

Photosensitization of a porous TiO₂ electrode with merocyanine dyes containing a carboxyl group and a long alkyl chain

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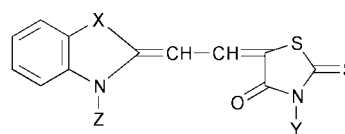
Porous TiO₂ electrodes sensitized using merocyanine dyes containing a carboxyl group and a long alkyl chain, in particular 3-carboxymethyl-5-[2-(3-alkyl-2-benzothiazolynylidene)ethylidene]-2-thioxo-4-thiazolidinone, showed remarkably high solar-energy efficiency (4.2%, AM-1.5, 100 mW cm⁻²).

Since Grätzel *et al.* reported a highly efficient solar cell (incident solar light–power conversion efficiency, $\eta_{\text{sun}} = 10\%$) based on a nanocrystalline TiO₂ semiconductor electrode sensitized by a Ru complex,^{1,2} the studies on dye sensitization of porous oxide semiconductors have been actively investigated. Most papers on the Grätzel type solar cell so far have focused on metal complex dyes such as bipyridyl and porphyrin derivatives, and little attention has been shown to the use of organic dyes as photosensitizers. There are some early works on the spectral sensitization of non-porous semiconductors using organic dyes,³ however, the efficiencies were quite low. It is worthwhile to develop highly efficient organic dye sensitizers from the standpoint of low cost, saving of limited precious metal resources and the easy handling for cell recycling without removal of metal, however, the efficiencies of Grätzel type cells sensitized by organic dyes were relatively low ($\eta_{\text{sun}} < 1.3\%$).^{4–10} Here we investigated various kinds of merocyanine organic dyes containing a carboxyl group as an anchor to attach the dye on the semiconductor surface. Merocyanine dyes have been studied on dye multi-layer photovoltaic cells based on a Schottky-type barrier at the metal/dye film contact,^{11–13} but have been rarely investigated on Grätzel cells. We report here, for the first time, that some merocyanine dyes show excellent efficiencies up to $\eta_{\text{sun}} = 4.2\%$ on porous TiO₂ semiconductor electrodes, and also investigate the relationship between solar cell efficiency and the structure of the dyes.

All dyes were synthesized by Hayashibara Biochemical Laboratories Inc. The preparation of the porous TiO₂ film electrode on a conducting glass support (F-SnO₂, 10 Ω sq⁻¹)

was *via* the published procedure.² TiO₂ powder (Nihon Aerosil, P-25) was mainly used in order to prepare a TiO₂ paste for coating. Adsorption of a dye on the TiO₂ surface was carried out by soaking the TiO₂ electrode in a 220 mg dm⁻³ dry ethanol solution of the dye at 80 °C for 1 h, and the electrode was washed with ethanol. The dye-sensitized TiO₂ electrode was incorporated into a thin-layer sandwich-type solar cell with a Pt/ conducting glass as counter electrode and electrolyte solution. To investigate the efficiency of dyes (Table 1), an Xe lamp with suitable band pass filters (3–4 mW cm⁻²) and UV cut off filter was used as the light source. The incident solar light–electric energy conversion efficiency (η_{sun}) was measured with a solar simulator (AM-1.5, WACOM Co.).

We mainly investigated the photoelectrochemical properties of indole type [Ma, X = C(CH₂)₂] and benzothiazole type [Mb, X = S] merocyanines, a widely used merocyanine dye, as shown in Scheme 1. Both Ma(2)-N and Mb(2)-N dyes containing a carboxyl group adsorbed strongly on the TiO₂ surface, and showed significantly high efficiencies. On the other hand, the Mb(2)' dye containing no carboxyl group scarcely adsorbed on TiO₂ and the cell efficiency was negligible, suggesting that the presence of anchoring groups to adsorb on the semiconductor surface is essential for efficient dye-sensitization. In the studies of solid photovoltaic cells using dye multi-layer electrodes without semiconductors,^{11,13} various kinds of merocyanine dyes including Ma and Mb dyes were examined, and the carboxyl group was not essential in contrast to the dye-sensitized semiconductor cells studied here. The



Scheme 1 Structure of merocyanine dyes; for the identity of X, Y and Z see Table 1.

Table 1 Photoelectrochemical properties of porous TiO₂ semiconductor solar cells sensitized with various merocyanine dyes^a

Dye	Dye structure			$\lambda_{\text{max}}^b/\text{nm}$	$\lambda_{\text{threshold}}^b/\text{nm}$	IPCE ^c (%)	Isc ^d /mA	Voc ^d /V	ff ^d (%)	η_{Xe}^d (%)
	X	Y	Z							
Ma(2)-N	CMe ₂	CH ₂ CO ₂ H	C ₂ H ₅	490(520)	550(600)	38.0	3.50	0.61	60	1.6
Mb(2)-N	S	CH ₂ CO ₂ H	C ₂ H ₅	520(560)	570(660)	33.3	3.92	0.62	60	1.8
Mb(5)-N	S	CH ₂ CO ₂ H	C ₅ H ₁₁	520(560)	570(660)	36.7	4.68	0.68	60	2.4
Mb(10)-N	S	CH ₂ CO ₂ H	C ₁₀ H ₂₁	520(570)	570(660)	41.7	5.35	0.68	60	2.7
Mb(18)-N	S	CH ₂ CO ₂ H	C ₁₈ H ₃₇	520(590)	580(670)	41.8	5.50	0.62	54	2.3
Mb(2)'	S	Me	Et	520(—)	570(—)	< 0.1	< 0.01	—	—	< 0.1
Mb(2)-M	S	Et	CH ₂ CO ₂ H	520(550)	570(650)	45.7	4.28	0.52	58	1.6
Ma(2)-NM	CMe ₂	CH ₂ CO ₂ H	CH ₂ CO ₂ H	500(540)	580(630)	26.5	2.30	0.50	63	0.9

^a TiO₂ film (thickness 7 μm , area 1 cm²) prepared from P-25. The electrolyte solution was a mixture of tetrapropylammonium iodide (0.5 M) and iodine (0.05 M) in ethylene carbonate–dry acetonitrile (60:40 v/v). ^b In ethanol; values in parentheses were measured on TiO₂. ^c IPCE was measured by monochromatic light at near λ_{max} using band pass filters. ^d Under white light from an Xe lamp >420 nm (80 mW cm⁻²).

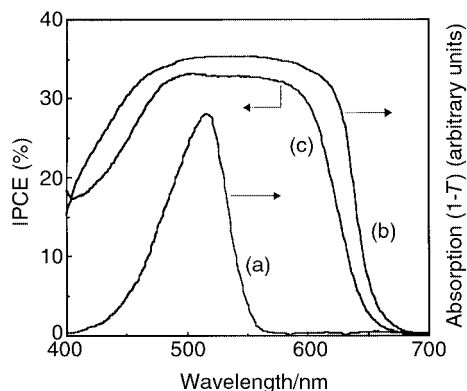


Fig. 1 Absorption spectra of Mb(2)-N in ethanol solution (a), Mb(2)-N on TiO₂ electrode (b) and IPCE action spectrum of the Mb(2)-N/TiO₂ cell (c). The TiO₂ electrode and the electrolyte were same as indicated in Table 1.

incident photon–current efficiencies (IPCE) of the dye-sensitized semiconductor cells in our study were superior to those of solid photovoltaic cells (IPCE < 22%).^{11–13}

Fig. 1 shows the light absorption spectra of Mb(2)-N in ethanol solution (a) and Mb(2)-N on a TiO₂ electrode (b), in addition to the IPCE action spectrum of the Mb(2)-N/TiO₂ cell (c). The absorption peak maximum (λ_{\max}) and the absorption threshold ($\lambda_{\text{threshold}}$) of various dyes in ethanol and on TiO₂ are also shown in Table 1. All merocyanine dyes had a narrow absorption band in ethanol solution, and the peak at around 500 nm was assigned to the monomer.¹² By adsorbing the dye on the TiO₂ electrode, a broadening of the absorption spectrum and a large red shift of the absorption threshold were observed in all electrodes. The IPCE action spectrum was as broad as the absorption spectrum on TiO₂. Similar broadening and red shifts have been reported on several merocyanine multi-layer electrodes without semiconductors.^{11,12} Therefore, it is suggested that the interaction between neighboring dyes causes the red shift and the broadening of the absorption. The changes of absorption on the merocyanine multilayer electrode are explained on the basis of exciton phenomena, calculated from the molecular packing structure of the dye aggregate and the coupling of transition dipoles.¹¹ It was reported that a J-aggregate of Mb(2)-N, which showed a large red shift and a sharp absorption peak at 610 nm, was formed in the TiO₂ mesoporous network after aqueous solution treatment.¹⁴ In our experiments, while a large red shift of the absorption was observed, no sharp absorption peak at ca. 610 nm was observed. Therefore, we speculate that small J-like aggregates were formed on the TiO₂, and that chemical anchoring on the TiO₂ surface restricted the formation of large and highly oriented J-aggregates.

We investigated the merocyanines [Mb(*m*)-N] with long straight alkyl chains (carbon number: *m* = 2, 5, 10 and 18) in detail, since it has been reported that the formation of J-aggregates is more facile with increasing length of alkyl chain in the study of dye multi-layer electrodes.^{12,13} The peak maximum and threshold of absorption for Mb(*m*)-N on TiO₂ were slightly shifted to the longer wavelength with an increase in *m* (Table 1). In addition the rise of absorption at the threshold became sharp with increasing *m*. The IPCE of Mb(*m*)-N/TiO₂ cells at ca. 520 nm increased with an increase of *m*, and these electrodes had the same values of light harvesting efficiency at 520 nm. Therefore, it is suggested that the intrinsic sensitization efficiency, *i.e.* quantum efficiency, increased with the length of alkyl chain.

In discussing the relationship between the sensitization efficiency and the presence of long alkyl chains the electron injection process from the excited state of the dye to the TiO₂ generally competes with other undesirable processes, and

photo-isomerization is one of the major decay pathways for merocyanine.¹⁰ The presence of long alkyl chains and aggregate formation probably prevents isomerization by the restriction of rotation around the methine chain. Moreover, in the J-aggregate crystal structure of Mb(2)-N sodium salt octahydrate,¹⁴ the alkyl chain is located at the opposite side of the carboxyl group, and the formation of single isomers and uniform orientation of the dye seem to be important factors for good J-aggregation. It is speculated that the repulsion between long alkyl chains and the TiO₂ surface might help form the predominant isomer, in which the alkyl chain lies far apart from the carboxyl group anchoring on the TiO₂ surface. Mb(2)-M, which has a carboxyl group at another position Z instead of position Y, showed almost same efficiency as Mb(2)-N. On the other hand, the photocurrent of Ma(2)-NM containing two carboxyl groups was very low compared with that of Ma(2)-N containing one carboxyl group. The configuration and aggregation of Ma(2)-NM on TiO₂ were very restricted by two anchors, and this might affect the photocurrent. From all the results, it is concluded that the control of configuration and aggregation of the merocyanine dye are very important factors in improving the solar cell efficiency.

Finally, we improved the efficiency of the Mb(18)-N/TiO₂ solar cell using thicker TiO₂ films (*ca.* 13 μm thickness) prepared by the alkoxide method using a different electrolyte solution consisting of a mixture of LiI (0.1 M), 1,2-dimethyl-3-propylimidazolium iodide (0.6 M), iodine (0.05 M), 4-*tert*-butylpyridine (1 M) and methoxyacetonitrile as solvent.^{2,15} The maximum η_{sun} value under solar simulated light (100 mW cm^{-2} , AM-1.5, 0.25 cm^2) was *ca.* 4.2% (Isc: 9.7 mA cm^{-2} , Voc: 0.62 V, ff: 69%), the best value among organic dye systems reported so far.^{3–10} The stability of these dyes in a sealed solar cell is now under investigation.

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