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Highly Efficient Photosensitization of Mesoporous TiO_2 Electrode with a Cyanine Dye

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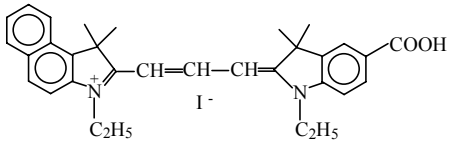
Abstract: A low cost cyanine dye, 1, 1-dimethyl-3-ethyl-2-[3-(1, 3-dihydro-3, 3-dimethyl-1-ethyl-5-carboxyl-2H-indol-2-ylidene)-1-propenyl]-1H-benz[e] indolium iodide (**1**) was synthesized and applied to sensitize mesoporous TiO_2 electrode. Photoresponse of the electrode was extended to the visible and remarkably high incident photon-to-current conversion efficiency (IPCE) over 70% was achieved from 500 nm to 600 nm.

Keywords: Cyanine dye, sensitization, photoelectrochemical cell, titanium dioxide.

Dye-sensitized mesoporous TiO_2 photoelectrochemical cell has attracted much interest for photoelectric conversion[1,2]. The most efficient charge transfer dye studied so far is $Ru(dcbpy)_2(NCS)_2$ (dcbpy=4, 4'-dicarboxy-2, 2'-bipyridine), with which IPCE of about unity has been achieved[3]. Considering the low cost, low toxicity, easy handling, non-metal complex dyes should also be right candidates. Here we report the highly efficient photosensitization of mesoporous TiO_2 electrode with a novel cyanine dye.

Preparation of mesoporous TiO_2 electrode has been described elsewhere[4]. Dye-coating of the electrode was done by soaking it in 0.5 mmol/L ethanol solution of **1**. A sandwich-type cell was constructed with **1** coated electrode and platinized counter electrode. The electrolyte was 0.5 mol/L LiI and 0.05 mol/L I_2 in propylene carbonate. Photoelectrochemical measurements were performed with a 150 W xeron lamp and a monochromator as light source.



1

The synthesis of **1**: Mixture of 1.25 mmol 1, 1-dimethyl-3-ethyl-2-(2-phenylamino ethylene)-1H-benz[e] indolium iodide, 1.25 mmol 1-ethyl- 2, 3, 3- trimethyl -5-carboxyl-3H-indolium iodide and 1.83 mmol sodium acetate in 10 mL acetic anhydride was heated at 100~ 110 °C under N_2 for 1 h, then poured into water. The precipitate was filtered, washed and recrystallized from methanol to give red crystals.

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^{1}H NMR (400MHz, d^6-DMSO, δ ppm): 1.33 (t, 3H, J=7.0 Hz, -CH_2CH_3), 1.41 (t, 3H, J=7.1 Hz, -CH_2CH_3), 1.75 (s, 6H, -$C(CH_3)_2$), 1.98 (s, 6H, -$C(CH_3)_2$), 4.16 (m, 2H, -CH_2CH_3), 4.37 (m, 2H, -CH_2CH_3), 6.55 (d, 1H, J=13.0 Hz, -CH=CH-CH), 6.73 (d, 1H, J=13.9 Hz, -CH=CH-CH), 7.49 (d, 1H, J=8.3 Hz, Ar-H), 7.57 (t, 1H, J=7.8 Hz, Ar-H), 7.69 (t, 1H, J=7.3 Hz, Ar-H), 7.87 (d, 1H, J=8.8 Hz, Ar-H), 8.02 (d, 1H, J=8.4 Hz, Ar-H), 8.13 (m, 3H, Ar-H), 8.35 (d, 1H, J=8.4 Hz, Ar-H), 8.49 (t, 1H, J=13.4 Hz, -CH=CH-CH). IR (KBr, cm^{-1}): 2400~3600 (broad, -OH), 1700 (strong, C=O).

Figure 1 (a) Photocurrent action spectrum and (b) absorption spectrum of **1** sensitized mesoporous TiO_2 electrode

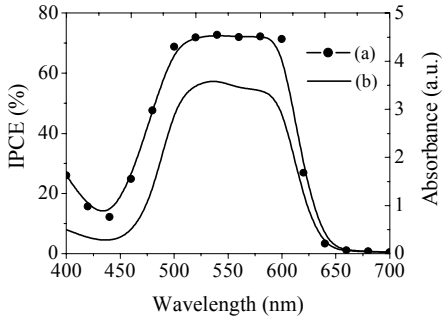

Figure 1 shows the photocurrent action spectrum and the absorption spectrum of **1** sensitized mesoporous TiO_2 electrode in the visible region. It can be seen that the action spectrum of **1** sensitized TiO_2 electrode corresponds well with its absorption spectrum. It confirms that the photocurrent arises from interface charge-transfer between **1** and TiO_2, since TiO_2 is a wide band gap semiconductor and only reponsive to UV light. The maxium IPCE is 73%, while the value is 85% for $Ru(dcbpy)_2(NCS)_2$ sensitized TiO_2 under the same condition. Under 27 mW/cm^2 white light illumination, overall energy conversion efficiencies of 3.9% were achieved for **1** sensitized photoelectrochemical cells. This shows that the **1** has commensurate performance with $Ru(dcbpy)_2(NCS)_2$ dye, while the cost is reduced greatly by excluding noble metal.

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