# Photoelectrochemical solar cells: Present status

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**This review focuses on the present status and emerging trends of photoelectrochemical (PEC) solar cells. PEC cells are wet photovoltaic systems with vital advantages over their solid-state counterparts. The important operational principles, classification and a historical account of development of PEC solar cells have been dealt with. Some of the earlier studied and recently discovered photoelectrode materials have been outlined. To make an efficient and viable PEC solar cell, some of the feasible efficiency enhancement processes such as electrode surface modification, electrolyte modification, etc. have been described. The high efficiency PEC solar cell developed in our laboratory, i.e. *n*-$WSe_2/I^-$, $I_3^-$/Pt cell ($\eta \sim 17\%$) and some of the important and efficient photoelectrosynthetic solar cells where solar-to-chemical energy conversion is possible have been discussed. Recent trends embodying the development of new and efficient photoelectrode materials and semiconductor septum (SC-SEP) cells have been reported. The case of a recent novel PEC cell incorporating nanostructured $TiO_2$ photoelectrode overlaid with special dye (ruthenium trinuclear cyanide complex) and exhibiting efficiencies of 7% (under usual solar illumination) and 12% (in diffuse solar light), has also been outlined. It is suggested that further efforts to develop new and efficient photoelectrode materials, e.g. nanocrystalline versions of known photoelectrode materials and novel cell designs to eventually obtain high conversion efficiency and long-term stability should form one of the priority areas of the chemical routes for trapping solar energy.**

THE ever-increasing demands of commercial energies (electricity and fuel) due to increasing global population, the depleting trend of the present sources of commercial energies – the fossil fuels, and the current concern about pollution leading to environmental degradation, acid rains, global warming, etc., have made it imperative to accelerate R&D and demonstration efforts in the area of renewable energy technologies on a priority basis. In this respect, solar energy is unique as it is inexhaustible, nonpolluting and does not contribute to global warming. The spectrum of solar energy received on the surface of earth is approximately 0.25 μm to 3.0 μm. Solar energy conversion devices can be classified into two main groups: (a) solar thermal conversion devices using the infrared part (~ 49%) of the solar spectrum e.g. solar heat collector and (b) solar photon conversion devices utilizing visible/near ultraviolet region (~ 51%) of solar spectrum. The solar photon conversion devices called solar cells can be classified into: (i) solid-state photovoltaic (*p*/*n* junction) solar cells, (ii) semiconductor metal-based Schottky barrier (M-S) solar cells, and (iii) semiconductor-liquid junction based photoelectrochemical (PEC) solar cells. Solid state photovoltaic solar cells are well suited for special applications e.g. for supplying power to space vehicles and to remote inaccessible localities. In contrast to solid-state photovoltaic devices the photoelectrochemical solar cells are inexpensive, can be easily fabricated and a possibility exists of *in situ* storage[1–3].

The semiconductor-liquid junction photoelectrochemical solar cell consists of photoactive semiconductor (SC) electrode immersed in electrolytic solution containing suitable redox couple and counter electrode which can be a metal or semiconductor. Irradiation of semiconductor/electrolyte junction with light of $h\nu \geq E_g$, ($E_g$ is the band gap of SC) results in generation and separation of charge carriers. The minority carriers (e.g. hole ($h^+$) in *n*-type SC) migrate to electrolyte and take part in electrochemical reaction. The majority carriers (e.g. electrons in *n*-type SC) go to counter-electrode through external circuit and take part in counter-reaction[1–3].

## Classification and general operation principles of photoelectrochemical solar cells

PEC solar cells can be classified on the basis of their Gibbs free-energy change ($\Delta G$), as (a) regenerative PEC solar cells (solar energy converted into electrical energy; $\Delta G = 0$) and (b) photoelectrosynthetic cells (solar energy converted to chemical energy, $\Delta G \neq 0$). Photoelectrosynthetic cells are of two types: (i) photoelectrolysis cells ($\Delta G > 0$) where solar energy is stored as chemical energy in endoergic reactions (e.g.

$2H_2O \rightarrow H_2 + O_2$) and (ii) photocatalytic cells ($\Delta G < 0$). *Solar energy provides activation energy for exoergic* reactions (e.g. $N_2 + 3H_2 \rightarrow 2NH_3$). Another type of PEC cell, termed as photogalvanic cell, uses metal electrodes and light-absorbing molecules in solution. The solar conversion efficiencies of photogalvanic cells are usually very low ($\leq 0.1\%$).

### *Regenerative photoelectrochemical solar cells ($\Delta G = 0$)*

This type of solar cell is used to convert solar energy to electricity. When the photosensitive *n*-type SC electrode is immersed in an electrolyte solution containing a suitable redox system where Fermi level of SC is more negative than that of the redox electrolyte, two chemical potentials equilibrate by transfer of electrons from SC to electrolyte leading to a positive space charge layer in the semiconductor. As a result, the conduction and valence band edges are bent upwards in *n*-type SC, forming a potential barrier against further electron transfer to the electrolyte. A schematic diagram of this cell is depicted in Figure 1.

When the semiconductor-electrolyte junction is illuminated with light corresponding to energy $h\nu \geqslant$ semiconductor band gap ($E_g$), the electron-hole pairs are generated in the semiconductor and separated under the influence of electric field present in the space charge region. Photogenerated minority carriers (e.g. holes in *n*-type SC and electrons in *p*-type SC) move towards the semiconductor surface where they are consumed for oxidation of reduced species (red) and reduction of oxidized species (oxi) of the redox system in *n*-type and *p*-type SC respectively, whereas majority carriers move to the bulk of the semiconductor. Under short circuit conditions or under certain load, the electrons (in *n*-type SC) reach the counterelectrode where they are used for reduction of oxidized species. If the electrolyte contains only one effective redox couple, then the oxidation *reaction at the anode is simply reversed at the cathode* and no net chemical change occurs in the electrolyte. The electrode reaction merely serves the charge transfer across the electrolyte and there is no change in Gibb's free energy ($\Delta G = 0$) of the electrolyte (Figure 1). The general energetics and kinetics of charge transfer reactions at semiconductor interfaces have been extensively studied by several workers[1–4].

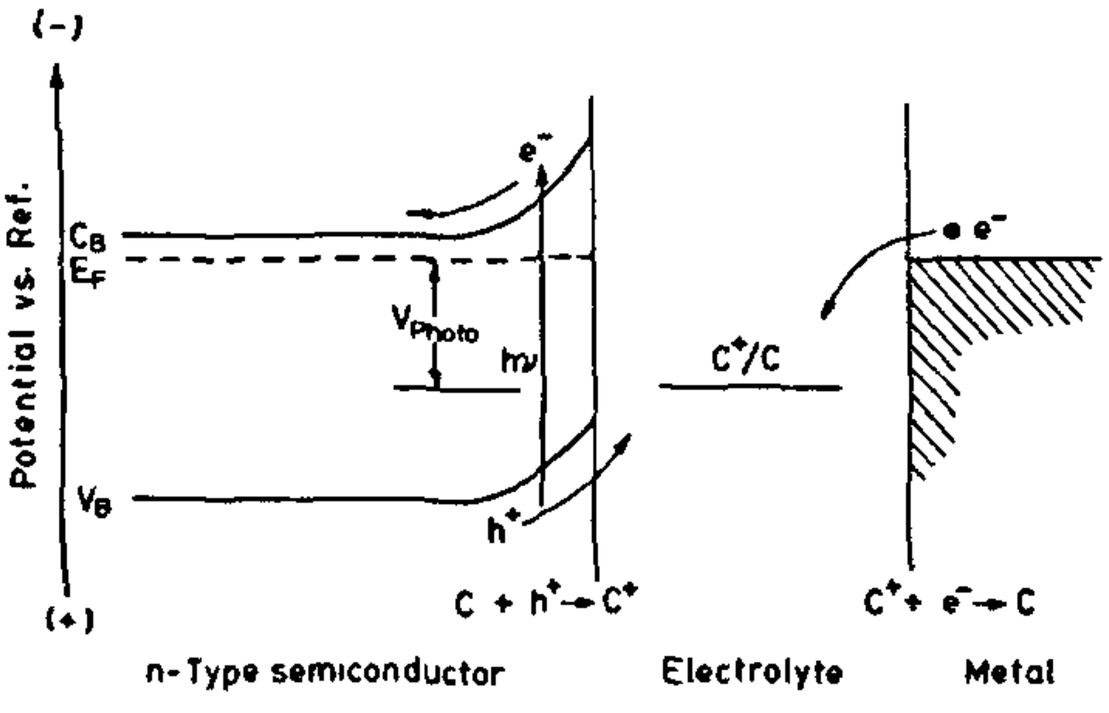


**Figure 1.** Schematic energy diagram for regenerative photoelectrochemical solar cell

### *Photoelectrolysis cells*

In a photoelectrolysis cell, the anodic reaction has a more positive redox potential than the cathodic reaction so that the overall cell reaction has a positive free energy change ($\Delta G > 0$). There are two types of photoelectrolysis cells. One electrode is a semiconductor and the second a metal. In the second type, one electrode is an *n*-type semiconductor and the second a *p*-type semiconductor. The energetics of the cell for the photoelectrolysis of water into $H_2$ and $O_2$ by using *n*-type semiconductor electrode with zero and applied bias has been shown in Figure 2[1–5].

## Photoelectrochemical conversion efficiency

There are three important electrical output quantities, which determine the conversion efficiency of liquid

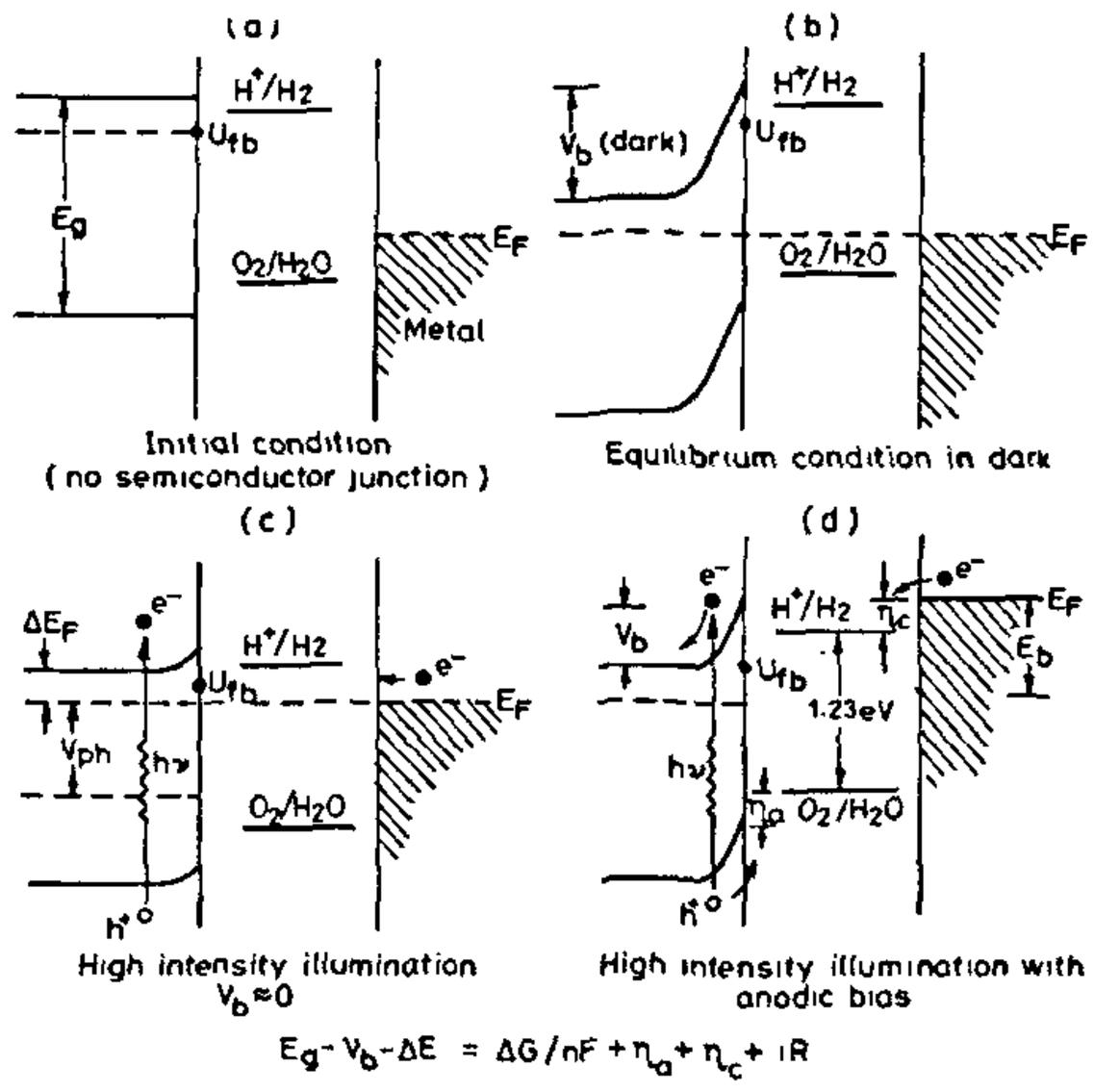


**Figure 2.** Sequence of energy level diagrams for a single semiconductor electrode photoelectrolysis cell from the initial condition to the final condition of photoelectrolysis with bias Energy balance is written for case of zero bias; if bias is present, $E_b$ is added to the left side of equation.

junction electrochemical PEC cell. They are (i) open circuit voltage ($V_{oc}$) (ii) short circuit photocurrent ($I_{sc}$) and (iii) the fill factor. For a given set of conditions (semiconductor, light intensity, cell temperature etc.), the fabrication of an efficient PEC device involves optimization of these three quantities.

### *Solar energy conversion efficiency of regenerative PEC solar cells*

The solar-to-electrical conversion efficiency ($\eta$) in a semiconductor/liquid junction solar cell is given as,

$$\eta = [(I \times V)_{max}/P] \times 100,$$

where $(I \times V)_{max}$ is the maximum output power of the solar cell and $P$ the optical power input[5]. In addition to $\eta$, a parameter namely fill factor (FF) is defined in a PEC solar cell as:

$$FF = \frac{(I \times V)_{max}}{(I_{SC} \times V_{OC})},$$

where $I_{SC}$ is the short circuit photocurrent and $V_{OC}$ the open circuit photovoltage. FF (< 1) indicates the extent of departure from the ideal $I$–$V$ behaviour.

### *Solar energy conversion efficiency of photoelectrosynthetic cells*

The photoelectrosynthetic (photoelectrolytic or photocatalytic) cells utilize photon energy input ($E \geq E_g$) to produce a net chemical change in the electrolyte solution ($\Delta G \neq 0$) when the reaction at the counterelectrode is not exactly opposite to the hole-transfer reaction at illuminated semiconductor-liquid interface. For photoelectrolysis cells which produce chemicals (e.g. $H_2$ from water) with an applied bias, solar energy conversion efficiency is given by

$$\eta = \frac{[(\text{energy stored as fuel}) - (\text{electrical energy supplied})]}{(\text{incident solar energy})}.$$

Several methods have been suggested for calculating the conversion efficiency of photoelectrosynthetic cells. For single electrode-based PEC employing semiconductors and band gaps 1.2–1.5 eV, the maximum $\eta$ for operation in regenerative (light to electricity) mode is 25–30% and for water photoelectrolysis is 20–30%. Considering the optimum band gap for photoelectrolysis to be 1.8 eV, the theoretical maximum $\eta$ estimate is 25%. For double photoelectrode based ($p$–$n$) water photoelectrolysis cells a maximum $\eta$ of 45% is given[2–5].

## High efficiency regenerative PEC cells for light-to-electricity conversion

The commercial viability of photoelectrochemical solar cells is dependent on its conversion efficiency and stability. Various efforts such as surface modification of the presently-known semiconductors, electrolyte modifications, photoetching of layered semiconductors, new configuration PEC solar cells (e.g. semiconductor-septum based PEC solar cells), and dye-sensitization have been directed to fabricate efficient and stable PEC solar cells. Recently, several novel developments in regard to higher efficiency and/or cost-effective PEC solar cells have been made. The important efficiency enhancement aspects of conventional PEC cells e.g. (a) photoelectrode and electrolyte modifications and (b) developments regarding new PEC cell designs leading to improved efficiencies or higher power output have been described below.

### *Photoelectrode surface modification for enhancing PEC conversion efficiency*

The surface recombination rates of SC/liquid junction-based PEC solar cells can be successfully controlled by

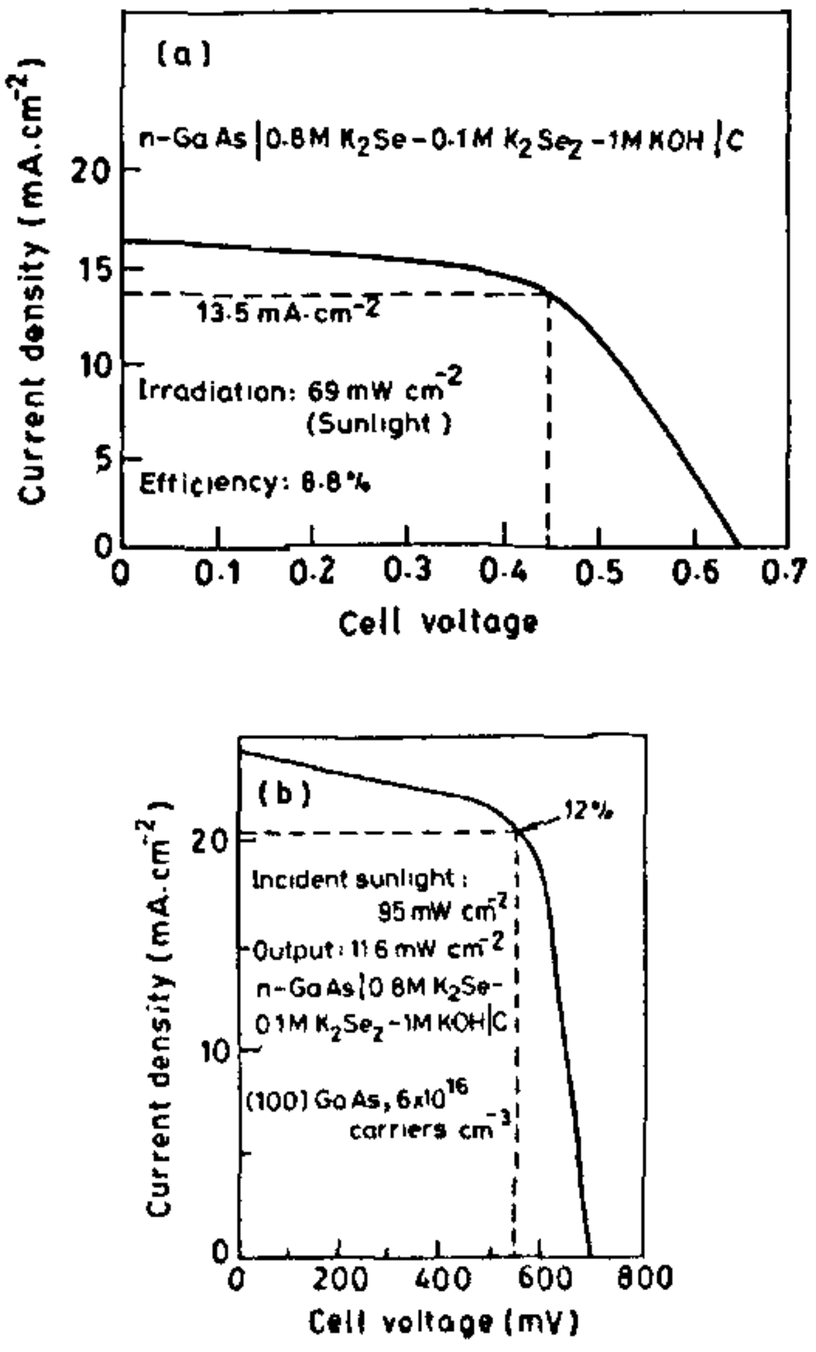


**Figure 3.** *a*, *n*-GaAs/0 8 M $K_2Se$-0.1 M $K_2Se_2$-1 M KOH/C PEC solar cell showing solar-to-electrical conversion efficiency of 8 8% without photoelectrode surface modification. *b*, High conversion efficiency (12%) *n*-GaAs/0.8 M $K_2Se$-0.1 M $K_2Se_2$-1 M KOH/C, PEC cell, after surface modification of *n*-GaAs with $Ru^{3+}$.

surface modification. A dominant effect of modification of photoelectrode surface is to introduce or alter existing semiconductor surface states. The *n*-GaAs/$Se^{2-}$, $Se_x^{2-}$, $OH^-$/C PEC solar cells show an $\eta$ value of ~ 8.8% under 75 mW/cm$^2$ insolation[6] (Figure 3*a*). This power conversion efficiency is significantly enhanced by surface modification of *n*-GaAs photoanode through ruthenium and osmium metal ions[6]. The ruthenium modification of *n*-GaAs photoanode surface is carried out by immersing the *n*-GaAs photoelectrode in 0.01 M ruthenium (III) solution prepared in 0.1 M $HNO_3$. The modified *n*-GaAs based PEC solar cell corresponding to configuration *n*-GaAs/$Se^{2-}$, $Se_x^{2-}$, $OH^-$/C resulted in enhancement of open-circuit voltage as well as the fill factor. The $\eta$ value of 12% (Figure 3*b*) was found to be stable even after the passage of 35000 C/cm$^2$. The PEC solar cell based on surface modified *n*-GaAs through $Os^{3+}$ ions (*n*-GaAs/$Se^{2-}$, $Se_x^{2-}$, $OH^-$/C) yielded superior current-voltage (*I–V*) characteristics. The open circuit photovoltage, short circuit current and fill factor are found to be 780–810 mV, 24–26 mA/cm$^2$ and 0.65–0.75 respectively. The $\eta$ value is 15%. The *I–V* characteristics of this cell remained constant at a maximum power point for ~ 3000 C/cm$^2$ of charge passed[5]. With $Te^{2-}$, $Te_x^{2-}$ electrolyte, $\eta$ = 14%[7].

## *Electrolyte modifications for enhancement of PEC efficiency*

An alternate approach to improve $\eta$ has been investigated by systematic modification of the electrolyte[5]. Licht and Peramunage[8] found that addition of 0.1 M potassium cyanide solution to *n*-cadmium selenide-based PEC solar cell (*n*-CdSe/0.25 M $K_4Fe(CN)_6$, 0.0125 M $K_3Fe(CN)_6$, 0.1 M KCN, 0.5 M KOH/Pt) achieved an open-circuit potential of 1.2 V and a $\eta$ value of 15.6 to 16.4%. The conversion efficiencies in *n*-CdSe/$[Fe(CN)_6^{3-\ 4-}]$ aqueous solar cell have been reported to be 12–14%, in which redox electrolyte containing a 1:1 ratio of $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$ salts in highly alkaline environment is employed. The observed photocurrents are, however, highly unstable and decay within hours. *Employing* $K_3Fe(CN)_6$ *to* $K_4Fe(CN)_6$ *in the ratio of* ~ 20:1, the charge transfer across *n*-CdSe/$Fe(CN)_6^{3-/4-}$ aqueous interface is found to be most facile. This ratio shows enhancement in photocurrent stability for the *n*-CdSe/$Fe(CN)_6^{3-\ 4-}$ system. After adding the KCN solution to *n*-CdSe/$Fe(CN)_6^{3-\ 4-}$ system, large improvements in photocurrent (~100 fold) and its stability have been observed. Recently, it has been suggested that 26% of the observed photocurrent in the KCN modified CdSe-based PEC solar cell was due to a 'virtual battery' resulting from electrochemical discharge of cyanide to cyanate at the photoelectrode[9]. Licht *et al.* did not observe this virtual battery effect and their investigations indicate that battery effects are artifacts of the experimental configuration in that study. Further studies indicate that no cyanide is electrochemically oxidized at either Pt or CdSe electrodes[10].

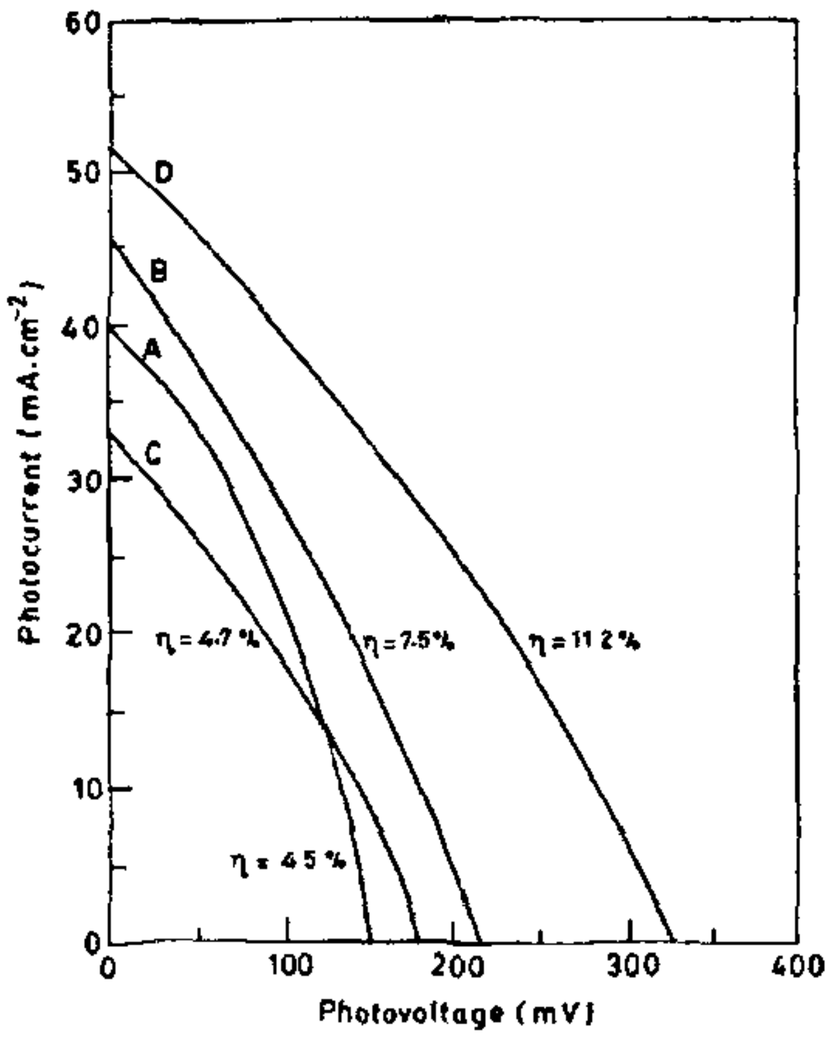


**Figure 4.** Power characteristics of the *n*-$CuInSe_2$/polysulphide electrolyte/Pt PEC solar cell; curve A, before electrolyte modification; curve B, after electrolyte modification with 10 mM $Cu_2S$; curve C, after electrolyte modification with 10 mM $In_2(SO_4)_3$; curve D, after electrolyte modification with 10 mM $Cu_2S$ and 10 mM $In_2(SO_4)_3$. Illumination intensity 40 mW cm$^{-2}$ (after ref. 11)

## *n-CuInSe$_2$/S$^{2-}$, S$_x^{2-}$, OH$^-$/Pt PEC solar cells*

PEC conversion efficiencies of *n*-$CuInSe_2$/polyiodide cell have been reported to be greatly enhanced up to $\eta$ ~ 12% when polyiodide redox electrolyte is suitably modified with $Cu^+$ and $In^{3+}$ ions through the addition of CuI and $In_2(SO_4)_3$, respectively[5]. In another work on enhancement of conversion efficiency in *n*-$CuInSe_2$-based PEC solar cell, the polysulphide electrolyte has been modified through the addition of $Cu^+$ and $In^{3+}$ ions obtained from 10 mM $Cu_2S$ and 10 mM $In_2(SO_4)_3$ solutions. This modification led to a conversion efficiency ($\eta$) of up to ~ 11.2%[11]. The power output characteristics of *n*-$CuInSe_2$/polysulphide PEC solar cell before and after electrolyte modification are shown in Figure 4. In a typical case, the addition of $Cu_2S$ and $In_2(SO_4)_3$ to the starting electrolyte enhanced the efficiency from ~ 4.5% to ~11.2% (Figure 4). This is significantly higher than the efficiency obtained either by addition of $Cu_2S$ or $In_2(SO_4)_3$ alone[5].

## *n-InP/nonaqueous redox electrolyte/Pt PEC solar cells*

Another kind of electrolyte modification consists of variation of the very nature of the electrolyte i.e. *p*-InP

and *p*-Si aqueous electrolyte junctions performed in $V^{3+/2+}$–6 M HCl electrolyte to nonaqueous medium. A recent example of such an electrolyte modification relates to the *n*-InP-based PEC solar cells. The nonaqueous redox electrolytes provide efficient photoelectrochemical solar cells e.g. 14% efficient PEC solar cell based on the *n*-Si/$CH_3OH$ junction. Heben *et al.*[12] reported the *n*-InP/$CH_3OH$, 1.0 M $LiClO_4$, 0.20 M-dimethylferrocene, 0.5 mM-dimethylferrocene$^+$ PEC solar cell, with $\eta$ of 7.3%[12]. However, *n*-InP/aqueous redox electrolyte-based PEC solar cell shows conversion efficiency less than 1%. The *n*-InP/0.20 M $Me_2Fe$, 0.5 mM $Me_2Fe^+$, 1.0 M $LiClO_4$, $CH_3OH$ junction under simulated AM 2 conditions (62 mW/cm$^2$), gives short circuit photocurrent of 14–15 mA-cm$^{-2}$, open circuit photovoltage ($V_{OC}$) of 0.59–0.61 V and PEC efficiencies of 6.5–7.0%. This represents a good PEC output for an *n*-InP surface-barrier device[12].

### *Tungsten diselenide-based photoelectrochemical solar cells*

Transition-metal chalcogenide, layered-type semiconductors like $WSe_2$ ($E_g \sim 1.1$–1.4 eV), have been shown to be attractive for use in regenerative photoelectrochemical solar cells due to their excellent properties. These are corrosion-resistant materials because of optical transitions which occur between two *d*-bands ($d_{z^2} \rightarrow d_{xy}, d_{x^2-y^2}$) of the metal and do not involve metal and chalcogen bonding orbitals, thus assuring good stability against photocorrosion[13]. In addition to some of the surface treatments like deposition of Pt metal islands on the surface of (W, Mo)$Se_2$ crystals, etc., photoetching treatment has been found advantageous in enhancing the PEC conversion efficiency of $MX_2$-type layered materials. Among the various etchants employed in our laboratory for photoetching *n*-$WSe_2$, aquaregia (0.1 M) has been found to be the most suitable etchant under forward bias (1.0 V vs SCE). Typical current-voltage (*I*–*V*) characteristics of *n*-$WSe_2/I^-$, $I_3^-$/Pt cell, before and after subjecting to photoetching has shown a photovoltage of 600 mV and photocurrent ($I_{ph}$) of 48 mA/cm$^2$. The net photovoltage of the cell (after photoetching) has been found to be 570 mV and $I_{ph}$ has undergone a significant enhancement from 48 to 95 mA/cm$^2$. Figure 5 shows the power characteristics of this *n*-$WSe_2$-based PEC cell. Photoetching of this cell in 0.1 M aquaregia under specified conditions enhanced the short circuit photocurrent of the cell from 18 to 38.4 mA/cm$^2$. The photovoltage of the cell slightly decreased from 600 to 570 mV. An estimation of conversion efficiency ($\eta$) for this cell typified by Figure 5 reveals that $\eta$ changed from 8.3% to 17.1%[13]. Consolidated PEC characteristics of some *n*-$WSe_2$ crystals (photoelectrodes) is given in

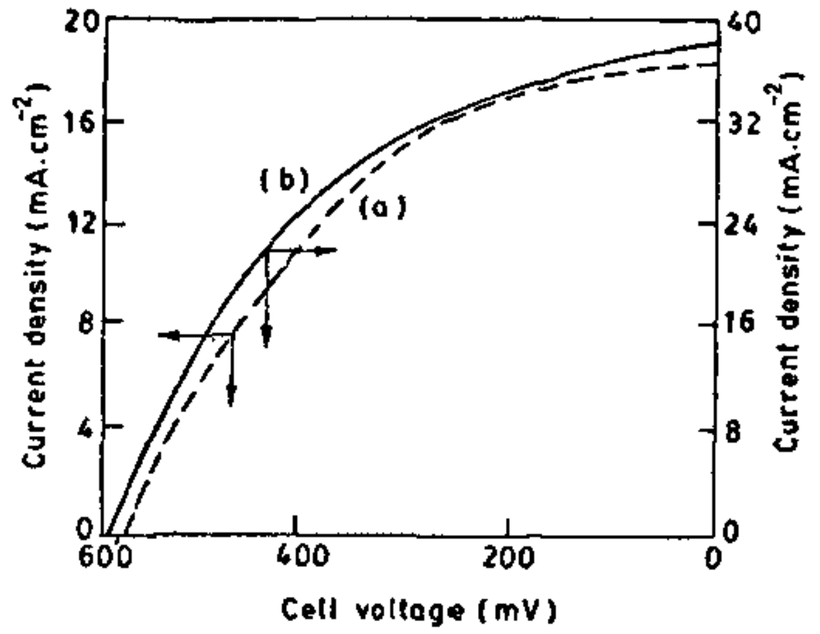


**Figure 5.** Power characteristics of the *n*-$WSe_2/I^-$. $I_3^-$/Pt PEC cell (*a*) as-grown (*b*) photoetched. The solar-to-electrical conversion efficiency enhanced from 8.3% to 17.1%.

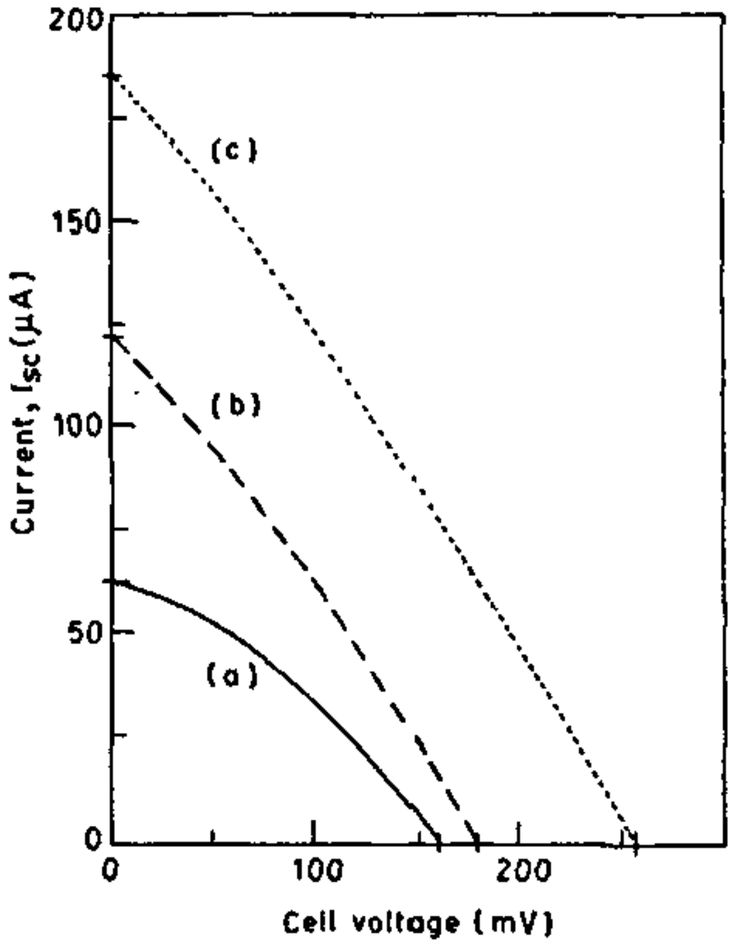


**Figure 6.** Power curve for the *n*-$WSe_2/I^-$, $I_3^-$/Pt PEC solar cell (*a*) with as-prepared (native) electrolyte, (*b*) in an electrolyte heated to ~ 42°C and then cooled to ~ 32°C and (*c*) in the preheated electrolyte cooled to room temperature.

Table 1, showing improvement in PEC parameters after photoetching. The output stability of these *n*-$WSe_2$ photoanodes has been tested in $I^-/I_3^-$ redox electrolyte and the cell was stable for at least 200 hours[13].

### *Electrolyte heating-induced enhancement of photoelectrochemical response in n-$WSe_2/I^-$, $I_3^-$/Pt PEC solar cells*

Among the various possible modes for enhancement of conversion efficiencies, variation of electrolyte characteristic is one of the promising options. This embodies the results of PEC conversion efficiency enhancements obtained through development of preheated electrolyte

**Table 1.** PEC characteristics of $n$-$WSe_2$-based PEC solar cells before and after photoetching[13]

| Open circuit voltage ($V_{oc}$) (Volts) | | Short circuit current ($I_{sc}$) (mA/cm$^2$) | | Fill factor | | Electrode area (cm$^2$) | Efficiency ($\eta$) % | |
|---|---|---|---|---|---|---|---|---|
| Before | After | Before | After | Before | After | | Before | After |
| 0 50 | 0 42 | 12 0 | 32 0 | 0.28 | 0.31 | 0 015 | 2 8 | 7 0 |
| 0 60 | 0 55 | 15.4 | 33.2 | 0.39 | 0.44 | 0 027 | 6.0 | 13.4 |
| 0 52 | 0 48 | 15 6 | 25 4 | 0.29 | 0 29 | 0 013 | 3.9 | 8.1 |
| 0 61 | 0.56 | 16 6 | 41.6 | 0 30 | 0.30 | 0.012 | 5.0 | 11 6 |
| 0 62 | 0 57 | 18 0 | 38 4 | 0 45 | 0 47 | 0 0125 | 8.3 | 17 1 |
| 0 61 | 0 46 | 15 0 | 44.0 | 0.39 | 0 48 | 0 010 | 6 0 | 16 2 |
| 0.57 | 0 54 | 13 1 | 35 0 | 0.43 | 0 46 | 0.016 | 5 3 | 14 4 |
| 0 62 | 0.64 | 20 6 | 31.7 | 0.41 | 0 46 | 0 025 | 8 7 | 15 7 |
| 0 64 | 0 64 | 8 4 | 20 0 | 0.45 | 0 50 | 0 012 | 4 0 | 10 6 |
| 0 64 | 0 62 | 17.3 | 33.0 | 0 40 | 0 41 | 0 013 | 7 4 | 14 0 |
| 0 62 | 0 60 | 9.0 | 24 0 | 0.45 | 0.51 | 0 015 | 4 2 | 12 2 |
| 0 62 | 0 60 | 15.6 | 48 0 | 0 34 | 0.34 | 0 010 | 5.5 | 16.3 |
| 0 30 | 0.40 | 34.6 | 46 6 | 0 45 | 0 45 | 0 007 | 7.8 | 14 0 |

(heated slowly to ~ 42°C at 0.1°C per minute, then the electrolyte was allowed to cool to room temperature) in PEC configuration corresponding to $n$-$WSe_2/I^- - I_3^-$/Pt[14]. The use of preheated electrolyte significantly improved the PEC characteristics and hence the efficiencies. Although both the important PEC parameters – the open circuit voltage ($V_{OC}$) and the short circuit photocurrent ($I_{SC}$) – were found to improve when *preheated rather than the as-prepared* $I^-/I_3^-$ *aqueous* electrolyte used, significant changes occurred in the short circuit photocurrent. For example, for one of the cells $I_{SC}$ changed from 44 μA to 215 μA, a five-fold increase. Figures 6*a–c* represent the *I–V* (power curve) and show that the observed change in $I_{SC}$ and $V_{OC}$ in a preheated electrolyte is a room temperature phenomenon. The results have been explained assuming the formation of $I_4^{2-}$ and $I_5^-$ species during electrolyte heating, which affected the PEC properties of the cell[14].

*New generation high efficiency PEC solar cell*

Using the concept of sensitization a new and efficient PEC solar cell was developed by O'Regan and Gratzel[15]. This cell which may be termed as 'artificial leaf cell', consists of two electrodes of $SnO_2$ conducting glass in contact with a redox electrolyte solution of iodine-iodide (Figure 7). One of the two electrodes is coated with nanostructured $TiO_2$ film having a large surface area. This $TiO_2$ is further coated with a special ruthenium trinuclear cyanide complex dye i.e., $[RuL_2(\mu\text{-}(CN)Ru(CN)L'_2)_2]$ where L is 2,2′ bipyridine, 4,4′ dicarboxylic acid and L′ is 2,2′ bipyridine. In this Ru-dye, a new concept of antenna-sensitizer molecular device was employed. The antenna fragment of the dye has the role of absorbing strongly the incident light and transferring efficiently the electronic energy to sensitizer fragment, which then gives charge (electron) injection into the $TiO_2$ semiconductor. Thus both the light directly absorbed by the sensitizer and that absorbed by the antenna can be used to effect charge injection. Another critical part in the design of this cell is to prepare nanoparticles of $TiO_2$ semiconductor deposited on conducting glass substrate. These nanostructured particles increase the effective surface area of the semiconductor film by at least 1000 times. This extremely high surface area $TiO_2$ electrodes adsorb very large amount of Ru-dye on the electrode surface, thereby increasing the quantum yield and conversion efficiency of this dye-based PEC solar cell.

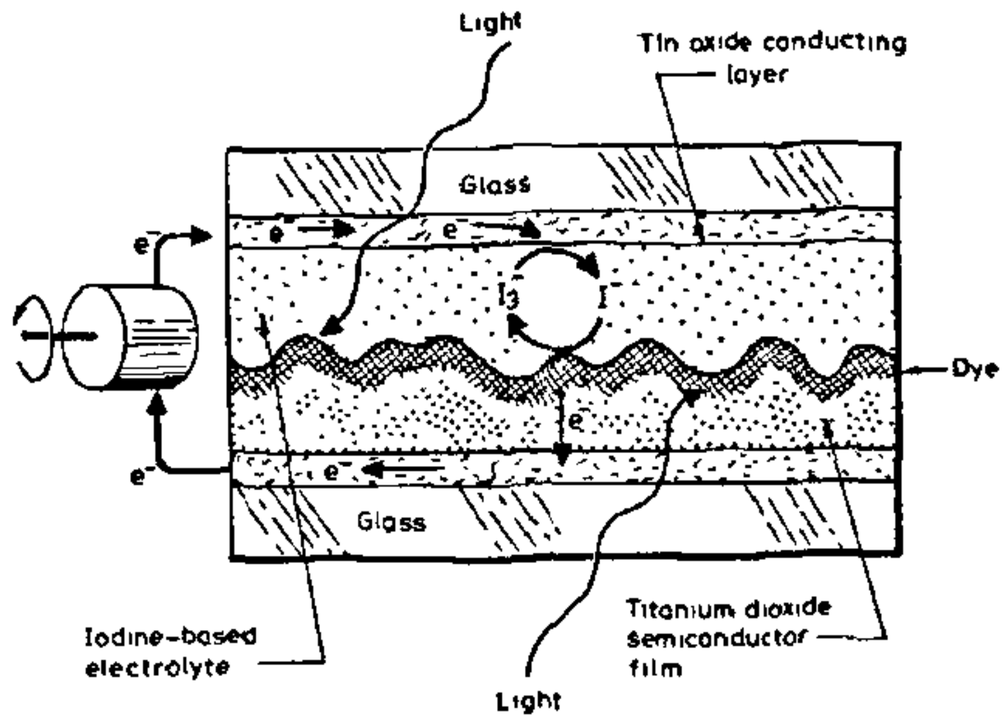


**Figure 7.** Schematic diagram of the new electrochemical photovoltaic cell termed as artificial leaf cell

This $SnO_2$ (glass)/$TiO_2$-dye//$I^-$, $I_3^-$//$SnO_2$(glass) cell acts as a renewable PEC solar cell and has solar-to-electrical conversion efficiency ($\eta$) of 7% under direct sunlight[15]. Under diffuse daylight the efficiency increased to 12%, indicating that under such conditions the cell is better than the conventional silicon solar cell.

**Table 2.** Some photoelectrosynthetic solar cells[2]

| Photoelectrode(s) | Type of cell | Products | Reactants | Energy cut-off (eV) |
|---|---|---|---|---|
| *n*-$MoSe_2$, *p*-InP(Pt) | *p-n* | $H_2$, $Br_2$ | HBr | 1.35 |
| *n*-$MoSe_2$, *p*-InP(Pt) | *p-n* | $H_2$, $I_2$ | HI | 1.35 |
| *n*-$MoSe_2$ | PE[a] | $H_2$, $SO_4^{2-}$ | $H^+$, $SO_2$ | 1.09 |
| *n*-$WSe_2$, *p*-$WSe_2$ | *p-n* | $H_2$, $I_2$ | HI | 1.20 |
| *p*-InP(Pt) | PAE[b] | $H_2$, $O_2$ | $H_2O$ | 1.35 |
| *p*-GaP | PC | $NH_3$ | $N_2$, $H^+$ | 2.3 |
| *p*-GaP | PE | $CH_3OH$, $CH_2O$ | $CO_2$, $H^+$ | 2.3 |
| *n*-$TiO_2$, *p*-GaP | PE | $H_2$, $O_2$ | $H_2O$ | 3.0 |
| *n*-$SrTiO_3$ | PE | $H_2$, $O_2$ | $H_2O$ | 3.2 |
| *p*-$LuRhO_3$, *n*-$TiO_2$ | *p-n* | $H_2$, $O_2$ | $H_2O$ | 3.0 |
| *p*-InP, *n*-$WSe_2$ | *p-n* | $S^{2-}$, $I_2$ | $S_x^{2-}$, $I^-$ | 1.35 |
| p-InP | PAE | $H_2$ , $O_2$ | $H_2O$ | 1.35 |
| *p*-InP | PAE | $HCO_2H$ | $H^+$, $CO_2$ | 1.35 |
| *n*-$TiO_2$ | PC[c] | $Ph_2C{=}O$ | $Ph_2C{=}CH_2$, $O_2$ | 3.0 |
| *p*-CdTe | PC | CO | $CO_2$, $H^+$ | 1.5 |
| *n*-$Fe_2O_3$, *p*-$Fe_2O_3$ | PE | $H_2$, $O_2$ | $H_2O$ | 1.2 |
| *n*-$Ru_x Fe_{1-x} S_2$ | PAE | $H_2$, $O_2$ | $H_2O$ | 1.2 |
| *n*-$TiO_2$ (Ti(I) / Ti(III)) | PC | propylene oxide | $CH_2{=}CH_2CH_3$ | 3.0 |
| *n*-CdS (polymer $RuO_2$) | PAE | $O_2$ | $H_2O$ | 2.5 |

[a] PE = photoelectrolysis; [b] PAE = photoassisted electrolysis; [c] PC = photocatalytic.

The normal loss mechanism, such as recombination normally encountered in semiconductor photoconversion devices involving carrier excitations across band gap has been minimized in this cell.

Some details about the synthesis of the nanostructured (particle size ~ 3–5 nm) $TiO_2$ semiconductor film having a very high effective surface area, and the synthesis of the trinuclear-Ru-cyanide complex have been briefly described by Vlachopoulos *et al.*[16] and Amadelli *et al.*[17]. Our recent efforts in this direction have led to the preparation of nanostructured $TiO_2$ (particle size 2–4 nm) having an extremely large surface area[18]. Further work on the development of new and highly quantum-efficient and cheap dyes may lead to the development of process scale-up for PEC solar cells.

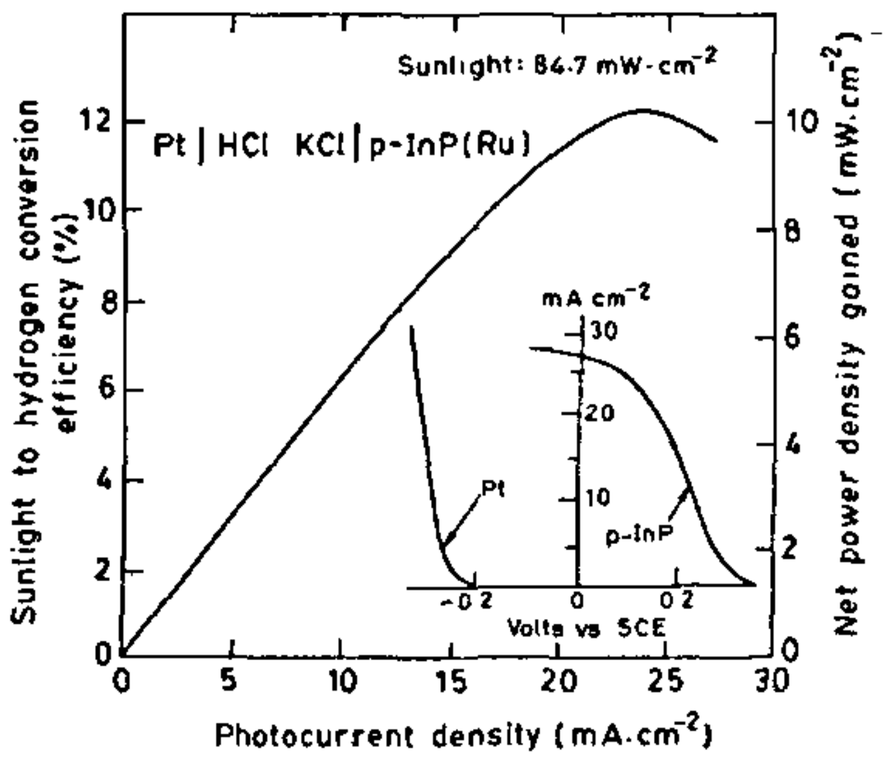


**Figure 8.** Solar-to-hydrogen conversion efficiency and power density gain at 84.7 mW/cm² sunlight as a function of photocurrent density. The gain is the product of the voltage difference between the Pt and p-type InP cathodes and the current density.

## Photoelectrosynthetic cells for light-to-chemical conversion

Some of the interesting and efficient photoelectrosynthetic cells are outlined in Table 2. Among the important photoelectrosynthetic cells, photoelectrochemical splitting of water into hydrogen and oxygen has been the main goal of semiconductor photoelectrochemistry since the demonstration of Fujishima and Honda (1972). Despite several papers reporting visible light-induced hydrogen production, up to now no semiconductor capable of direct splitting of water in a one-photon process is known besides $SrTiO_3$, $KTaO_3$ etc., which use only the UV part of the light spectrum. It has been suggested that an efficiency higher than that obtained in a one-photon water splitting is achievable using two photons in a system with two effective junctions of small band gap semiconductors. The two systems *p*-GaP/*n*-$Fe_2O_3$ and *p*- and *n*-$Fe_2O_3$ using *p/n* in addition to semiconductor/electrolyte contacts have been tested. Several double junction photoassisted electrolysis cells have been studied earlier[1, 2, 5].

### *Efficient photoassisted electrolysis*

Among the several hydrogen-generating photocathodes which have been studied, important materials include *p*-GaP, *p*-$LuRhO_3$ and *p*-Si, *p*-$WSe_2$ etc. Already, efficient

photocathode-based semiconductor liquid junction solar cell *p*-InP/$VCl_3$-$VCl_2$-HCl/C giving a $\eta$ value of 11.5% has been reported[2]. In the *p-InP* ($E_g \sim 1.35$ eV) based high efficiency photoassisted electrolysis cell, islands of ruthenium, rhodium or platinum have been electrodeposited on *p-InP up to 100 Å and the electrodes have* been etched in dil. acid. Typical performance of these cells has been shown in Figure 8. The Pt cathode starts to generate $H_2$ at –0.24 V vs SCE and reaches a current density of 20 mA-cm$^{-2}$ at $-0.31$ V. The *p*-InP photocathode starts to produce hydrogen at + 0.34 V vs SCE. Under 84.7 mW-cm$^{-2}$ sunlight, the cell operated *at a current density of 20 mA/cm*$^2$ and +0.15 V vs SCE. The anode voltages for Pt have been 0.98 at the threshold and 1.12 V at 20 mA/cm$^2$ (see Figure 8). The maximum solar-to-chemical conversion (the equivalent of the maximum power point in a solar cell) is at 23.5 mA and at +0.11 V vs SCE or 0.4 V versus an $H_2$-generating Pt electrode operating at similar current density. This translates to a gained power density of 10.1 mW/cm$^2$ or to a net hydrogen-production efficiency of 12% referred to sunlight (see Figure 8). This cell has *been described to be the most efficient system for* photoassisted electrolysis that uses a semiconductor/liquid junction[19].

*In* another study, a stable *oxide cathode*, *p-LuRhO*$_3$ has been reported to possess sufficient photopotential when used with *n*-$TiO_2$ anode to photoelectrolyze water with no externally applied potential. In recent years, research has been concentrated on silicon: starting with the combination of an electrolyte/*n*+/*p* or *n*+/*n*-Si electrode, *n*-Si/*p*-NiO(OH) heterojunction was added by Li and Wang. Tsubomura and coworkers used [*p-i-n-p-i-n*] stacks of amorphous Si and *p*-type cryst Si [*n-p-i-n-p-i-n* aSi:H] electrode combined with an $RuO_2$ counterelectrode to directly split water with an efficiency of up to 2.9%[20]. A similar *n-i-p-n-i-p-n-i-p* stack with directly painted $RuO_2$ on the anode and platinum islands on the cathode side used by Bockris and coworkers have reported 5% efficiency[21]. In another study, a *p*-InP has been decorated with platinum and combined with an *n*-type gallium arsenide electrode which has been protected against photocorrosion by depositing a thin film of Mn-oxide, has been employed to demonstrate significant increase in self-driven *photoelectrolysis of water. It has been indicated that the* two electrodes when placed together in a cell would spontaneously give rise to hydrogen and oxygen when photoirradiated with an intensity of ~1 sun. Evaluation of the solar conversion efficiency for production of *hydrogen and electricity showed a maximum total conversion efficiency of 8.2%, the conversion being* predominantly to hydrogen[22]. The Pt *n*-Si/Pt or Ir cathode and $n^+$ *p*-Si/$IrO_x$ (anode) system has been developed for HBr splitting, in which illumination was carried out from the back side of the semiconductor. The combined photovoltage of anode and cathode has been able to split HBr without any additional bias. With this *system, it has been demonstrated that it is possible to* build a compact solar energy storer. In yet another recent study, Si wafer has been coated with Ni or Co. *These studies suggest that the best corrosion resistance* was when Ni or Co have been sputtered on the *n*-Si surface, which gave technically applicable multilayer semiconductor electrodes on silicon for hydrogen production[23]. Solid polymer membrane of sulphonated *polytetrafluoroethylene has been used as solid polymer electrolyte for splitting water into* $H_2$ *and* $O_2$ *at* $SrTiO_3$ or $TiO_2$ photoanode. Quantum efficiency of 80% has been reported in the electrolysis of aqueous $H_2SO_4$ solution[24]. Photoelectrolysis of water, and in situ storage of hydrogen in the form of a fuel cell has been reported by Chandra *et al.*[14]

## Semiconductor-septum based photoelectrochemical solar cell

The work of Tien *et al.* on pigmented bilayer lipid membranes (BLM) suggests that energy transduction is possible even if semiconductor electrolyte contacts are made on both sides of the semiconductor. A recent attempt in this direction has been made by Tien and his coworkers, by constructing a PEC cell with a semiconductor separator. In the semiconductor-septum photoelectrochemical (SC-SEP, PEC) cell, the semiconductor (SC) septum electrode connects the two compartments containing two different redox electrolytes. In this system, the light-induced charge separation of electrons ($e^-$) and holes ($h^+$), across the photoactive septum electrode causes reduction on one side of the septum electrode and oxidation on the other. In the earliest SC-SEP, *PEC solar cell cadmium* chalcogenides in the configuration of CdS/Ti, CdS/Ni, CdSe/Ti, CdSe/Ni, $CdS_{1-x}Se_x$/Ti, $CdSe_{1-x}Te_x$/Ni etc. have been employed as semiconductor septum electrodes and a solar-to-electrical conversion efficiency of >10% *and solar-to-chemical energy* conversion efficiency of ~ 10% has been reported[25–26]. Tien *et al.* in their initial studies employed pellets of CdS, CdSe, *p*-$Fe_2O_3$, *n*-$Fe_2O_3$, and thin film electrode materials of CdS/Ti, CdSe/Ti, CdSe/Ni, etc. as semiconductor *septum electrodes. Thin films of CdS or CdSe were* slurry-painted on Ti or Ni metals. Initially they prepared a dual electrolyte-semiconductor contact CdSe-based SC-SEP, PEC cell, and demonstrated the possibility of generating high photovoltage and photo*current of 1 to 1.24 V and 25* mA/cm$^2$. They also employed CdSe pellets for photoreduction of metal ions like Sn, Fe, Cu, Ag, Pt, Pd etc from solutions in the dark compartment of semiconductor septum-based PEC solar cell. From these studies, they have suggested that this

**Table 3.** Photoelectrochemical characteristics of CdSe/Ti-based SC-SEP, PEC cell: Pt / 1M 3S//CdSe/Ti// Redox electrolyte in dark compartment / Pt[32]

| Electrolyte in dark compartment (0.1 M) | Flatband potential $V_{Fb}$(V) vs SCE | $E_{redox}$ of electrolyte in dark compartment (V) vs SCE | Theoretical photovoltage $V_{OC}$ (Theor.)/V | Experimental photovoltage $V_{OC}$ /V | Short-circuit photocurrent $I_{SC}$ /mA cm$^{-2}$ |
|---|---|---|---|---|---|
| NIL | – 1.0 | – | – | 0.64 | 6 |
| $SnCl_4/SnCl_2$ | – 1.0 | – 0.17 | 0.83 | 0.82 | 2 |
| $K_4[Fe(CN)_6]$/ $K_3[Fe(CN)_6]$ | – 1.0 | 0.22 | 1.22 | 1.0 | 3.5 |
| KI / $I_2$ in 1 M $Na_2SO_4$ | – 1.0 | 0.29 | 1.29 | 1.20 | 2.5 |
| $FeCl_3$ / $FeCl_2$ | – 1.0 | 0.53 | 1.53 | 1.14 | 6 |
| $AgNO_3$ / Ag | – 1.0 | 0.50 | 1.50 | 1.42 | 20 |
| $Ce(SO_4)_2$ /$Ce_2(SO_4)_3$ | – 1.0 | 1.19 | 2.19 | 1.22 | 2 |

**Table 4.** Photoelectrochemical characteristics of $TiO_2$ /Ti-based SC-SEP solar cell: Pt, 1 M NaOH, $SCE_{(A)}$ //*n*-$TiO_2$ /Ti//$SCE_{(B)}$ electrolyte, $AE_{(B)}$ $V_{Fb}$ of the semiconductor: – 0.94 V vs SCE[31]

| Electrolyte in compartment B (0.1 M) | Auxillary electrode in compartment B | $E_{redox}$ of electrolyte in compartment B $V$ ($V_s$ SCE) | Theoretical photovoltage (V) | $V_{OC}$ dark $V_{OC}$ (d) $V$ ( $V_s$ SCE) | $V_{OC}$ light $V_{OC}$ (l) $V$ ($V_s$ SCE) | Photovoltage $V_{OC} = V_{OC}$ (l) – $V_{OC}$ (d) $V$ | Short-circuit current $I_{SC} = I_{SC}$ (l) – $I_{SC}$ (d) mA-cm$^{-2}$ |
|---|---|---|---|---|---|---|---|
| – | – | – | 0.8 | – 0.2 | – 0.9 | 0.7 | 5 |
| NaOH | Pt | – | 0.8 | – 0.25 | – 0.98 | 0.73 | 4 |
| $AgNO_3$ | Pt | 0.53 | 0 | 0.42 | 0.42 | 0 | 0 |
| – | – | – | 0 | 0.24 | 0.24 | 0 | 0 |
| $SnCl_2$ / $SnCl_4$ | Pt | – 0.22 | 0.72 | – 0.26 | – 0.88 | 0.6 | 0.1 |
| $CuCl_2$ / CuCl | Pt | – 0.2 | 0.74 | – 0.24 | – 0.9 | 0.66 | 0.8 |
| $CuSO_4$ in 1 M KCl | Pt | 0.17 | 1.01 | 0.02 | – 0.92 | 0.94 | 1 |
| $K_4Fe(CN)_6$ / $K_3Fe(CN)_6$ | Pt | 0.19 | 1.13 | 0.14 | – 0.86 | 1.00 | 1.5 |
| $Cu(NO_3)_2$ in 1 M $KNO_3$ | Cu | 0.25 | 1.19 | 0.10 | – 0.94 | 1.04 | 0.25 |
| KI / $I_2$ in 0.5 M $Na_2SO_4$ | Pt | 0.27 | 1.21 | 0.2 | – 0.92 | 1.12 | 3.5 |
| $FeCl_3$ /$FeCl_2$ | Pt | 0.50 | 1.44 | 0.24 | – 0.94 | 1.18 | 0.5 |
| $AgNO_3$ in 1M $KNO_3$ | Pt | 0.53 | 1.47 | 0.3 | – 0.90 | 1.2 | 15 |
| $PdCl_2$ in 1 M KCl | Pd | 0.72 | 1.66 | 0.34 | – 0.94 | 1.28 | 9 |
| $H_2PtCl_6$ in 1 M KCl | Pt | 0.93 | 1.87 | 0.48 | – 0.92 | 1.40 | 12 |
| $Ce(SO_4)_2$ /$Ce_2(SO_4)_3$ | Pt | 1.19 | 2.13 | 0.6 | – 0.96 | 1.56 | 6 |

SC-SEP cell may be a good choice for photochemical reduction of metal ions and recovery of precious metals from mixtures or industrial wastes. In another study, *p*-$Fe_2O_3$ and *n*-$Fe_2O_3$ pellets were joined with silver epoxy to make a bipolar semiconductor septum electrode and this was used for water decomposition and hydrogen production[27]. In yet another study, Tien *et al.* produced hydrogen from sea water using semiconductor septum electrode of CdSe/Ti and CdSe/Ni with visible light of $\lambda > 390$ nm. These findings of Tien *et al.* demonstrate that SC-SEP cell can be used not only to convert visible light ($\lambda > 390$ nm) of solar spectrum to electricity but into stored chemical energy in the form of hydrogen as well. Following similar lines, several others[2, 3, 28-30] reproduced the findings of Tien *et al.* Xiao and Tien[27] developed a star-like configuration of SC-SEP cell and demonstrated efficient hydrogen production from water.

The preliminary and subsequent studies of Tien and coworkers appear to lack the investigation on stability of CdSe/Ti, SC-SEP-bearing PEC solar cells and exploration of other possible semiconductor-septum electrode-bearing PEC solar cells. Keeping these in view, we have investigated the synthesis, structural and photoelectrochemical characterization of SC-SEP, PEC cells, based on CdSe/Ti and $TiO_2$/Ti semiconductor septum electrodes. The *n*-CdSe/Ti septum electrodes were prepared by the slurry painting method[26, 32]. The *n*-$TiO_2$/Ti septum electrode was prepared by anodically oxidizing Ti sheets under high current density and glow discharge conditions[31]. The cell design, fabrication and characterization methods of SC-SEP, PEC cells have been described in detail elsewhere[31, 32]. The electrolyte in the illuminated compartment facing $TiO_2$ side of $TiO_2$/Ti septum electrode was chosen to be 1 M NaOH, and 1 M ($Na_2S$ + NaOH + S) ( ≡ 1M3S) was used as the

electrolyte facing CdSe of CdSe/Ti electrode. The various electrolytes used in the dark compartment facing Ti surface of SC-SEP electrode were 0.1 M $SnCl_2|SnCl_4$, $CuCl_2|CuCl$, $CuSO_4$, $K_4Fe(CN)_6|K_3Fe(CN)_6$, $Cu(NO_3)_2$; $PdCl_2$, $H_2PtCl_6$, and $Ce(SO_4)_2|Ce_2(SO_4)_3$. In addition, other acidic electrolytes of 1 M $K_2SO_4$, $Na_2SO_4$, $(NH_4)_2SO_4$ were used in the dark compartment for hydrogen production experiments. The photoelectrochemical characteristics i.e., $V_{OC}$, $I_{SC}$ etc. of various cells having different electrolytes in the dark compartment were measured and given in Tables 3 and 4.

Figure 9 shows the current-voltage ($I$–$V$) characteristics of Pt, I M 3S//CdSe/Ti and Pt, 1 M 3S//CdSe/Ti//0.1 M $AgNO_3$ Pt cells, giving photovoltage ($V_{OC}$) and short circuit current ($I_{SC}$) of 0.64 V, 6 mA-cm$^{-2}$ and 1.42 V, 20 mA-cm$^{-2}$ respectively. To monitor the stability of this SC-SEP cell, the power output characteristics of the cell were measured under prolonged PEC operation for 100 h. In Pt, 1 M-3 S//CdSe/Ti//0.1 M $AgNO_3$, Pt cell; after 100 h, the power output of the cell decreased from $V_{OC}$ and $I_{SC}$ of 1.42 V, 20 mA-cm$^{-2}$ to 1.3 V, 13 mA-cm$^{-2}$ respectively. The PEC output parameters ($V_{OC}$ and $I_{SC}$) could be restored with the modification of polysulphide electrolyte by the addition of 0.1 M Se[32]. Figure 10 shows the current-voltage ($I$–$V$) characteristics of Pt, 1 M NaOH//$TiO_2$/Ti, and Pt, 1 M NaOH//$TiO_2$/Ti//0.1 M $AgNO_3$ Pt cells, which gave $V_{OC}$, $I_{SC}$ of 0.7 V, 6 mA-cm$^{-2}$ and 1.2 V, 15 mA-cm$^{-2}$ respectively. The results in Tables 3 and 4 confirm that when redox couples of higher $E_{redox}$ potential are added into the dark compartment, keeping ingredients of the illuminated compartment unchanged, there is an increase in the photovoltage of the SC-SEP, PEC cell, as compared to single compartment PEC cell (see Figures 9 and 10). Based on these findings, a schematic band diagram and probable reaction mechanism have been proposed[31]. The short circuit photocurrent characteristics of this cell monitored under prolonged PEC operation revealed that SC-SEP cell is quite stable, with negligible change in its structural, compositional and power output characteristics. This new configuration of SC-SEP, PEC solar cell, which promises to yield high power output and therefore high conversion efficiency, deserves further study in regard to the electrode/solution junction potentials, capacitances and other characteristics.

## Recent studies in photoelectrochemical solar cells

There has been renewed interest recently in the photoelectrochemical conversion of solar energy for producing electricity, chemicals and their utilization in cleaning hazardous chemicals (e.g. oil slicks) and has rekindled explorations in this field. Several efforts have been made worldwide to develop high efficiency PEC solar cells on an economically viable basis. Glimpses of recent developments will be outlined in the following.

### *New semiconductor electrode materials*

A wide variety of pure and mixed oxides, chalcogenides, pnictides etc., have been examined for possible use as photoelectrodes in PEC cells. Some of these materials are listed in Table 5.

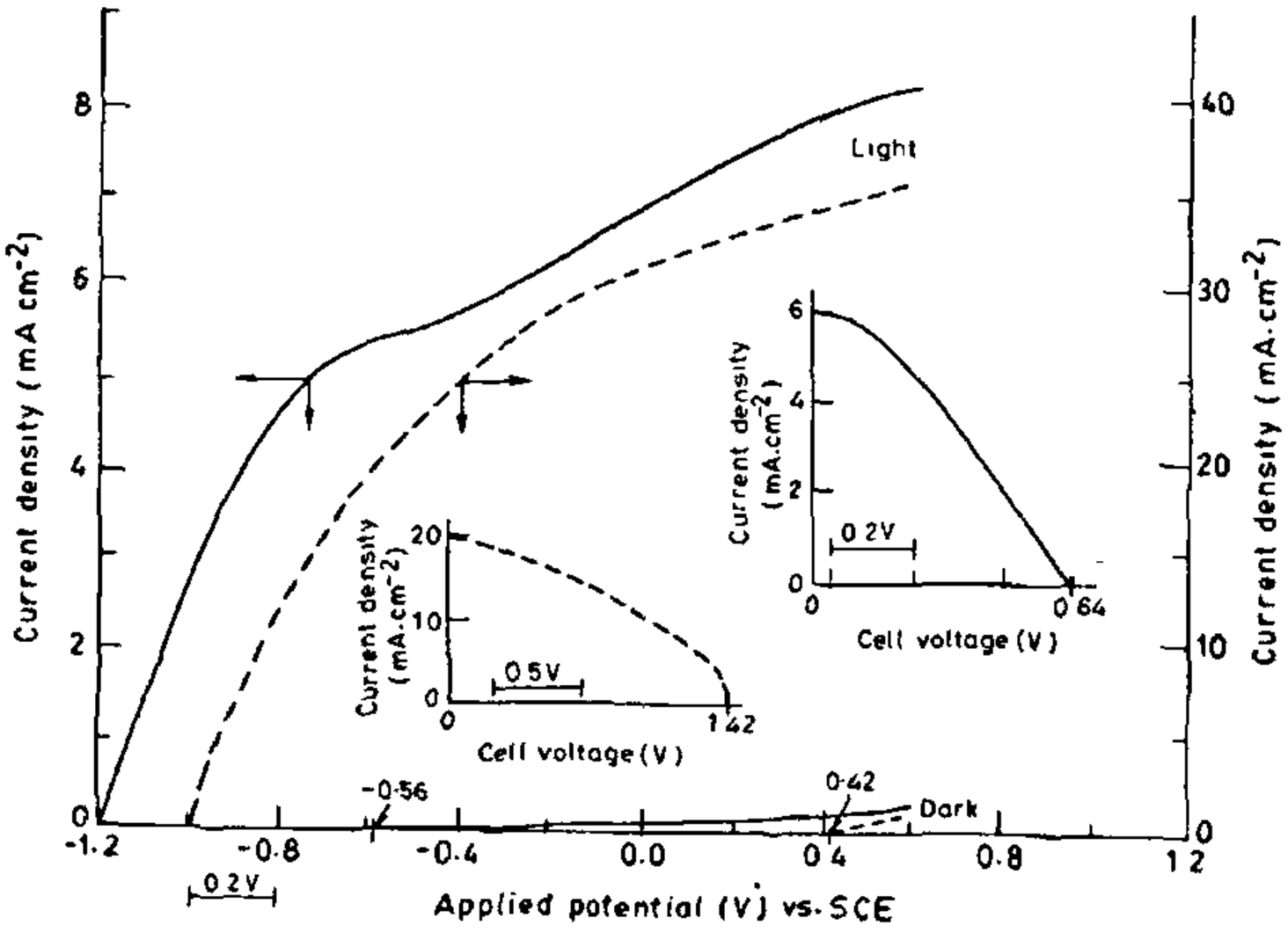


**Figure 9.** Current-voltage ($I$–$V$) characteristics of photoelectrochemical cell Pt, 1 M 3S//CdSe/Ti and Pt, 1 M 3S//CdSe/Ti//0 1 M $AgNO_3$, Pt cell (inset shows power characteristics) (see text).

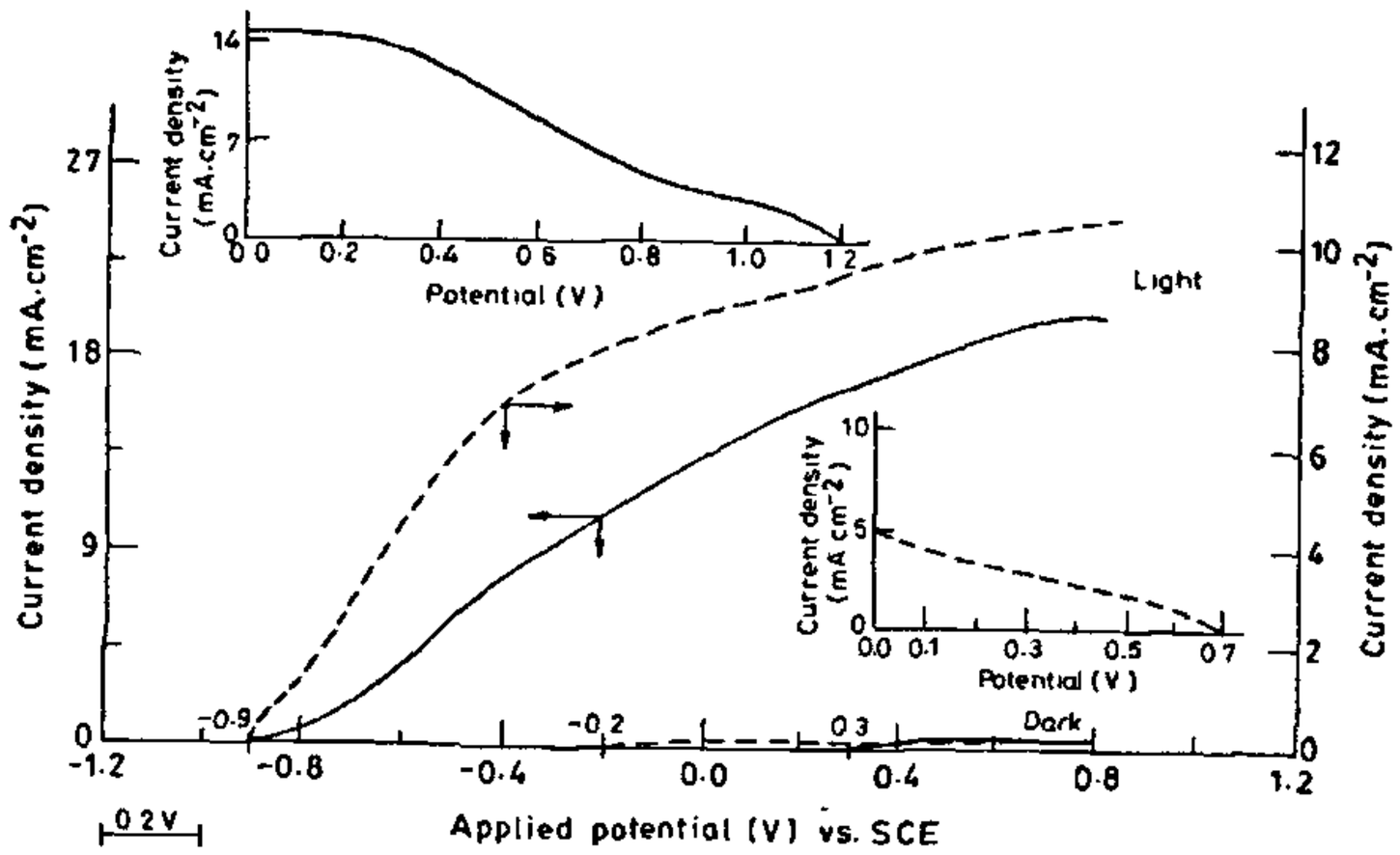


**Figure 10.** Current-voltage ($I$–$V$) characteristics of Pt, 1 M NaOH//$TiO_2$/Ti cell and Pt, 1 M NaOH//$TiO_2$/Ti//0.1 M $AgNO_3$, Pt cell under dark and illumination (inset shows power characteristics) (see text).

**Table 5.** Some of the new semiconductor photoelectrode materials studied in recent years

| Material | References | Material | References |
|---|---|---|---|
| $p$-$Mo_{0.50}W_{0.5}Se_2$ , $p$-$Mo_{0.2}Wo_{0.8}Se_2$ | Smstad[33] | SiC | Osgod *et al.*[42] |
| $Zn_3In_2S_6$ | Poulios *et al.*[34] | TiN | Massiani *et al.*[43] |
| $p$-$CuInSe_2$ | Lincot[35] | $Re_{60}X_8Br_2$ (X = S, Se) | Tributsch *et al.*[44] |
| $CuIn_{0.75}Al_{0.25}Se_2$ | Lewerenz[36] | Porous Si | Koshida *et al.*[45] |
| $CdSe_{0.65}Te_{0.35}$ | Gutierrez[37] | Amorphous Si | Gutierrez *et al.*[46] |
| $CuGaSe_2$ | Kessler[38] | $MnMoO_4$ , $YBaCuO_3$ | Kharat *et al.*[47] |
| $CuIn_{11}S_{17}$ | Basaveswaran *et al.*[39] | p-GaP | Kaname Ito *et al.*[48] |
| InP Zeolitecage | Yoneyama *et al.*[40] | GaSb-AlGaAsSb, InGaAsSb | Shou Yun Lu *et al.*[49] |
| $n$-$ZnIn_2S_4$ | Savadogo *et al.*[41] | | |

### *Surface modification of known photoelectrode materials*

Several attempts have been made to stabilize the low band gap semiconductor electrode materials. Recently, a very thin discontinuous layer of metals such as Pt, W or Mo has been deposited on Si and a high photocurrent of 20 mA-cm$^{-2}$ of reasonable stability has been reported. GaAs and $CuInSe_2$ electrodes have been suitably modified by coating with thin oxide layers to give enhanced stability and better PEC performance. Polybiothiophene (PBT), polystyrene and polypyrrole films have been photoelectrochemically grown on CdS and CdSe, and the stability of the photoelectrodes has been enhanced. Recently, effects of metals like Ni, Pb, Al and Langmuir-Blodgett (LB) films of several organic compounds like coumarin have been studied. The short-circuit current of $n$-Si/Ni/LB3/$Fe(CN)_6^{3-\,4-}$/Pt PEC cell has been increased by 40% and its stability substantially increased[50]. Ultrathin layers of nanocrystalline semiconductors of $FeS_2$, $RuS_2$, $PtS_2$ etc. have been employed for sensitization of high band gap semiconductors like $n$-$TiO_2$[51]. Wide band gap metal oxide films of ZnO and $TiO_2$ were deposited on amorphous silicon and an increased stability of a-Si in electrolyte was reported[52]. Submonolayers of lead have been deposited on $n$-GaAs and enhanced PEC characteristics have been reported. Ultrafine metal islands of several metals (Pt, Ni, Au etc.) were deposited on Si photoelectrodes and its stability and PEC properties have been enhanced[53]. Polypyrrole has been photoelectrochemically deposited on $TiO_2$ enhancing its PEC properties. Thin film of indium hexacyanoferrate (III) has been deposited on CdSe for stabilizing its PEC characteristics. $n$-GaAS has been coated with $SrTiO_3$ and its PEC properties stabilized in the cell configuration of $n$-GaAs/$SrTiO_3$//$I_3^-$ , $I^-$//Pt cell[54]. $n$-Si was coated with $TiO_2$-$RuO_2$ films and the stability of the cell enhanced. $n$-Si was also coated with evaporated metal films of Ni, Pt, Ni/Pt and immersed in electrolyte solution of $Br_2/Br^-$ or $Fe(CN)_6^{4-\,3-}$ yielding an $V_{OC}$ and $I_{SC}$ of 0.5 V and 45 mA/cm$^2$ with high conversion efficiency of 12.3%. Pt was electrodeposited on $p$-Si to protect the photoelectrode during photosplitting of water. $n$-$MoSe_2$ was

grafted with polycarbazone for an extended life of the PEC cell. In addition, several other modifications of the photoelectrodes have earlier been attempted[24].

### *Photogalvanic cells and rechargeable PEC cells*

Photogalvanic cells use metal electrodes and produce electricity as a result of irradiation of light absorbing molecules in the solution. Albery *et al.* set a practical upper limit of about 4% solar energy conversion efficiency for photogalvanic cells. One photogalvanic cell of Pt (or $SnO_2$)/$Fe^{2+}$/$Fe^{3+}$, thionine, Leucothionine/Pt cell having an efficiency of 0.03% has been reported. Simultaneous generation of oxidized and reduced chemical species is possible in a suitably designed two-compartment photoelectrochemical cell, resulting in a storage device. The cell can be discharged in the dark, producing a current flow opposite to that during light-induced charging step. Keita and Udajo[55] reported power conversion efficiency of > 9% in the system of $n$-$WSe_2$/1 MKI + 0.1 $MI_2$ + 0.5 M $Na_2SO_4$/ $3.5 \times 10^{-2}$ M AQ + $3.5 \times 10^{-2}$ M $AQH_2$/C-based storage cell. They studied several photocathodic and photoanodic reactions in storage PEC cells, using sodium 9,10 anthraquinone-Zb, disulphonate (AQ) and numerous heteropoly acids (HPA) which are soluble in acidic water and have coupled with $n$-$MX_2/I^-$, $I_3^-$/Pt cell, and found them stable for long periods of operation. Another two compartment storage PEC cell has been developed by Kraljic *et al.* In the first half of this cell, photo-oxidation of a redox couple (compact complexes of EDTA) diethylene triamine pentaacetate (DTPA) etc. sensitized by sensitizing dye (flavin dyes etc.) occurs. In the second half cell, photoreduction has been achieved by addition of an electron donor (D) such as EDTA, DTPA etc. Two inert electrodes (Pt or Au) serve for measurements of electrochemical potential. In this, the best electrochemical performances have been obtained with flavin dyes (riboflavin, lumiflavin) whereas other classes of sensitizers (xanthenes, porphyrins, Ru-bipyridine complex etc.) have been found to be less efficient.

### *New configurations of PEC cells*

*Bipolar photoelectrodes and multiple electrode arrays for unassisted photolytic water splitting*: Studies of water photoelectrolysis with $TiO_2$ and Pt electrodes date from the work of Honda and Fujishima. As the potential developed by this cell is inadequate to drive the water splitting reaction at a useful rate, an external bias must be applied. Connecting several photoactive junctions in series will generate a sufficient driving force to decompose $H_2O$ to $H_2$ and $O_2$ without an external bias. Bard *et al.* constructed bipolar electrodes consisting of $TiO_2$ or CdSe film with a sputtered Pt backing and the series assembly of these into multiple arrays giving 3–3.6 V could split water when irradiated with light[56].

Another new configuration of heterogeneous electrochemical photovoltaic cell has been developed by Honda *et al.* which consisted of two separated cells having (i) CdS/polysulphide and (ii) oxidizing electrolyte/Pt. When both these cells have been connected through a salt bridge, a photovoltage of 2.0 V, which is 80% of the band gap of the semiconductor ($E_g$ ~ 2.4 eV), has been obtained[31].

*Semiconductor septum-photoelectrochemical solar cell*: Semiconductor septum-based PEC cells have recently generated a lot of interest in the study of PEC cells. Some of the recent findings of the pioneer workers and some of our own work was described in an earlier section of this article.

### *New experimental techniques*

Various new experimental techniques have been developed and applied to study the PEC behaviour. Some of them are (i) time domain spectroscopy (TDS) for capacitance measurements, (ii) double beam illumination ($h\nu \geq E_g$; $h\nu \leq E_g$) to study intrinsic semiconductors, (iii) electromodulated infrared spectroscopy for *in situ* measurements, (iv) laser spot scanning for correlation of grain boundaries and defects at the SC surface, (v) photothermal beam depletion technique for *in situ* observation and detection of unstable species during cell reaction, (vi) electrochemical photocapacitance spectroscopy (EPS) for identification of energy levels and concentration before and after surface modification of semiconductors and (vii) Raman spectroscopy to identify composition of modified surface.

Recently, microwave interfacial photoelectrochemical techniques have been developed to characterize and optimize photoactive interfaces and for tracking down *mechanisms responsible for charge carrier losses*[57]. Another technique aimed at improving the knowledge on the interrelation of surface structure and composition with photoactivity involves photoelectron spectroscopy (XPS) combined with *in situ* determination of photovoltages[57]. Time-resolved UV-vis spectroscopic technique has been suggested as a useful technique in photoelectrochemistry for detecting groups containing π-electrons, non-bonding lone-pairs of electrons, complex molecules and charge transfer complex molecules which exist widely in photoelectrochemical, electrochemical and bioelectrochemical systems[58]. Surface photovoltage spectroscopy (SPS) has been found to be sensitive to surface electronic properties of photoelectrode material and give information about the photoinduced charge transfer processes at molecular

semiconductor and gas/molecular semiconductor surface interface. Intensity-modulated photocurrent spectroscopy (IMPS) has been described to be the optical equivalent of ac electrical techniques and can be used to investigate the kinetic processes at semiconductor/electrolyte interface[59]. Laser scanning microprobe photoelectrochemical technique has also been described to be one of the important techniques to study photoelectrochemistry[24].

*Theory, models and mechanisms*

A Schottky barrier model was developed by Chandra *et al.* to explain the *I–V* characteristics and the fermi-level pinning observed in GaAs-based PEC cells. Mechanistic studies of etchpit formation by PEC etching were reported by Marce and Tenne, whereas a kinetic model for the quantized electron transfer from superlattice photoelectrodes ($GaAs/GaAs_{0.5}P_{0.5}$) was proposed by Nozik *et al.* Some theoretical investigations using spectrum-response-curve (SRC) have been carried out to investigate new materials for raising the energy conversion efficiency of PEC cells[60]. Several theoretical developments have been made to understand electron transfer (ET) interfaces at metal/liquid semiconductor/liquid, liquid/liquid, and ET at monolayer bridged interfaces[24].

*Nanocrystalline photoelectrode material-based PEC cells*

During the past decade, 'small particle or nanoparticle', research has become quite popular in various fields of chemistry and physics[61]. By 'small or nanoparticles' are meant clusters of atoms or molecules of metals and semiconductors ranging in size from < 1 nm to almost 10 nm or having agglomeration numbers from < 10 up to a few hundred, i.e., species representing the neglected dimension between single atoms or molecules and bulk materials. The interesting properties exhibited by these small particles including 'size quantization effects' make this an interesting new field of research. This small particle research is a new branch of colloidal science where photochemical, radiation, chemical and electrochemical methods and theories are applied. For example CdS particles > 6 nm absorb close to 515 nm (2.4 eV), and with decreasing size, the absorption threshold shifts to shorter wavelength (2.2 eV). This effect is known as size quantization effect[61]. Several photophysical and photoelectrochemical studies of nanoclusters of $Fe_2O_3$, $Mn_2O_3$, $Cr_2O_3$, $Co_2O_3$, PbS, CdS, $TiO_2$ etc. have been reported. Size-quantized nanocrystalline photoelectrodes of CdS, CdSe were studied in PEC cells[61]. Presently, several other studies have been carried out on nanoparticle-based PEC cells. In some recent studies, ultrathin (10–15 nm) semiconductor layers of $FeS_2$, $PtS_2$, $RuS_2$ etc. have been suggested as alternatives for sensitization of high band gap oxide semiconductor-based PEC cells. The advantages of such sensitization will be cheap and material-saving production of these ultrathin semiconductor films, small real oxide surfaces, and good preconditions for developing solid-state contacts. The nanoparticle-based semiconductor thin films can open a new era in the development of efficient PEC solar cells.

## Conclusions – Recent trends and prospects

A survey of available literature in the area of photoelectrochemical conversion of solar energy reveals that the principal thrust and recent trends are on two aspects of PEC cells: (i) development of materials i.e., discovery of new materials or modification of the known materials (ii) development of new PEC cell designs. In regard to the first, comparatively less encouraging results have been obtained on the discovery of altogether new and efficient photoelectrode materials. Most developments have been on the modification of known materials with particular emphasis on improving their solar spectral response and increasing the stability under PEC conditions. Some new materials studied recently are listed in Table 5. Considering the requirements for an efficient and viable photoelectrode material, it appears that the most viable materials may be (i) the surface-modified versions of the presently known low band gap materials so that their stability and efficiency can be increased. For example, GaAs-$Os^{3+}/Ru^{3+}$, Si/polymer, Si/metals etc. and (ii) bulk modified forms of wide band gap oxide materials of the type $Ti_{1-x}V_xO_2$; $Ti_{1-x}Nb_xO_2$, etc. One important class of photoelectrode materials which may prove stable and viable because of their *d-d* phototransition, corresponds to the layered transition metal chalcogenides. Some of the newly studied chalcogenides and oxides are $FeS_2$, $RuS_2$, $PtS_2$, $Mo_2Re_4Se_8$, $Zn_2Mo_3O_8$, etc. whereas the layered chalcogenide semiconductor materials which are still being studied with a view to improving their PEC efficiency correspond to $WS_2$, $WSe_2$, $MoS_2$, $MoSe_2$, etc. An interesting and important new brand of materials recently under study are the nanocrystalline versions (sometimes called nanoparticles, quantum dots, Q particles... etc.) of the earlier known photoelectrode materials. For example, it has recently been found that the well-known photoelectrode material $TiO_2$, when synthesized in the new form (nanoparticle) possessing extremely high surface area (1000 times more), can improve the PEC properties of the cell. This appears promising and further efforts are necessary to exploit the full potential of the photoelectrode material in nanocrystalline forms. Some of the new materials which

possess potential promise as PEC photoelectrodes but which have been sparsely studied are porous silicon, Langmuir-Boldgett film modified semiconductors, some interesting organic semiconductors and high temperature superconductors etc.

Another aspect of the recent trends concerns the novel design of PEC cells. One simple variation leading to higher PEC conversion efficiency and long-term stability under PEC conditions correspond to electrolyte modification. Suitable modification of the electrolytes in *n*-CdSe, *n*-InP, *n*-$CuInSe_2$, *n*-$WSe_2$-based PEC cells has been reported to give encouraging results. More innovative PEC cell designs embody changes in conventional PEC solar cell configurations which correspond to single compartment and single electrolyte PEC cell. One of the new PEC cell designs correspond to semiconductor-septum-based PEC (SC-SEP, PEC) solar cell. The principle of this SC-SEP PEC cell has been borrowed from thylakoid membranes in chloroplasts. In the SC-SEP cell, the membrane separator has been replaced by semiconductor septum electrode. Although the concept of efficiency in this two compartment (dark and illumination compartments in SC-SEP cell are separated by SC-SEP electrode) PEC cell is not yet intelligible, the higher electrical output energy which is invariably higher than the single compartment cell, makes this new design of PEC cell very attractive. The SC-SEP electrode-based PEC cells presently studied are Pt, 1 M, –3 S//CdSe/Ti//0.1 M $AgNO_3$, Pt and Pt, 1 M NaOH//$TiO_2$/Ti//0.1 M $AgNO_3$, Pt.

Finally, it is expected that if both the foregoing aspects are properly coupled, a novel PEC solar cell may result. One PEC cell which may be taken to correspond to such an effort is the 'artificial leaf cell' developed by Gratzel *et al.* (1991), where the new photoelectrode is in the form of nanocrystalline $TiO_2$, coupled with a very efficient light-harvesting trinuclear Ru-cyanide dye (antenna-sensitizer complex). The recombination losses normally encountered in a conventional PEC cell are negligible in this new PEC cell and the electrolyte is sandwiched between two electrodes. This cell is novel in design in that it can be mounted as window panels of houses for direct and economical conversion of solar energy to electrical power. Further efforts in the development of new and efficient photoelectrode materials and novel PEC cell designs for eventually obtaining high conversion efficiency and long-term stability should form one of the priority areas on the renewable energy scenario.


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# Molecular assemblies for solar energy conversion – Biomimetic approach

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**Excitation energy migration followed by electron transfer forms the main components of natural photosynthesis. An understanding of these aspects is essential to reenact the primary processes in laboratory under conditions that are precisely repeatable. Here we describe the state of understanding of the natural process and several model systems designed to harvest solar energy and conversion to useful form of chemical energy. The molecular assemblies constituting the model systems offer a great advantage in terms of better comprehension of the mechanistic aspects and yield valuable information on the design of molecular photonic devices.**

NATURAL photosynthesis represents efficient energy conversion process. Excitation energy and electron transfer reactions form important primary processes in the natural photosynthesis. The transduction of light energy to chemical energy has been carried out by green plants and bacteria and in this process approximately $3.0 \times 10^{21}$ J of free energy is stored annually. An effective way to understand the mechanism of these primary processes is to conceptualize a photosynthesis unit (PSU), a composite of an antenna protein and a reaction centre (RC) protein. The antenna system is a light-harvesting pigment protein complex (LHC) comprising an ensemble of chlorophyll molecules which harvests the light energy extending from near-UV to near-IR. The radiant energy is transferred to specialized chlorophyll molecules called RC where the actual charge separation (CS) occurs. This trapped energy in the RC initiates a series of electron transfer reactions mediated through cytochromes till the final reductant NADPH is formed leading to the synthesis of ATP. Plant and bacterial systems have a judicious combination of LHC and RC. This is essential since the cross-section for the absorption of light by chlorophyll (Chl) molecule is small and thus if each RC contains a few Chl molecules, the turnover will be small even

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