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Visible-Light Sensitisation of Nanocrystalline TiO_2 Film by Mg Chlorophyll-*a* through the Axial Imidazole-4-acetic Acid Ligand

Keiko Aoki, Yumi Takeuchi, and Yutaka Amao*

Department of Applied Chemistry, Oita University,
Dannoharu 700, Oita 870-1192

Received May 24, 2004; E-mail: amao@cc.oita-u.ac.jp

Mg chlorophyll-*a* (MgChl-*a*) with imidazole-4-acetic acid (Im) as the axial ligand (MgChl-*a*–Im), adsorbed on a nanocrystalline TiO_2 film electrode, was prepared. Further, the photoelectrical properties of a solar cell using visible-light sensitisation of the nanocrystalline TiO_2 film through an axial Im ligand of MgChl-*a* were investigated.

Dye-sensitised nanocrystalline solar cells have attracted much attention as low-cost conventional solid state photovoltaic conversion devices.[1] Many studies on dye-sensitised nanocrystalline solar cells have been reported.[2–6] The most successful photoinduced electron-transfer sensitizers employed so far in these cells have been ruthenium(II) polypyridyl complexes. The photovoltaic conversion efficiency was 10% in dye-sensitised nanocrystalline solar cells using ruthenium(II) polypyridyl complexes.[2–4] To further improve the performance of dye-sensitised nanocrystalline solar cells using ruthenium(II) polypyridyl complexes, it is imperative to enhance their near-infrared response, which is weak due to the small extinction coefficient of such ruthenium(II) complexes above 600 nm. On the other hand, Mg chlorophyll-*a* (MgChl-*a*), which acts as an effective photosensitizer in a photosynthesis reaction,[7] has an absorption maximum in the visible-light region. Thus, MgChl-*a* is an attractive compound as a visible photosensitiser. The carboxylic acid substituents in Ru(II) polypyridyl complexes are essential for anchoring the dye onto the surface of TiO_2. The carboxylate groups establish an electronic coupling with the 3d conduction-band orbital manifold of Ti. The interfacial binding between the dye with a carboxyl group and the TiO_2 surface is considered to have three types of carboxylic coordination modes: unidentate, bidentate chelating, and bridging.[8,9] These coordination modes are formed between the carboxyl group and Ti. Because MgChl-*a* does not have a carboxyl group, chlorin-e_6 (Chl-e_6) formed by the hydrolysis of MgChl-*a* has two carboxyl groups in the molecule. We previously reported on a solar cell based on the visible-light photosensitisation of Chl-e_6 adsorbed on a nanocrystalline TiO_2 film electrode; the maximum peak of the photocurrent action spectrum of a cell using Chl-e_6 was 670 nm.[10] In photosynthesis proteins, MgChl-*a* is not fixed via a covalent bond, but is fixed via coordination with an imidazole site of the histidine residue as an axial ligand. Grätzel et al. previously reported on the visible-light sensitization of nanocrystalline TiO_2 by the ruthenium(II) phthalocyanine through the axial 3,4-dicarboxylpyridine ligands.[11] By using MgChl-*a*, which is coordinated by an imidazole with a carboxyl group as an axial ligand, the direct use of MgChl-*a* can be carried out as the photosensitiser of a solar cell.

In the present work, MgChl-*a* with imidazole-4-acetic acid (Im) as an axial ligand (MgChl-*a*–Im) adsorbed on a nanocrystalline TiO_2 film (MgChl-*a*–Im/TiO_2) electrode was prepared, and the photoelectrical properties of a solar cell using the visible-light sensitisation of the nanocrystalline TiO_2 film by MgChl-*a* were studied.

MgChl-*a* was purchased from Juntech Corporation. Titanium dioxide powder (P25) was purchased from Degussa. The 0.05 $\mathrm{mol\,dm^{-3}}$ I_2/0.5 $\mathrm{mol\,dm^{-3}}$ LiI in an ethylene glycol/acetonitrile solution was obtained from Sol Ideas Technology Development. The other chemicals were of analytical grade or the highest grade available. A conductive glass plate (10–15 Ω/square SnO_2: fluorine coated) (OTE) was obtained from Nihon Sheet Glass Co. Ltd.

MgChl-*a*–Im was synthesized by refluxing MgChl-*a*, 10.0 mg (1.12×10^{-5} mol), with about 10-times the molar equivalent of Im, 18.2 mg (1.12×10^{-4} mol), in 50 mL of methanol at 60 °C for 6 h. The synthetic reaction of MgChl-*a*–Im was monitored by the UV–vis absorption spectrum using a Shimadzu Multispec 1500 spectrophotometer. When Im was added to the MgChl-*a* in methanol, the Soret band of MgChl-*a* changed with the isosbestic point at 421 nm by the coordination of Im to the axial site of MgChl-*a*. After the mixture was cooled to room temperature, the solvent was removed under a vacuum. The residue was dissolved in acetone, and then the unreacted Im was removed as precipitation. Finally, MgChl-*a*–Im was obtained by removing the solvent under a vacuum. The yield of MgChl-*a*–Im was 3.1 mg (26%) (TOF-MS m/z 1018 $[M + H^+]$). The nanocrystalline TiO_2 film was prepared by a similar procedure to that described in the literature.[2,5,6] A MgChl-*a*–Im/TiO_2 electrode was prepared as follows. An OTE glass plate with a nanocrystalline TiO_2 film was dipped into a 0.2 $\mathrm{mmol\,dm^{-3}}$ methanol solution of MgChl-*a*–Im at room temperature for 24 h. After dipping, the plate was washed with methanol several times, and then dried under a vacuum overnight. MgChl-*a* adsorbed on nanocrystalline TiO_2 film (MgChl-*a*/TiO_2) electrode was also prepared as a reference. The photocurrent–photovoltage characterization of the MgChl-*a*–Im/TiO_2 electrode was measured with a sandwich-type cell. The working electrode with MgChl-*a*–Im/TiO_2 was gently squeezed together with a platinum-coated OTE glass electrode using a spring, and irradiated from the substrate side of the working electrode. A platinum-coated electrode was prepared by the thermal decomposition of H_2PtCl_6 from 2-propanol on an OTE substrate, and annealed at 380 °C for 30 min under an ambient condition. The 0.05 $\mathrm{mol\,dm^{-3}}$ I_2/0.5 $\mathrm{mol\,dm^{-3}}$ LiI in ethylene glycol acetonitrile was used as a redox electrolyte. A solar simulator (YSS-40, Yamashita Denso) was used as a light source (A.M. 1.5, 100 $\mathrm{mW\,cm^{-2}}$). The photocurrent and photovoltage were measured by two dig-

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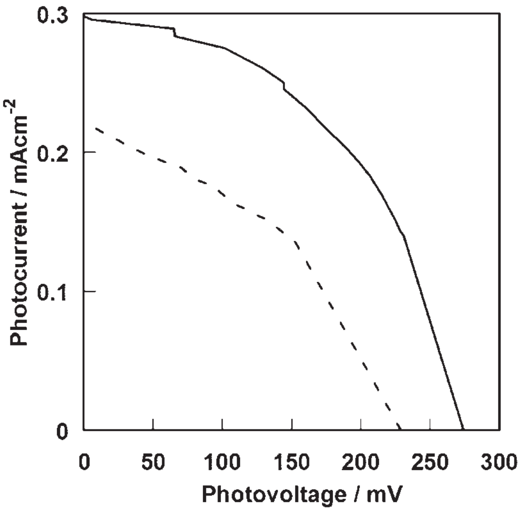

Fig. 1. Photocurrent–photovoltage characteristic of cell using MgChl-*a*–Im/TiO_2 electrode under A.M. 1.5 (100 mW cm^{-2}) condition. The dotted line shows that of the cell using MgChl-*a*/TiO_2 electrode.

ital multimeters with model 2000-J (Keithley) and model 34401A (Agilent), respectively. The active electrode area was typically 1.0 cm^2.

A 400 W xenon lamp with a monochromator was used as a 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 900 nm. The IPCE was then calculated according to the following equation:

$$\mathrm{IPCE} = 1240 i_{\mathrm{ph}}(\mu\mathrm{A})/P(\mu\mathrm{W})\lambda(\mathrm{nm}), \qquad (1)$$

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

Figure 1 shows the photocurrent–photovoltage characteristics of the sandwich solar cell based on the MgChl-*a*–Im/TiO_2 electrode irradiated with 100 mW cm^{-2}. The short-circuit photocurrent (I_{SC}) was 0.30 mA cm^{-2} and the open-circuit photovoltage (V_{OC}) was 275 mV. The maximum power was estimated to be 38.4 µW cm^{-2} and the fill factor (FF) was estimated to be 46.5%. In contrast, the I_{SC}, V_{OC}, maximum power, and FF of a solar cell based on the MgChl-*a*/TiO_2 electrode (dotted line) were 0.22 mA cm^{-2}, 229 mV, 20.7 µW cm^{-2}, and 41.1%, respectively.

Figure 2 shows the photocurrent action spectrum of a solar cell based on the MgChl-*a*–Im/TiO_2 electrode (bold line), where the IPCE is plotted as a function of the wavelength. It is similar to that of the UV–vis absorption spectrum of MgChl-*a*–Im in methanol, as shown in Fig. 2 (dotted line). The IPCE values reach a maximum at around the wavelength of the absorption maximum (3.4% at 400 nm and 1.2% at 680 nm). On the other hand, the action spectrum of a cell using a MgChl-*a*/TiO_2 electrode (plain line) was also similar to that of the UV–vis absorption spectrum of MgChl-*a* in methanol. However, the IPCE values were lower than that of a cell using a MgChl-*a*–Im/TiO_2 electrode (0.9% at 400 nm and 0.1% at 680 nm). To investigate the photoinduced electron injection process form the photoexcited singlet state of MgChl-*a* to the conduction band of TiO_2, the emission spectra of MgChl-*a*–Im/TiO_2 and MgChl-*a*/TiO_2 were measured with 600 nm excitation. First, the emission spectra of MgChl-*a*–Im/Al_2O_3 and MgChl-*a*/Al_2O_3 were measured and the emission peak was observed at 700 nm. In both cases, no fluorescence quenching of MgChl-*a*–Im or MgChl-*a* by an insulator Al_2O_3 was observed. The fluorescence intensity of MgChl-*a*–Im/Al_2O_3 or MgChl-*a*/Al_2O_3 was used as a reference (I_0). For MgChl-*a*–Im/TiO_2, the fluorescence intensity ($I_{\mathrm{MgChl}\text{-}a\text{-Im}}$) at 700 nm decreased and the $I_0/I_{\mathrm{MgChl}\text{-}a\text{-Im}}$ value was estimated to be 100. For MgChl-*a*/TiO_2, in contrast, the fluorescence intensity ($I_{\mathrm{MgChl}\text{-}a}$) at 700 nm also decreased, and the $I_0/I_{\mathrm{MgChl}\text{-}a}$ value was estimated to be 73. These results indicate that the emission of MgChl-*a*–Im was effectively quenched by electron injection from the excited singlet state of MgChl-*a*–Im into the conduction band of TiO_2 particles. Thus, MgChl-*a*–Im anchored on nanocrystalline TiO_2 film through the axial Im ligand is an efficient visible sensitiser for a photovoltaic injection cell based on the nanocrystalline TiO_2 film electrode.

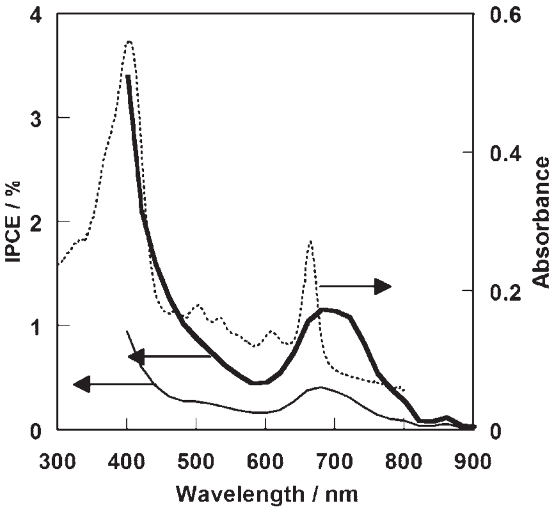

Fig. 2. Photocurrent action spectra of solar cell based on the MgChl-*a*–Im/TiO_2 (bold line), MgChl-*a*/TiO_2 electrode (plain line), and UV–vis absorption spectrum of MgChl-*a*–Im in methanol (dotted line). The IPCE is plotted as a function of wavelength.

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