

Review
Solar cells based on dyes

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Abstract

From early developments to recently developed stages of solar cells have been discussed in details, considering the effect of different parameters. In this paper, primitive photoelectrochemical (PEC) cell and PEC cell with Fe–thionine and different dyes-reducing agent have been reviewed. Solar cell with phenazine dyes have also been pointed out separately since these dyes give more output in solar cell. The use of inorganic semiconductor electrode (e.g. SnO₂, In₂O₃ and ZnO) and utilization of semiconducting properties of organic dyes in PEC cell have been mentioned. Furthermore, utilization of surfactant media for storage of solar energy and production of hydrogen from solar cell using dye are also included. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Dyes; Photochemical cells; Photopotential; Photocurrent

1. Introduction

The search for renewable sources of energy has led to an increasing interest in photochemical cells because of their possible role as transducers of solar to electrical energy. The photoeffects in electrochemical systems were first observed by Becquerel [1] in his investigation on the solar illumination on metal electrodes in 1839. Later it was observed by Moser [2] and Rigollot [3] that the sensitivity of silver/silver halide and copper/copper oxide electrode could be increased by coating them with a dye stuff. Thompson [4] and Stora [5] reported that pure metal electrodes were also sensitive to light when coated with a dye or immersed in a dye solution. The result of the first 100 years had been reviewed by Copeland and co-workers [6]. A summary of the properties of photoelectrochemical (PEC) cells described in the literature upto 1965 was compiled by Kuwana [7] and later work has been reviewed by Archer [8].

This review paper is comprised of evolution of solar cell from the very beginning stage and it includes vast field of research in PEC cell in which dyes are used for photoeffected electron-transfer reaction. The basic principles of PEC cell are not discussed here. PEC cell are of three types i.e. photogalvanic (PG), photovoltaic (PV) and photogalvanovoltaic (PGV). So, these three types of PEC cell are considered in different sections of this paper.

A list of abbreviations and symbols is mentioned at the end of this paper as a large numbers of chemical systems have been cited here.

1.1. A primitive PEC cell

Anciently a photochemical cell is composed with inert metal electrodes immersed in two redox couple [i.e. A/B (light sensitive) and Y/Z] and the best performance is obtained if one couple (e.g. A/B) is highly reversible and the other (Y/Z) is highly irreversible [9]. As a result, the reaction occurs in the light and dark are as follows:



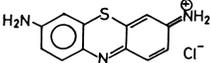
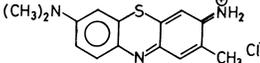
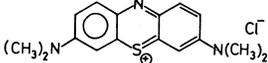
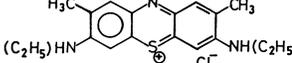
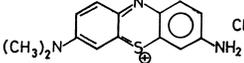
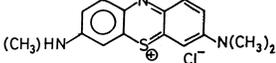
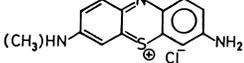
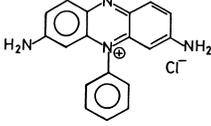
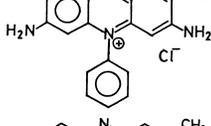
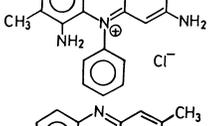
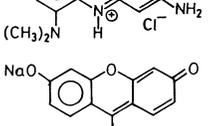
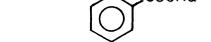
Furthermore, optimum output of power depends on the cell length, the concentration of A, Y and Z, the kinetics of the homogeneous reaction B+Y, the extinction coefficient of A, and the cell load [10,11].

In this comprehensive mode cell, five major types of process [12] occurs which are (i) the intermolecular oxidation–reduction reactions in the dark of the solution and at the electrode, (ii) the electrodic charge transfer reactions, (iii) the steps for the conversion of bulk species to surface species with or without the possibility of adsorption, (iv) direct photochemical pathways, and (v) the photochemical side reactions.

1.2. PEC cell with dyes

Generally inorganic elements possess redox properties because of large electronegativity difference between bonded elements. The organo-metallic and heterocompounds (e.g. dye) like inorganic element also show redox property although they are covalent in nature. So dye molecules, having redox property as well as light sensitivity, can be used in comprehensive solar cell as a redox couple among the two which is mentioned in model primitive cell. The structure and absorption wavelength maxima of some dyes are listed in Table 1. They are commonly used in this paper.

Table 1
The structure and absorption maxima of five classes of dyes

Dye	Class	Structure	λ_{\max} (nm)
Thionine (TH ⁺)	Thiazines		596
Toluidine blue (Tb ⁺)	Thiazines		630
Methylene blue (MB)	Thiazines		665
New methylene blue	Thiazines		650
Azure A	Thiazines		635
Azure B	Thiazines		647
Azure C	Thiazines		620
Phenosafranin (PSF)	Phenazines		520
Safranin-O (Saf-O/SO)	Phenazines		520
Safranin-T (Saf-T/ST)	Phenazines		520
Neutral red (NR)	Phenazines		534
Fluorescein	Xanthenes		490

1.2.1. Iron–thionine system

A particularly striking example of an oxidation–reduction system, in which light is converted to a marked proportion into chemical energy, is the iron–thionine system observed by Weber [13] firstly. The reaction was reversible in the dark, but could be driven in an irreversible manner by precipitation of the simultaneously formed ferric ions (Weiss) [14]. The PEC effect of this Fe(II)–thionine system was first seriously considered by Rabinowitch [15].

The cell characteristics of Fe(II)–thionine PG cell are reported by many authors, few of them are mentioned in Table 2.

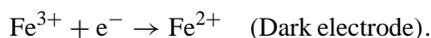
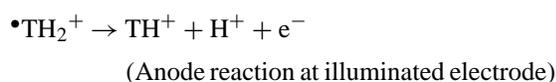
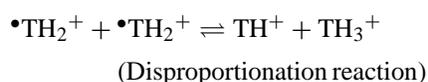
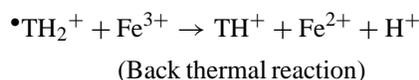
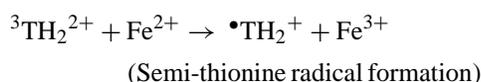
Table 1. (Continued)

Dye	Class	Structure	λ_{max} (nm)
Erythrosin	Xanthenes		530
Erythrosin B	Xanthenes		525
Rhodamine B (Rh. B)	Xanthenes		551
Rose bengal	Xanthenes		550
Pyronine Y (PY)	Xanthenes		545
Eosin	Xanthenes		514
Rhodamine 6G	Xanthenes		524
Acridine orange (AO)	Acridines		492
Proflavin (PF)	Acridines		444
Acridine yellow (AY)	Acridines		442
Fuchsin	Triphenyl methane derivatives		545
Crystal violet	Triphenyl methane derivatives		578
Malachite green	Triphenyl methane derivatives		423, 625
Methyl violet	Triphenyl methane derivatives		580

Table 2
Cell characteristics of PG cell with Fe(II)–thionine system

Photovoltage (mV)	Short-circuit current (I_{SC}) (μ A)	Solar energy efficiency (SEE) %	Reference
10–240	–	–	[15]
185	–	3×10^{-4}	[16]
–	–	30-fold of [16]	[17]
230 (pH 4.0)	–	–	[18]
–	–	2.36×10^{-1}	[19]
138	26.3	–	[20]
900	80.0	–	[21]
–	–	1.1×10^{-2}	[22]

The thionine–Fe(II) aqueous PG system was studied extensively [23–30] but the basic mechanism of the PG effect was unknown initially. However, Hatchard et al. [31] and Albery et al. [32] established the sequence of reactions in Fe–thionine cell which are as follows:



Thionine was represented by TH^+ , since in the dark thionine is in the oxidized form TH^+ .

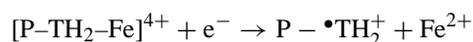
Still, the photoenergy conversion is very low mainly due to back thermal reaction between reduced dye and Fe(III) [33,34] and formation of local cells. Last factor can be reduced if the Fe(II)–thionine system is studied in heterogeneous cell. Kamat et al. [35–38] reported the better power output of heterogeneous cell than homogeneous cell which are 0.022 and 0.001%, respectively.

In order to decrease the back reaction of this system, Natarajan et al. [39] constructed a PG cell with Fe(II) and thionine coated with poly(*N*-methyl acrylamide), and observed that open-circuit voltage (V_{OC}) and I_{SC} of this system increased with increase in ratio of P/D (polymer/dye) and reached maxima with

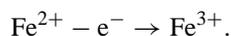
P/D=33. Yamad et al. [40] also observed greater photo-potential with thionine-poly(imino-ethylene) compared to thionine-monoamine. Even thionine coated electrode [41–44] favours irreversible oxidation process over reduction process but Harrison et al. [45] reported 19 times reduced power conversion efficiency with thionine coated gold electrode compared to uncoated electrode. Kamat [46] also reported very low efficiency i.e. $10^{-4}\%$ with thionine dye incorporated Pt clay modified electrode.

Lichtin et al. [47] developed the totally illuminated thin layer (TITL) iron–thionine PG cell and studied the electrodic phenomena at the anode of this cell. Albery [48] also discussed theoretical principles regarding kinetics, electrode selectivity and efficiency of the TITL cell. Natarajan et al. [49,50] approached the electrode coated method to TITL system using polymer bounded thionine coated on SnO_2 electrode and clean Pt electrode, and obtained maximum power output compared to earlier study [39]. They proposed the following mechanism

at the cathode:



at the anode:



Mechanism shows that the oxidation of the thionine in the complex $[\text{P}-\text{TH}_2-\text{Fe}]^{4+}$ present near the electrode, occurs slowly for which efficiency of cell increases. The photocurrent of TITL system [51] with bare and thionine coated Pt electrode increases to some extent by the addition of F^- ion.

The Kinetics of iron–thionine system have been studied by the steady state illumination [23,24,26,52–54] and flash photolysis techniques [55,56]. Employing a cross beam illumination kinetic spectrophotometry technique, Kamat et al. [57] studied the oxidation of leuco-thionine by Fe(III) in aqueous solution i.e. the kinetics of photobleaching recovery. The photobleaching recovery follows pseudo first-order kinetics through complex formation between TH_4^{2+} and Fe(III), and the rate constant increases with increase in pH, light intensity and temperature. The experimental kinetics

of photobleaching process is in good agreement with theoretical approach, concerning the efficiency of a photoredox system for Fe(II)–thionine PG cell [58].

All sorts of stability, thermodynamic stability and kinetic phase diagram diffusion of reactants were investigated with a model Fe(II)–thionine PG cell [59]. These studies suggest that if a PG cell is driven very hard, non-linear effect may modulate, considering the evaluation and maintenance of a photostationary state. The output of the Fe(II)–thionine cell [60] can be enhanced if the standard potential of leuco dye/dye couple decreases and/or standard potential of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ increases. The influence of parameters i.e. temperature, pH, the concentrations of, Fe^{3+} , Fe^{2+} , TH^+ , halide ions, and organic solvents on the Fe(II)–thionine homogeneous system [38] was studied. Considering PG cell potential, the optimum condition of these parameter are: temperature ≤ 280 K, $[\text{Fe}^{3+}] \sim 10^{-4}$ M, $[\text{Fe}^{2+}] = 5 \times 10^{-3}$ M, $[\text{TH}^+] = 2 \times 10^{-5}$ M, pH=2.0, and light intensity 150 mW cm^{-2} . But addition of halide ions and different organic medium except acetonitrile decreases the photopotential of PG cell. The dye molecule has a property of self-quenching at higher concentration which can be reduced to some extent using new thionine dye [61] in the place of traditional dye in PG cell.

Albery [62] reported that the efficiency of electrolyte cell is less compared to semiconductor cell. So combining the principles of photogalvanic (PG) and photovoltaic (PV), the photogalvanovoltic (PGV) cell [63,64] was designed to utilize the solar spectrum from UV to IR region. This type of cell can be used for direct conversion of solar energy to electrical energy and short term storage also.

1.2.2. Different dyes — reducing agents

Molecules capable of absorbing light in the visible region of the electromagnetic spectrum behave at electrodes like other light insensitive molecules and can be either reduced or oxidized. The reduction of an electronically excited molecule can take place by reaction with a reducing substance which will not reduce the molecules in the ground state. PG cells arising from the photoredox reactions in solutions of various dyes have been studied, a few have been enlisted in Table 3 [65]. It can be noted from this table that especially high photovoltage and photocurrents were obtained in systems with sacrificial electron donors like ethylene diamine tetra acetic acid (EDTA) or triethanolamine (TEA), against thionine and riboflavin compared to the case of reversible reducing agents like Fe^{2+} or hydroquinone. But for rhodamine B, proflavin and rose bengal, much smaller photovoltages and photocurrents were obtained with EDTA or TEA as the reducing agents due to high negative potential of the dyes. The photoresponses for proflavin–EDTA or TEA systems were enhanced drastically by the addition of methyl viologen (MV^{2+}), and the enhanced values were almost of same order as those for thionine or riboflavin with EDTA and TEA as reducing agents. Such enhancement by MV^{2+} could not be seen for thionine and riboflavin and

Table 3
Photocurrents (i_p) and photovoltages (v_p) in various photogalvanic cells^a

Dye ^b	Redox reagent ^c	i_p ($\mu\text{A cm}^{-2}$)	v_p (mV)
Thionine	Fe^{2+}	3.3	140
	Hydroquinone	2.8	20
	EDTA	12	190
	TEA	18	250
	TEA+ MV^{2+}	18	210
Riboflavin	Hydroquinone	0.83	20
	EDTA	58	720
	TEA	35	500
	TEA+ MV^{2+}	37	430
Proflavin	Hydroquinone	0.43	1.9
	Hydroquinone+ MV^{2+}	0.41	2.4
	EDTA	0.79	140
	EDTA+ MV^{2+}	25	350
	TEA	0.25	60
	TEA+ MV^{2+}	6.25	320
Rhodamine B	MV^{2+}	0.038	5.0
	EDTA	0.092	28
	EDTA+ MV^{2+}	0.092	10
Rose bengal	EDTA	0.025	19
	EDTA+ MV^{2+}	0.017	20

^a Taken from [65] and references therein.

^b The concentrations are $10^{-4} \text{ mol dm}^{-3}$ for the dye, except thionine ($5 \times 10^{-4} \text{ mol dm}^{-3}$).

^c $10^{-2} \text{ mol dm}^{-3}$ for the reducing agent, $10^{-3} \text{ mol dm}^{-3}$ for MV^{2+} .

also not for proflavin with hydroquinone. Thus the effect of MV^{2+} arises only for the proflavin and aliphatic amine system. The role of MV^{2+} is firstly to oxidize the dye to dye cation by reducing to MV^+ itself, then the dye cation react with the sacrificial donor — the presence of MV^{2+} thus catalyses the photoredox reaction, acting as a mediator.

Hann et al. [66] had first studied the photoredox reaction of dye methylene blue (MB)– Fe^{2+} system for a PG cell. Getoff and Solar have investigated the same system at pH 1.8, the quantum yield for the photochemical reaction being 0.038 at 292–400 nm. The photogalvanic effect of MB and various reducing agents were studied by Murthy and Reddy [67]. Photopotentials upto 550 mV have been reported for MB–EDTA PG cell with power conversion efficiency of $\sim 0.04\%$, using Pt electrodes in both compartments. Using TEA and triethyl amine in the same set up, instead of EDTA, photovoltages of 432 and 397 mV, and photocurrents of 43 and 40 μA were obtained.

While working with the Fe(II)–thionine system, an elegant approach to store the light energy had been proposed [68] by illuminating a water–ether binary solvent system, where the reduced form of the dye could be extracted into the ether layer and Fe^{3+} in the aqueous layer, thereby preventing dark back recombination reactions, and photovoltage of 300 mV was obtained. The same kind of system with thionine–EDTA, however, gave only 200 mV [69]. Murthy et al. [67] had also studied the MB– Fe^{2+} system in H_2O –ether binary system, and also in H_2O – C_6H_6 and H_2O – CCl_4 binary systems. The photopotentials obtained were much higher

Table 4
Photopotentials of iron–MB and EDTA–MB PG cells in the two-phase solvent systems

System	Solvent	Photopotential (mV)
Fe ²⁺ –MB	Diethyl ether	254
	C ₆ H ₆	293
	CCl ₄	295
EDTA–MB	Diethyl ether	350
	C ₆ H ₆	750
	CCl ₄	812

than ordinary aqueous systems as depicted in Table 4. The higher photopotential in non-polar solvents like C₆H₆ and CCl₄ is due to absence of any side reaction. However, by replacing Pt electrode with SnO₂ electrode, so that both electrodes could be illuminated, the EDTA–MB, triethyl amine–MB and TEA–MB systems gave lower photopotentials.

Srimvasalu and Mathew [70] investigated photogalvanic effect in MB and 2-hydroxy ethylene diamine triacetic acid (HEDTA). HEDTA is an efficient electron donor at pH 13.0. The cell with Pt–calomel electrode generates photovoltage and photocurrent 730 mV and 420 μ A, respectively at 200 W illumination in presence of HEDTA. The suitability of new methylene blue NN as a dye was investigated by Alberly and Foulds [71], though solar energy conversion efficiency of it is low even in lower concentration (10–25 μ M) due to self-quenching [72] similar to thionine dye [73].

While studying the various steps in photogalvanic process MB–Fe²⁺ system, Hay et al. [74] and Nicodem et al. [75] have studied the kinetics, equilibria and solvent effect on the disproportionation reaction of semi-MB and oxidation of leuco-MB by MB and Fe²⁺, and the behavior of MB–Fe²⁺ was found to be analogous to thionine–Fe²⁺ system. But the photogalvanic output of Fe²⁺-dye (i.e. MB, New MB and Azure A) [76] can be enhanced by using better complexing agent KH₂PO₄ with produced Fe³⁺ compared to NH₄HF₂ or EDTA through suppression of back recombination reaction.

The photoresponses of the dye toluidine blue (Tb⁺) with reversible as well as sacrificial donors like Fe²⁺, EDTA, TEA and triethyl amine were studied [77]. The results are given in Table 5.

It was observed that photoredox reaction of Tb⁺ with reversible reducing agent like Fe(II) was completely reversible, whereas with amines it is not completely reversible. Ameta et al. [78] have enable to generate photocurrent 10 μ A

and photovoltage 73 mV from toluidine blue–nitrilo triacetic acid PG cell, and obtained maximum power 7.3×10^{-7} W from this cell. The maximum photocurrent and photovoltage yielded by toluidine–mannitol [79] (a reducing agent) at pH 13.0 are 70 μ A and 900 mV, respectively.

Another photoredox that has been studied in detail [80,81] is rhodamine B and Fe²⁺/Fe³⁺ system, by using Au electrodes. The power conversion efficiency of such a cell is very low $(2.4 \pm 0.2) \times 10^{-6}\%$. However, by using a rotating disc electrode and dye layers deposited on Au electrodes, the efficiency of the cell could be increased upto 14 times.

Photoreduction of 3,7-diamino phenoxy azymylum chloride (oxamine) by Fe(II) was studied as a model system for singlet state driven PG cell [82]. Fawcett et al. [83] have investigated the same system and reported V_{OC} , I_{SC} and SEE which are 21 mV, 2.6 μ A and $2.9 \times 10^{-4}\%$ (578 nm), respectively.

Photosystem (I) mediated and proflavin catalyzed photoreduction of methyl viologen when taken in a PG cell, was reported to yield photopotential of 800 mV, I_{SC} of 3 mA and power of 1 mW at 300 Ω applied resistance. Photoreduction of methyl viologen was proposed to give a large photocurrent [84].

A flavinmononucleotide (FMN)–EDTA system had been studied in a PG cell [85] and an efficiency of 0.048% was established.

Riboflavin–diethanolamine PG system [86] generates maximum photopotential of 520 mV at pH 8.4. Murthy et al. [87] reported that SEE of riboflavin–EDTA PG cell is $\sim 0.018\%$ though photoinduced current is low.

The possible mechanisms are obtained from a short survey, by which phenolphthalein dye molecules may convert the absorbed radiation energy into chemical energy, electrical energy or heat [88]. The SEE of PEC cell [89] with fluorescence dye can be improved by the complete separation of the absorption and emission bands of this dye by embedding in polymer plates.

Morel et al. [90] have made a systematic study of the influence of chemical structure on the performance of merocyanine and squarylium dyes as solar energy converters. The highest sunlight efficiencies have been investigated with binuclear structures, however certain trinuclear structures, which exhibit broader spectral width and hence show higher quantum efficiencies.

The quenching rate of the triplet state of eosin by different transition metal ions follow decreasing order [91]: Cu²⁺ > Fe²⁺ > Cu⁺ > Fe(CN)₆³⁻ > Fe(CN)₆⁴⁻ > CrO₄²⁻ having magnitude from 2.5×10^9 to 7.2×10^7 l mol⁻¹ s⁻¹. A kinetic study of the photochemical reaction of Azure B–EDTA [92] system informs that the rate of photoreduction of triplet dye is maximum at pH 6.8 and is first-order w.r.t. dye, EDTA and absorbed light intensity. It is also observed that only the small amount of iodide ions, not other halides or metal ions retards the life time of triplet dye in presence of EDTA. Another PEC cell [93] with Azure C–glucose generates photovoltage and photocurrent of 536 mV and

Table 5
 V_{OC} and I_{SC} of toluidine blue PG cells

System	pH	V_{OC} (mV)	I_{SC} (μ A)
Toluidine blue–Fe ²⁺	1.9	24	5.0
Toluidine blue–EDTA	5.9	330	8.5
Toluidine blue–triethyl amine	9.8	318	8.6
Toluidine blue–TEA	9.0	315	7.5

230 μA , respectively. The maximum power obtained from the cell was 68.4 μW .

When a bilayer lipid membrane (BLM), pigmented with a stearyl substituted monomethin cyanine dye was illuminated, photovoltage was obtained 15 mV under symmetric conditions (in BLM bathed on both sides with 0.1 mol dm^{-3} KCl solution) and 200 mV under asymmetric condition (in BLM bathed on one side with electron donor and other with electron acceptor) [94].

A two compartment PEC cell was constructed utilizing the photoreduction of dyes MB, rhodamine B, rose bengal and 1,10-phenanthroline by photogenerated ketyl radicals, to test their efficiencies as mediators. One of the compartments was filled with a solution of alcoholic benzophenone and dye, and the dark cathode with 1 mol dm^{-3} HClO_4 . The reduction of dye was reversible in the dark and the time taken to attain the original state is quite long with a conversion efficiency of 11.6% [95].

PG cell containing iminodiacetic acid and brilliant cresyl blue dye [96] generates photovoltage 688 mV and the effect of pH, concentration of dye and reductant on photovoltage was studied.

Most of the PEC cells discussed till now are heterogeneous type cell in nature. Kamat et al. [97] have studied both homogeneous and heterogeneous type cells, and pointed out that the power output of heterogeneous cell is about 10 times higher than the homogeneous cell under similar experimental conditions. Furthermore, the advantages of the heterogeneous cell are: (i) the dark compartment need only be formally dark, it need not be protected from light since there is no photoactive material therein, (ii) compared to heterogeneous, the homogeneous cell does not permit use of higher $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio than 0.02 as at higher Fe^{3+} concentration, V_{OC} itself decreases, (iii) with the heterogeneous cell, it should also be possible to store the light energy in the form of chemical free energy, and then release it by discharging through an external load. Pigments like inorganic compounds behave as semiconductor which will be discussed later. These semiconductor pigments can be used for conversion of solar energy in homo and heterogeneous systems [98].

From the survey of PEC cell with different dyes, it is observed that photochemical solar energy conversion and storage depend on the structures, reduction potentials and absorption maxima of dyes used in solar cell. Mohammad et al. [99] also studied the effect of the dye concentration, reducing agent, pH, temperature, wavelength maxima of dye in PG cells containing dyes thionine, lumiflavin, fluorescein, eosin, Rhodamine 6G, rhodamine B, rose bengal and methylene blue.

To convert the broad solar spectrum, mixed dyes instead of single dye may be used in solar cell. Abdul-Ghani et al. [100] observed that the solar energy conversion capability of mixture of dyes in liquid collector is controlled by dye-dye interactions, photodegradation and susceptibility to photo-oxidation. The photodegradation of methyl

violet [101] absorbed onto a P-CuCNS photocathode is suppressed by any fluorescent dye e.g. rhodamine B or fluorescein present in electrolyte through energy transfer between excited dye molecule in the solution and the absorbed dye.

1.2.3. Solar cell with phenazine dyes

In 1961, Eisenberg and Silvermann [102] started the preliminary studies of the PEC cell with phenosafranin (PSF), a phenazine dye and EDTA, and the system generates photovoltage of 600 mV. Bharadwaj et al. [103] showed that PSF could serve as an acceptor for photosystem (I). Moreover, they have shown that PSF could be used to generate power in a PEC cell in the presence of an electron donor like EDTA or tricene. An open-circuit voltage of 670 mV and a short-circuit current of 1.6 mA were obtained. The front face power conversion efficiency of the cell was about 0.2% at 110 W cm^{-2} light intensity.

During the investigation of the characteristics of the PSF-EDTA aqueous system, Rohatgi-Mukherjee et al. [104] observed that both photopotential and photocurrent increase with increase in temperature but the solar conversion efficiency of this cell is very low ($\sim 10^{-3}\%$) due to high activation overpotential. Roy et al. [105] noted the critical temperature and activation energy of phenazine dyes (i.e. PSF, safranin-O, safranin-T and neutral red) during the study of temperature effect on solar cell with these phenazine dyes, which has theoretical importance for further study. From the kinetics study of the PSF-EDTA system, Bhowmik et al. [106] computed the rate constants of forward and backward reaction at 25°C which are $k_1 = 2.0 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$ and $k_2 = 4.15 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$. The reaction follows the first order w.r.t. PSF concentration only. The calculated free energy across the electrode/electrolyte interface is about $-3.92 \text{ kJ mol}^{-1}$.

The PEC cells [107] consisting of redox system PSF-aliphatic amines generate photovoltage which increases from monosubstituted to trisubstituted amine as the ionization potential of amines decreases. A PGV tandem cell [108], a combination of PG cell (consisting of PSF-EDTA aqueous system) and wet PV cell [metal tetraphenyl porphyrin (ZnTPP) coated electrodes in KCl solution] was constructed. When ZnTPP electrode was modified by polymer, an increase in power from 0.461 to 1.063 μW was obtained.

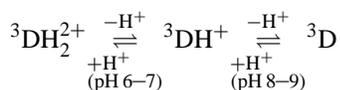
Tien et al. [109] have recently reported redox systems consisting of different dyes and EDTA, employed to photoproduction of hydrogen from water. The dyes used were phenazine dyes — safranin-O (Saf-O), safranin-T (Saf-T) along with other dyes such as proflavin (PF), acridine orange (AO), and acridine yellow (AY). In the two safranin systems, H_2 production was observed even in absence of a Pt catalyst, and an electron mediator like methyl viologen. The AY-EDTA system with K_2PtCl_6 was estimated to give best performance. The photopotentials in PG cells were also studied, as depicted in Table 6.

Table 6
Photopotentials of some PG cells

PG system	Photopotential (mV)
PF-EDTA	476
Saf-O-EDTA	844
Saf-T-EDTA	926
AO-EDTA	940
AO-EDTA-K ₂ PtCl ₆	830
AY-EDTA	900
AY-EDTA-K ₂ PtCl ₆	820
AY-EDTA-K ₂ PtCl ₆ -TX-100	830
AY-EDTA-K ₂ PtCl ₆ -SDS	460
AY-EDTA-K ₂ PtCl ₆ -HDTAC	480

Kaneko and Yamada [110] obtained high photopotential of 844 mV and quantum yield of the order of 0.1–0.2% from the Saf-T-EDTA system.

Flash photolysis study of PSF, SO, and neutral red (NR) [111–113] with EDTA were done to investigate the nature of the electroactive species. They reported that three triplet species of these dyes appeared at two specific pH range and attain equilibrium in the absence of reducing agent.

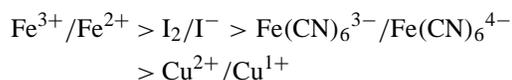


Mainly long lived ${}^3\text{DH}_2^{2+}$ is responsible for photoeffect.

From flash photolysis and cyclic voltammetry study [111,114], the reduction of PSF in the presence of EDTA indicated that PSF forms CT complex with EDTA. An attempt has been made to suggest the mechanism of reactions of this system at the illuminated electrode [115]. From electrode kinetics study of photoinduced redox reactions of phenazine dyes (i.e. PSF, Saf-O, Saf-T and NR)–EDTA aqueous systems at different pH, Jana and Bhowmik [116,117] reported that each dye PSF, Saf-O, and Saf-T have two pK_a values of the triplet species corresponding $\text{pH} \sim 7.0$ and ~ 9.0 but only one pK_a value of triplet species of dye NR is obtained at pH 6.0. It indicates that only two triplet species of NR are produced and form one CT complex at low pH i.e. ${}^3\text{DH}_2^{2+} \dots \text{HY}^{3-}$, whereas other phenazine dyes having structural similarity produce three triplet species during photovoltage generation and form two CT complexes i.e. at lower pH, ${}^3\text{DH}_2^{2+} \dots \text{HY}^{3-}$ and at higher pH, ${}^3\text{DH}^+ \dots \text{Y}^{4-}$. The SEE of PSF-EDTA system [118] with PSF coated photoanode and bare Pt photocathode have improved compared with the system using two bare Pt electrodes due to prevention of back combination reaction. Furthermore, it has been reported that two CT complex formed by triplet PSF dye species and ionized EDTA at two specific pH which support the above statement.

A new type of PEC cell [119] has been developed using PSF and EDTA aqueous solution and saturated aqueous solution of I₂ separated by a pyrex sintered glass membrane (G-4). An appreciable photovoltage of 740 mV was generated and SEE of 0.023% is obtained. For an improvement of

SEE and storage capability, we [120] have studied the above cell extensively using phenazine dye (i.e. PSF, Saf-O, Saf-T and NR) and electron donor EDTA aqueous solution and aqueous solution of different redox couples (i.e. $\text{Cu}^{2+}/\text{Cu}^{1+}$, $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$, I_2/I^- and $\text{Fe}^{3+}/\text{Fe}^{2+}$) separated by a glass membrane. The cell characteristics such as V_{OC} , I_{SC} , fill factor (FF), Power efficiency (PE) and SEE have been determined. The results indicate that the photovoltages generated in the presence of different redox couples follow the order:



which follows the standard reduction potential of redox couples. For different phenazine dyes, the photovoltage generated follows the order: PSF>Saf-O>Saf-T>NR which is consistent with the reduction potential of dyes. One of the seven systems, Pt|PSF-EDTA||Fe²⁺, Fe³⁺|Pt generates large photovoltage of 631 mV and SEE of $2.97 \times 10^{-2}\%$. The PEC cell containing alkali Saf-T and EDTA system [121] exhibits maximum photovoltage 926 mV under the optimum condition and also shows storage capacity which increases with increasing dye concentration.

Many photochemists have studied PEC cell with reducing agents EDTA and aliphatic amines. For the comparison between the role of EDTA and other reducing agents such as Fe²⁺, I⁻, Cu⁺ and Fe(CN)₆⁴⁻ in photoredox reaction with PSF, we [122] developed the PEC cell with PSF and these reducing agents. From photovoltage generation and spectral study, we concluded that these inorganic reducing agents (i.e. reductant species of redox system) are reversible but EDTA is irreversible in nature.

To utilize the broad spectrum of visible region of solar radiation, we constructed a solar cell [123] with mixed dyes instead of single dye system. The dyes are of four groups i.e. phenazine, thiazine, xanthene and acridine. An enhancement in power output of solar cell consisting of mixed dyes is observed when compared to the solar cell with single dye.

From the survey of dye-solar cell, it is noted that phenazine dyes-EDTA systems give higher photopotentials when compared to other dyes. So the research works connecting with phenazine dyes will be given special importance for the topics which will be discussed latter.

1.3. PEC cells based on semiconductor dyes

In the past few years, the semiconducting and photoelectric properties of different kinds of organic dyes have been reported [124–128]. These dyes can be classified into p-type and n-type semiconductors. It should be pointed out that if the concentrations and mobility of the electrons and defect electrons (holes) are equal, one speaks of intrinsic conduction. The predominant migration of electrons in the conduction band is referred to as n-conduction, and the predominance of holes as p-conduction (Fig. 1).

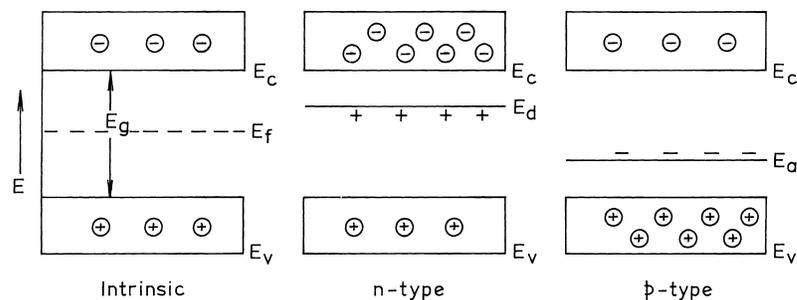


Fig. 1. Schematic presentation of intrinsic, n-type and p-type semiconductors. E_v , valence band energy; E_c , conduction band energy; E_f , Fermi energy; E_g , energy band gap; E_d , donor energy level; E_a , acceptor energy level; (+), hole and (–), electron.

Photocells based on organic semiconductor compounds offer the prospects of inexpensive energy conversion. In these cells, the photovoltaic effect arises from the dissociation of excitons into charge carriers in the built-infield region of a rectifying contact. Rectification and photovoltaic effects have been observed in four types of organic cells: (i) Metal–insulator–organic semiconductor (MIS) cells, (ii) Conductor [e.g. indium tin oxide (ITO), ZnO]–insulator–organic semiconductor (CIS) cells, (iii) Organic p–n junctions cells, and (iv) Redox electrolyte–organic semiconductor cells. Few research works of said organic cells are discussed.

1.3.1. 1st type

Morel et al. [127] obtained SEE upto 0.7% from organic solar cell by depositing merocyanine dyes on semitransparent Al electrode. They also approached the doping, dye mixing and multiple layering to obtain high quantum efficiency. One member of merocyanine family [128] placed between metal Al and Ag, yields V_{OC} of ~ 1.5 V. The photovoltaic effect in sensitized and pure crystal violet dye (n-type) [129] was studied by using Al, Zn and Ag electrode materials, and AgBr and AgI sensitizers. The dark conductance and photoconductance of Erochrome Black-T, Erochrome blue Black-B, crystal violet and Rhodamine B (Rh. B) dye films [130] increases by doping with I_2 or sensitizing by CdS due to decrease of the carrier activation energy through shifting the Fermi level towards the conduction band. The energy conversion efficiency of solar cell with these organic dyes film also increases by doping and sensitization.

1.3.2. 2nd type

Rohatgi-Mukherjee et al. [131] constructed a sandwich cell by placing a pellet (completely dried and powdered PSF–EDTA mixture in different ratios) between a semi-transparent conducting glass coated with SnO_2 and a Pt foil. On illumination of the SnO_2 electrode, photovoltage generated, and for composition variation from 1 to 0 mole fraction of PSF dye, the photovoltage varied from 90 mV in pure PSF to a maximum value of 326 mV at 0.67 mole fraction of PSF, and gradually decreasing to zero. The dye PSF was found to behave as a p-type [132], whereas SnO_2 is an n-type semiconductor. But the SEE

was low ($6.3 \times 10^{-4}\%$), due to high resistance of SnO_2 and PSF–EDTA pellet. Current-applied voltage study [133] indicated that thin film solar PV cell: Al|Rhodamine-6G| SnO_2 behaves as photodiode for the forward biased direction. Kang et al. [134] constructed another thin film solar cell: Al|poly phenyl acetylene (PPA)–dye pyronine Y (PY) or MB| SnO_2 which behaves as a diode under dark condition and follows the Schottky–Richardson equation. Utilizing the semiconducting properties of PSF, a thin film solar cell [135] has been constructed with PSF dye in a thin film of polyvinyl alcohol (PVA) placed between conducting glass coated with In_2O_3 and a Pt foil. The current-applied voltage curve indicated that this cell behaves like a diode in the dark and a photodiode under illumination, when the junction is forward-biased. The efficiency in photovoltage generation has also been found to increase due to the decrease of self-quenching caused by aggregation of dye. Above study was extended using other p-type phenazine dyes i.e. Saf-O, Saf-T [136] and NR [137] under both forward and reverse biases. The conductivities of semiconductor phenazine dyes in thin films of PVA increase exponentially with temperature according to the relation [138] $\sigma_T = \sigma_0 \exp(-E/2kT)$. With the help of this equation, band gaps of PSF, Saf-O, Saf-T and NR are of 2.02, 2.14, 2.26 and 2.38 eV determined which are theoretically important for further study.

Panoyotatos and co-workers [139,140] studied the characteristics of p–n junction cells using perylene and some metal substituted phthalocyanines and concluded that the dyes should be considered for the photocell which generates more excitons by the absorbed quanta at the dye–dye interface.

The maximum solar efficiency of 0.1% was obtained from this photocell. They also studied about 350 p–n heterojunction cells using 25 different dyes. The most efficient cell is SnO_2 |bis-methylimide of perylenetetra carboxylic acid–chloroaluminium phthalocyanine|Ag which gives I_{SC} of 1.25 mA cm^{-2} and short-circuit quantum efficiency of 19% with light absorption of 60–80% over the visible range of the solar spectrum.

1.3.3. 3rd type

The photoelectric properties of p-type and n-type dyes allow the construction of p–n junction photocell which have

a specific sensitivity. Meier et al. [141–147] studied p–n junction photoelectric cells using organic dye and inorganic semiconductors. They proposed the mechanism that the dark current and stationary photoelectric current are generated due to transport of charge carriers from the ground state to excited state and then recombination via defect centers which capture electrons in the first step and allow them to recombine in the second step with the holes of the valence band.

Recently new impetus on organic p–n junction photocell is observed due to low material and fabrication costs compared to inorganic solar cell. As organic dyes have narrow absorption spectrum profiles in the visible light region and their spectra can be changed easily by chemical substitutions, a p–n junction cell using organic dyes will also have many attractive features for device application. Meier et al. [148] studied the photovoltaic effect of organic semiconductor/electrolyte system using n-type dye, crystal violet, pinacyanol or p-type dye, vanadyl phthalocyanine, merocyanine A 10, and observed photovoltage of ≤ 0.8 V and photocurrent of ≤ 0.3 mA cm⁻², respectively. The photoinduced potentials and photocurrents are explained similarly to inorganic semiconductor PG cells by the separation of photogenerated hole–electron pairs in a space–charge layer of the electrolyte/organic semiconductor interface. Kudo et al. [149] constructed p–n junction photocells with p-type merocyanine dyes and n-type dyes like rhodamine B, malachite green which generate V_{OC} of 750 mV and I_{SC} of 130 μ A cm⁻² but the power conversion efficiency of the cell is 0.05%. They also considered that the cell with merocyanine family as a p-type dye and the triphenyl methane derivatives (crystal violet, malachite green, and fuchsin etc.) as n-type dye can cover almost the full range of visible light spectrum and improve the efficiency of solar conversion. The most efficient device by Chamberlain [150] consisted of a sandwich of thin layers of ITO|malachite green|a benzothiazole rhodamine merocyanine|Au on pyrex in the absence of air which improved the sunlight efficiency to 0.12%. He suggested the mechanism which shows that the creation of excitons in the organic material is involved by light absorption and the excitons can produce charge carrier (e⁻ and h⁺) by electron transfer to dopant sites. Chamberlain [151] rectified the above cell only replacing benzothiazole rhodamine merocyanine by p-type merocyanine and observed PV properties that a depletion layer of about 65 nm and a barrier height of about 0.8 eV are formed between the two dyes. For improvement in energy conversion efficiency of solid-state organic PV cell, he [152] used merocyanines (six species i.e. A, B, C, D, E and F) of low ionization potential in PV cells with electronegative dopant iodine. The PV cell with E species (660 nm) generates high SEE of 0.18% compared to other system. Morel et al. [90] tried to correlate between cell performance and molecular structures of 126 dyes of group eight in organic PV cells. They noted that squarylium dyes, a special class of merocyanine demonstrate high potential efficiency. Huang et al. [153] also developed PV cell

with squarylium dyes which generate V_{OC} of 1 V and photoelectric conversion efficiency of 0.8% in the 50–80°C range. The V_{OC} obtained upto 0.8–1.0 V from the PV cell [154] using four kinds of n-type merocyanine (MX) dyes and p-type distearyl paraquat (PQ). This cell behaves like p–n junction diode. Uehara et al. [155] constructed a sandwich cell with p-type polymer and n-type dye i.e. Au|poly(*N*-vinyl carbazole)|Rh. B|Al which showed a rectifying effect in the dark as well as photovoltaic effect in light.

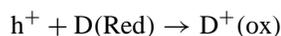
1.3.4. 4th type

The maximum photovoltage i.e. 1.2 V was observed in a liquid junction cell [156] of the type: Metal|merocyanine|redox electrolyte|Pt, using acceptor MV²⁺ at high light intensity. Iodine doping dye is effective to the generation of efficient cells.

1.4. PEC cells involving semiconductor electrode

For PEC cells which involve the use of semiconductors, immersed in suitable electrolytes, require absorption of photons by semiconductor with energy greater than the band gap so that promotion of electrons from valence to conduction band is possible. The physical and chemical processes which occur in a liquid junction PEC cell are as follows [157]:

1. A junction capable of separating electrons from oxidants is formed spontaneously by band bending in the semiconductor in the region adjacent to its interface with the solution.
2. Absorption of photon by semiconductor promotes electrons (e⁻) from the valence band to the conduction band in the region adjacent to the interface leaving an excess of holes (h⁺).
3. Holes, at the energy level of the valence band, oxidize the reduced electroactive species (D) i.e. reductants of a solution containing redox couple (D/D⁺) at the interface of the photoanode.



4. Electron flow from the interface through the band-bending region into the bulk of the semiconductor and are pumped by light to the conduction band (Fig. 2).
5. Electrons at the energy level of the conduction band, move away from the interface, through the external circuit to an inert cathode and reduce oxidants of the solution at its interface with the electrolyte.

Liquid junction devices have several advantages [158]:

1. The simplicity of fabricating a junction by immersing a semiconductor in an electrolyte solution.
2. Ability to control junction characteristics (i.e. band-bending) by varying the composition of the electrolyte.
3. Improved absorption of light by the semiconductor due to diminished reflection.

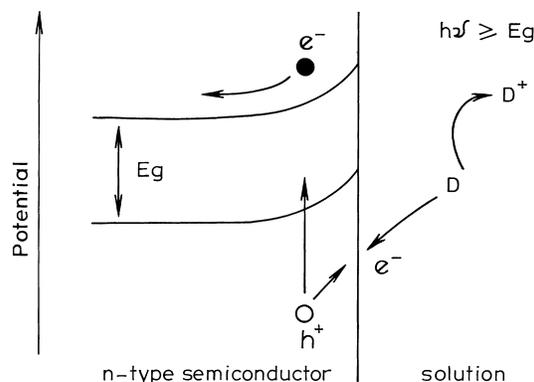


Fig. 2. Electron-hole flow upon irradiation of n-type semiconductor immersed into solution with redox couple D/D⁺.

4. Efficiencies using cheaper randomly oriented polycrystalline semiconductor photoelectrode approach those obtained with expensive single crystals.

With addition of these advantage, corrosion is a main problem in liquid junction devices which can be resisted using semiconductor of large band gap (>3 eV) but it can absorb very little of the insulation flux in the longer wavelength. Gerischer [159] have reported stabilization of photoelectrodes by impurity doping e.g. chromium doped TiO₂, but reasonable efficiencies have not been obtained. Bard [160] has classified semiconductor electrode PEC cells into three categories i.e. (i) regenerative type, (ii) photosynthetic type and (iii) photocatalytic type, depending on the relative position of the Fermi level of the semiconductor electrode and the redox potential of the electrolyte in the solution phase. The characteristics of the PEC cells [161] containing a number of redox couples (i.e. Br₂/Br⁻, Fe³⁺/Fe²⁺, I₂/I⁻, Fe(CN)₆³⁻/Fe(CN)₆⁴⁻, and MV²⁺/MV¹⁺) and n-, p-type WSe₂ single crystal electrodes were studied. Among these cells, n-WSe₂|I₃⁻, I⁻|Pt system showed maximum photovoltage 0.74 V, I_{SC} 65 mA cm⁻² and power efficiency ~14%.

Suda et al. [162] investigated the photogalvanic effect in the aqueous thionine-Fe(II) system with semiconductor electrode. The results were explained on the basis of the band structure of semiconductor and the redox levels of the photoreaction products in solution and not on the basis of interaction between the semiconductor and the excited dye molecules absorbed on it.

Here PEC cells with SnO₂, In₂O₃ and ZnO as n-type semiconductor electrode are discussed systematically.

1.4.1. SnO₂ electrode

Clark and Eckert [17] invented a Fe(II)-thionine TITL cell employing a SnO₂ anode and Pt cathode separated by 25 or 80 μm spacers. At 25 and 80 μm spacers, V_{OC}=130 and 113 mV; I_{SC}=0.255 and 0.242 mA and power 27 and 26 μW were obtained taking Fe(II) and thionine in 0.01 and ~10⁻³ mol dm⁻³ in this cell. The advantage of using

semiconductor is that due to definite band gap, reaction of Fe²⁺/Fe³⁺ couple is completely blocked at the illuminated electrode. The Fe(II)-thionine PG cell [163] using SnO₂ as anode generates SEE 0.03% and it is higher than the PG cell with two Pt electrodes due to encompassing semi-conduction band overlap with the energy level of TH⁺/TH₃⁺.

Gessmer [164] obtained a reproducible conversion efficiency of ~5 × 10⁻³% from Fe-thionine PG cell using semiconductor SnO₂ electrode. Mesmaeker et al. [165] reported that the V_{OC} and I_{SC} of SnO₂|thionine-Fe²⁺/Fe³⁺|Au photogalvanic cell are 110 mV and 20 μA at Fe³⁺ and thionine concentrations of 10⁻⁴ and 4.8 × 10⁻⁵ mol dm⁻³, respectively. These values are greater than other systems of different dye and Fe³⁺ concentrations. High concentration of Fe³⁺ is harmful to the cell concerning the life time of leuco-thionine as well as photocurrent.

The photoredox reactions and photogalvanic effects of gel systems [166] containing Fe(II)-thionine and gelation agents were studied in thin-layer photocell with SnO₂ and Pt electrodes. The structure of gelation agent is the predominant factor for electron exchange reaction. The thionine coated Pt-SnO₂ electrode systems [167] produced improved results than the traditional wet PG cell. The PEC mechanism of dye-SnO₂ electrode-photocell [168] was studied in detail using not only thionine but also other dyes e.g. methyl violet, malachite green, erythrosin and rhodamine with reactants.

During the study of photoelectrochemistry of erythrosin-hydroquinone system at SnO₂ electrode, Mesmaeker and Dewitt [169] pointed out three types of photocurrent due to photo-oxidation originating (i) from the physically absorbed excited molecules, (ii) from the solution triplet, and (iii) from the electrochemically deposited irreversibly adsorbed dye film. Yoshikawa et al. [170] studied the sensitization of SnO₂ electrode with crystal violet and different sulfites as reducing agent in PV cell. They noted that increase in the concentration of Na₂S₂O₃, increases the photocurrent and decreases the light absorption but efficiency increases in PEC cell due to formation of a new dye during photoadsorption at the electrode. The same effect was also observed with ZnO electrode instead of SnO₂.

At high concentration, dyes show self-aggregation property which is observed with different dyes e.g. crystal violet, methyl violet B, malachite green, *para*-rosaniline and Rh. B in a SnO₂ electrode sensitized PEC cell [171] from the action spectra as well as spectral study. Electrode kinetics study of PSF-EDTA system [172] in the solid polycrystalline state, using illuminated SnO₂ electrode reveals that PSF and EDTA composes 2:1 ratio during voltage generation. Power conversion efficiency of PEC cell [173] enhanced several times by using Rh. B deposited on Au and SnO₂ glass but it reduced several times using rhodamine 110 (rh-110) instead of Rh. B. The anodic sensitized photocurrent at a SnO₂ electrode [174] with Rh. B containing acetonitril-water electrolyte solution depends markedly on the solvent composition i.e. with increasing water concentration [H₂O] in acetonitril, photocurrent remains fairly

constant upto $[H_2O]=1\text{ M}$, where it starts to decrease to reach a 1/20-fold lower level at $[H_2O]=3\text{--}20\text{ M}$, and then abruptly increases to a maximum value in a pure aqueous solution. The overall SEE of the PG cell [175] with rose bengal dye coated n-SnO₂ photoanode in poly(4-vinyl pyridine) matrix, dipped into an aqueous solution of Fe²⁺/Fe³⁺ redox couple is 10⁻²%. This efficiency is an order of magnitude higher than that obtained in an analogous PG cell in which this same dye is dissolved in or adsorbed from homogeneous solution due to achievement of high dye concentration near the electrode surface, minimization of dye aggregation and retardation of self-quenching leads to longer lived excited states. The PV cell [176] with erythrosin B dye coated n-SnO₂ photoelectrode in poly(4-vinyl pyridine) film yields maximum power and SEE of $\sim 0.5\ \mu\text{W}$ and $<10^{-2}\%$, respectively. The PEC cell [177] with Chl a (670) or Chl a (740)–PVA complex film on SnO₂ electrode-reducing agent hydroquinone (H₂Q) generates photocurrent through an electron transfer from excited Chl a molecules to the conduction band of SnO₂. This system is very stable against strong light radiation and is very useful in vitro.

The photovoltaic and rectification properties of CdS and AgBr sensitized sandwich cells [178] SnO₂|CdS–Eriochrome Black-T (EBT)|Ag and SnO₂|AgBr–EBT|Ag study indicate p–n junction formation and power conversion efficiencies of the two cells are 0.02 and 0.016%, respectively. Panayotatos et al. [139] developed a new type p–n heterojunction solar cell fabricating dye pair on SnO₂ semiconductor glass and obtained SEE $\sim 0.1\%$ which is twice time higher than the other p–n junction solar cell with single dye. They also studied about 350 p–n junction cells [140] using 25 dyes and the most efficient cell is SnO₂|DMP|ClAlPc|Ag whose short-circuit cum quantum efficiency is 19% with light absorption of 60–80% over the visible range of the solar spectrum, obeying the Förster radiationless energy transfer of the absorbed quanta to the dye–dye interface.

1.4.2. In₂O₃ electrode

The PEC cell [179] with In₂O₃ film gives $\sim 90\%$ quantum efficiency at 310 nm and the band gap energy is determined as 2.8 eV (indirect) and 3.6 eV (direct), but electron affinity of In₂O₃ is 4.45 eV [180] which was obtained from the photovoltaic characteristics study of heterojunction solar cells e.g. In₂O₃/Ge, In₂O₃/GaAs and In₂O₃/InP.

In₂O₃ and indium tin oxide (ITO) [181] are good window materials for solar cells because they have high transparency and low resistivity compared to CdS. The n-In₂O₃/p-CdTe cell yields high efficiency i.e. V_{OC} 892 mV, I_{SC} 20.1 $\mu\text{A cm}^{-2}$ and FF 0.745 corresponds to the active area efficiency of 14.4% due to formation of a buried homojunction.

It is observed that In₂O₃/A^{II} B^{IV} C₂V behaves as heterocell [182] using broad spectrum above 0.3 eV. In₂O₃ electrode coated with crystal violet (II) dye whose methyl group is substituted by octadecyl group, PEC cell [183]

using quinone (Q)/hydroquinone (H₂Q) redox system generates ~ 200 -fold photocurrent compared to the PEC cell with non-coated In₂O₃ electrode and crystal violet (I). Thin film solar cells [135–137] have been studied extensively using phenazine dyes as p-type and In₂O₃ as n-type which are discussed in a previous topic 1.3. A PEC cell [184] i.e. In₂O₃|PSF dye–EDTA|redox couple|Pt, has been developed using redox couples e.g. Cu⁺/Cu²⁺, and Fe(CN)₆⁴⁻/Fe(CN)₆³⁺, I⁻/I₂ and Fe²⁺/Fe³⁺. The cell efficiency increased 2–3-fold compared to the same cell when illuminated at a Pt electrode. A thin film of X-metal-free phthalocyanine [185] dispersed in a polymer and placed between SnO₂ and Indium electrode exhibit high power conversion efficiency but SEE is low due to the low transmission of light through the indium barrier electrode.

The photocell [186] was studied using electrolytes KCl, Glutathione (GSH), reduced GSH (GSSG), flavinmononucleotide (FMN), tryptophan and two different chlorophyll electrodes. The best cell was Pt|Chl|5 mM FMN, 5 mM tryptophan|Chl, IQ|In₂O₃ which produces highest photovoltage 143 mV at pH 7.

1.4.3. ZnO electrode

Optimum donor density of semiconductor [187] ZnO is few times larger than of SnO₂ for enhancement of the quantum yield of the dye-sensitized photocurrent. The stability of a PEC cell [188] depends on the photoanodic corrosion of an n-type semiconductor. The corrosion can be suppressed if the electron supply from a reductant to the electrode is faster. Tsubomura et al. [189] studied the ‘wet’ photocell using dye and ZnO electrode and established a mechanism for the decay photocurrent. They evaluated the effect of reducing agent and determined intrinsic quantum efficiency of the electron injection from dye to semiconductor electrode. The variation of surface potential in photocell consisting dye fabrication on ZnO semiconductor [190] depends on the absorption of light by dye, electron injection from dye to ZnO layer and decrease in the strength of electric double layer at the ZnO surface. Darwent and Lepre [191] observed the photosensitization function of ZnO for the oxidation of methyl orange in aerobic solution accompanied by the reduction of oxygen to H₂O₂. Tsubomura et al. [192] and Matsumura et al. [193] have developed PEC cell containing semiconductor ZnO and rose bengal dye with and without I₂ and reported the power conversion efficiency 1.5%. They suggested that only electrode absorbed dye molecules generate photocurrent which increases with increasing dye concentration and light intensity.

1.5. Photoelectrochemical cells in surfactant micellar solution

Among the most important properties of surfactants are their ability to solubilize a variety of molecules insoluble in aqueous solution and their substantial catalytic effect on

many chemical reactions. On the other hand, studies of photoinduced electron transfer reactions in surfactant solutions above critical micellar concentration (CMC) have added a new dimension for efficient energy conversion and storage. The power conversion efficiency as well as storage of PEC cell may be enhanced if the charge carriers in the photochemical reaction dispersed into the core of micelle and can not recombine with oxidized species readily, but not prohibitively.

An elegant approach for storing light energy in a Fe-thionine cell [194] have been proposed: the photoproducts are separated by solubilization of the reduced thionine in an ether layer in which the oxidized thionine is insoluble. The importance of organized molecular assemblies, such as micelles, bilayers and membranes in controlling the course of chemical reactions, particularly those related to the problem of light energy conversion and storage has been recognized [195]. The addition of Triton X-100 (TX-100) micelles to an Fe-thionine PG cell [196] leads to an increased solubilization of the dye, and an overall increase in conversion efficiency by a factor of 5 relative to the micelle-free PG cell, due to retardation of back recombination reaction of reduced dye and suppression of dimer formation of thionine. Srivastava et al. [197] investigated the thionine-Fe(II), methylene blue-Fe(II) and riboflavin-EDTA system in polyvinyl methyl ether (PVME) surfactant and found that the reduced form of the dye was incorporated in the hydrophobic core of the micelle. As a result, all systems with surfactant have good storage of solar energy. They [198] also studied the PG behavior of Fe-thionine and Fe-methylene blue systems in sodium lauryl sulfate (SLS), cetyl pyridinium bromide and Tween-80 micellar solution.

Dixit and Mackay [199] have found that the current and voltage responses of a TITL photogalvanic cell, consisting of a newly synthesized thionine-surfactant complex $C_{10}Th H^+$ and Fe^{2+}/Fe^{3+} in a 60% microemulsion (anionic) medium are enhanced and the effect is larger in an anionic medium than the cationic cetyltrimethyl ammonium bromide (CTAB) and water. On investigation of electrochemical and photochemical properties of the Fe-thionine PG system in SLS micellar solution [200], it is observed that micellar solution solubilizes significantly thionine and reduces the efficiency of photochemical formation of leuco-thionine. So surfactant SLS is unfavorable for this system. The photoreduction of thionine and MB by EDTA is inhibited due to electrostatic repulsion between the anionic micelle and the reductant, but the photoreduction of eosin bound to a cationic micelle by EDTA is enhanced [201].

The anionic surfactant SDS micelle suppress the back electron transfer in photoredox process of Zn-tetraphenyl porphyrin trisulfonate-triethanolamine-methyl viologen (MV^{2+}) system [202] due to absorption of positive charged viologen (reduced and oxidized form) molecules in the anionic micelle. This suppressing property of micelle also observed in the system [203] e.g. fluorescence dyes

(fluorescein, eosin, rose bengal)-iso-PrOH with photosensitizer Ph_2CO . We [204] constructed the PSF-EDTA, PEC cell with surfactants. The surfactants used are ionic CTAB, SLS, and non-ionic TX-100. From the cell characteristic study of this system with surfactants below, at and above CMC, it is revealed that electrical performance of the cell is decreased in SLS, increased slightly in TX-100. An appreciable 50-fold increased in SEE ($1.2 \times 10^{-1}\%$) as well as increase storage capability (4–5 days) is observed where CTAB (above CMC) is used in comparison with the cell without surfactant. The possible mechanisms of the cell in the various surfactant are discussed. Bi et al. [205] obtained remarkable results from mesotetra phenyl porphine sensitized SnO_2 coated electrode containing PGV cell with addition of surfactant SLS, here photocurrent increases by a factor of ≥ 2 in the presence of it.

From the transient spectra and decay kinetics study [206] of Fe-thionine system in SDS micellar media, it is noted that the decay of the semi-thionine species is pseudo first-order but it behaves as a second-order in non-surfactant media. From photogalvanic and photo-conductivity studies of cationic dyes (Rh. B, fuchsin, crystal violet, PSF)-TX-100 system, Bhowmik et al. [207,208] reported that the formation of 1:1 CT complex and generation of photovoltage in every system. The dyes used in this system behave as electron acceptor which follow the order $PSF > crystal\ violet > fuchsin > Rh. B$.

1.6. Solar cell with production of hydrogen

Most interesting and fairly successful experiment is the photosensitized decomposition of water to H_2 and O_2 . Hydrogen is a non-polluting fuel which burns in air to produce water again releasing large amount of heat. Alternatively, H_2 and O_2 may be made to recombine in a fuel cell generating. The thermodynamic break down energy for water is 1.23 eV. The electrochemical decomposition of water requires two electrons in consecutive steps. Therefore, it should be possible to decompose water with two quantum photochemical process with the input of at least 2.46 eV per molecule. For one quantum process, the light of wavelength shorter than 500 nm can only be effective.

Fujishima and Honda observed photoelectrolysis of water first, using semiconductor TiO_2 as anode and Pt as cathode in 0.1 N NaOH solution. Later many scientists have studied the production of hydrogen utilizing band gap of semiconductor. Nowadays, H_2 is being produced from PEC cell using inorganic complex and organic dyes as photosensitizer. Some of this type of research work is mentioned below.

The reduced form of methyl viologen of proflavinmethyl viologen-EDTA aqueous solution [209] reduces H_2O to H_2 in the presence of solid catalyst e.g. Pt, TiO_2 , ZnO during illuminating condition by visible light. Irradiation of the system [210] containing acridine yellow as a sensitizer, EDTA or cysteine as an electron donor and methyl viologen, europium(III) salicylate, europium(III) EDTA complex

or vanadium(III) salicylate as electron acceptor and in the presence of catalyst [Ni, Pd, Pt(IV) oxide or colloidal [Pt], reduction of water is accompanied by evolution of hydrogen.

The PG cell [211] (Pt|FMN–EDTA (pH=7)||5 N H₂SO₄|Pt) leads to the production of H₂ at the cathode. 1.1 μmol of H₂ were produced after the irradiation of 25 h and the quantum yield for hydrogen production was 0.008 but V_{OC} was 600 mV. Using eosin dye [212] photosensitizer, CdS photoanode generates 50 ml h⁻¹ H₂ from water photoelectrolysis under illumination and 35 mA current was obtained in the PEC cell. Photoresponse of chlorophyll/ascorbic acid and chlorophyll/buffer acetate junction has been studied [213] at different pH and light intensity. The photovoltage and photocurrent reach maximum at the region of pH 4–5. Furthermore, hydrogen gas evolution supports the photoinduced charge transfer at the chlorophyll–electrolyte interface. The photosensitizer [214] proflavin, acridine yellow and tris(2,2-bipyridyl) ruthenium instead of methyl viologen showed the same ability to promote H₂ evolution. When CdS was used as a sensitizer instead of dyes 10 times less hydrogen was obtained.

2. List of abbreviations and symbols

BLM	bilayer lipid membrane
Chl	chlorophyll
CIS	conductor–insulator–semiconductor
ClAlPc	chloro aluminium phthalocyanine
CMC	critical micellar concentration
CT	charge transfer
CTAB	cetyl trimethyl ammonium bromide
DMP	bis-methylimide of perylenetetra carboxylic acid
EDTA	ethylene diamine tetra acetic acid
FF	fill factor
FMN	flavinmononucleotide
GSH	glutathione
GSSG	reduced GSH
HDTAC	hexadecyl trimethyl ammonium chloride
HEDTA	2-hydroxy ethylene diamine triacetic acid
H ₂ Q	hydroquinone
IQ	2-(<i>cis</i> -10-hepta decenyl)-6-methoxy- <i>p</i> -benzoquinone
IR	infrared
I _{SC}	short-circuit current
ITO	indium tin oxide
MIS	metal–insulator–semiconductor
MV ²⁺	methyl viologen
P/D	polymer/dye
PE	power efficiency
PEC	photoelectrochemical
PG	photogalvanic
PGV	photogalvanovoltaic
PPA	poly phenyl acetylene
PQ	p-type distearyl paraquat

PrOH	propyl alcohol
PV	photovoltaic
PVA	polyvinyl alcohol
PVME	polyvinyl methyl ether
Q	quinone
SDS	sodium dodecyl sulfate
SEE	solar energy efficiency
SLS	sodium lauryl sulfate
TEA	triethanolamine
TITL	totally illuminated thin layer
Tween-80	polyoxyethylene sorbitan mono-oleate
TX-100	Triton X-100
UV	ultra violet
V _{OC}	open-circuit voltage
ZnTPP	zinc tetraphenyl porphyrin
<i>E</i>	band gap energy
<i>i</i> _p	photocurrent
<i>σ</i> _{<i>T</i>}	conductivity at temperature <i>T</i>
<i>σ</i> ₀	conductivity at infinite temperature
<i>v</i> _p	photovoltage

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References

- [1] C. Becquerel, C.R. Acad. Sci. Paris 9 (1839) 14.
- [2] J. Moser, Mh. Chem. 8 (1887) 373.
- [3] H. Rigollot, C.R. Acad. Sci. Paris 116 (1893) 878.
- [4] G.E. Thompson, Phys. Rev. 5 (1915) 43.
- [5] C. Stora, J. Chim. Phys. 34 (1937) 536.
- [6] A.W. Copeland, O.D. Black, A.B. Garrett, Chem. Rev. 31 (1942) 177.
- [7] T. Kuwana, Electroanal. Chem. 1 (1966) 197.
- [8] M.D. Archer, J. Appl. Electrochem. 5 (1975) 17.
- [9] W.J. Albery, M.D. Archer, J. Electrochem. Soc. 124 (1977) 688–697.
- [10] W.J. Albery, M.D. Archer, J. Electroanal. Chem. Interfacial Electrochem. 86 (1978) 1–18.
- [11] W.J. Albery, M.D. Archer, J. Electroanal. Chem. Interfacial Electrochem. 86 (1978) 19–34.
- [12] T.I. Quickenden, G.K. Yim, J. Phys. Chem. 83 (1979) 2796–2804.
- [13] K. Weber, Z. Physik Chem. B15 (1931) 18.
- [14] J. Weiss, Nature 136 (1935) 794.
- [15] E. Rabinowitch, J. Chem. Phys. 8 (1940) 551.
- [16] A.E. Potter, L.H. Thaller, Sol. Energy 3 (1957) 1.
- [17] W.D. Clark, J.A. Eckert, Sol. Energy 17 (1975) 147.
- [18] H.T. Tien, J.M. Mountz, J. Electrochem. Soc. 125 (1978) 885–886.
- [19] M. Sudoh, T. Murakami, T. Shivotsuka, J. Chem. Eng. Jpn. 16 (1983) 61–66.
- [20] A.S.N. Murthy, K.S. Reddy, Electrochim. Acta 28 (1983) 473–476.
- [21] S.C. Ameta, S. Khamesra, S. Lodha, R. Ameta, J. Photochem. Photobiol. A 48 (1989) 81–86.
- [22] L. Pezza, M.G. Neumann, F. Gessner, Eclética Quim. 13 (1988) 127–140.
- [23] R. Hardwick, J. Am. Chem. Soc. 80 (1958) 5667.

- [24] I. Schlag, *Z. Phys. Chem. N.F.* 20 (1959) 53.
- [25] R. Havemann, H. Pietsch, S. Wolff, *Z. Wiss. Phot.* 57 (1963) 88.
- [26] S. Ainsworth, *J. Phys. Chem.* 64 (1960) 715.
- [27] R. Bonneau, J. Jousset-Dubien, J. Faure, *Photochem. Photobiol.* 17 (1973) 313.
- [28] R. Bonneau, J. Jousset-Dubien, J. Faure, *Photochem. Photobiol.* 19 (1974) 129.
- [29] R. Bonneau, J. Jousset-Dubien, J. Faure, *Photochem. Photobiol.* 21 (1975) 159 and 190.
- [30] J.C.M. Brokken-Zijp, M.S. De Groot, P.A.J.M. Hendriks, *Chem. Phys. Lett.* 81 (1981) 129–135.
- [31] G.G. Hatchard, E. Parker, *Trans. Faraday Soc.* 57 (1961) 1093.
- [32] W.J. Albery, M.D. Archer, *Nature* 270 (1977) 399.
- [33] K. Shigehara, E. Tsuchida, *J. Phys. Chem.* 81 (1977) 1883–1886.
- [34] N.N. Lichtin, P.D. Wildes, T. Osif, D.E. Hall, *Adv. Chem. Ser.* 173 (1979) 296–306.
- [35] P.V. Kamat, M.D. Karkhanavala, P.N. Moorthy, *Ind. J. Chem.* 18A (1979) 210–212.
- [36] P.V. Kamat, M.D. Karkhanavala, P.N. Moorthy, *Ind. J. Chem.* 20A (1981) 718–720.
- [37] P.V. Kamat, M.D. Karkhanavala, P.N. Moorthy, *Ind. J. Chem.* 15A (1977) 342.
- [38] P.V. Kamat, M.D. Karkhanavala, P.N. Moorthy, *Ind. J. Chem.* 18A (1979) 206–209.
- [39] R. Tamilarasan, P. Natarajan, *Ind. J. Chem.* 20A (1981) 213–215.
- [40] M. Kaneko, S. Sato, A. Yamada, *Makromol. Chem.* 179 (1978) 1277–1283.
- [41] W.R. Bowen, *Acta Chem. Scand. Ser. A* 34 (1980) 437–442.
- [42] W.J. Albery, W.R. Bowen, *Proc. Electrochem. Soc.* 80 (1979) 148–166 (published 1980).
- [43] W.J. Albery, W.R. Bowen, *J. Electroanal. Chem. Interfacial Electrochem.* 107 (1980) 37–47.
- [44] M.D. Archer, M.I.C. Ferreira, W.J. Albery, A.R. Millman, *J. Electroanal. Chem. Interfacial Electrochem.* 111 (1980) 295–308.
- [45] T.I. Quickenden, I.R. Harrison, *J. Electrochem. Soc.* 132 (1985) 81–88.
- [46] P.V. Kamat, *J. Electroanal. Chem. Interfacial Electrochem.* 163 (1984) 389–394.
- [47] D.E. Hall, P.D. Wildes, N.N. Lichtin, *J. Electrochem. Soc.* 125 (1978) 1365–1371.
- [48] W.J. Albery, *NATO Adv. Study Inst. Ser., Ser. B*, B69 (1981) 313–347.
- [49] R. Tamilarasan, P. Natarajan, *Curr. Sci.* 50 (1981) 713–715.
- [50] R. Tamilarasan, P. Natarajan, *Nature* 292 (1981) 224–225.
- [51] M.D. Archer, J.H. Wilford, M.I.C. Ferreira, *Isr. J. Chem.* 22 (1982) 142–146.
- [52] R. Havemann, H. Pietsch, *Phys. Chem. (Leipzig)* 208 (1957) 98.
- [53] R. Havemann, K.G. Reimer, *Z. Phys. Chem. (Leipzig)* 211 (1959) 26.
- [54] J.C.M. Brokken-Zijp, M.S. De Groot, *Chem. Phys. Lett.* 76 (1980) 1–6.
- [55] P.D. Wildes, N.N. Lichtin, *J. Phys. Chem.* 82 (1978) 981.
- [56] T.L. Osif, N.N. Lichtin, M.Z. Hoffman, *J. Phys. Chem.* 82 (1978) 1778.
- [57] P.V. Kamat, M.D. Karkhanavala, P.N. Moorthy, *J. Phys. Chem.* 85 (1981) 810–813.
- [58] W.J. Albery, P.R. Benson, A.W. Foulds, *J. Photochem.* 13 (1980) 1–12.
- [59] M.H. Dung, J.J. Kozak, *J. Photochem.* 14 (1980) 205–232.
- [60] M.S. De Groot, P.A.J.M. Hendriks, J.C.M. Brokken-Zijp, *Chem. Phys. Lett.* 97 (1983) 521–527.
- [61] W.J. Albery, P.N. Bartlett, J.P. Davies, A.W. Foulds, A.R. Hillman, F.S. Bachiller, *Faraday Discuss. Chem. Soc.* 70 (1980) 341–357.
- [62] W.J. Albery, *Acc. Chem. Res.* 15 (1982) 142–148.
- [63] J.I. Tsipouridis, B.M. Gibbs, *IEE Conf.* 192 (1981) 87–91.
- [64] H.T. Tien, J.M. Mountz, *Int. J. Energy Res.* 2 (1978) 197–200.
- [65] H. Tsubomura, Y. Shimoura, S. Fujiwara, *J. Phys. Chem.* 83 (1979) 2103.
- [66] R.A. Hann, C. Read, R.C. Rosseinsky, P. Wassell, *Nature Physical Sci.* 244 (1973) 126.
- [67] A.S.N. Murthy, K.S. Reddy, *Energy Res.* 3 (1979) 205.
- [68] K.G. Mathai, E. Rabinowitch, *J. Phys. Chem.* 66 (1962) 663.
- [69] R.N. Tarafdar, K.K. Rohatgi-Mukherjee, *Int. Conf. on the Photochemical Conversion and Storage of Solar Energy*, Ontario, Canada, 1976.
- [70] K. Srimvasalu, G. Mathew, *National Solar Energy Conversion*, PC: 02, 1981, pp. 8–21.
- [71] W.J. Albery, A.W. Foulds, *J. Photochem.* 10 (1979) 41.
- [72] W.J. Albery, A.W. Foulds, *J. Photochem.* 15 (1981) 321–328.
- [73] P.V. Kamat, N.N. Lichtin, *J. Phys. Chem.* 85 (1981) 814–818.
- [74] D.W. Hay, S.A. Martin, S. Ray, N.N. Lichtin, *J. Phys. Chem.* 85 (1981) 1474.
- [75] D.E. Nicodem, S.M.C. De Menezes, *Sol. Energy* 26 (1981) 365–366.
- [76] A.S.N. Murthy, K.S. Reddy, *J. Chem. Soc. Perkin Trans. II*, 12 (1984) 2023–2026.
- [77] A.S.N. Murthy, K.S. Reddy, *Solar Energy* 30 (1983) 39.
- [78] S.C. Ameta, G.C. Dubey, T.D. Dubey, R. Ameta, *Z. Phys. Chem. (Leipzig)* 226 (1985) 200–203.
- [79] S.C. Ameta, R. Ameta, D. Sharma, T.D. Dubey, *Hung. J. Ind. Chem.* 16 (1988) 245–252.
- [80] T.T. Quickenden, R.L. Bassett, *J. Phys. Chem.* 85 (1981) 2232.
- [81] T.I. Quickenden, G.K. Yim, *Sol. Energy* 19 (1977) 283–289.
- [82] D. Creed, N.C. Fawcett, R.L. Thompson, *J. Chem. Soc., Chem. Commun.* 1991 (1981) 497.
- [83] N.C. Fawcett, D. Creed, R.L. Thompson, D.W. Presser, *J. Chem. Soc., Chem. Commun.* 11 (1985) 719–720.
- [84] R. Bharadwaj, R.L. Pan, E.L. Gross, *Photochem. Photobiophys.* 3 (1981) 19.
- [85] A.S.N. Murthy, R. Bhargava, K.S. Reddy, *Int. J. Energy Res.* 6 (1982) 389.
- [86] K. Prajuntaboribal, N. Chaikum, *Sol. Energy* 38 (1987) 149–153.
- [87] A.S.N. Murthy, H.C. Dak, K.S. Reddy, *Int. J. Energy Res.* 4 (1980) 339–343.
- [88] H. Labhart, *Nature Wissenschaften* 64 (1977) 247–252.
- [89] C.D. Eisenbach, R.E. Sah, G. Baur, *J. Appl. Polym. Sci.* 28 (1983) 1819–1827.
- [90] D.L. Morel, E.L. Stogryn, A.K. Ghosh, T. Feng, P.E. Purwin, R.F. Shaw, C. Fishman, G.R. Bird, A.P. Piechowski, *J. Phys. Chem.* 88 (1984) 923.
- [91] G.V. Zakharova, A.K. Chibisov, *Teor. Eksp. Khim.* 18 (1982) 174–179.
- [92] T. Perez-Ruiz, C. Martinez, J. Ochotorena, *Talanta* 29 (1982) 479–484.
- [93] S.C. Ameta, A.K. Chittora, K.M. Gangotri, S. Khamesra, *Z. Phys. Chem. (Leipzig)* 270 (1989) 607–612.
- [94] B.B. Bhowmik, R. Dutta, P. Nandy, *Ind. J. Chem.* 24A (1985) 1046.
- [95] V. Bhanumathi, B. Sethuram, T. Navneeth Rao, *Ind. J. Chem.* 24A (1985) 463.
- [96] P.K. Jain, O.P. Jajoo, R.C. Ameta, S.C. Ameta, *Z. Phys. Chem.* 267 (1986) 1230–1232.
- [97] P.V. Kamat, M.D. Karkhanavala, P.N. Moorthy, *Ind. J. Chem.* 15A (1977) 342–344.
- [98] J. Setsune, *Shikizai Kyokaishi* 54 (1981) 344–354.
- [99] M.S. Mohammad, Aw.A.R. Al-Sadoon, *Iraqi J. Sci.* 29 (1988) 161–170.
- [100] A.J. Abdul-Ghani, M.A. Al-Abbasi, I.G. Mohamad, B.A. Ziada, S.H. Razoooki, *J. Sol. Energy Res.* 5 (1987) 27–37.
- [101] K. Tennakone, J. Karunamuni, M. Dewasurendra, *Sol. Energy Matter* 13 (1986) 447–452.
- [102] M. Eisenberg, P. Silverman, *Electrochim. Acta* 5 (1961) 1.
- [103] R. Bharadwaj, R.L. Pan, E.L. Gross, *Photochem. Photobiol.* 34 (1981) 215.
- [104] K.K. Rohatgi-Mukherjee, M. Bagchi, B.B. Bhowmik, *Electrochim. Acta* 28 (1983) 293.

- [105] S. Roy, A.K. Jana, B.B. Bhowmik, *Sol. Energy* 48 (1992) 215–219.
- [106] B.B. Bhowmik, S. Roy, K.K. Rohatgi-Mukherjee, *Ind. J. Chem.* 26A (1987) 183.
- [107] B.B. Bhowmik, S. Roy, *Energy* 12 (1987) 519.
- [108] J. Basu, A.B. Chatterjee, K.K. Rohatgi-Mukherjee, *Ind. J. Chem.* 24A (1985) 550.
- [109] Z.C. Bi, H.T. Tien, *Int. J. Hydrogen Energy* 9 (1984) 717.
- [110] M. Kaneko, A. Yamada, *J. Phys. Chem.* 81 (1977) 1213.
- [111] K.K. Rohatgi-Mukherjee, M. Bagchi, *Ind. J. Chem.* 23A (1984) 623.
- [112] C.E. Baumgartner, H.H. Richtol, D.A. Aikens, *Photochem. Photobiol.* 34 (1981) 17.
- [113] G.T. Marks, E.D. Lee, D.A. Aikens, H.H. Richtol, *Photochem. Photobiol.* 39 (1984) 323.
- [114] J. Basu, K.K. Kundu, K.K. Rohatgi-Mukherjee, *Ind. J. Chem.* 23A (1984) 630.
- [115] K.K. Rohatgi-Mukherjee, M. Bagchi, B.B. Bhowmik, *Ind. J. Chem.* 24A (1985) 1002.
- [116] A.K. Jana, B.B. Bhowmik, *Ind. J. Chem.* 28A (1989) 351–355.
- [117] A.K. Jana, B.B. Bhowmik, *J. Photochem. Photobiol. A: Chem.* 110 (1997) 41–46.
- [118] B.B. Bhowmik, S. Roy, K.K. Rohatgi-Mukherjee, *Ind. J. Chem.* 25A (1986) 714.
- [119] B.B. Bhowmik, S. Roy, K.K. Rohatgi-Mukherjee, *Ind. J. Technol.* 24 (1986) 388.
- [120] A.K. Jana, S. Roy, B.B. Bhowmik, *Energy* 13 (1988) 161–166.
- [121] S-Kang, Wu, Xi-Jun, Zhou, Tzu Jan Tsa Chih 3 (1980) 715–716.
- [122] A.K. Jana, S. Roy, B.B. Bhowmik, *Chem. Phys. Lett.* 168 (1990) 365–370.
- [123] A.K. Jana, B.B. Bhowmik, *J. Photochem. Photobiol. A: Chem.* 122 (1999) 53–56.
- [124] F. Gutmann, L.E. Lyons, *Organic Semiconductor*, Wiley, New York, 1967.
- [125] H. Meier, *Organic Semiconductors Monographs in Modern Chemistry*, Verlagchemie, Weinheim, 1974.
- [126] H. Meier, W. Albrecht, U. Tschirwitz, *Photogr. Sci. & Eng.* 18 (1974) 276.
- [127] D.L. Morel, A.K. Ghosh, T. Feng, E.L. Stogryn, P.E. Purwin, R.F. Shaw, C. Fishman, *Appl. Phys. Lett.* 32 (1978) 495–497.
- [128] K. Iriyama, M. Shiraki, K. Tsuda, A. Okada, M. Sugi, S. Iizima, K. Kudo, S. Shikawa, T. Moriizumi, T. Yasuda, *Jpn. J. Appl. Phys.* 19 (1980) 173–177.
- [129] G.D. Sharma, A.K. Tripathi, S.C. Mathur, D.C. Dube, *Mater. Sci. Lett.* 2 (1983) 433–436.
- [130] S.C. Mathur, D.C. Dube, G.D. Sharma, *Thin Solid Films* 164 (1987) 249–253 (published 1988).
- [131] K.K. Rohatgi-Mukherjee, M. Roy, B.B. Bhowmik, *Sol. Energy* 31 (1983) 417.
- [132] B.L. Kurbatov, F.I. Vilesov, *Dokl. Akad. Nauk SSSR* 141 (1961) 1343.
- [133] J. Muto, Y. Tsunekawa, *Phys. Stat. Sol. (a)*, 79 (1983) K109–K112.
- [134] E.T. Kang, P. Ehrlich, W.A. Anderson, *Mol. Cryst. Liq. Cryst.* 106 (1984) 305–316.
- [135] B.B. Bhowmik, A.K. Jana, *Energy* 13 (1988) 755–759.
- [136] A.G. Majumder, A.K. Jana, B.B. Bhowmik, *Energy* 27 (1992) 1233–1237.
- [137] A.G. Majumder, A.K. Jana, B.B. Bhowmik, *Ind. J. Chem.* 32A (1993) 605–607.
- [138] S.M. Sze, *Physics of Semiconductor Devices*, 2nd Edition, Wiley Eastern, New Delhi, 1983.
- [139] P. Panayotatos, D. Parikh, *Sol. Cells* 18 (1986) 71.
- [140] P. Panayotatos, G. Bird, R. Sauer, A. Piechowski, S. Husan, *Sol. Cells* 21 (1987) 301.
- [141] H. Meier, A. Haus, Z. *Electrochem.* 64 (1960) 1105.
- [142] H. Meier, W. Albrecht, *Ber. Bunsenges. Physik. Chem.* 68 (1964) 64.
- [143] H. Meier, W. Albrecht, *Ber. Bunsenges. Physik. Chem.* 69 (1965) 160.
- [144] H. Meier, *J. Phys. Chem.* 69 (1965) 719.
- [145] H. Meier, *Angew. Chem.* 77 (1965) 633.
- [146] H. Meier, *Angew. Chem. Int. Edit.* 4 (1965) 619.
- [147] H. Meier, W. Albrecht, U. Tschirwitz, *Angew. Chem. Int. Edit.* 11 (1972) 1051.
- [148] H. Meier, W. Albrecht, U. Tschirwitz, E. Zimmerhackl, N. Gaheew, BE. *Bunsenges. Phys. Chem.* 81 (1977) 592–598.
- [149] K. Kudo, T. Moriizumi, *Jpn. J. Appl. Phys.* 20 (1981) L 553.
- [150] G.A. Chamberlain, *Mol. Cryst. Liq. Cryst.* 93 (1983) 369.
- [151] G.A. Chamberlain, *Sol. Cells* 10 (1983) 199–210.
- [152] G.A. Chamberlain, P.J. Cooney, S. Dennison, *Nature* 289 (1981) 45–47.
- [153] S. Huang, Q. Yin, R. Fan, Z. Zhu, *Huadong Huagong Xueyuan Xuebao* 12 (1986) 745–750.
- [154] K. Sakai, M. Saifu, M. Sugi, S. Lizima, *Jpn. J. Appl. Phys. Part I.* 24 (1985) 865–869.
- [155] K. Uehara, K. Takagishi, M. Tanaka, *Chem. Express* 2 (1987) 129–132.
- [156] G.A. Chamberlain, R.E. Malpas, *Faraday Discuss. Chem. Soc.* 70 (1980) 299–310.
- [157] N.N. Lichtin, *CHEMTECH* 10 (1980) 252.
- [158] J.T. mc Devitt, *J. Chem. Education* 61 (1984) 217.
- [159] H. Gerischer, *Power generation by photoelectrolysis*, in: J.R. Bolton (Ed.), *Solar Power and Fuels*, Academic Press, New York, 1977, p. 77.
- [160] A.J. Bard, *J. Photochem.* 10 (1979) 59.
- [161] F-R.F. Fan, H.S. White, B.L. Wheeler, A.J. Bard, *J. Am. Chem. Soc.* 102 (1980) 5142–5148.
- [162] Y. Suda, Y. Shimoura, T. Sakata, H. Tsubomura, *J. Phys. Chem.* 82 (1978) 268.
- [163] D.E. Hall, W.D.K. Clark, J.A. Eckert, N.N. Lichtin, P.D. Wildes, *Am. Ceram. Soc., Bull.* 56 (1977) 408.
- [164] F. Gessmer, *Contrib. Cient. Tecnol. (Numero Espec)* 13 (1983) 47–49.
- [165] A. Krisch-De Mesmaeker, M. Wyart-Rermy, J. Nasielski, *Sol. Energy* 25 (1980) 117–122.
- [166] K. Shigehara, M. Nishimura, E. Tsuchida, *Electrochim. Acta* 23 (1978) 855–860.
- [167] W.J. Albery, A.W. Foulds, K.J. Hall, A.R. Hillman, *J. Electrochem. Soc.* 127 (1980) 654–661.
- [168] T. Nasielski, A. Krisch-De Mesmaeker, *Eur. Communities [Rep] EUR* 1982, EUR 7795, p. 97.
- [169] A. Krish-De Mesmaeker, R. Dewitt, *Electrochim. Acta* 26 (1981) 297–302.
- [170] A. Yoshikawa, S. Yasuhira, M. Yoshioka, *Mem. Fac. Lib. Arts. Educ. Part 2*, 35 (1984) 31–34.
- [171] M. Shimura, K. Shakushiro, Y. Shimura, *J. Appl. Electrochem.* 16 (1986) 683–692.
- [172] K.K. Rohatgi-Mukherjee, S. Roy, B.B. Bhowmik, *Ind. J. Chem.* 24A (1985) 5–7.
- [173] I.R. Harrison, T.I. Quickenden, *J. Phys. Chem.* 91 (1987) 1481–1486.
- [174] M. Nakao, T. Watanabe, K. Honda, *Chem. Lett.* 2 (1984) 225.
- [175] P.V. Kamat, M.A. Fox, *J. Electrochem. Soc.* 131 (1984) 1032–1037.
- [176] P.V. Kamat, *Res. Dev.* 31 (1989) 87, 89–90.
- [177] I. Inamura, H. Ochiai, K. Toki, T. Araki, *Chem. Lett.* 10 (1984) 1787–1790.
- [178] G.D. Sharma, D.C. Dube, S.C. Mathur, *Sol. Cells* 15 (1985) 189–197.
- [179] L.C. Schumacher, S. Mamiche-Afara, M.J. Dignam, *J. Electrochem. Soc.* 133 (1986) 716–722.
- [180] L. Hsu, E.Y. Wang, *Comm. Eur. Communities, [REP.] EUR* 1978, EUR 5913, *Photovoltaic Sol. Energy Conf.* 1977, pp. 1100–1108.
- [181] T. Nakazawa, K. Takamizawa, K. Ito, *Appl. Phys. Lett.* 50 (1987) 279–280.
- [182] A.A. Abdurakhimov, Yu.V. Rud, K.V. Sanin, M. Serginov, V.E. Skoryukin, *Zh. Tekh. Fiz.* 53 (1983) 325–328.

- [183] F. Mizutani, K. Sasaki, *Denki Kagaku Oyobi. Kogyo Butsuri Kagaku* 51 (1983) 77–78.
- [184] A.K. Jana, S. Roy, B.B. Bhowmik, *Sol. Energy* 51 (1993) 313–316.
- [185] R.O. Loutfy, J.H. Sharp, C.K. Haiso, R. Ho, *J. Appl. Phys.* 52 (1981) 5218–5230.
- [186] F. Takahashi, T. Komori, *Bull. Chem. Soc. Jpn.* 54 (1981) 1305–1307.
- [187] M. Nasako, K. Itoh, K. Honda, *Phys. Chem.* 88 (1984) 4906–4907.
- [188] M. Matsumura, K. Mitsuda, H. Tsubomura, *J. Phys. Chem.* 87 (1983) 5248–5251.
- [189] H. Tsubomura, M. Matsumura, K. Nakatani, Y. Nomura, *Proc. Electrochem. Soc.* 77 (1977) 178–185.
- [190] T. Yoshimura, K. Kiyota, H. Ueda, M. Tanaka, *Jpn. J. Appl. Phys.* 19 (1980) 1007–1008.
- [191] J.R. Darwent, A. Lepre, *J. Chem. Soc. Faraday Trans. 2*, 82 (1986) 1457–1468.
- [192] H. Tsubomura, M. Matsumura, Y. Nomura, T. Amamiya, *Nature* 261 (1976) 402.
- [193] M. Matsumura, Y. Nomura, H. Tsubomura, *Bull. Chem. Soc. Jpn.* 50 (1977) 2533.
- [194] K.G. Mathi, E. Rabinowitch, *J. Phys. Chem.* 66 (1962) 663.
- [195] J. Kiwi, K. Kalyansundaram, M. Grätzel, *Struct. Bonding (Berlin)* 49 (1982) 37.
- [196] E.J.J. Groenen, M.S. de Groot, R. de Ruiter, N. dewit, *J. Phys. Chem.* 88 (1984) 1449–1454.
- [197] R.C. Srivastava, R. Srinivasan, P.R. Marwadi, S.B. Bhise, S.S. Mathur, *Curr. Sci.* 51 (1982) 1015–1017.
- [198] R.C. Srivastava, P.R. Marwadi, P.K. Latha, S.B. Bhise, *Int. J. Energy Res.* 6 (1982) 247–251.
- [199] N.S. Dixit, R.A. Mackay, *J. Phys. Chem.* 86 (1982) 4593–4598.
- [200] W.R. Bowen, *Acta Chem. Scand. Ser. A*, A35 (1981) 311–315.
- [201] Y. Usui, K. Saga, *Bull. Chem. Soc. Jpn.* 55 (1982) 3302–3307.
- [202] I. Okura, T. Kita, S. Aono, N. Kaji, *J. Mol. Catal.* 32 (1985) 361–363.
- [203] S. Lingamurthy, V. Bhanumathi, B. Sethuram, T.N. Rao, *Sol. Energy* 42 (1989) 359–364.
- [204] S. Battacharya (Roy), A.K. Jana, B.B. Bhowmik, *J. Photochem. Photobiol. A: Chem.* 56 (1991) 81–87.
- [205] Z-Chu. Bi, Tu-Shu. Li, Z-Mui. Liu, *Tai Yang Neng Hsueh Pao* 1 (1980) 140–147.
- [206] S.N. Guha, P.N. Moorthy, K.N. Rao, *J. Photochem.* 28 (1985) 37–51.
- [207] K.K. Rohatgi-Mukherjee, R. Chaudhuri, B.B. Bhowmik, *J. Colloid & Interface Sci.* 106 (1985) 45–50.
- [208] B.B. Bhowmik, R. Chaudhuri, K.K. Rohatgi-Mukherjee, *Ind. J. Chem.* 26A (1987) 95–98.
- [209] O.I. Mičić, M.T. Nenadović, *Glas. Hem. Durs. Beograd* 45 (1980) 77–83.
- [210] O.I. Mičić, M.T. Nenadović, *J. Chem. Soc. Faraday Trans. I.* 77 (1981) 919–925.
- [211] T. Yamase, *Photochem. Photobiol.* 34 (1981) 111–114.
- [212] I. Gulya, *Energy Atomtech.* 41 (1988) 198–203.
- [213] S. Chandra, B.B. Srivastava, N. Khare, *Solid State Commun.* 56 (1985) 975–979.
- [214] M.T. Nenadović, O.I. Mičić, T. Rajh, D. Savic, *J. Photochem.* 21 (1983) 35–44.