Highly Efficient Photon-to-Electron Conversion of Mercurochrome-sensitized Nanoporous ZnO Solar Cells

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Mercurochrome showed efficient performance as an organic dye photosensitizer for a solar cell based on nanoporous ZnO thin film electrodes. A 2.5% solar energy conversion efficiency was accomplished under AM 1.5 (99 mW cm^{-2}) with a short-circuit photocurrent density (*J*sc) of 7.44 mA cm^{-2}, an open-circuit photovoltage (*V*oc) of 0.52 V, and a fill factor of 0.64. A monochromatic incident photon-to-current efficiency (IPCE) reached 69% at 510 nm.

Grätzel and co-workers reported that a dye-sensitized solar cell based on *cis*-dithiocyanato bis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) ($Ru(dcbpy)_2(NCS)_2$) as a photosensitizer and nanoporous TiO_2 thin film electrodes with an I^-/I^{3-} redox electrolyte (Grätzel cell) showed a highly efficient solar energy conversion to electricity of 10% under 1 sun (AM 1.5).[1] Since then, many workers have been investigating extensively this dye-sensitized electrochemical solar cells using various metal complex photosensitizers and nanoporous TiO_2 electrodes because of its high performance and low cost.[2,3] We have also developed a new efficient Ru-dye, a Ru phenanthoroline complex (*cis*-dithiocyanato bis(4,4'-dicarboxy-2,2'-biphenanthoroline)ruthenium(II)), which shows good performance as a sensitizer for a nanoporous TiO_2 thin film electrode with an iodine redox system. The solar energy conversion efficiency under 100 mW cm^{-2} was 6.1% and a high IPCE value, 60% was obtained at 500 nm.[4]

Recently dye-sensitized solar cells using organic dyes as the sensitizer have been positively investigated because they are supposed to be manufactured with a low cost compared to Ru dye-sensitized solar cells. For example, rhodamine 6G/SnO_2,[5] perylene/SnO_2,[6] and, anthocyanin/TiO_2[7] solar cells have been reported so far. However, these solar energy conversion efficiencies are quite low (< 1.0%). In order to develop efficient organic dye-sensitized solar cells, we have examined various organic dyes as photosensitizer for dye-sensitized nanocrystalline oxide semiconductor solar cell. As a result, we found eosin Y (9-phenylxanthene dye) showed a good performance as a sensitizer for TiO_2 nanoporous thin film electrodes.[8] An IPCE of 51% at 533 nm and a solar energy conversion efficiency of 1.3% (AM1.5, 100 mW cm^{-2}) were obtained, indicating that 9-phenylxanthene dyes also perform as good photosensitizer for dye-sensitized solar cell. Mercurochrome, one of 9-phenylxanthene dyes, whose absorption peak is 517 nm in solution as well as eosin Y, is also expected to be a good photosensitizer for the dye-sensitized solar cell. Although Gomes et al. discussed mechanism of the dye-sensitization using a single crystal ZnO and xanthene dyes such as rhodamine B, eosin, mercurochrome,[9] the photovoltaic property of mercurochrome-sensitized nanoporous ZnO thin film solar cells with an iodine redox electrolyte has never been studied so far. In this letter, we report for the first time highly efficient organic dye-sensitized solar cell based on mercurochrome-adsorbed nanocrystalline ZnO thin film electrodes with an iodine redox.

Nanoporous ZnO thin film electrodes were prepared by screen printing method using ZnO paste made from ZnO nanoparticle (Sumitomo Osaka Cement, #100, particle size: 10–20 nm), polyvinyl acetal, and α-terpineol. The paste was printed on a SnO_2-coated conducting glass substrate and then calcined for 1 h at 420 °C. The ZnO thin films were immersed into a 0.5 mmol dm^{-3} ethanolic solution of mercurochrome and then refluxed at 80 °C for 1 h to fix dye on the surface of ZnO electrodes. After dye adsorption, the color of thin films change into dark red.

The electrochemical cell for photovoltaic measurement consisted of a dye-adsorbed ZnO electrode, a counter electrode, a polyethylene film spacer (120 μm thickness), and an organic electrolyte. The counter electrode was a Pt film sputtered on a transparent conducting glass. The electrolyte was a 0.5 mol dm^{-3} Pr_4NI-0.05 mol dm^{-3} I_2/ethylene carbonate-acetonitrile (60:40) solution. Apparent surface area of the dye-adsorbed ZnO electrodes was 0.09–0.25 cm^2. The photoelectrochemical performance of the solar cells was measured with a potentio/galvanostat, a digital multimeter, and an X-Y recorder. An AM 1.5 solar simulated light source was used for the light source. A 500 W halogen lamp, a monochromator, a scan controller, and a multimeter were used for the IPCE measurements.

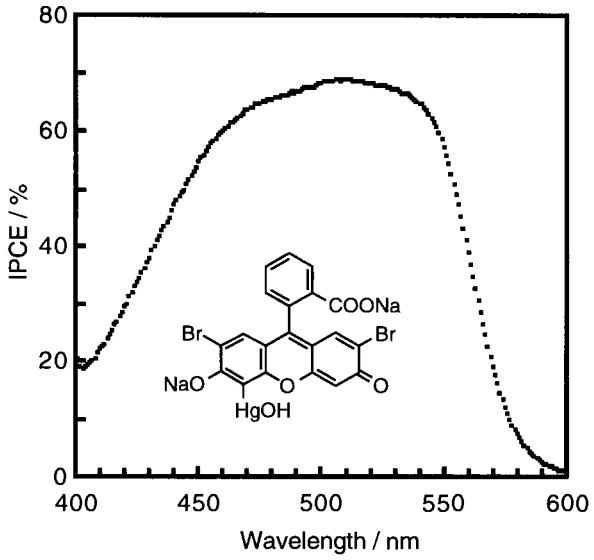

Figure 1. An action spectrum of IPCE for a mercurochrome-sensitized nanocrystalline ZnO solar cell.

Figure 1 shows an action spectrum of IPCE for a mercurochrome-sensitized nanoporous ZnO electrode (20 μm thickness and 0.5 cm^2) with an I^-/I_3^- redox electrolyte. This photoelectrode can convert efficiently visible light in the range from 400 to 600 nm to photocurrent, as shown in this figure. The IPCE reached 69% at 510 nm. This high IPCE indicates that electron transfer from excited state of mercurochrome to the conduction band of ZnO and that from I^- ion to the oxidized mercurochrome occurred effectively. It was reported that the IPCE for $Ru(dcbpy)_2(NCS)_2$-sensitized TiO_2 electrode reached 85–90% in the range from 510 nm to 570 nm.[2] On the other hand, a monochromatic IPCE for $Ru(dcbpy)_2(NCS)_2$ adsorbed on a ZnO electrode (7 μm thickness) was 58% at 540 nm, which is lower than that of $Ru(dcbpy)_2(NCS)_2/TiO_2$ system.[10] It should be noted that the IPCE performance of mercurochrome for a ZnO electrode exceeds that of $Ru(dcbpy)_2(NCS)_2$ dye. The amount of adsorbed mercurochrome on a 20 μm-thick ZnO electrode was 1.6×10^{-7} mol cm^{-2}. This large amount of mercurochrome adsorbed on the ZnO surface leads to an increase of the light harvesting efficiency and the high IPCE performance.

Kamat and co-workers measured transient absorption for rhodamine 6G/SnO_2 nanoparticles in solution and reported that the fast back electron transfer from the conduction band of SnO_2 to oxidized dye occurred with 27 ns, resulting in low efficiency for light energy conversion into electricity.[13] We have been conducting the study of transient absorption measurement for mercurochrome/ZnO system and found that the back electron transfer is very slow process with more than 1 ms.[14] We suppose that the slow back electron transfer from the conduction band of ZnO to oxidized mercurochrome is one of factors that leads to the high IPCE performance.

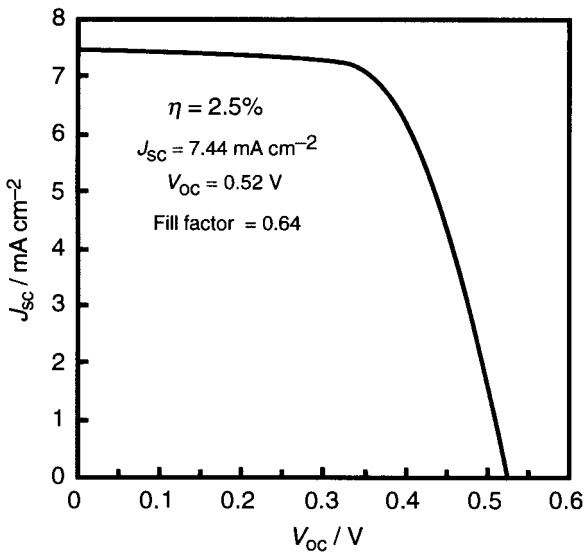

Figure 2. Photocurrent-voltage curve for a mercurochrome-sensitized nanoporous ZnO solar cell obtained under irradiation intensity of 99 mW cm^{-2} (AM 1.5).

Figure 2 shows photocurrent-voltage curve for a mercurochrome-sensitized ZnO solar cell (36 μm, 0.09 cm^2) with an iodine redox electrolyte. The total solar-energy conversion efficiency η at 99 mW cm^{-2} reached 2.5% with a short-circuit photocurrent density (J_{sc}) of 7.44 mA cm^{-2}, an open-circuit photovoltage (V_{oc}) of 0.52 V, and a fill factor of 0.64. The η for a $Ru(dcbpy)_2(NCS)_2$-sensitized ZnO solar cell was 0.4% at 119 mW cm^{-2} for 0.7 μm-thick ZnO[11] and 2% at 56 mW cm^{-2} for a 30 μm-thick ZnO.[10] Note that the solar cell performance of mercurochrome-sensitized nanocrystalline ZnO thin film exceeds that of $Ru(dcbpy)_2(NCS)_2$/ZnO system, although mercurochrome can not absorb light from 600 to 800 nm, where $Ru(dcbpy)_2(NCS)_2$ dye shows strong absorption. This suggests that combination of dye and semiconductor material is very important for the construction of efficient dye-sensitization system. Mercurochrome is one of the best sensitizers for a ZnO photoanode. Detailed studies of mercurochrome-sensitized nanoporous oxide semiconductor solar cells are now being studied.

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