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Invited feature article

Fabrication of a dye-sensitized solar cell containing a noncarboxylated spiropyran-derived photomerocyanine with cyclodextrin

Tatsuya Takeshita, Takao Umeda, Michihiro Hara*

Department of Environmental and Food Sciences, Fukui University of Technology, Fukui, Japan

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ABSTRACT

The fabrication, photovoltaic conversion, and photo-response of dye-sensitized solar cell (DSSC) containing a noncarboxylated spiropyran 1,3,3-trimethylindolino-β-naphthopyrylospiran (**1**) and carboxymethyl-β-cyclodextrin sodium salt (CM-β-CD) were investigated for the first time. In fact, we found the adsorption of photomerocyanine form (PMC) of **1** and inclusion complexes between the PMC and CM-β-CD (PMC/CM-β-CD) to the TiO_2 surface. The formation of PMC/CM-β-CD was confirmed by fluorescence spectroscopy. The incident photon-to-current conversion efficiency (IPCE) of the PMC-containing DSSC obtained 4.1% under 570-nm light irradiation, and the highest IPCE reached 11.1% by inclusion effect of CM-β-CD. Similar, the fillfactor and the open-circuit voltage were improved by CM-β-CD layer. The IPCE value of PMC/CM-β-CD-containing DSSC was decreased by visible light treatment, and it was considered that decrease of IPCE values are attributed to the formation of PMC isomer. Therefore, we demonstrated the photovoltaic conversion and photoresponsivity of the DSSC by incorporating a noncarboxylated PMC with inclusion effect of CM-β-CD layer.

1. Introduction

Dye-sensitized solar cell (DSSC) is one of the photovoltaic solar cells, which have various features such as low manufacturing cost, simple manufacturing processes, and lightweight. Ru based dyes (*i.e.*, N3, N719, black dye and so on) are typical photosensitizing dye, which has excellent properties such as broad absorption band, high molar absorption coefficient and efficient electron injection to the oxide semiconductor, and photovoltaic conversion of DSSC containing a Ru based dyes has been achieved more than 10% [1–3]. Additionally, it has been also reported that metal free organic dyes acts as photosensitizing dye, and it is well known that merocyanine dyes indicate the high photovoltaic conversion compared with the other organic dyes, broadened and longer wavelength shift of absorption spectrum by formation of *J*-aggregate [4,5], and fatigue-resistant [6].

In general, it is well known that photosensitizing dye acts *via* the ester bond between the carboxyl groups of photosensitizing dye and hydroxyl group of TiO_2 nanoparticles surface [7]. Introducing of carboxyl groups to the photosensitizing dye needs in order to satisfy such a requirement, and it limits the choice of the dye compound for application in DSSC. We previously investigated the fabrication of photoelectrode containing a cyclodextrin (carboxymethyl-β-cyclodextrin sodium salt: CM-β-CD) layer and reported the application of noncarboxylated Ru based dye by inclusion effect of CM-β-CD [8]. CM-β-CD-based DSSC indicated the offer potential of other function by incorporating an external stimulus response molecules without carboxyl groups.

Spiropyran derivatives are one of the photochromic molecule and occurs the spiropyran form (SP) → photomerocyanine form (PMC) isomerization by using light irradiation, as shown in Scheme 1 [9–12]. Structures between the SP and PMC are quite different; SP has a nonplanar structure *via* the spiro C—O bond, whereas structure of PMC indicates the planar by cleavage of spiro C—O bond. Therefore, SP and PMC indicates the colorless and colored, respectively by change of the conjugated system. Conjugated PMC can be light harvesting at visible region, and it has been demonstrated that PMC acting as photosensitizing dye as with the merocyanine dyes. Chen et al. reported the DSSC containing a spiroindolinobenzothiopyran with adsorbed group and the self-regulation of photovoltaic conversion by SP → PMC isomerization and PMC → SP isomerization [13]. Dryza et al. investigated the photochromic reaction of spiropyran incorporated into γ-cyclodextrin onto metal oxide nanoparticles and reported the electron injection to the titania conduction band and FRET to the photosensitizing dye by excitation of PMC [14]. However,

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* Corresponding author at: Department of Environmental and Food Sciences, Fukui University of Technology, 3–6–1 Gakuen, Fukui 910–8505, Japan.
E-mail address: hara@fukui-ut.ac.jp (M. Hara).

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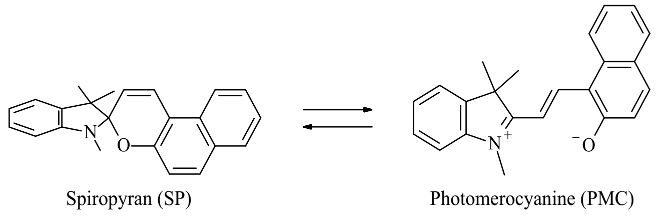

Scheme 1. Isomerization of 1,3,3-trimethylindolino-β-naphthopyrylospiran (**1**).

photovoltaic conversion of DSSC containing a noncarboxylated spiropyran and cyclodextrin layer has not been demonstrated, therefore, this area requires further investigation.

In this article, we investigated the fabrication and photovoltaic conversion of DSSC containing a noncarboxylated spiropyran and cyclodextrin layer. Additionally, photoresponsivity was investigated in order to demonstrate the offer of stimulus responsivity function with incorporating a noncarboxylated molecules by inclusion effect of cyclodextrin. We expected that the inclusion complex of spiropyran and cyclodextrin layer gives the self-regulation of photovoltaic conversion as with the report of Chen et al. [13]

2. Experimental

2.1. Materials

TiO_2 paste (Ti-nanoxide T-L) and electrolyte (Iodolyte Z-50) were purchased from Solaronix. Spiropyran 1,3,3-trimethylindolino-β-naphthopyrylospiran (**1**) was purchased from Tokyo Kasei (Japan). CM-β-CD was purchased from Sigma-Aldrich (Japan). The fluorine-doped tin oxide (FTO)-coated glass with a sheet resistance of $9.3\ \Omega/\text{cm}^2$ was purchased from Asahi Glass Co., Ltd. Benzene (spectroscopic grade) was purchased from WAKO. All materials were used as received.

2.2. Fabrication

TiO_2 paste was applied onto the FTO-coated glass substrates by a doctor-blade method, and sintered for 30 min at 450 °C. The temperature was set to rise from room temperature to 450 °C for 20 min. Active area was 0.5 cm × 0.5 cm. Two photoelectrodes were fabricated in the absence and presence of a CM-β-CD layer. Adsorption of CM-β-CD onto the TiO_2-based DSSC was performed by immersing the photoelectrodes in aqueous solution containing a CM-β-CD for 6 h. Each amount of CM-β-CD (1.0×10^{-2} g/mL, 1.5×10^{-2} g/mL and 2.0×10^{-2} g/mL) were investigated. Following immersion, photoelectrodes were rinsed off by water, and dried at room temperature. After that, photoelectrodes were immersed in benzene solution containing a **1** (0.16 M) for 5 min. The counter electrode was fabricated by Pt sputtering the FTO-coated glass in Ar atmosphere. DSSC was assembled as sandwich type cell with spacer film (thickness is ~80 μm) between the photoelectrode and counter electrode.

2.3. Measurements

The UV–vis absorption and fluorescence spectra of the prepared samples were recorded on a spectrophotometer (Hitachi, U-3310) and a fluorescence spectrophotometer (PerkinElmer, LS55), respectively. The current (I)-voltage (V) profiles of the DSSCs under light irradiation (light source comprised 500 W Xe lamp; USHIO UXL-500SX, and MT10-T monochromater; BUNKOUKEIKI Co., Ltd.) were recorded on an Advantest R6243 power source meter. A condensing lens was also used. The I-V measurements were performed on the open cell. The light intensity was measured using a power meter (Broadband Power/Energy Meter, 13PEM 001, Melles Griot). When measurement of I-V profile and light intensity, aperture mask ($0.16\ \text{cm}^2$) was set on the DSSCs and power meter. The short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fillfactor (FF) and incident photon-to-current conversion efficiency (IPCE) were evaluated from the I-V profiles. The reported values are the average obtained from more than five data for all measured DSSCs. All measurement was performed at 25 °C.

3. Results and discussion

3.1. Absorption and fluorescence spectra

Fig. 1 illustrated the UV–vis absorption spectra of **1** (1.7×10^{-4} M) in benzene, and strong absorption was observed at UV region (black line). Additionally, absorption peak with very weak intensity was also observed at ~530 nm (black line in Fig. 1), and solution color was indicated the red-purple without 254-nm irradiation (*i.e.*, coloring of solution was observed when dissolved the **1** to benzene). It has been reported that small amount of PMC exists in the crystal, and reflectance spectra of PMC was observed in the region 400–600 nm [15]. Therefore, absorption peak at ~530 nm was assigned to the formed PMC by spontaneous isomerization of **1**. However, new absorption peak was observed at ~400 nm after 254-nm irradiation (red line in Fig. 1), and solution color slightly changed to the yellow. It has been reported that PMC exist four isomer by *cis* (C) or *trans* (T) configuration of methine bridge between the indole and benzene parts [16,17]. Additionally, it was also reported that most stable isomer TTC undergo TTC → TTT isomerization and TTC → CTC/CTT isomerization. From these reports, it was assumed that absorption peaks at ~400 nm is attributed to the PMC isomer. However, ^{1}H NMR measurements carried out on irradiated solution in order to decide the structure of PMC isomer did not allows us to confirm the direct isomerization of the ethylenic bridge and we are still investigating the structure of PMC isomer.

In the case of **1** with a solution molar concentration of 0.16 M, absorption peaks were observed at ~530 and ~560 nm (black line in Fig. 2(a)), and this spectrum band agree with the reflectance spectra band of PMC in the crystal [15]. Fluorescence spectrum was

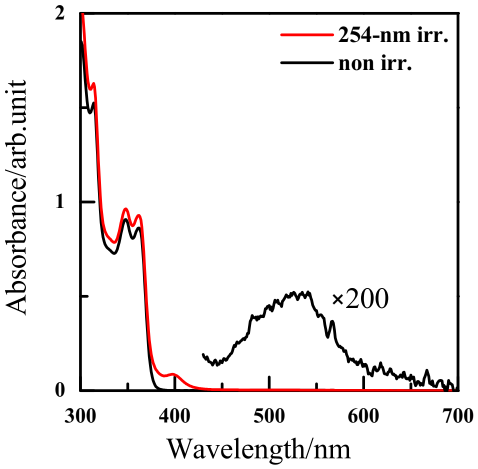

Fig. 1. Absorption spectra of **1** (1.7×10^{-4} M) in benzene before and after 254-nm irradiation (Irradiation time is 10 min). The 530 and 400 nm absorption bands are assigned to the PMC and PMC isomer, respectively. (For interpretation of the references to colour in the text, the reader is referred to the web version of this article.)