the usage of poisonous chemicals such as hydrofluoric acid, boron trifluoride, arsenic, cadmium, tellurium and selenium compounds. The photoelectrochemical cell has not yet provided an answer to these problems in utilization of solar energy for power needs. There is hope that a solution may be eventually found through the photoelectrochemical route.

It is abundantly clear that India can ill afford to neglect effort in this area of Chemtrapse, if it wishes to avoid the danger of being in a pitiable position to borrow or buy the technology, when it is available. Just as in nuclear energy, where we got in at the beginning of the game, it would be visionary if we support effort at a viable level so that we contribute to the development of this futuristic area and keep abreast with the developments and hence be able to absorb and adapt quickly any significant developments, to our needs.

Artificial photosynthesis: Efficient dye-sensitized photoelectrochemical cells for direct conversion of visible light to electricity

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Significant advances have been made in recent years on the design of dye-sensitized photoelectrochemical cells for the direct conversion of visible light to electricity. One approach extensively developed in Lausanne involves textured, nanocrystalline TiO_2 membrane films as the charge separation/collection device and polypyridyl complexes of Ru as photosensitizers. Efficient solar cells have been made that give short-circuit photocurrents exceeding 17 mA/cm^2, open-circuit photovoltage of 700 mV and sunlight to electrical conversion efficiencies of 10%. Herein the principles and recent advances in this area are reviewed.

GROWING energy requirements of the modern society, dwindling fossil fuel reserves and the energy crisis of the seventies forced a number of research groups around the world to reassess their research priorities and orient them towards search for alternate energy resources. In this context, direct conversion of sunlight to electricity is a very attractive goal to pursue. Indeed considerable effort has been devoted to this area in the last three decades. Commercially available solar cells based on silicon[1] as the light-absorbing material are clear-cut examples of how one can harness sunlight.

In Lausanne, for many years, we have been interested in photochemical approaches for the conversion and storage of solar energy[2-5]. This goal led us to look at a variety of photochemical systems such as photoredox reactions of organic and inorganic dyes in the presence of finely divided redox catalyst, photochemical processes in organized media and photoredox reactions of semiconductor electrodes, dispersions and colloids. The topic of this review article is the outcome of cross-fertilization of our experience in these areas. It involves the design of an efficient photoelectrochemical cell for the direct conversion of light to electricity, one that is based on the concept of 'dye sensitization'[6-8]. It is the outcome of coordinated efforts of chemists of different interests and backgrounds – organic, inorganic, electrochemistry, colloids and interfaces, photochemistry and material science – a true interdisciplinary effort. The principles or dye-sensitized photoelectrochemical cells are outlined first followed by description of the features and performance characteristics of the solar cells.

Photoelectrochemical cells

A conventional photovoltaic/solar cell consists of two layers of a semiconducting material, usually Si. One is chemically treated to have an excess of electrons (*n*-type) and the other carries an excess of positively charged holes (*p*-type). When the two layers are brought into contact, electrons flow from the *n* to the *p* side, producing an electric field at the interface. The resulting

solid-state device is called a *pn* junction. When photons of light energy from the sun strike the semiconductor, they excite the electrons to higher energy levels, leaving 'holes' behind. These electron-hole pairs recombine rapidly unless the electrons are carried away quickly to create useful electric current. When electron-hole pairs are created near the *pn* junction, the build-in electric field forces the positively charged holes to the *p* side and the negatively charged electrons to the *n*-side. This movement of free charges causes a current between the positive *p* region and the negative *n* region. Together with the voltage difference, electric power is generated. This in essence constitutes the principles of commercially available solar cells based on silicon.

For many years chemists have been interested in examining two forms of photoelectrochemical cells for the direct conversion of light to electricity: semiconductor-based 'wet photovoltaic' or 'liquid-junction solar cells' and dye-based photogalvanic cells. The former one is a variation of the dry photovoltaic cell indicated earlier and its involves irradiation of a *n*- or *p*-type semiconductor immersed in a redox electrolyte. Absorption of photons of light energy equal or higher than the bandgap energy leads to creation of electron-hole pairs. Under the influence of space-charge layer present at the semiconductor-electrolyte interface, spatial separation of charges occur. In *n*-type semiconductor, for example, electrons flow to the back contact and holes move to the interface where they cause oxidation of redox reagents present in the solution. The conduction band electrons flow from the back contact of the illuminated semiconductor to the counter-electrode where the reduction (hence regeneration) of the redox reagents is achieved (an inversion situation occurs in cells composed of *p*-type semiconductors). The net effect of irradiation with light is driving electrons over the external circuit or conversion of light to electricity.

Over a thousand publications appeared in the seventies and eighties describing the results of investigations on a number of photoelectrochemical cells involving different semiconductors[9–11]. A number of cells with sunlight to electrical conversion efficiencies in the range of 20–25% have been identified[12, 13], particularly those based on low-bandgap materials such as Si, InP and WSe_2. High efficiencies however were obtained only with cells composed of single crystal materials. As with dry photovoltaic cells, efficient recombination of electrons and holes occur at smallest defect or impurity sites. For this reason, cells composed of polycrystalline materials give light conversion efficiencies of an order of magnitude smaller. Such low values ($\eta \leq 5\%$) render them unattractive as potential candidates for practical applications.

Photogalvanic cells are based on photoredox reactions of organic or inorganic dyes with electron donors or acceptors dispersed in solution (equation (1)):

$$S + A \xrightleftharpoons{h\nu} S^{+} + A^{-} \qquad (1)$$

and for this reason, they are more closer to the interests of photochemisits. The photogenerated redox products are selectively oxidized/reduced using suitable metal/catalytic electrodes. Here also the overall effect of light irradiation is conversion of light to electricity. In spite of the very simple design, performance of these cells is extremely poor[14, 15]. Cells of this kind never gave sunlight to electrical conversion efficiency (η) even 0.01%. There are several factors that are responsible for the very poor performance of the photogalvanic cells. It is useful to review them here, for they also play important roles in the dye-sensitized photoelectrochemical cells that we will discuss later. Firstly, the kinetics of electron transfer processes on electrodes are much slower as compared to rates of forward and back electron transfers in photoredox processes. Hence, reasonable currents can be obtained if and only if significant differences in the rate constants of forward and back electron transfer exists. If the back electron transfer, for example, is 100 times slower than in the forward direction, then, in the steady state, the equilibrium shifts to the right. With slight excess of photoredox products present under steady state photolysis conditions, even sluggish electrodes can compete for them. Ideally one would like to have a million-fold (or large) differences between the two rate constants. If such rate differences do not exist inherently in the chemical nature of the system, they must be introduced by external means. For many years, we and several others examined the possibility of using different types of organized media (micelles, vesicles, etc.) to introduce such rate differences.

Secondly, efficient performance of photogalvanic cells requires high 'selectivity' on the part of the electrodes to selectively interact with one particular oxidized/reduced species in solution without affecting others. If the electrodes are not selective, they only function as additional recombination centres for photogenerated charges and an overall decrease in the efficiency of the device. Electrode selectivity is a problem that worried electrochemists for many years and only very limited success has been obtained in few cases with modified electrodes. To circumvent some of these problems, chemists also examined photogalvanic cells composed of dyes coated onto different electrodes (metal, SnO_2, etc.)[16–18]. Here again, only the first few monolayers of the dye were effective in contributing to photocurrent. Thicker layers were either insulating or had problems such as concentration quenching of the excited state. It may be obvious from the discussions up and until now that, design of an efficient solar cells depends largely on the success in two key steps: conversion of sunlight (photons) to electrical charges (photoproducts) and the

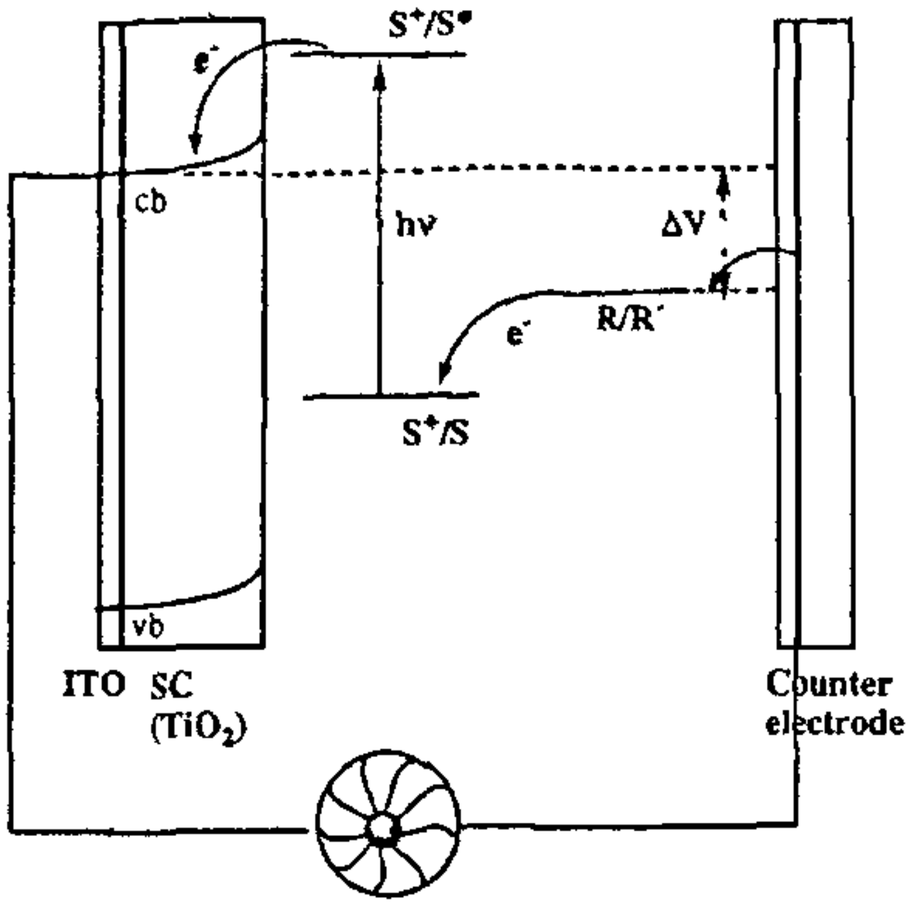


Figure 1. Principles of operation of dye-sensitized photoelectrochemical cell.

charge separation/collection step leading to photocurrent generation.

Dye-sensitized photoelectrochemical cells

The topic of this article, viz. dye-sensitized photoelectrochemical cell can be considered as a hybrid of the above two approaches, trying to put together in a single device the principal advantages of liquid-junction and photogalvanic cells[19–21]. Figure 1 shows schematically the principles of operation of these cells. The key component of the cell is organic or inorganic dyes adsorbed onto a textured, porous, membrane film composed of nanocrystalline TiO_2. Optical excitation of the adsorbed dye leads to injection of an electron from the excited dye to the conduction band of TiO_2. The oxidized dye is subsequently reduced back to its native state by external donor (redox couple) present in the electrolyte. The electrons in the conduction band trickles down the particles in the membrane film to arrive at the collector/back electrode. As in photogalvanic cells, the reduction (regeneration) of the donor is achieved at the counter electrode. The overall effect of visible light irradiation of the dye-coated electrode is to drive electrons over the external circuit or generation of electric current.

Figure 2 presents a cartoon of the actual cell design currently examined in our laboratories. The solar cell consists of two conducting glass electrodes sandwiched with an organic electrolyte containing the redox mediator (R/R^-). On one of the conducting glass (ITO) electrode is coated a few-micron thick porous, membrane film made of nanocrystalline colloidal TiO_2. The TiO_2 electrode is coated with the sensitizer by immersing it in

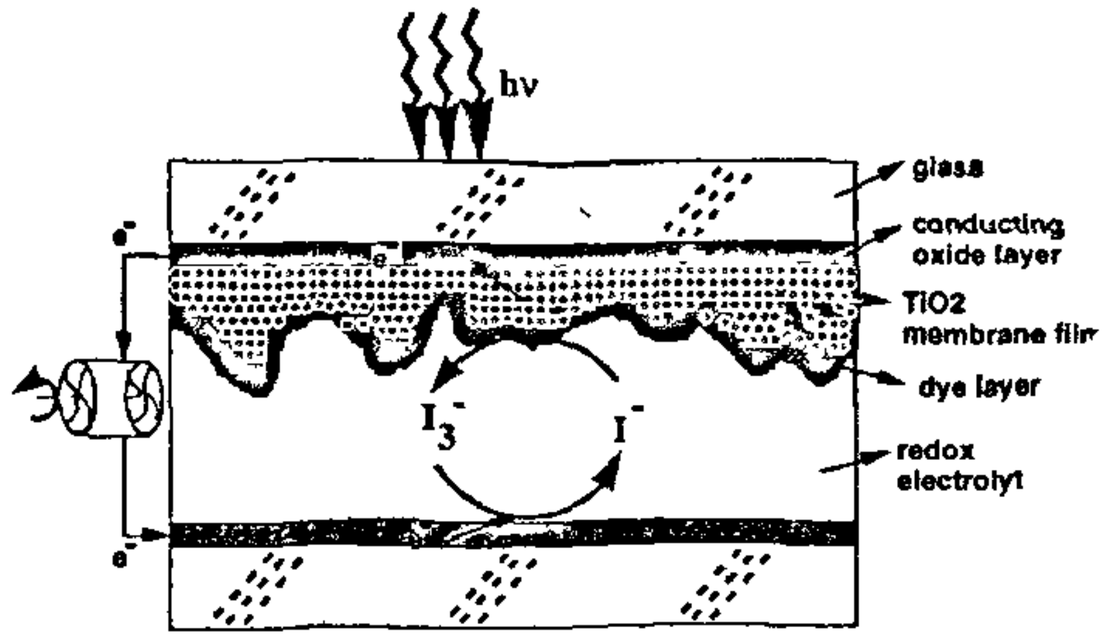


Figure 2. Schematic presentation of TiO_2-based dye-sensitized photoelectrochemical cell.

a solution containing the dye and subsequent drying. Due to the porous nature of the film, there is efficient uptake of the dye and visible light absorbances of ≥3 are readily obtained in such μm-size films. A mixture of I_2 and LiI constitutes the active mediator redox couple. A thin film of Pt mirror is sputtered onto the counter-electrode on the side exposed to the electrolyte.

Dye-sensitization of single crystal semiconductor electrodes has been examined earlier[7, 8] by a number of scientists including Tributsch, Gerischer, Memming, Honda and Tsubomura. The process is often considered as a model system for the commercially important photographic process, where adsorbed dyes are used to extend the spectral range of silver halide grains. The optimized efficiency of spectral sensitization of silver halide grain is known to be very high. In the present version, the dye-sensitized cell allows more efficient light harvesting (charge injection and collection) than what is possible in earlier model studies. Cells of this kind presently give very high white light to electrical conversion efficiency (η) (≥10%). We will elaborate on the reasons for the drastic enhancements in the performance as we go along. It may be fair to state that we came to examining photoelectrochemical cells of the present kind indirectly or through back door. Studies of photoredox processes on colloidal semiconductors showed how one can manipulate electron-transfer rates on semiconductors[22–24]. It was also found that the excited state of a number of adsorbed dyes was efficiently quenched by electron-transfer mechanisms.

Features and performance characteristics

The charge separation and collection process has been made efficient by using a textured, porous TiO_2 layer as the electron acceptor. Studies on the excited state decay by luminescence have shown that the charge injection step (equation (2)) is extremely rapid, occurring in time-

scales of ≤100 ps[25]. The back reaction between the electrons in the conduction band of TiO_2 and oxidized dye is extremely slow. Transient absorption studies indicate this process to occur on a timescale of 10–50 μs[26]. The architecture of the cell and the large differences in the forward and back electron transfer rates allow quantitative collection and separation of photogenerated charges.

The TiO_2 layer is prepared from nanocrystalline colloidal particles of TiO_2 through a well-controlled annealing process. The colloidal particles in turn are prepared via controlled hydrolysis of $TiCl_4$ or titanium *isopropoxide*. Charge separation and charge collection are two key steps in the processing of sunlight to electricity and both take place on the textured TiO_2 film. The structure and morphology of the layer play important roles and it is important that procedures for the preparation of the TiO_2 layer takes into account the delicate nature of this annealing process. Annealing is carried out so that there is physical contact between the various TiO_2 particles and the bulk resistivity of the film is low. Extensive annealing is also undesirable as it can cause sintering and reduce the porosity of the film. Over the years we have developed a recipe for reproducible formation of active TiO_2 layers and this is elaborated in detail in a recent publication from this laboratory[27]. The preparation of the TiO_2 film indeed is a delicate process and large differences in the performance of the film can be observed if strict adoption of the procedure is not enforced.

The performance of the cell has been examined using several criteria. The efficiency with which monochromatic photons are converted into electrons (photocurrent) is given by *incident photon-to-current conversion efficiency* (IPCE):

$$\text{IPCE} = \text{no. of electrons flowing through/no. of photons incident.} \quad (2)$$

This is determined by three factors: (a) light harvesting efficiency (depends on the spectral and photophysical properties of the dye): (b) the charge injection yield (depends on the excited state redox potential and lifetime) and (c) the charge collection efficiency (depends on the structure and morphology of the TiO_2 layer). The IPCE values were measured at various excitation wavelengths (leading to photocurrent action spectrum). The sunlight to electrical conversion efficiency (η) is obtained by integrating the IPCE values over the solar spectrum.

Figure 3 shows the photocurrent action spectra obtained for TiO_2 films coated with some Ru-complexes including $Ru(dcbpy)_2(SCN)_2$, in a thin-layer cell containing 0.03 M I_2 and 0.3 M LiI in acetonitrile as the redox electrolyte. The photocurrent was measured at short circuit where the TiO_2 film is poised at a potential

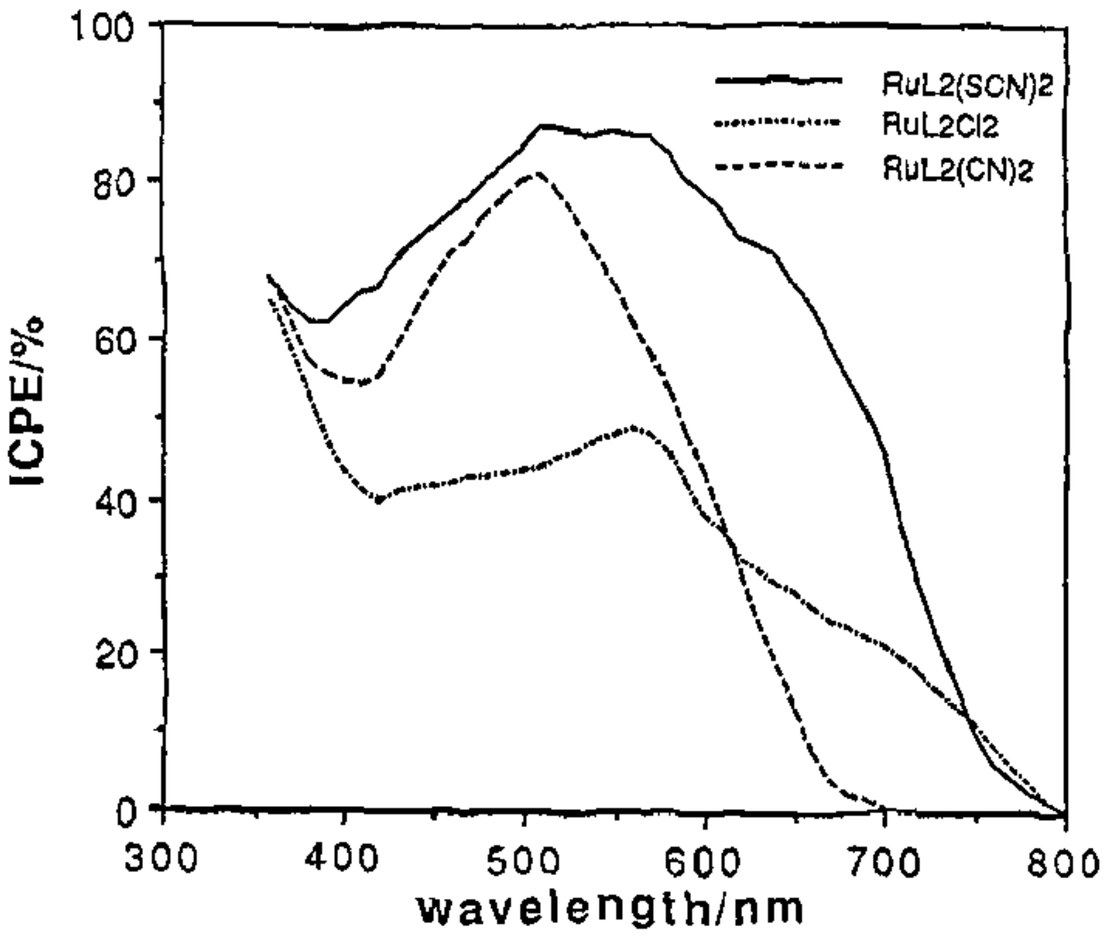


Figure 3. Photocurrent action spectra for a thin layer cell composed of nanocrystalline TiO_2 films coated with different Ru-complexes and a solution of 0.03 M I_2 and 0.3 M I_2 in acetonitrile: (——) $Ru(dcbpy)_2(SCN)_2$; (-.-.-.-) $Ru(dcbpy)_2Cl_2$ and (- - - -) $Ru(dcbpy)_2(CN)_2$.

Table 1. Performance characteristics of photovoltaic cells based on nanocrystalline TiO_2 films sensitized by cis-$[Ru(dcbpy)_2(SCN)_2]$

Light intensity (mW/cm²)	i_{sc} (mA/cm²)	V_{oc} (mV)	ff	η (%)
24.1	5.0	640	0.76	10.4
38.2	7.9	660	0.76	10.4
55.6	11.5	670	0.74	10.3
96.0	18.2	720	0.73	10.0

of around 0.1 V measured against SCE. The IPCE values exceed 80% in the wavelength range between 480 and 600 nm, attaining a plateau of 85–90% between 510 and 570 nm. The yields are uncorrected for the absorption and scattering (ca. 10–15%) by the glass. Taking this into account, the conversion of photon flux into electrical current is nearly quantitative in this wavelength domain. Table 1 presents data on the performance characteristics of the solar cell based on this photosensitizer. It may be recalled that the solar energy input at tropical mid-day is about 100 mW/cm². The overall light-to-electrical conversion efficiency is in the range of 10%. The short circuit current increases linearly with light intensity up to about 1 sun. This linearity implies that the photocurrent is not limited by diffusion of the triiodide ions within the nanocrystalline film up to current densities of at least 20 mW/cm².

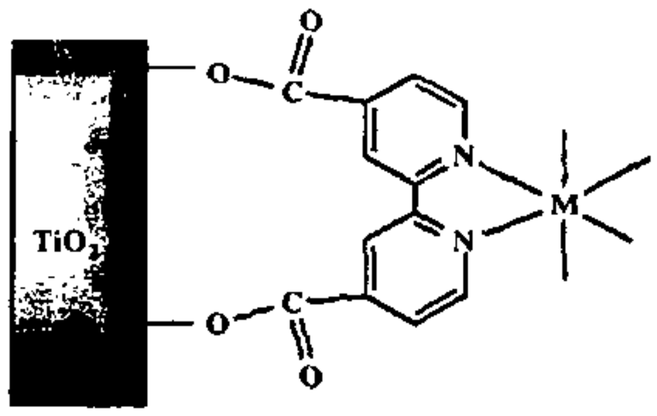
It should be mentioned that even the best performing dye, when coated onto a flat surface of a TiO_2 single crystal, gives very low photocurrent (few μA/cm²). In such a configuration only the first few dye layers are active (as in photogalvanic cells). The purpose of the

textured layer to enhance the surface area available for the TiO_2-dye intimate contact. The textured TiO_2 layer can be considered as an arrangement of small grape clusters tightly packed in a rectangular box. One would like to have optimal electrical contact between the individual TiO_2 particles (grapes) so that, the electrons (no matter which particle originally received it from the excited state of the dye) efficiently trickle down the matrix to arrive at the back collector plate (ITO layer in the present case). Isolated TiO_2 particles can act only as trap sites, for they cause quenching of the excited state of the dye without contributing electrons to the bottom collector plate.

Design of photosensitizers

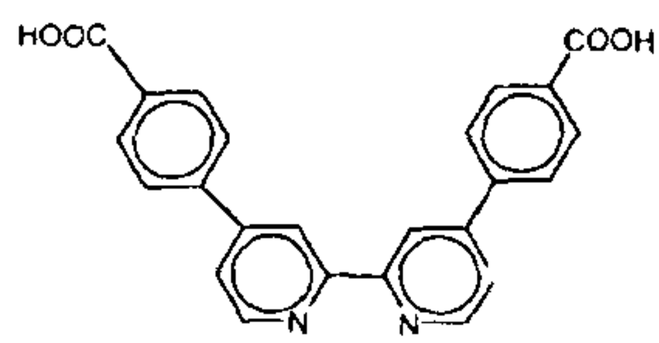
In the last five years, a wide variety of organic and inorganic dyes have been examined as possible sensitizer for the above cell. Other than good visible light absorption properties, a key requirement for the sensitizer is its excited state redox potential (cf. Figure 3). The excited state should have enough driving force thermodynamically to inject electrons into the conduction band of TiO_2. Figure 4 shows the structures of two polypyridyl complexes of Ru that have been found to be the most efficient sensitizers. One is a mononuclear Ru complex with two 4,4′-dicarboxy-2,2′-bipyridine (dcbpy) and two thiocyanato ligands[27]. The other is a trinuclear complex of Ru that has various Ru-bipyridyl units linked through the cyanide bridge[28, 29]. The central unit of this supramolecule is the lowest energy chromophore and this carries also the dcbpy unit.

It may be noted that in both cases, the key chromophore carries carboxylic groups. In fact, it turns out, the presence of a carboxylic group as a peripheral substituent enhances sensitization capacity of the dye, sometimes as much by a factor of 10. It is likely that some sort of surface chelation or derivatization takes place with the carboxylic group as shown below:



The electronic coupling is enhanced due to possible overlap of the π^*-orbitals of 4,4′-dcbpy with the $3d$ orbitals of Ti(IV). As an amphoteric oxide, the surface of TiO_2 carries a number of hydroxylic groups and surface chelation with a number of dyes has been documented earlier. The surface chelation is not irreversible for the dyes can be bleached out by stirring of the dye-coated electrode in alkaline solutions.

It has been found that the position of the carboxylic group in the 2,2′-bipyridine ligand also plays an important role. For example, the Ru complexes with 4,4′-disubstituted dcbpy ligand are more efficient sensitizers than those that have the two carboxylic groups in the 5,5′- or 6,6′-. Examination of the structures obtained upon geometry optimization procedures in MM2 calculations showed that only in the 4,4′-dcbpy complex, there are two carboxylic groups that have the right orientation for efficient chelation to the TiO_2 surface. In order to improve the molar absorbance of the dye, Ru-complexes were synthesized with phenyl group introduced before the carboxylic group of the 2,2′-bpy, as in the ligand 4,4′-dicarboxyphenyl-2,2′-bipyridine:



Even though the Ru-complex derived using this ligand did show increased molar absorbance, its performance as a sensitizer in the TiO_2-based solar cell was inferior to that of the parent complex with dcbpy ligand[30]. Clearly introduction of phenyl group as a spacer between the 2,2′-bipyridine and the chelating carboxylic group reduces the coupling between the electronic excited state of the dye and the semiconductor. The promoted electron resides primarily within the bpy ligand and does not go far into the carboxylic group.

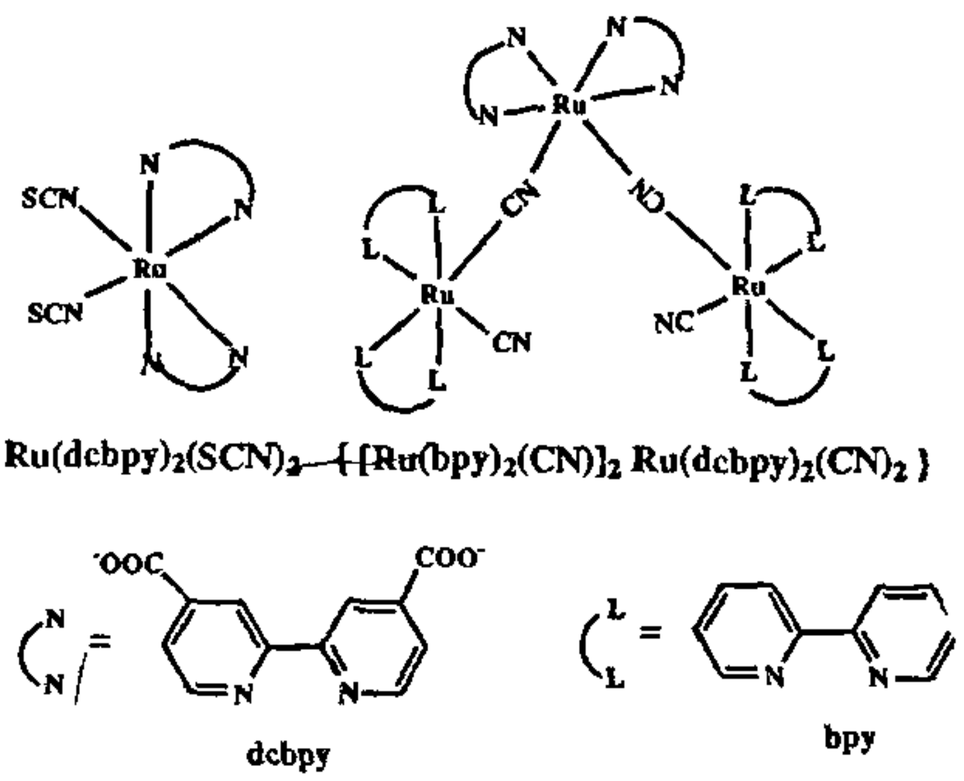


Figure 4. Structures of some of the most efficient photosensitizers: *The mononuclear complex, [Ru(dcbpy)₂(SCN)₂] and the cyano-bridged trinuclear complex,* [(CN)(bpy)₂Ru-CN-Ru(dcbpy)₂-NC-Ru(bpy)₂(CN)]

These studies show the subtleties involved in the excited state electron transfer to the conduction band of the semiconductor.

Optimization of the cell output

The performance of the cell has been optimized using two important procedures. One of them, viz. sputtering a shiny Pt mirror (≈2 μm thickness) on the counter electrode was mentioned earlier. This serves two purposes. A shiny mirror back reflects the light, increasing the efficiency of light absorption. A light-reflecting counter electrode increases the photocurrent yields in the long wavelength region (600–800 nm) where the absorption of the dye-coated electrodes decreases sharply. Such procedures are known in amorphous silicon solar cell technology. A conducting glass electrode itself is a poor catalytic electrode for the mediator redox couple and Pt islands improves considerably the electrochemical processes at the counter-electrode.

Exposure of the dye-coated electrode to 4-tert-butylpyridine was found to improve dramatically the fill factor (ff) and the open-circuit voltage (V_{OC}) of the device without affecting the short-circuit photocurrent (i_{SC}) in a significant fashion. This is illustrated in Figure 5 which presents current-voltage curves of the cell before and after such surface treatment. The untreated electrode gave i_{SC} = 17.8 mA/cm^2, V_{OC} = 0.38 V and ff = 0.48, corresponding to an overall conversion (η) of 3.7%. After the electrode is dipped in 4-*t*-butyl-pyridine, V_{OC} increases to 0.66 V, ff to 0.63 and η to 8.5%. The increase in the open-circuit voltage and fill factor is due to the suppression of the dark current at the semiconductor electrolyte junction. The effect of substituted pyridine can be rationalized in terms of adsorption at the TiO_2 surface blocking surface states that are active intermediates in the heterogeneous charge transfer.

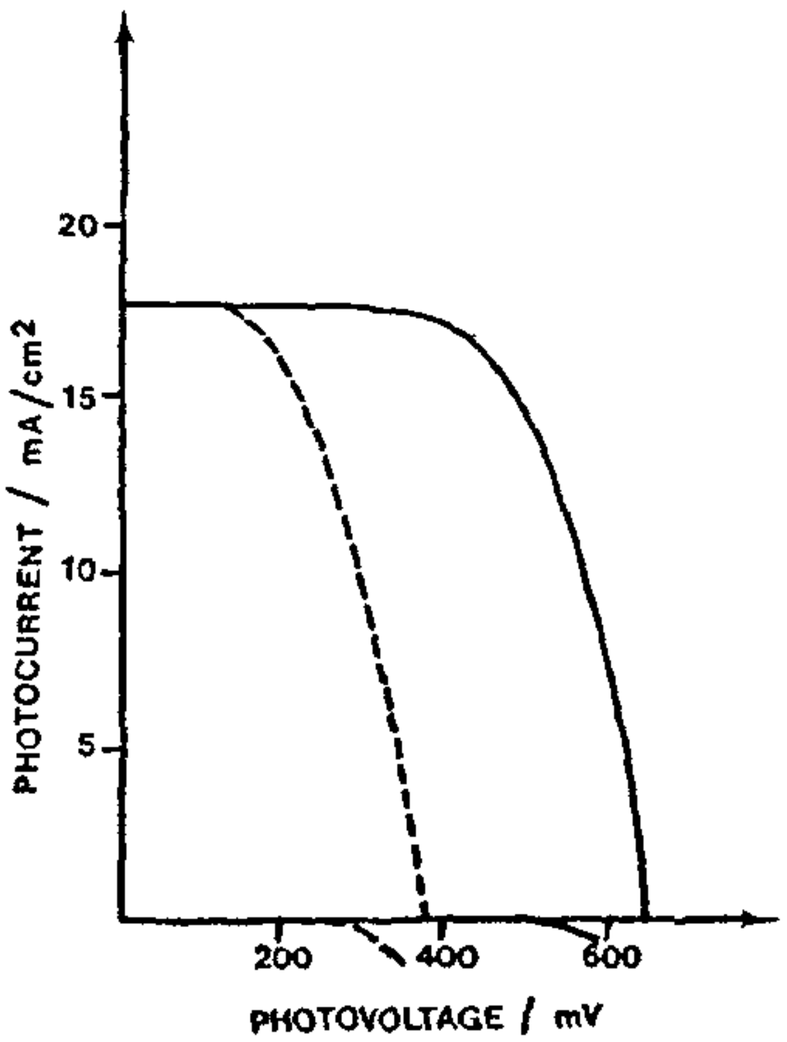


Figure 5. Effect of treatment of the dye-coated electrode on the photocurrent-potential characteristics of a cell based on colloidal TiO_2, $Ru(dcbpy)_2(SCN)_2$ as the sensitizer and I_2/I^- as the redox mediator. (- - - -) untreated electrode; (——) same electrode after dipping for 15 min in 4-*t*-butylpyridine after dye coating.

Light energy harvesting in polynuclear complexes

Polypyridine complexes of transition metal ions of d^6-electronic configuration (such as Ru(II), Os(II), Re(I),..) show strong visible light absorption properties. The lowest electronically excited state is invariably metal-to-ligand charge transfer (MLCT). The MLCT excited state is emissive in fluid solution, fairly long lived and undergoes redox reactions with a number of electron donors and acceptors. Extensive literature is available on the 'tunability' of photophysical and redox properties[31–33]. For these reasons we chose to examine a large number of transition metal polypyridine complexes as potential sensitizers.

The tunability of visible light absorption was examined[34] in a series of mixed ligand complexes of the type $[Ru(dcbpy)_2(X)(Y)]$ where X and Y are electron-rich non-chromophoric ligands or 2,2′-bi-pyridines with donor substituents. In these complexes, the lowest excited state is Ru → dcbpy CT. The auxiliary ligands allow tuning of the energy of the Ru → dcbpy CT excited state by increasing the charge density at the metal centre. Increasing the charge density at Ru raises the energy of the donor (t_{2g}) level, thereby decreasing the energy of the associated MLCT transition. Figure 6 illustrates schematically this principle. In the three complexes $Ru(dcbpy)_3$, $[Ru(dcbpy)_2(DEA\text{-}bpy)]$ and

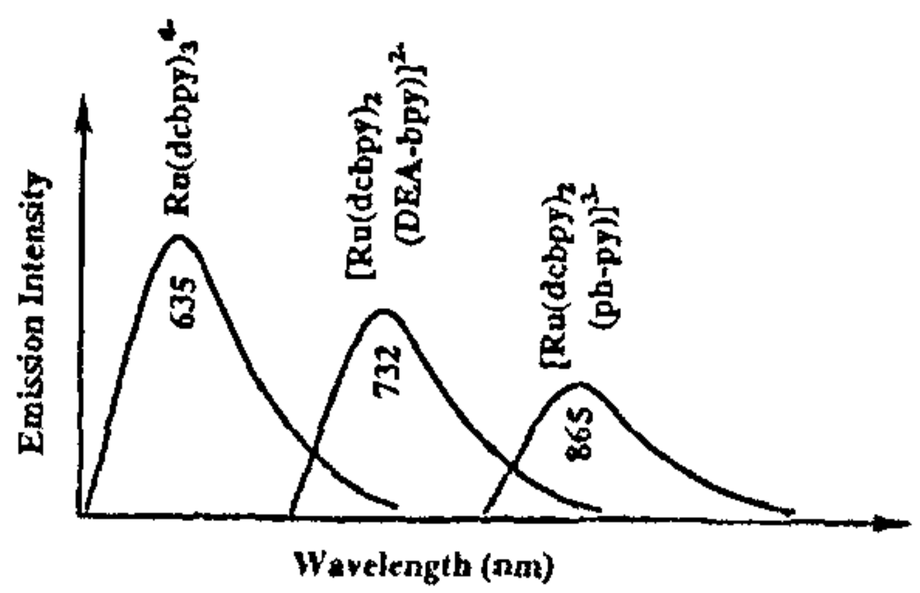
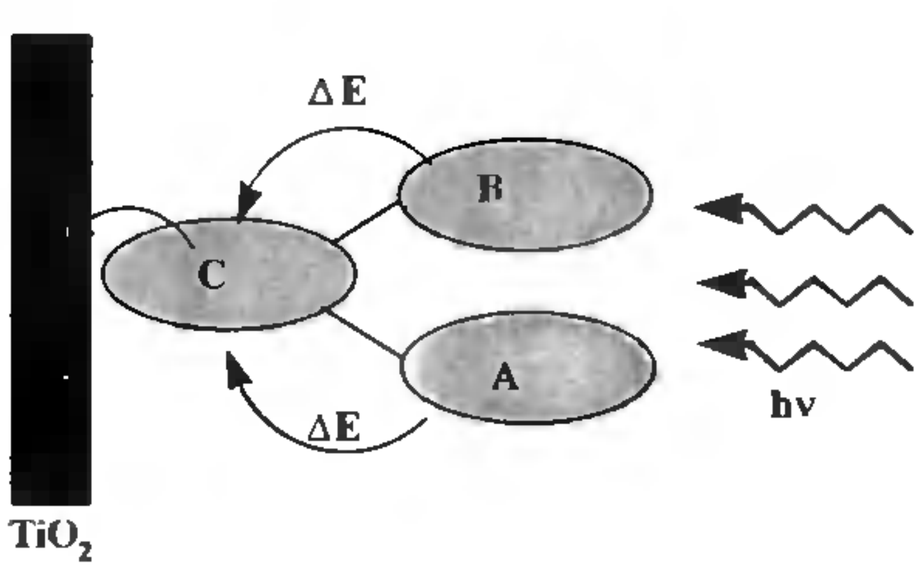


Figure 6. Tuning of the lowest energy MLCT transition in mixed ligand complexes of Ru, $[Ru(dcbpy)_2X_2]$.

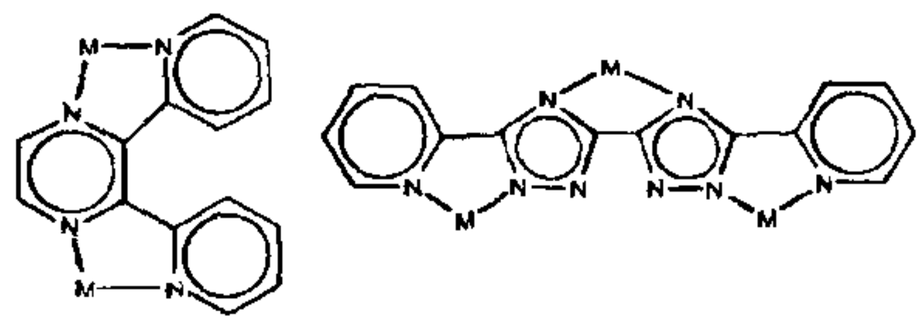
[Ru(dcbpy)$_2$(ph-py)], there is a gradual lowering of the energy of the MLCT excited state due to the presence of electron-rich ligands 4,4′-diethylamino-2,2′-bipyridine and phenylpyridine. The lowering of the energy of the MLCT excited state is accompanied by decreased emission quantum yield and shorter excited state lifetime. *Quantitative analysis for about twenty mixed* ligand complexes showed that the enhanced decay of the MLCT excited state is due to enhanced radiationless decay. The rate parameters can be quantitatively explained in terms of *energy gap law*.

It was mentioned earlier that the mononuclear complex Ru(dcbpy)$_2$(SCN)$_2$ is an efficient sensitizer[27] but its spectral response decreases very rapidly above 700 nm. In the above type of 'tuning' of lowest energy MLCT transition the bandwidth of the transition in the mononuclear complexes remains the same. So one approach for efficient harvesting of sunlight would be to link several such graded series of chromophores in a 'supramolecule' using appropriate bridging or spacer units. Higher energy chromophores transfer the excitation energy to the lowest energy one and charge injection process will take place from this unit, as shown below:



The efficiency of intramolecular electron- and energy-transfer processes in such polynuclear complexes will depend on the extent of electronic coupling between different chromophoric units as modulated by the bridge. In cases where the bridge is 'truly innocent', the properties of the supramolecule would be described in terms of mononuclear parent compounds ('localized description'). When the bridge efficiently mediates electronic coupling between the chromophores, care must be taken in describing the polynuclear complex in terms of its precursors. In favourable cases, metal-to-metal charge transfer (also called inter-valence) transitions allow quantifying of the extent of electronic coupling between the chromophores.

In our laboratories, photophysical and redox properties of polynuclear complexes have been examined, particularly for those with cyanide as the bridging ligand[35, 36] or polyimines (such as 2,3-bis(2-pyridyl)-pyrazine (dpp)[37] or 2,2′-bis(2-pyridyl)-5,5′-bis(1,2,4)-triazole (BPBT))[38] as template ligand. The dpp ligand can chelate two and the BPBT ligand up to three metal centres:



When fragments such as Ru(bpy)$_2$- are chelated as in complexes of the type [(bpy)$_2$Ru]$_3$(BPBT), the bridging ligand behaves as a template to tie up different chromophores. Due to the electron-rich character of the bridging ligand, the lowest energy transitions involve spectator ligand bpy (i.e. Ru → bpy) and not the bridging ligand. The lowest energy chromophore is identified from a combined analysis of absorption and redox properties of model compounds and resonance Raman spectra[39] obtained at various excitation wavelengths within the lowest energy absorption band. Presence of the peripheral carboxylic group in the ligands of this chromophoric unit would ensure efficient channelling of photons.

The cyano-bridged trinuclear complex mentioned earlier as an efficient sensitizer[28, 29], [(CN)(bpy)$_2$Ru-CN-Ru(dcbpy)$_2$-NC-Ru(bpy)$_2$(CN)] is a typical example of this category. Analysis of the absorption and redox properties of model compounds and resonance Raman spectra measured at various excitation wavelengths within the lowest energy visible absorption band, it can be shown that the lowest energy chromophore is based on the central -Ru(dcbpy)$_2$-unit. Time-resolved emission, absorption and resonance Raman studies[40] also show that there is efficient intramolecular energy transfer from the peripheral units to the central chromophore as shown in Figure 7. Quite recently we have made systematic photophysical and spectroscopic

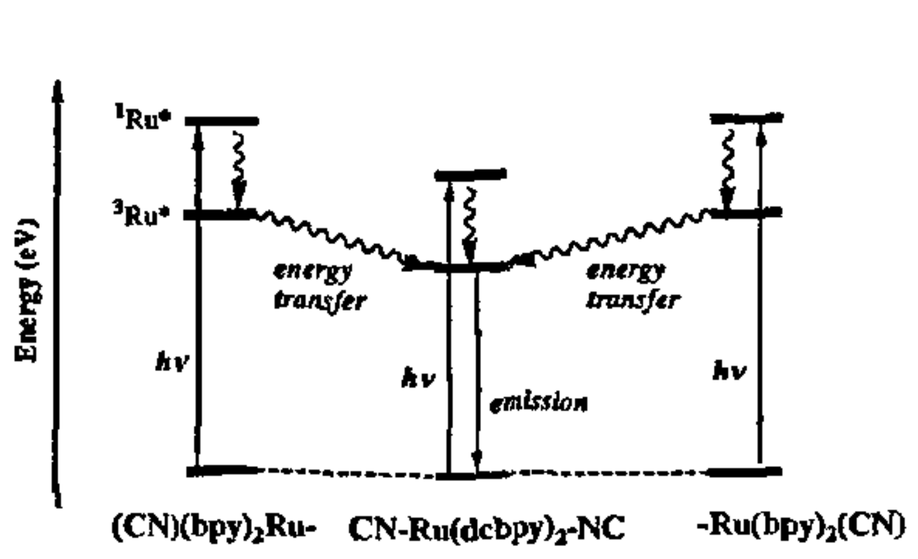


Figure 7. Schematic presentation of intramolecular energy transfer from the CT excited states of peripheral units to the central chromophore in the complex, [(CN)(bpy)$_2$Ru-CN-Ru(dcbpy)$_2$-NC-Ru(bpy)$_2$]

studies[41] of cyano-bridged trinuclear complexes of the type $[(X)(LL)_2M_1\text{-}CN\text{-}M_2(NN)_2\text{-}NC\text{-}M_1(LL)_2(X)]$, M_1, M_2 = Ru, Os; LL, NN = bpy, dcbpy, X = Cl, H_2O, CN, etc. In this series, depending on the nature of the metal, polypyridine and spectator ligands, the lowest energy chromophore can be placed on the central or on the peripheral units[41]. Thus, by appropriate design, it is possible to construct a supramolecule carrying a graded series of chromophores and follow energy cascade upon excitation of higher energy units.

Stability

One final point concerns the stability or long-term performance of the solar cell. A weak point on the solar cells based on TiO_2 is their sensitivity to near-UV component of the sunlight. Membrane films produced from colloids contain typically 30% rutile and rest anatase. The bandgap of rutile is 3.0 eV as compared to 3.2 eV for anatase, corresponding to fundamental absorption edge of 413 and 388 nm respectively. It is well known that excitation within the bandgap of TiO_2 using near-UV light (in the wavelength range 350–420 nm) causes generation of 'holes'. The 'hole' is a very strong oxidant ($E \geq 2.0$ eV) being capable of oxidizing the solvent, dye, redox mediator, etc. For this reason, the stability of the solar cells decreases significantly upon exposure to concentrated sunlight. In practice, a polycarbonate filter that cuts off all the light below 390 nm is placed on the cell on the dye-coated TiO_2 electrode side. With such protection to the near-UV light, the stability of the cells to sunlight is greatly enhanced. Unfortunately such an added filter adds to the cost of the device but cannot be avoided.

Results obtained up till now in our laboratories have been very encouraging. There are some solar cells that have been running continuously for several months. On the contents of the cell, the dye sensitizer is considered to be the weakest point. Under continuous photolysis, dye undergoes two critical phases. The first is electronically excited state. Fortunately the charge injection is extremely rapid, taking place in ≤ 50 ps, providing a very fast channel for the deactivation of this state. The second state of concern is one after the injection where the sensitizer has lost one charge. Losing a charge can mean instability for many organic dyes. With inorganic metal complexes, charge variations often occur at the metal ion and this ion is quickly returned to its original state by the electrons from the electrolyte. Based on the amount of photocurrent obtained (charge passing through the cell) in laboratory experiments, it has been found that the sensitizer can sustain 10^7–10^8 turnovers without degradation. One may expect this many turnovers in about 20 years in operating in sunlight.

Conclusions

Using a combination of textured membrane film based on finely dispersed TiO_2 and polypyridine complexes of Ru, it is possible to construct efficient photoelectrochemical cells for the direct conversion of sunlight to electricity. White light to electrical conversion efficiencies of over 10% strongly suggests potential for practical applications on a future date. The main attractions of solar cells of this kind are low material cost for the key components. With few milligrams of the Ru-complex it is possible to cover several square meters of a solar panel. TiO_2 is available cheaply as a bulk chemical, being used in quantity in paints, cosmetics, health products and the paper industry. The cell as of date is not yet ready for large scale applications. There is excellent scope for improvement in many areas, especially in the choice of the sensitizer and redox mediator. Currently photovoltaic technology as a means of power generation has only a very limited market. It is mainly for power generation in remote areas but this is bound to change. Solar cells have an important role to play in small electrical devices, for lighting, communications, storage of food and pharmaceuticals, water supply and purification, to name but a few examples.

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