Dye Sensitization of ZnO by Unsymmetrical Squaraine Dyes Suppressing Aggregation

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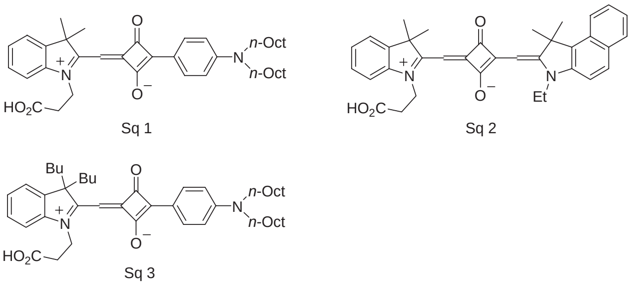
We have developed an efficient, cyan-colored, and novel squaraine-dye-sensitized ZnO solar cell, producing a maximum incident photon-to-electron conversion efficiency (IPCE) of 59% at 630 nm. The solar cell sensitized by Sq 3 having bulky groups to prevent aggregation of dyes has achieved a 1.5% solar-to-electricity conversion efficiency (η) with a short-circuit current density of 4.04 mA cm^{-2}, an open-circuit photovoltage of 0.61 V, and a fill factor of 0.61 under standard AM 1.5 irradiation (100 mW cm^{-2}).

Dye-sensitized solar cells (DSSCs) have attracted a great deal of interest due to their reasonably high conversion efficiencies for low cost.[1] Attractive characteristics of DSSCs are also found in the possibilities to fabricate flexible and colorful solar cells, unlike the conventional silicon cells.

Recently, a novel electrochemical method to prepare porous ZnO thin film at a low temperature (70 °C) has been introduced.[2] The process can be applied to the plastic film substrates, thus leading to the realization of flexible DSSCs. Our final goal is to accomplish multi-colored DSSCs proving the versatile products. They were fabricated by using appropriate combinations of organic dyes, especially yellow-, magenta-, and cyan-colored dyes.[3] So far, coumarin and eosin as yellow- and magenta-colored dyes respectively produced high incident photon to current conversion efficiency (IPCE) over 80%.[2] Further, merocyanine dyes as yellow- and magenta-colored dyes produced high energy-conversion efficiencies.[4,5] Although cyanine,[6] merocyanine,[3] phthalocyanine,[7] and squaraine dyes[8,9] as cyan-colored dyes have been reported, their IPCE values were lower than 50% as yet.

It is well known that squaraine dyes easily form H-aggregates, which result in the decrease of their sensitization efficiency in DSSCs.[8,9] Very recently, Das et al. have reported that unsymmetrical squaraine dyes as sensitizers exhibit much higher efficiencies than the symmetrical squaraine dyes.[9] These literatures led us to design and synthesize new cyan-colored unsymmetrical squaraine dyes as photosensitizers. They have been derivatized in the structures as shown in Scheme 1 to suppress H-aggregation on the ZnO surface.

We report here the synthesis and application of new unsymmetrical squaraine dyes as sensitizers for the ZnO solar cell, prepared by cathodic electrodeposition method. The best result has been obtained with Sq 3 dye achieving an IPCE = 59% at 630 nm.



Scheme 1. Molecular structures of unsymmetrical Sq dyes.

Sq 1 was synthesized as follows. Condensation of 1-(4-*N*,*N*-dioctylaminophenyl)-2-hydroxycyclobutene-3,4-dione with 1-(2-carboxyethyl)-2,3,3-trimethyl-3*H*-indolium iodide under reflux in the mixed solvent of benzene and 1-butanol (v/v = 1:1) using Dean–Stark condenser and purified by column chromatography using silica gel with the mixed solvent of dichlorometane and methanol (v/v = 10:1), producing Sq 1 in 18% yield. Sq 2 and Sq 3 were synthesized in 30 and 35% yields by the same method, respectively.

Porous ZnO layer (thickness: 3 µm) was electrodeposited onto an F-doped SnO_2 (FTO) coated glass (Asahi Glass, 10 Ω/sq.) using eosinY as a template molecule. The details of the film preparation is described elsewhere[2] After dried at 100 °C for 1 h, the film was immersed in an ethanol solution of Sq 1–3 (100 µmol dm^{-3}) without or with deoxycholic acid (DCA) (500 µmol dm^{-3}) and kept at room temperature for appropriate times (Sq 1: 1 h, Sq 2: 20 min, Sq 3: 1.5 h, Sq 3 with DCA: 3 h). Photovoltaic measurements were carried out for sandwich-type cells (two electrode) consisting of a dye-coated ZnO electrode and a Pt-sputtered FTO glass counter electrode as attached in a face-to-face configuration using a polymer film spacer. The electrolyte was 0.5 mol dm^{-3} tetrabutylammonium iodide and 0.05 mol dm^{-3} iodine in the mixed solvent of acetonitrile and ethylenecarbonate (v/v = 1:4). The cell area was regulated to 0.2 cm^2 using a photomask. The photocurrent action spectra were recorded at short circuit under monochromatic light illumination at a constant photon number (5×10^{14} cm^{-2} s^{-1}). The photovoltaic performances were measured under simulated AM 1.5 irradiation (100 mW cm^{-2}).

Figures 1 and 2 show the absorption spectra of the dye-coated ZnO thin films and the action spectra of the cells employing them, respectively.

The absorption peaks ($\lambda_{\max}$) in ethanol solution were observed at 620, 647, and 623 nm for Sq 1, Sq 2, and Sq 3, respectively. As shown in Figure 1, the blue-shifted absorptions around 590 nm are observed for the dyes adsorbed on ZnO indicating the formation of H-aggregates. It is known that H-aggregation usually quenches fluorescence efficiently and would consequently be a loss mechanism competing with electron injection, resulting

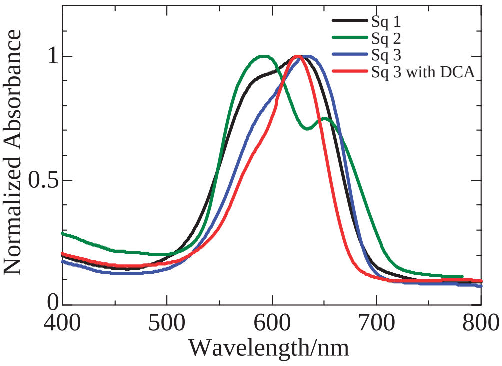


Figure 1. Absorption spectra of Sq 1, Sq 2, Sq 3, and Sq 3 with DCA absorbed on ZnO film whose absorbance is normalized.

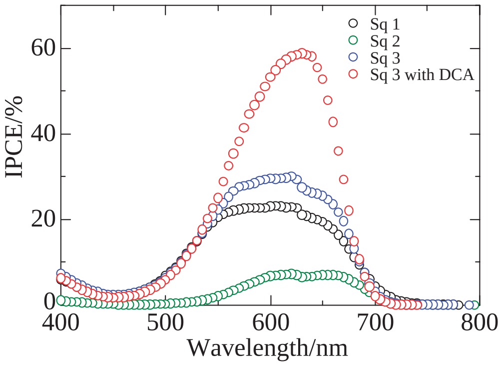


Figure 2. Action spectra obtained for ZnO solar cells sensitized by Sq 1, Sq 2, Sq 3, and Sq 3 with DCA.

in lower IPCEs.[10] Comparison of the absorption spectra in Figure 1 reveals that the formation of aggregates of Sq 1 is much less than that of Sq 2. As a result, much higher IPCE (22% at 620 nm) of Sq 1 was obtained than that (7% at 620 nm) of Sq 2, as shown in Figure 2. The difference between Sq 1 and Sq 2 is presumably due to the decrease in polarization of the π-electrons in Sq 2[11] as well as the steric hindrance caused by the presence of the dioctylamino groups on the phenyl group in Sq 1.

In addition, the introduction of the dibutyl group into the indolium moiety (Sq 3) to enhance steric hindrance was effective for the inhibition of H-aggregation even at a higher degree than the dimethyl group in Sq 1, as seen in the absorption spectra and to the achievement of the higher IPCE (30% at 620 nm). Optimization of immersion conditions of Sq 3 using DCA[12] as a co-adsorbent has resulted in the best photovoltaic performance. As recognized from the monomeric character of the absorption spectrum in Figure 1, the addition of DCA to a solution of Sq 3 almost completely prohibits the formation of dye aggregates on ZnO. Consequently, the highest IPCE (59% at 630 nm) has been attained.

Table 1 summarizes the photovoltaic performance of the DSSCs employing the new squaraine dyes. It is noticed that the suppression of dye aggreration contributes not only to the increase of photocurrent but also to the increase of photovoltage.

Table 1. Photovoltaic performance of dye-sensitized solar cells

	IPCE	J_{sc} /mA cm^{-2}	V_{oc}/V	*ff*	η/%
Sq 1	22	2.32	0.53	0.64	0.78
Sq 2	7	0.40	0.48	0.66	0.13
Sq 3	30	3.05	0.51	0.58	0.89
Sq 3 with DCA	59	4.04	0.61	0.61	1.50

It is likely that co-adsorption of DCA suppresses the back electron transfer and thus increases the photovoltage. Consequently, the solar cell sensitized by Sq 3 with DCA has achieved the highest solar energy-to-electricity conversion efficiency (η) of 1.5% with a short-circuit current density of 4.04 mA cm^{-2}, an open-circuit photovoltage of 0.61 V, and a fill factor (*ff*) of 0.61 under illumination with AM1.5 simulated sun light (100 mW cm^{-2}), almost equivalent to the efficiencies of the cells employing yellow- and magenta-colored sensitizer dyes.[2] Especially encouraging with the new cyan-colored dye is its relatively high photovoltage despite of the smaller energy of the absorbed photons. Such a character gives us a chance to mix these dyes with three primary colors without deteriorating their activities to cover the wide range of the sun spectrum as well as to furnish the solar cells in all color variations.

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References and Notes

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