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Electrochimica Acta 53 (2007) 42–45

ELECTROCHIMICA Acta

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Chlorophyll assembled electrode for photovoltaic conversion device

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Received 29 November 2005; received in revised form 26 February 2007; accepted 27 February 2007
Available online 4 March 2007

Abstract

Chlorophyll-*a* (Chl-*a*) assembled in hydrophobic domain by fatty acid with long alkyl hydrocarbon chain such as myristic acid (Myr), stearic acid (Ste) and cholic acid (Cho) modified onto nanocrystalline TiO_2 electrode is prepared and the photovoltaic properties of the nanocrystalline TiO_2 film by Chl-*a* are studied. Incident photon to current efficiency (IPCE) value at 660 nm in photocurrent action spectrum of Chl-*a*/Ste-TiO_2, Chl-*a*/Myr-TiO_2 and Chl-*a*/Cho-TiO_2 electrodes are 5.0%, 4.1% and 4.1%, respectively. Thus, the IPCE is maximum using Chl-*a*/Ste-TiO_2 electrode. From the results of photocurrent responses with light intensity of 100 mW cm^{-2} irradiation or monochromatic light with 660 nm, generated photocurrent increases using Chl-*a*/Ste-TiO_2 electrode compared with the other Chl-*a* assembled TiO_2 electrodes. These results show that the hydrophobic domain formed by stearic acid with long alkyl hydrocarbon chain is suitable for fixation of Chl-*a* onto TiO_2 film electrodes and photovoltaic performance is improved using Chl-*a* onto Ste-TiO_2 film electrode.

Keywords: Chlorophyll; Photosynthesis; Nanocrystalline TiO_2 film; Photovoltaic conversion system; Hydrophobic effect

1. Introduction

Chlorophyll-*a* and -*b* (Chl-*a* and -*b*) act as the light-harvesting in photosynthesis of green plant and exhibit physiological functions of the photolysis of water, the reduction of $NADP^+$ and carbon dioxide fixation under visible light irradiation [1]. Chlorophylls consist of Mg porphyrin ring and phytol group. Chl-*a* has absorption maxima at 432 and 670 nm and is attractive compound as a visible photosensitizer for the means of converting solar energy to chemical energy or such as a photoinduced hydrogen evolution to electrochemical energy. Many studies on the photovoltaic conversion system using chlorophyll derivatives have been reported [2–8]. In these reports, the photovoltaic conversion system using chlorophyll derivatives is directly immobilized onto electrode such as optical transparent electrode (OTE) with TiO_2 layer. For cell based on dye-sensitized TiO_2 [9], the carboxylic acid substituents in dye molecule are essential for anchoring on the surface of TiO_2. The carboxylate groups establish an electronic coupling with the 3d conduction band orbital manifold of Ti [10,11]. As Chl-*a* is attractive compound as a visible photosensitizer, no carboxylate group exists in Chl-*a* molecules. However, Chl-*a* is not fixed via covalent bond and fixed via coordination with an imidazole site of the histidine residue as an axial ligand in the hydrophobic domain of proteins plays an important in the natural photosynthesis proteins [12–14]. Thus, the hydrophobic domain of proteins will act as an important role for the fixation of Chl-*a* molecules in the natural photosynthesis systems.

In this work, Chl-*a* assembled in hydrophobic domain by fatty acid with long alkyl hydrocarbon chain such as myristic acid, stearic acid and cholic acid (chemical structures are shown in Fig. 1) modified onto nanocrystalline TiO_2 electrode is prepared and the photovoltaic properties of the nanocrystalline TiO_2 film by Chl-*a* are studied.

2. Experimental section

2.1. Materials

Chl-*a* was purchased from Juntech Corporation. Myristic acid, stearic acid and cholic acid were purchased from Tokyo Kasei Chemicals. Titanium dioxide powder (P25) was purchased from Degussa. The 0.05 mol dm^{-3} I_2/0.5 mol dm^{-3} LiI 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

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doi:10.1016/j.electacta.2007.02.071

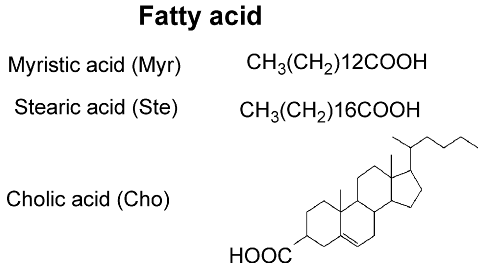


Fig. 1. Chemical structures of myristic acid (Myr), stearic acid (Ste) and cholic acid (Cho).

(10–15 Ω/□ SnO_2: fluorine coated) as an optical transparent electrode (OTE) substrate was obtained from Nihon Sheet Glass Co. Ltd.

2.2. *Preparation of nanocrystalline TiO_2 film electrode*

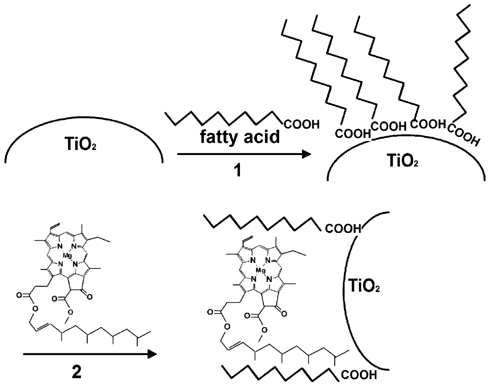
The nanocrystalline TiO_2 film was prepared by a similar procedure to that described in the literature [15,16]. TiO_2 powder was dispersed by grinding in concentrated nitric acid aqueous solution (pH 1.0). The viscous suspension was spread onto OTE (1 cm × 3 cm) at room temperature using scotch tape 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 TiO_2 film electrode. The thickness of the film, determined by using a micron-sensitive caliper, was about 10 μm. The geometric area of electrode was $1.0\,cm^2$.

2.3. *Preparation of platinum-coated OTE electrode*

The platinum-coated OTE electrode was prepared by thermal decomposition of H_2PtCl_6 from 2-propanol on an OTE substrate as following method. An OTE glass plate was dipped into $1.0\,mmol\,dm^{-3}$ H_2PtCl_6 in 2-propanol at room temperature for 30 min. After dipping, the plate was dried at room temperature for 30 min under ambient condition and then annealed at 380 °C for 30 min under ambient condition. The geometric area of electrode was $1.0\,cm^2$.

2.4. *Preparation of Chl-a assembled onto nanocrystalline TiO_2 film electrode*

Chl-*a* assembled onto nanocrystalline TiO_2 electrode was prepared according to the method as shown in Scheme 1. At first, nanocrystalline TiO_2 film electrode was dipped into $0.2\,mmol\,dm^{-3}$ methanol solution of fatty acid such as myristic acid (Myr), stearic acid (Ste) and cholic acid (Cho) at room temperature for 24 h (step 1 in Scheme 1). After dipping, the electrode was washed with methanol several times and then was dried under vacuum overnight. Fatty acid adsorbed on a nanocrystalline TiO_2 film electrode was dipped into $0.2\,mmol\,dm^{-3}$ methanol solution of Chl-*a* at room temperature for 24 h (step 2 in Scheme 1). After dipping, the electrode was washed with methanol several times and then was dried under vacuum overnight. Each electrode is referred to as Chl-*a*/Ste-TiO_2, Chl-*a*/Myr-TiO_2 and Chl-*a*/Cho-TiO_2, respectively. The amount of Chl-*a* molecules adsorbed onto nanocrystalline TiO_2 electrode was determined using a spectrophotometer (Multispec-1500 Shimadzu) according to a method previously reported [17]. The UV–vis absorption spectra of Chl-*a*/Ste-TiO_2 (solid), Chl-*a*/Myr-TiO_2 (dash) and Chl-*a*/Cho-TiO_2 (dotted) are shown in Fig. 2.



Scheme 1. Procedures of preparation of Chl-*a* assembled onto fatty acid modified TiO_2 film electrodes. 1: Modification of fatty acid onto TiO_2 film electrodes; 2: immobilization of Chl-*a* onto the electrode.

2.5. *Photocurrent action spectra measurement*

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 without applied potential. Photocurrent action spectrum was measured with a sandwich type cell. The working electrode with Chl-*a* assembled on TiO_2 film was gently squeezed together with a platinum-coated OTE glass electrode as a counter electrode using spring and irradiated from the working electrode side. The $0.05\,mol\,dm^{-3}$ $I_2/0.5\,mol\,dm^{-3}$ LiI in ethylene glycol/acetonitrile solution was used as the redox electrolyte. The distance between the working and counter electrode was 0.1 mm. The photocurrent is measured with the digital multimeters with model 34401A (Agilent). The

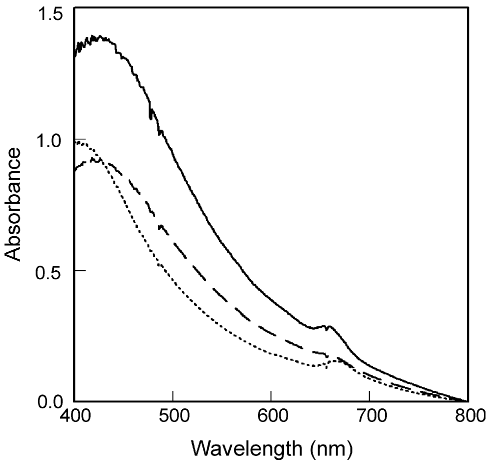


Fig. 2. UV–vis absorption spectra of Chl-*a*/Ste-TiO_2 (solid), Chl-*a*/Myr-TiO_2 (dash) and Chl-*a*/Cho-TiO_2 (dotted).