Solid-state Solar Cells Sensitized with Indoline Dye

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A solid-state solar cell sensitized with an indoline dye is found to have an efficiency of 4.2%. This value is higher than that of similar cells sensitized with the N3 dye, indicating that organic dyes adsorbing strongly onto TiO_2 and forming nonquenching aggregates are more suited for application in solid-state cells.

Dye-sensitized photoelectrochemical cells (DS PECs) made from nanocrystalline films of TiO_2 sensitized with ruthenium bipyridyl dyes have attained efficiencies exceeding 10%.[1,2] Although extensive efforts were made to develop organic sensitizers,[3–7] ruthenium dyes remained well ahead of organic dyes. Recently, an indoline dye-based DS PEC was found to yield an efficiency of ca. 9% with a peak incident photon to photocurrent efficiency exceeding 80%.[8] This dye adsorbs strongly onto the TiO_2 surface and remain highly stable. Organic dyes are cheap, they degrade into nontoxic constituents, and conventional synthesis procedures can be adopted to tailor the structure to suit requirements. Furthermore, in general, organic dyes possess higher molecular extinction coefficients compared to inorganic sensitizers. An advantage of high molecular extinction coefficient happens to be the possibility of achieving a sufficient light absorption cross section at a reduced film roughness factors. This is advantageous as the diffusive electron transport in the nanocrystalline semiconductor matrix sets an upper limit to the film thickness. Again, nanocrystalline films of the type required for dye-sensitized solid-state cells (DSSCs), where the electrolyte is replaced by a solid hole-collector, have roughness factors smaller than that of DS PEC type films, and here dyes with higher extinction coefficients are more useful. In this paper, we describe the photovoltaic properties of a DSSC sensitized with an indoline dye.

The precursor for deposition of TiO_2 films was prepared by the procedure described below. Titanium isopropoxide (5 mL) mixed with few drops of glacial acetic acid is homogenized after addition of 20 mL of propan-2-ol. Water (5 mL) is quickly transferred and the mixture was ground to form a milky paste. Paste was mixed with 0.65 g of TiO_2 (Nihon Aerosol, median particle size 30 nm), ground again, spread on fluorine-doped conducting tin oxide (FTO) glass plates (Nihon Sheet Glass), and heated to 150 °C. Once the liquid component of paste evaporates, the powder not adhered to the surface is blown off, the process was repeated several times, and the film is sintered in air for 4 min at 500 °C. Above steps are repeated until the film grows to a thickness of ca. 6 µm. TiO_2 films were coated with the indoline dyes (D-149, structural formula shown in Figure 1) by soaking plates in a solution of the dye in *tert*-butyl alcohol/acetonitrile (1/1, 4×10^{-4} M) for 3 h.

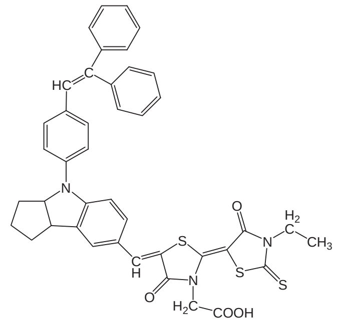

Figure 1. Molecular structure of indoline dye (D-149).

The amount of the dye adsorbed was determined by extracting the dye into warm glacial acetic acid. The heterojunction TiO_2/Dye/CuI was formed by deposition of CuI from an acetonitrile solution containing a trace amount triethylamine hydrothiocyanate (THT) which acts as CuI crystal growth inhibitor.[9] For comparison, cells were also fabricated excluding THT from the CuI solution. A gold-plated conducting glass firmly clamped to CuI surface served as the back contact to the cell. *I–V* characteristics and photocurrent action spectra were recorded using a calibrated solar cell evaluation system. CuI films were also examined by XRD (RINT 2000, X-ray diffractometer, Rigaku) to determine phases of CuI and the effect of aging.

Figure 2 shows the absorption spectra of indoline dye in alcoholic solution and deposited on nanocrystalline TiO_2 film (TiO_2/indoline). The latter spectrum is broader owing to dye aggregation. The adsorbed amount of indoline dye (9.42×10^{-8} mol/cm^2) is found to be higher than that of N3 dye on similar films (5.53×10^{-8} mol/cm^2). The photocurrent action spectrum of the cell TiO_2/Indoline/CuI (Figure 3) is also

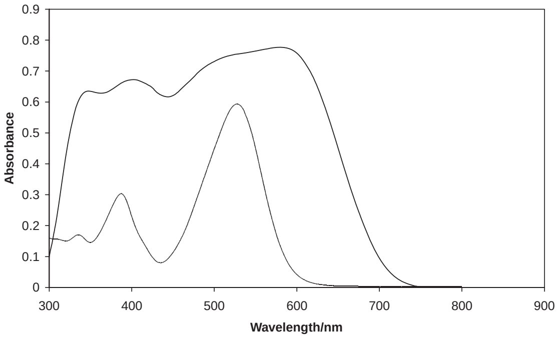

Figure 2. Absorption spectra of indoline dye (D-149) in *t*-butyl alcohol/acetonitrile (dashed line) and adsorbed on TiO_2 film (solid line).

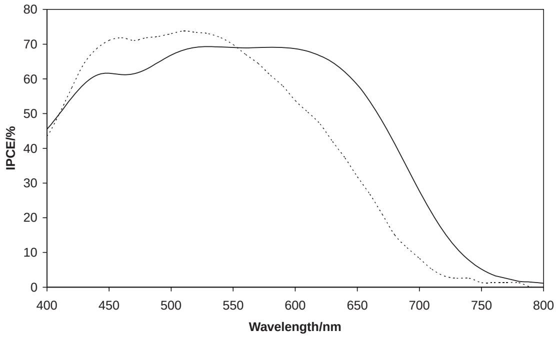

Figure 3. Incident photon-to-current conversion efficiency (IPCE) of indoline dye (D-149)-(solid line) and N3 (dotted line)-sensitized solid-state solar cell.

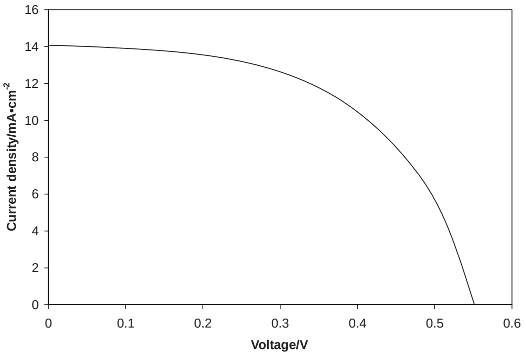

Figure 4. Photocurrent–voltage curve obtained with indoline dye (D-149)-sensitized solid-sate solar cell.

broad and commensurate with the adsorption spectrum of TiO_2/Indoline indicating that the aggregated dye effectively injects electrons to TiO_2. The observed peak (500–650 nm) of incident photon-to-photocurrent conversion efficiency (IPCE) of 70% is quite high for a DSSC.

It has been reported that indoline dyes forms J-aggregates that are not susceptible to concentration quenching.[4] In this respect, indoline dyes have several major advantages in use as sensitizers for DSSCs. Nanocrystalline TiO_2 films of the type needed for DSSCs generally have effective surface areas smaller than that of DS PEC type films, this could be compensated by thick film of a dye with very high extinction coefficient. Again a thicker dye layer serves as a barrier suppressing recombination of electrons injected to TiO_2 with holes injected to CuI. Furthermore, the coverage of a dye on the TiO_2 without leaving voids is an effective means suppressing recombinations, as direct contacts between CuI and TiO_2 are more susceptible.

Figure 4 indicates *I*–*V* characteristics of the cell, and the *I*–*V* parameters (Jsc = short-circuit photocurrent, Voc = open-circuit voltage, FF = fill factor, η = efficiency) are summarized in Table 1. The measured efficiency 4.2% is quite high for a cell based on a organic dye. Just as in CuI-based DSSCs sensitized with N3 dye, the cells where CuI is deposited from a CuI solution incorporating a crystal growth inhibitor (THT), remained more stable during operation. Indoline-sensitized CuI cells also showed similar signs of instability on continued illumination just as N3-sensitized CuI cells.

Table 1. Photovoltaic performance of dye-sensitized solid-state solar cells with indoline dye (D-149) and with N3 dye

Dye	Jsc/mA·cm^{-2}	Voc/mV	FF	η/%
D-149	14.1	551	0.54	4.2
N3	12.7	542	0.53	3.7

We have constructed solid-state solar cells of the configuration n-TiO_2/D/p-CuI, with D = indoline dyes and found that the efficiency is higher than the cells of similar configuration sensitized with N3 dye. The higher molecular extinction coefficient of indoline dyes and coverage on the TiO_2 surface minimizing formation of voids seem to be the cause of better performance of the cells sensitized with these dyes.

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