



An enhancement of photo-performance of dye sensitized solid-state cell by avoiding formation of dye aggregates



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ABSTRACT

Aggregation of indoline dye molecules was found to be decreasing performance of dye-sensitized solar cells. The effect of spacers which minimize formation of aggregates on the sensitization process of $\text{TiO}_2/\text{dye}/\text{CuI}$ solar cell was examined. Maximum power conversion efficiency of 3.6% and photovoltage of 580 mV were observed for D149 and D205 sensitized $\text{TiO}_2/\text{dye}/\text{CuI}$ solar cells, respectively.

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1. Introduction

The generation of green energy is one of the important scientific and technological challenges in 21st century. Most of the commercially available solar cells are currently based on silicon. The demand and the cost of silicon solar cells will be dramatically increased in next few decades. Dye-sensitized solar cell (DSSC), appear to be a highly promising and cost-effective alternative for the photovoltaic energy sector [1]. These cells are composed of a wide band gap semiconductor (TiO_2 , SnO_2 or ZnO) deposited on a semi-transparent conducting substrate, molecular sensitizer and a redox electrolyte, p-type semiconductor or p-type hole conductor. Generally, sensitizer is anchored on the n-type wide-band gap semiconductor. When dye molecules absorb light, the photo-excited electrons are rapidly transferred to the conduction band of the semiconductor. The oxidized dye molecule reaches to its neutral state via receiving of electron from redox couple, p-type semiconductor or p-type hole conductor. The positive charge is migrated toward the counter-electrode [2]. Natural pigments, phthalocyanines, coumarin, carboxylated derivatives of anthracene, metal complex sensitizers, metal-free organic sensitizers, and porphyrins have been used for the sensitization of semiconductors [3,4]. However, metal complex sensitizers are not suitable for cost-effective, environmentally friendly photovoltaic systems. These drawbacks

limit applications of DSSCs in day-to-day life. Indoline dyes replace the expensive ruthenium based sensitizers and also improve the electronic properties of devices. The photoelectric properties of these dyes could be tuned or matching with different substituents by altering the structure. For example, in order to control the aggregation between D102 and D149 dye molecules, a new indoline dye (D205) with an n-octyl substituent on the rhodanine ring was synthesized [5]. Indoline dyes D102, D149 and D205 were used as sensitizers in $\text{TiO}_2/\text{dye}/\text{CuI}$ solar cell and photo-performances of these cells are compared with and without spacers. The morphology of titania film plays major role in the performance of this type of cells. The influence of the preparation condition of titania electrodes in the performance of this type of cells has been studied [6]. However, the technique we used in this work produces the highest photo-performance of indoline-based solar cells, so far.

2. Experimental

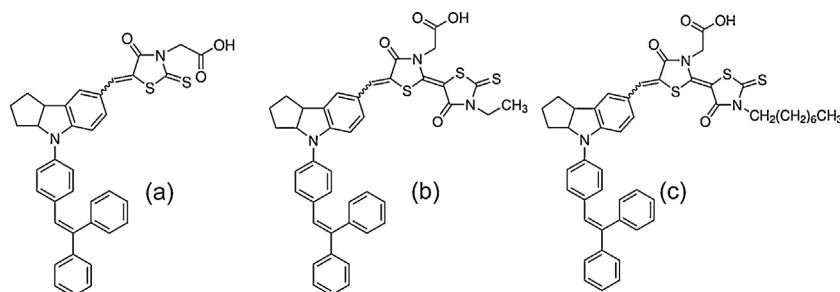
2.1. Deposition of compact TiO_2 layer on conducting glass plates

Conducting glass plates (FTO) were cut into $1 \times 2.5 \text{ cm}^2$ pieces, cleaned by detergent, thoroughly washed with distilled water and dried in an oven. One of the edges of FTO ($1 \times 1 \text{ cm}^2$) was covered with 3M tape and placed horizontally on a hotplate facing the conducting side to air. Temperature of the hotplate was gradually increased to 450°C . A solution of titanium diisopropoxide bis(acetylacetonate) (Sigma-Aldrich) in isopropanol (1:9) was sprayed over the FTO quickly at the thermal equilibrium at 450°C and allowed to reach to room temperature by disconnecting power of the hotplate.

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Scheme 1. Molecular structure of (a) D102, (b) D149 and (c) D205.

2.2. Deposition of mesoporous TiO_2 layer on the compact layer

A 5.5 ml of glacial acetic acid and 5 ml of tetraisopropyl titanate (Sigma–Aldrich) were mixed with 10 ml of 2-propanol. 3 ml of distilled water was added to the above mixture followed by adding TiO_2 powder (0.65 g, Nihon Aerisol) and kept under vigorous stirring for 2–3 h. Resulted TiO_2 semi-colloidal suspension was used as the stock solution. A small amount of TiO_2 stock solution was spread on compact layer coated FTO preheated at $\sim 150^\circ\text{C}$ by a plastic dropper and allowed to dry for few minutes. TiO_2 coated glass plate was fired at 450°C for 30 min and taken out after reaching them to room temperature by shutting down the power supply of the furnace. Loosely, bounded crust was removed by wiping TiO_2 film smoothly by piece of cotton wool. The thickness of TiO_2 film was achieved as $10\ \mu\text{m}$ by repeating the coating procedure, successively. Finally, TiO_2 coated conducting glass plates were cleaned by washing with acetonitrile.

2.3. Dye coating procedure on TiO_2 film

Dyes were purchased from well-reputed manufactures and used as purchased, in the present experiment. Dyes were separately dissolved in acetonitrile until concentration reaches $\sim 5 \times 10^{-4}\ \text{M}$. Various types of organic molecules with COOH group were used as the spacer in to the dye solutions. The concentration of spacer in the dye solution was maintained as 1 mM. TiO_2 coated glass plates were kept immersed in the dye solution (with and without space) and temperature of the dye solution was maintained as 40°C . Duration of immersion is controlled dye amount on the film. Dye-coating process was carried out in an oil bath.

2.4. Coating procedure of hole-conductor on dyed TiO_2 film

$\text{TiO}_2/\text{dye}/\text{CuI}$ cells were prepared by depositing CuI on dye coated TiO_2 electrodes as the hole-conductor. A 0.6 g CuI (Nacalai Tesque) was mixed with 15 ml of moisture-free acetonitrile and excess CuI was allowed to precipitate. The filtrate was separated. A single drop of triethyl-amine-hydro-thiocyanate was added to the CuI solution as surfactant. A small amount of above solution was carefully spread on the surface of the dye-coated TiO_2 plate heated at 150°C . This procedure was repeated until the conductivity of the CuI film reaches $50\ \Omega\ \text{cm}^{-1}$.

2.5. Measurements

Absorption spectra of dye solutions and dye coated TiO_2 films were measured by using UV–vis–NIR spectrometer (Jasco V-570). The cell was constructed by pressing a Ni-coated FTO glass plate on the $\text{TiO}_2/\text{dye}/\text{CuI}$ electrodes. Photo-effects of the cell were studied by illuminating the cell through TiO_2 layer. The variation of photocurrent current with the wavelength was measured

using monochromator (Jasco) coupled with single-phased lock-in amplifier (NF Instrument-5600 A), under constant photon energy illumination mode. Current-voltage characteristics were recorded with a solar simulator (Wacom) coupled with semiconductor parameter analyzer (Hewlett Packard HP 4145B), under 1.5 AM condition. Scan speed was maintained as $0.01\ \text{V}\ \text{min}^{-1}$. The interfacial electrical properties of the cells were studied by under natural bias and applying 0.4 V on the working electrode under a three-electrode configuration, at the dark and under illumination by using a multi-channelled potentiostat (Princeton Applied Research) coupled with a computer. The charge transfer resistance at the electrolyte–electrode interface was evaluated from EClab software.

2.6. Results and discussion

Molecular structures of (a) D102, (b) D149 and (c) D205 are shown in Scheme 1. These dyes have common bulky group (phenyl rings), central indoline group and a rhodanine ring with a cyanoacrylic acid group. Difference between D149 and D102 dyes is the rhodanine substitute to replace the S atom of D102. Absorption spectra for (a) D102, (b) D149 and (c) D205 in acetonitrile are shown in Fig. 1. The dye D102 absorbs visible light with the absorption onset at 508 nm and maximum at 456 nm. Dye D149 absorbs visible light with the absorption onset at 598 nm and maximum at 526 nm. It seems to be rhodanine substitute in D149 shifted absorption toward the longer wavelength due to change of main structure. The difference between D205 and D149 dye is the octyl substitute on the terminal rhodanine ring to replace the ethyl group of D149. The absorption spectrum of D205 shows almost similar properties to that of D149 in acetonitrile, due similarities in the main

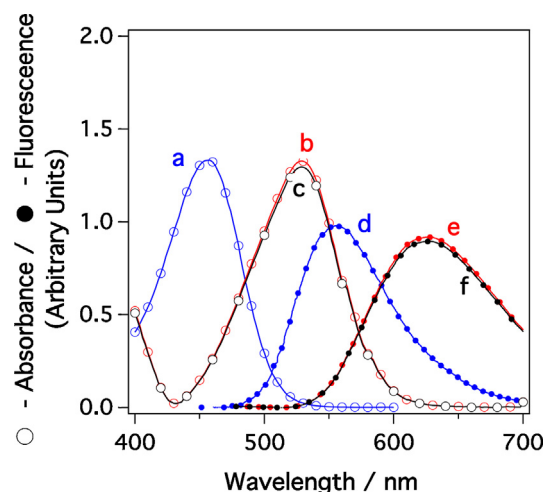


Fig. 1. Absorption spectra of (a) D102, (b) D149, (c) D205 and luminescence spectra of (d) D102, (e) D149 (f) D205 in acetonitrile.

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