



Enhancement in power output of solar cells consisting of mixed dyes

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Abstract

A new type solar cell consisting of dye-redox system have been developed. Instead of single dye, mixture of two dyes along with a reducing agent, EDTA was taken in the illuminated compartment of an H-shaped cell in which I^-/I_2 redox couple in the dark compartment are separated by glass membrane (Porosity G-4). The dyes used for mixed system are of four classes: phenazine, thiazine, xanthene and acridine. Calculated solar energy efficiency (SEE) and other cell characteristics of mixed dye-solar cell is larger in comparison to the cell with single dye. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

One area of recent interest relevant to the direct conversion of light energy to electrical energy is the study of dye-redox systems capable of generating photogalvanic effect. Initially, thionine-Fe(II) system, a widely studied photogalvanic (PG) system, has yielded important information on the photochemical and electrochemical determinants of power conversion efficiency in PG cell [1–3].

Later scientists have been studied extensively many photovoltaic and photogalvanic solar cells using different classes of dye. Solar cells based on organic photovoltaic compounds offer the prospects of inexpensive energy conversion. However, the photovoltaic energy conversion efficiency is quite low because of the high rate of carrier recombination [4].

A redox system consisting of phenosafranin (PSF) and reducing agent EDTA has been found to generate a large photovoltage in aqueous solution [5,6] as well as in the solid polycrystalline state [7]. Interest in photoelectrochemical (PEC) cells consisting of dyes and reducing agents is waning because of low SEE and a lack of solar energy storage capability. The problem of storage may be partly overcome if the reversible dark reaction occurs sufficiently slowly to allow the oxidized and reduced photoproducts to be separated or else allows coexistence in appreciable concentrations in solution so that radiant energy is converted to

chemical energy on recharge and chemical energy to electrical energy on discharge [8,9]. Recently, we have developed a new type of PEC cell [10] consisting of (i) an aqueous solution of PSF-EDTA and different inorganic redox couples and (ii) the aqueous solutions of phenazine dyes – EDTA and I^-/I_2 separated by a pyrex-sintered glass membrane with porosity G-4. The glass membrane does not allow the solutes to flow but facilitates the transport of electrons generated by the double-electrode phenomenon.

As organic dyes have narrow absorption spectrum profiles in the visible light region, we have prepared the PEC cell consisting of mixed dyes instead of single dye system to utilize the broad spectrum of sunlight. The cell characteristics of mixed dyes as well as single dye system are reported here.

2. Experimental details

The dyes used for this study are phenosafranin (3,7-diamino-5-phenyl phenazinium chloride), neutral red (3-amino-6-dimethyl amino-2-methyl-phenazine hydrochloride), methylene blue [3,7-bis(dimethyl amino)-phenothiazinium chloride], fluorescein (3-keto-6-hydroxo-9-benzoate xanthene disodium salt), acridine orange [3,6-bis(dimethylamino)-acridine], azure A (3-amino-7-dimethyl-amino-phenothiazinium chloride), azure B (3-dimethyl amino-7-methyl amino-phenothiazinium chloride), and azure C (3-amino-7-methyl amino-phenothiazinium chloride), supplied by Sigma Chemicals and Fluka. A list of these dyes of

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Table 1
The structure, absorption and emission wave length maxima of four classes of dyes

Dye	Class	Structure	λ_{\max} (nm) (absorption)	λ_{\max} (nm) (emission)
Phenosafranin	Phenazines		520	572
Neutral red (NR)			534	590
Methylene blue (MB)	Thiazines		665	752
Azure A			635	722
Azure B			647	728
Azure C			620	692
Fluorescein	Xanthene		490	514
Acridine orange (AO)	Acridine		492	522

different group with their absorption and emission wavelength maxima are given in Table 1. They were twice recrystallized from ethanol-water mixtures. EDTA (disodium salt, dihydrate) and all other chemicals were of the AR grade supplied by BDH and Merck and were used without further purification. All of the solutions were prepared in doubly-distilled water.

The PEC cell and the detail of the experimental setup for the measurement of photovoltage has been described earlier [10]. The illuminated (anode) compartment consisted of either single or mixed dye and EDTA deoxygenated aqueous solution and the dark (cathode) compartment contains a redox couple I^-/I_2 . The photovoltage and photocurrent were measured with the Keithley digital electrometers (models 196 and 642). The light source was a projector tungsten lamp (220 V, 300 W) focused to 30 mW cm^{-2} . Intensity of the incident light was checked with YSI-Kettering Radiometer model 65, by placing the probe of the radiometer in front of the incident light at the same distance, where the PEC cell is placed.

3. Results and discussion

On illumination of the anode compartment of the cell consisting of deoxygenated aqueous solution of single dye of phenazine or thiazine group and EDTA generates photo-

potential and attains its maximum value (V_{OC}) within a few minutes. When the illumination is stopped, the generated photovoltage gradually decreases and the time required to reach the original dark value is 1–2 days; however, the decay time varies with the nature of the dye used. But the photovoltage generation with xanthene or acridine dye of Table 1 in PEC cell is nearly zero.

However, the PEC cell with mixed dye system consisting of phenazine dye PSF and the dye of any other class produces slightly improved photovoltage compare to PSF-EDTA system [10] except PSF-Azure B-EDTA system, where photovoltage decreases $\sim 20\%$ compared to the cell with PSF only. We have studied only seven mixed dye systems. Of them, PSF-Azure C-EDTA system generates $\sim 15\%$ enhanced photovoltage i.e., 704 mV compared to single dye PSF system. The growth and decay with time of irradiation of the photovoltage of the solar cell consisting of single dye PSF, Azure B, Azure C and mixed dye PSF-Azure B and PSF-Azure C with EDTA are shown in Fig. 1.

The solar energy efficiency (SEE) of PSF-EDTA redox system has been enhanced on mixing with dyes of difference classes. Particularly, the PEC cell with PSF and MB mixed dyes produce 20% more SEE compare to only PSF dye containing cell, whereas mixed system with PSF and acridine or flurescein dye give 50% more SEE. Mixing two phenazine dye i.e., PSF and NR yield SEE which is 80%

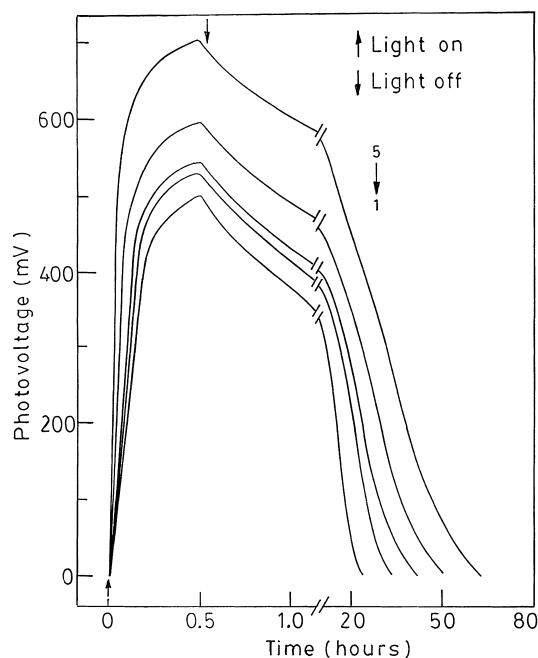


Fig. 1. Growth and decay curves of photovoltage in solar cells containing a saturated aqueous solution of iodine in iodide in the cathode compartment and PSF-Azure B-EDTA (1), Azure C-EDTA (2), Azure B-EDTA (3), PSF-EDTA (4), and PSF-Azure C-EDTA (5) in the anode compartment at 298 K. Concentrations of dye and EDTA are 2×10^{-5} and 0.1 mol dm^{-3} , respectively.

larger compare to PSF-EDTA system and 47 fold greater w.r.t. NR dye PEC cell.

The current–voltage characteristics of PSF-EDTA, NR-EDTA, and PSF-NR-EDTA are shown in Fig. 2. In comparison to PSF-EDTA system, the photovoltage production as well as SEE of PSF-Azure B-EDTA system decreases 40% but it increases 40% with PSF-Azure C-EDTA. All the cell characteristics of single dye and mixed dye systems have been calculated from $V-t$ as well as $I-V$ curves which are enlisted in Table 2.

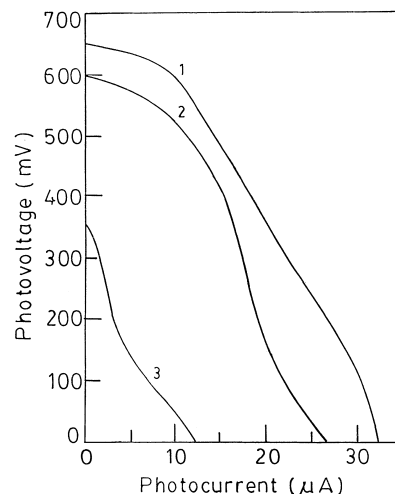


Fig. 2. Current-voltage characteristics of solar cells containing a saturated aqueous solution of iodine in iodide in the cathode compartment and (1) PSF-NR-EDTA (2) PSF-EDTA and (3) NR-EDTA in the anode compartment at 298 K. Concentrations of dye and EDTA are 2×10^{-5} and 0.1 mol dm^{-3} respectively.

The steps that lead to photovoltage generation in single dye-redox system [11–14] are as follows: the dye is excited to its triplet state (3D), which then undergoes protonation ($^3DH^+$ or $^3DH_2^+$), followed by charge transfer (CT) interaction between the protonated triplet dye and the ionized EDTA (HY^{3-} or Y^{4-}). The reduced dye ($^{\bullet}DH^+$; semi-dye; the electroactive species as determined from flash photolysis studies on pheanzine dye, PSF) [15] is the charge carrier; it diffuses to the illuminated electrode surface, and release the electron to the electrode. This electron flows through the external circuit to the cathode compartment, reduces iodine to I^- , which is oxidized again on the membrane surface and thus, the cycle is completed.

Morel et al. [16] investigated the improved quantum efficiency in photovoltaic device with merocyanine dye

Table 2
Characteristics of the single dye-EDTA and mixed dyes-EDTA solar cell at 298 K

Single or mixed dye	Open circuit photovoltage (mV)	Short circuit current (μA)	Fill-factor	Power efficiency ($\mu\text{W cm}^{-2}$)	SEE ($10^{-2}\%$)
PSF	600	26.00	0.41	7.61	2.54
MB	425	7.92	0.64	1.79	0.10
NR	354	12.00	0.16	0.81	0.27
Fluorescein	1	–	–	–	–
AO	4	–	–	–	–
Azure A	465	26.00	0.51	7.70	1.83
Azure B	547	31.20	0.25	6.46	1.54
Azure C	532	40.00	0.33	10.64	2.53
PSF + MB	665	22.75	0.32	6.05	3.02
PSF + Fluorescein	625	24.75	0.30	7.73	3.87
PSF + AO	685	24.00	0.33	9.04	4.50
PSF + NR	650	32.50	0.35	9.24	4.62
PSF + Azure A	651	23.75	0.32	8.25	1.96
PSF + Azure B	504	19.50	0.36	5.89	1.40
PSF + Azure C	704	45.50	0.28	14.94	3.56

mixing deposited on Al electrode. Abdul-Ghani et al. [17] observed that the photothermal energy conversion capability of mixed dyes in liquid solar cell is controlled by dye-dye interface. In PEC cell with mixed dye-EDTA system, triplet dye species are produced more by absorption of wide range of visible solar spectrum. The generated triplet dye molecules become protonated and give enhanced photovoltage as well as solar energy efficiency by CT interaction between protonated dye and ionized EDTA molecule. We have already mentioned [18] the possible mechanism for photovoltage generation in dye-EDTA system. Furthermore, the dye-dye interaction is also responsible for improved cell performance i.e., ${}^3\text{DH}_2^+ + {}^3\text{D}' \rightarrow {}^3\text{DH}^+ + {}^3\text{D}'\text{H}^+$. Where, ${}^3\text{DH}^+$, ${}^3\text{DH}_2^+$ are mono- and di-protonated triplet dye; ${}^3\text{D}'$ and ${}^3\text{D}'\text{H}^+$ are triplet and monoprotonated triplet of another dye.

In the case of PSF-Azure B-EDTA system, Azure B is highly fluorescent due to more N-methyl substitution in amine groups compared to Azure A and Azure C. Hence excited singlet Azure B molecules become more deactivated radiatively before H^+ transfer step by dye-dye interaction, which causes the decrease of cell efficiency.

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