Photosensitization of Porous TiO_2 Semiconductor Electrode with Xanthene Dyes

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Solar cell composed of Eosin Y-sensitized porous TiO_2 electrode treated with $TiCl_4$ showed remarkably high photon-to-current efficiency (51% at 533 nm) and solar-to-energy efficiency (1.3%, AM-1.5, 100 mW/cm^2 with UV cutoff filter). Eosin Y dimer supposed to be more efficient than monomer. Turnover number of Eosin Y for excitation was more than 2.7 x 10^6 cycles, suggesting that Eosin Y was fairly stable unless UV light was irradiated.

Dye sensitization of wide bandgap semiconductors has been investigated from the standpoint of simple production of highly efficient solar cell. Especially, xanthene organic dyes were widely studied in early works. Tsubomura et al. demonstrated that the efficiency of photo-electrochemical cell was improved by increase of electrode surface area using porous ZnO semiconductor electrode sensitized with rose bengal.[1] An incident monochromatic photon-to-current efficiency (IPCE) and an incident monochromatic light-to-power conversion efficiency (η_{563nm}) were 15% and 1.5% at 563 nm, respectively. Recently, Grätzel et al. reported the most efficient cell (IPCE > 80% at 520 nm and incident solar light-to-power conversion efficiency, η_{sun} = 10%) based on a porous TiO_2 semiconductor electrode sensitized with Ru-complex.[2,3] One of the key features for the high efficiency is very large surface area of TiO_2 film electrode on a conducting glass. Though most of recent works which investigated new sensitizers in such cell have focused on metal complex dyes such as bipyridyl and porphyrin derivatives, little attention has been given to the use of organic dyes, because organic dyes have been considered to be less stable and less efficient than metal complexes. Although some organic dye-sensitized Grätzel type cells such as Rhodamin B(RhB)/ZnO,[4] Rh6G/SnO_2,[5] perylene/SnO_2[6] and natural dye /TiO_2[7,8] have been reported, their IPCE and η_{sun} were low (< 30% and < 0.9%). However, it should be noteworthy, compared with metal complex, that there are several advantages to organic dyes in the following points; a wide variety such as natural dyes, high absorption coefficient, low cost, saving of limited precious metal resources, easy handling for cell recycle without removing metal and so on. In this paper, we report highly efficient solar cell using porous TiO_2 electrode sensitized with organic dyes, 9-phenyl xanthene dye, and also mention high stability of the dye in the cell.

Preparation of porous TiO_2 film electrode (7 µm thickness) on a conducting glass support (Nihon Sheet Glass Co., F-doped SnO_2 overlayer, 10 Ω/sq), by spreading a viscous slurry of TiO_2 powder (Nihon Aerosil, P25) and heating at 500 °C, were referred to the published procedure.[3] Adsorption of a dye on TiO_2 surface was carried out by refluxing the TiO_2 electrode in a 3.2 × 10^{-4} mol·dm^{-3} dry ethanol solution of 9-phenyl xanthene dye (e.g. eosin Y, Aldrich, high purity) at 80 °C for 30 min. The amount of adsorbed dye was determined by desorbing the dye from semiconductor surface into a solution of NaOH (0.1 mol·dm^{-3}) in a mixture of water and ethanol, and measuring its absorption spectrum. The dye sensitized TiO_2 electrode was incorporated into a thin-layer sandwich-type solar cell with a polyethylene spacer (0.12 mm thickness). The counter electrode consisted of a thin platinum layer sputtered on a conducting glass. The electrolyte solution was a mixture of 0.5 mol · dm^{-3} tetra-n-propylammonium iodide and 0.05 mol· dm^{-3} iodine in an ethylene carbonate and dry acetonitrile mixed solvent (60:40 by volume). In search of efficient dyes, Xe lamp with proper band pass filters (3 - 4 mW/cm^2) near absorption peak was used, and illuminated area was 1 cm^2. Action spectrum of the photocurrent was measured under light through monochrometer (resolution: 4 nm), and the illuminated area was 0.49 cm^2. The photocurrent, photovoltage and potential-current curve were measured using potentiostat equipped with non-resistance ammeter and XY recorder. For all of the cell characterization techniques, the resulting data are not corrected for intensity losses due to passing through electrode and light reflection by the glass support.

First, more than 80 organic dyes including 9-phenyl xanthene derivatives, coumarin derivatives, acridine derivatives, tetraphenylmetane derivatives, quinone derivatives and azo compound derivatives were tested as photosensitizers for porous TiO_2 electrode. As a result, 9-phenyl xanthane derivatives showed good properties. Among 9-phenyl xanthane derivatives, Eosin Y (EY) was found to be the best sensitizer on IPCE near absorption peak as the following order; EY > Dibromfluorescein > Fluorescein = Fluorescin > Rhodamin B >

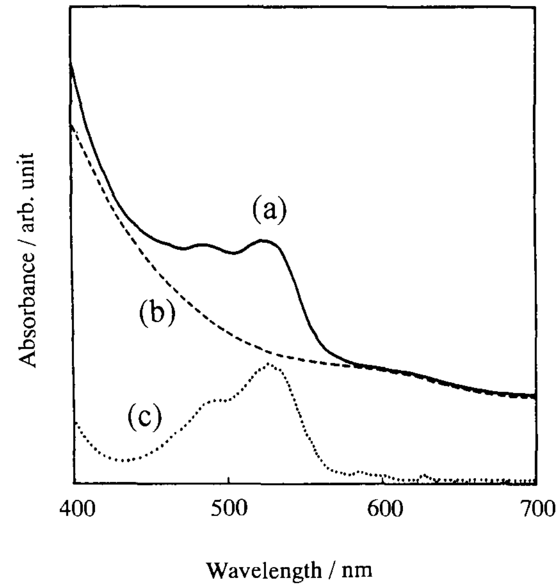

Figure 1. Absorption spectra of EY/TiO_2 cell measured in transmission mode. (a) EY/TiO_2 cell, (b) cell without EY, (c) absorption spectrum of EY in working state ((a)-(b)).

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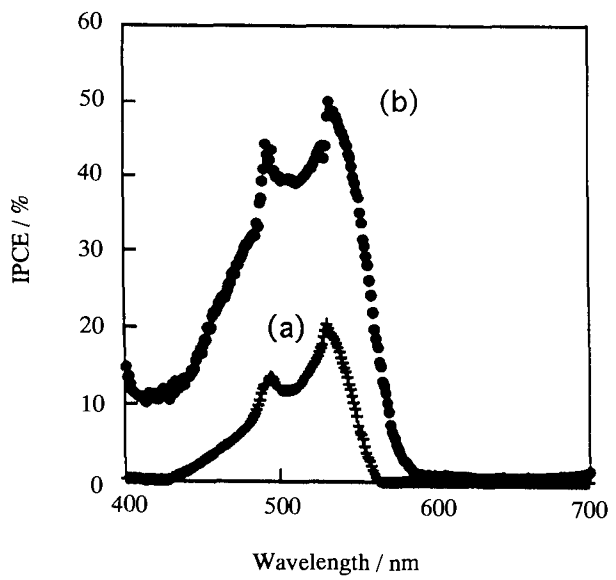

Figure 2. Photocurrent action spectra of EY/TiO_2 cell. (a) TiO_2 electrode was not treated with $TiCl_4$, (b) TiO_2 electrode was treated with $TiCl_4$ aqueous solution for 18 h.

Dichlorofluorescein > Uranine = Pyrogallol > Fluoresceinamine 2 > Erythrosine B = Rose bengal = Phloxine B > Tetrachlorofluorescein > Eosin B > Rhodamin 6G. The IPCE of the EY cell was ten times larger than that of rose bengal, one of the famous dyes as a good sensitizer. Photovoltages and fill factors of the highly efficient cells were almost same in the range of 0.53±0.03 V and 60±3%. We speculated that the redox potential of the dyes in the ground and excited states was very important factor to obtain the high IPCE value, and it is now under investigations.

The absorption spectra of EY adsorbed on TiO_2 electrode were shown in Figure 1. The absorption peak of EY on TiO_2 (528 nm) was almost same as that in ethanol (526 nm). Figure 2 shows the photocurrent action spectra of the EY/TiO_2 cell, however, the action spectrum shape was different from the absorption spectra shown in Figure 1(c), and two distinct peaks were observed (21% at 531 nm and 13% at 495 nm at (a)). This observation is very unique, because the shapes of action spectra usually showed good accordance with those of absorption spectra in dye-sensitization of semiconductors. The absorption peak of EY monomer was at ca. 520 nm, while dimer peaks were at ca. 485 and 540 nm.[9] Therefore, it was considered that both monomer and dimer were adsorbed on TiO_2 surface, and dimer was more efficient than monomer on photocurrent generation.

It was reported in the case of TiO_2 electrode sensitized with Ru-complex dye that the photocurrent was promoted by treatment of TiO_2 electrode with $TiCl_4$ aqueous solution.[3] According to the report, we investigated the effect of the $TiCl_4$ treatment on the EY/TiO_2 cell. The maximum IPCE was significantly improved to 51% at 533 nm by the treatment of $TiCl_4$ solution (0.2 mol·dm^{-3}) for 18 h as shown in Figure 2(b). This IPCE value was not corrected for passing and reflection of incident light, and it was significantly high compared to other cells reported so far using organic dyes.[1,4-8] In order to correct the loss of light passed through the electrode, a light harvest efficiency (LHE) was estimated by the following eq., LHE = $1\text{-}10^{-\Gamma\sigma}$, where Γ is the number of moles of EY per square centimeter (4.5 × 10^{-9} mol/cm^2) and σ is the absorption cross section of EY (1.1 × 10^8 cm^2/mol).[3] The LHE at 533 nm were calculated at 0.68, therefore, the absorbed photon-to-current efficiency (APCE) was estimated to be 75%. On the other hand, the incident solar light-to-electric energy conversion efficiency (η_{sun}) of the EY/TiO_2 cell was ca. 1.3% (Isc: 2.9 mA/cm^2, Voc: 0.66, ff: 67%), which was measured with solar simulator (AM-1.5, 100mW/cm^2, with 420 nm cutoff filter, 1×1 cm^2). The η_{sun} and the IPCE values were much larger than that sensitized by other xanthene dyes, and were the largest in all organic dye systems reported so far.[1,4-8] It is considered that simultaneous adsorption of various kinds of organic dyes which utilize light in different wavelength can improve the solar power conversion efficiency.

Concerning on the stability of the EY/TiO_2, both Isc and Voc were stable up to 400 h under visible light (tungsten lamp with two 440 nm cutoff filters, 25 mW/cm^2), and then Isc decreased gradually. Total electric charge for 1700 h was more than 1200 C, and turnover number of the dye was calculated to be more than 2.7 × 10^6 cycles. The large turnover number suggests that EY itself is fundamentally stable in this system unless UV light is irradiated. The red color of EY was immediately disappeared when UV light was directly irradiated because of the photocatalytic decomposition of the dye over TiO_2. It is considered that the leakage of electrolyte might be one of causes for the decrease of Isc after 400 h, because behavior of bubbles growing in the cell was in accord with the decrease of Isc. Improvement of sealing method is very important to prolong the cell life.

References and Notes

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