 0.012 \text{ mA cm}^{-2}$, $426 \pm 10 \text{ mV}$, and 45.0%, respectively. The overall photoenergy conversion efficiency (η) was 0.73%.

Key Words : Dye-sensitized Solar Cell, Chlorine- e_6 , Visible and Near-infrared Sensitization

1 Introduction

Dye-sensitized nanocrystalline solar cells have attracted much attention as low cost conventional prevailing photovoltaic cells.¹⁾ In recent years, many studies on the dye-sensitized nanocrystalline solar cells have been reported.²⁻¹⁸⁾ The most successful photoinduced electron transfer sensitizers employed so far in these cells are ruthenium(II) polypyridyl complexes yielding overall photovoltaic conversion efficiencies was 10% in the dye-sensitized nanocrystalline solar cells using ruthenium(II) polypyridyl complexes under light intensity of 100 mW cm^{-2} , the equivalent of one sun at AM 1.5.^{2-4, 16)} To improve further the performance of the dye-sensitized nanocrystalline solar cells using ruthenium(II) polypyridyl complexes, it is imperative to enhance their near-infrared response. Metallo-phthalocyanines possess intense absorption band in the far-red and near-infrared region and excellent photostability, chemical and thermal stability. The dye-sensitized nanocrystalline solar cells using the far-red and near-infrared sensitization of methallophthalocyanines have been reported.^{17, 18)} Despite their potential of the near-infrared sensitization, a methallophthalocyanines and ruthenium(II) polypyridyl complexes contain a heavy metal ion, these compounds would be undesirable photosensitizer from environmental

point of view. On the other hand, chlorophyll- α , which act as an effective visible and near-infrared photosensitizer in photosynthesis of green plant,¹⁹⁾ has absorption maximum at 670 nm. Thus, chlorophyll- α is an attractive compound for dye-sensitized solar cell as a photosensitizer in visible and near-infrared region. The carboxylic acid substituents in Ru(II) polypyridyl complexes are essential for anchoring the dye on the surface of TiO_2 .^{20, 21)} The carboxylate groups establish an electronic coupling with the 3d conduction band orbital manifold of Ti. Chlorine- e_6 (Chl- e_6), formed by the hydrolysis of chlorophyll- α , was used in this work (the structure is shown in Fig. 1). As Chl- e_6 does not contain a heavy metal ion, Chl- e_6 can be an environment-friendly photosensitizer. As shown in Fig. 2, the absorption spectrum of Chl- e_6 is similar to that of chlorophyll- α , indicating the Chl- e_6 is a attractive visible and near-infrared photosensitizer for dye-sensitized solar cell.

In this work Chl- e_6 derived from chlorophyll- α adsorbed nanocrystalline TiO_2 film electrode was prepared

Fig. 1 Chemical structure of chlorine- e_6 (Chl- e_6).

Fig. 2 UV-vis absorption spectra of Chl- e_6 (solid line) and chlorophyll- α (broken line) in methanol solution.

and the photoelectrical properties of the solar cell using visible and near-infrared sensitization of nanocrystalline TiO₂ film by Chl-e₆ were investigated.

2 Experimental

Chl-e₆ trisodium salt and eosin-Y were 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.^{2, 5-9} 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. The solar cell using eosin-Y adsorbed on nanocrystalline TiO₂ film electrode also was prepared as a standard solar cell. 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 34401 A (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 Optonics, Inc). The fill factor (FF) is defined by

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

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 200 W tungsten lamp with optical color filter was used as a light source for the investigation of the effect of the wavelength of light source on the short-circuit photocurrent density of solar cell using Chl-e₆ adsorbed on nanocrystalline TiO₂ film electrode. The optical color filters used were blue filter (BLF-410B, wavelength of maximum transmittance: 370~480 nm), green filter (GRF-533G, wavelength of maximum transmittance: 530~550 nm) and IR transmittance filter (SCF-60R, wavelength of maximum transmittance: >600 nm). The optical color filters were obtained from Sigma Koki Co. Ltd.

3 Results and Discussion

Figure 3 shows the photocurrent-photovoltage and power-photovoltage characteristics of a sandwich solar cell based on the Chl-e₆ (solid line) and eosin-Y (dotted line) adsorbed on nanocrystalline TiO₂ film electrode irradiated using 200 W tungsten lamp with a light intensity of 80 mW cm⁻² as a light source. The I_{SC} and V_{OC} , values of solar cell using Chl-e₆ adsorbed on nanocrystalline TiO₂ film electrode were 0.305 ± 0.012 mA cm⁻² and 426 ± 10 mV, respectively. The maximum power output and FF were 58.6 μW cm⁻² and 45.0%, respectively. The η value calculated using eqn. (2) was estimated to be 0.73%. For a eosin-Y adsorbed on nanocrystalline TiO₂ film electrode, on the other hand, I_{SC} , V_{OC} , FF and η were 0.205 ± 0.020 mA cm⁻², 250 ± 11 mV, 38.0%, and 0.02%, respectively. The maximum power output was 19.0 μW cm⁻². We can see that all factors for Chl-e₆ adsorbed on nanocrystalline TiO₂ film electrode are higher than those of the eosin-Y adsorbed electrode.

Next let us focus on the effect of wavelength region of light source on the short-circuit photocurrent density changes of the solar cell using Chl-e₆ and eosin-Y adsorbed on nanocrystalline TiO₂ film electrode. For solar cell using Chl-e₆ adsorbed on nanocrystalline TiO₂ film electrode, the photocurrents with the irradiation through

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

the blue, green, and IR transmittance filters were 0.101 ± 0.011 , 0.090 ± 0.008 , and $0.260 \pm 0.011 \text{ mA cm}^{-2}$, respectively. Especially, little change in the photocurrents between the irradiation with near-infrared region light and the irradiation without optical color filter ($0.305 \pm 0.012 \text{ mA cm}^{-2}$) was observed. The photoresponse of the Chl- e_6 adsorbed electrode extends well into the near-infrared region. Thus, the solar cell using visible and near-infrared sensitization of Chl- e_6 was achieved. For the solar cell using the eosin-Y adsorbed on nanocrystalline TiO_2 electrode, on the other hand, the photocurrents with the irradiation through the blue, green, IR transmittance filters and without optical filter were 0.04 ± 0.011 , 0.16 ± 0.016 , 0.007 ± 0.0003 and $0.205 \pm 0.020 \text{ mA cm}^{-2}$, respectively. The photocurrent decreased with the irradiation without optical color filters. Since the absorption band of eosin-Y is around at 520 nm, little change in the photocurrents between the irradiation with green region light and the irradiation without optical color filter was observed. These results show that the visible and near-infrared sensitized solar cell was attained using Chl- e_6 adsorbed on nanocrystalline TiO_2 electrode.

The photocurrent action spectrum and photocurrent-photovoltage characteristics of solar cell using Chl- e_6 adsorbed on nanocrystalline TiO_2 electrode under light intensity of 100 mW cm^{-2} , the equivalent of one sun at AM 1.5, are being studied in detail.

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