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The Artificial Leaf, Molecular Photovoltaics Achieve Efficient Generation of Electricity from Sunlight

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The Artificial Leaf, Molecular Photovoltaics Achieve Efficient Generation of Electricity from Sunlight

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A new molecular photovoltaic system for solar light harvesting and conversion to electricity has been developed. It is based on the spectral sensitization of a thin ceramic membrane by suitable transition metal complexes. The film consists of nanometer-sized colloidal titanium dioxide particles sintered together to allow for charge carrier transport. When derivatized with a suitable chromophore these membranes give extraordinary efficiencies for the conversion of incident photons into electric current, exceeding 90% for certain transition metal complexes within the wavelength range of their absorption band. The present paper discusses the underlying physical principles of these astonishing findings. Exploiting this discovery, we have developed a new type of photovoltaic device whose overall light to electric energy conversion yield is 11% in diffuse daylight and 6% under direct (AM1) solar irradiation.

Key Words: *light energy conversion, membrane, colloidal TiO_2 sensitization, photovoltaics*

In a conventional p-n-junction photovoltaic cell, made, e.g., from silicon, the semiconductor assumes two roles at the same time: it harvests the incident sunlight and conducts the charge carriers produced under light excitation. In order to function with a good efficiency the photons have to be absorbed close to the p-n interface. Electron–hole pairs produced away from the junction must diffuse to the p-n contact where the local electrostatic field sepa-

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rates the charges. In order to avoid charge carrier recombination during the diffusion the concentration of defects in the solid must be small. This imposes severe requirements on the purity of the semiconductor material rendering solid state devices of the conventional type very expensive.

Molecular photovoltaic systems separate the function of light absorption and carrier transport. The light harvesting is carried out by a sensitizer which initates electron transfer events leading to charge separation. This renders unnecessary the use of expensive solid state components in the system. While simple from the conceptual point of view the practical implementation of such devices must overcome formidable obstacles if the goal is to develop molecular systems that convert sunlight to electricity with an efficiency comparable to that of silicon photovoltaic devices. The approach taken by us will now be outlined in more detail. We begin by giving a very brief account of some basic principles employed by green plants, algae and cyanobacteria to harvest and convert solar energy which have inspired us in the choice of our strategies.

1. PRINCIPLES OF LIGHT ENERGY HARVESTING AND CONVERSION IN GREEN PLANTS

The light reaction in plants is called photophosphorylation. It involves the reduction of an electron carrier, i.e., nicotinamide adenine dinucleotide phosphate ($NADP^+$), by water to produce NADPH and oxygen. This photoinduced redox reaction is coupled to the generation of adenosine triphosphate (ATP) from adenosine diphosphate:

$$2H_2O + 2NADP + 3ADP + 3P \rightarrow 2NADPH + H^+ + 3ATP + O_2. \quad (1)$$

The electron transfer process takes place in the thylakoid membranes located in the interior part of the chloroplasts of plant cells. The photosynthetic unit assembled in these membranes is com-

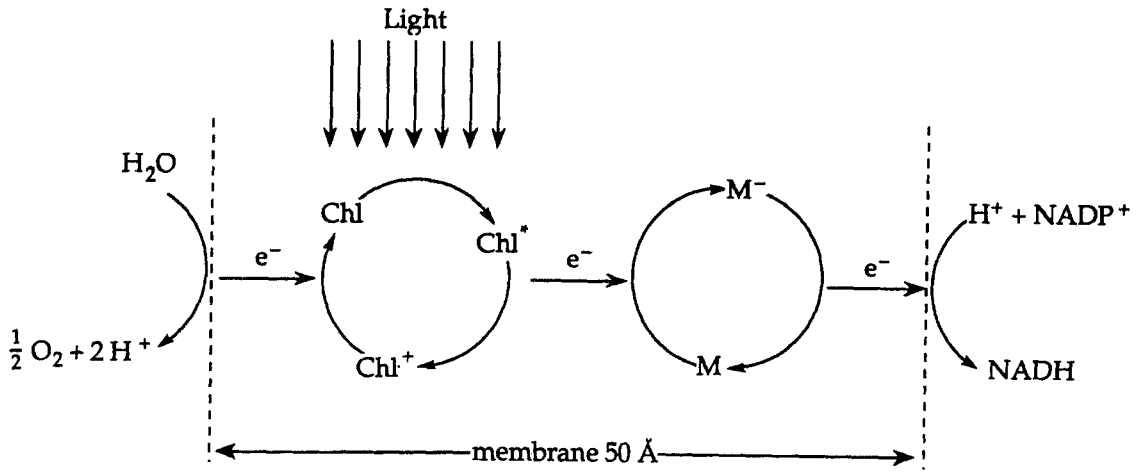
posed of antenna pigments and a reaction center consisting of two photosystems. The absorption of light causes electrons to be ejected from chlorophyll reaction centers and then passed between various electron-transfering mediators (M) of the photosystems. In that way, a chain of redox reactions is induced by light. Chlorophyll and the participating mediators, for example pheophytin, ferrodoxin, cytochromes, and various quinones, are spatially ordered in such a way that the electron transfer takes place directionally ("vectorially") from the inner to the outer section of the photosynthetic membrane (Fig. 1). The spatial arrangement of the mediators is known from the recent successful isolation of the reaction center protein of *Rhodopseudomonas viridis*.[1] This transmembrane electron flow is completed within a few hundred microseconds, resulting in light-induced charge separation. The negative charge is then located on the outer side of the membrane, and is ultimately used for the reduction of the $NADP^+$. (The NADPH thereby produced is employed in the dark reaction, the Calvin cycle, for the fixation of carbon dixoide.) The positive charges remaining on the inner side of the membrane in the form of chlorophyll cations serve for the oxidation of water to oxygen. The overall reaction, despite its complexities in detail corresponds to the simple equation above.

In summary, the stategy employed by nature to accomplish this thermodynamically uphill chemical conversion is to use a molecular absorber and not a solid state device such as a silicon p-n junction. The key element to achieve light induced charge separation is the presence of a membrane which serves to organize spatially the electron transfer mediators in an optimal fashion. This allows for the vectorial displacement of photogenerated electrons from the inside to the outside of the thylakoid vesicles. The conversion efficiency achieved in the primary charge separation step of plants' photosynthesis is rather high, i.e., ca 12%. Unfortunately, the overall conversion yield drops to at most 3–4% for top efficiency crops under optimal conditions of biomass generation.

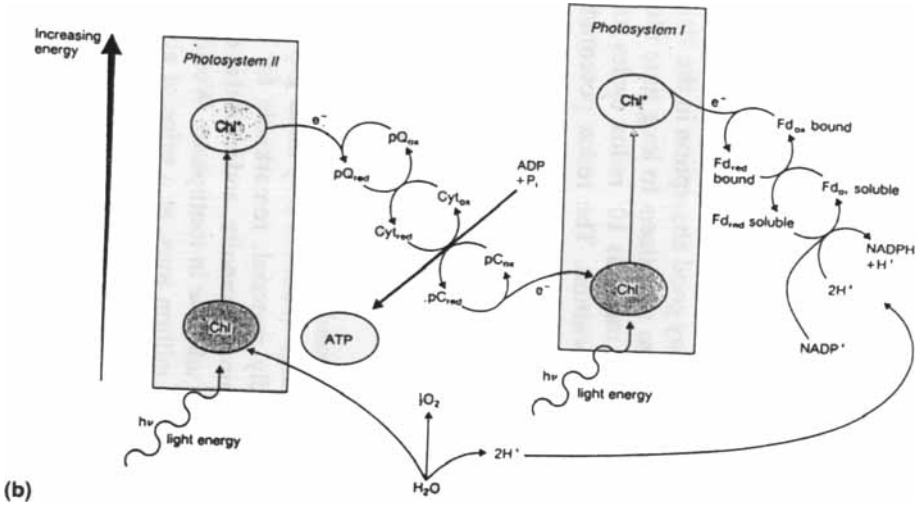
2. MOLECULAR PHOTOVOLTAICS AND ARTIFICIAL PHOTOSYNTHESIS

Our newly developed photovoltaic cell replicates the most important principles of its prototype, photosynthesis. In any case, the

THE MOLECULAR MACHINE OF CHLOROPLASTS



Chl = chlorophyll
(a) M = electron relay (mediator)



Coupling of the two photosystems in photophosphorylation
Chl = chlorophyll; Chl* = electronically excited chlorophyll; pQ = plastoquinone; Cyt = cytochrome; pC = plastocyanine; Fd = ferrodoxine. The subscripts 'red' and 'ox' refer to reduced and oxidized form, respectively.

FIGURE 1 Light energy harvesting and light-induced charge separation in photosynthesis: (a) the light driven molecular electron pump operating in green leafs, (b) a more detailed presentation of the redox events occurring in the photosynthetic reaction centers of green plants.

components of the synthetic system must be selected to satisfy the high stability requirements encountered in practical applications. A photovoltaic system must remain serviceable for 20 years without signficant loss of performance. In living systems this stability is less significant, since unstable components are continuously renewed. Because chlorophyll, and likewise the lipid membrane, are labile *in vitro*, they cannot be adopted directly. In artificial photosynthesis chlorophyll is therefore substituted by a more stable sensitizer molecule (S). One of the most remarkable achievements of research in inorganic chemistry during the last two decades has been the development of a great variety of transition metal complexes[2] mainly of the elements osmium and ruthenium which are exceptionally stable and display good absorption in the visible. We have submitted some of these sensitizers to long time illuminations where they sustained as much as 10^7 redox cycles under light without noticeable decomposition. The redox potentials of these complexes can be adjusted to the desired value by suitable choice of the ligands and their substituents.

The role of the sensititzer is the same as that of chlorophyll: it must absorb the incident sunlight and exploit the light energy to induce a vectorial electron transfer reaction. In place of the biological lipid membrane, a titanium dioxide ceramic membrane is employed.

Titanium dioxide is a semiconductor, which does not absorb visible light because of its large (about 3 eV) band gap. It is a harmless environment-friendly material, remarkable for its very high stability. It occurs in nature as ilmenite, and is used in quantity as a white pigment and as an additive in toothpaste. World annual product is of the order of a million tons, at a price of about US $1.-/kg. Since the membrane is about 5 microns thick, about 10 g of titanium dioxide is used per square meter of solar collector surface, representing an investment of only 1 cent per square meter.

The role of the titanium dioxide film is to provide a support for the sensitizer which must be applied to the surface of the membrane as a monomolecular layer. Furthermore, the conduction band of the titanium dioxide accepts the electrons from the electronically excited sensitizer. The electron injected into the conduction band travels very rapidly across the membrane. Its diffusion is at least 10^4 times faster than that of a charged ion in solution. The time

required for crossing a TiO_2 membrane, say five micrometer thick, is only about 2 microseconds. During migration the electrons maintain their high electrochemical potential which is equal to the Fermi level of the semiconductor. Thus, the principal function of the TiO_2, apart from supporting the sensitizer, is that of charge collection and conduction. The advantage of using a semiconductor membrane rather than a biological one as employed by natural photosynthesis is that such an inorganic membrane or film is more stable and allows extremely fast transmembrane electron movement. The charge transfer across the photosynthetic membrane is less rapid since it takes about 100 μs to displace the electron across the 50 Å thick thylakoid layer. Moreover, nature has to sacrifice about half of the absorbed photon energy to drive the transmembrane redox process at such a rate. In the case of the semiconductor membrane, the price to pay for the rapid vectorial charge diplacement is small. It corresponds to about 0.2–0.3 V of voltage drop required to establish the electrical field in the space charge layer at the semiconductor/electrolyte junction.

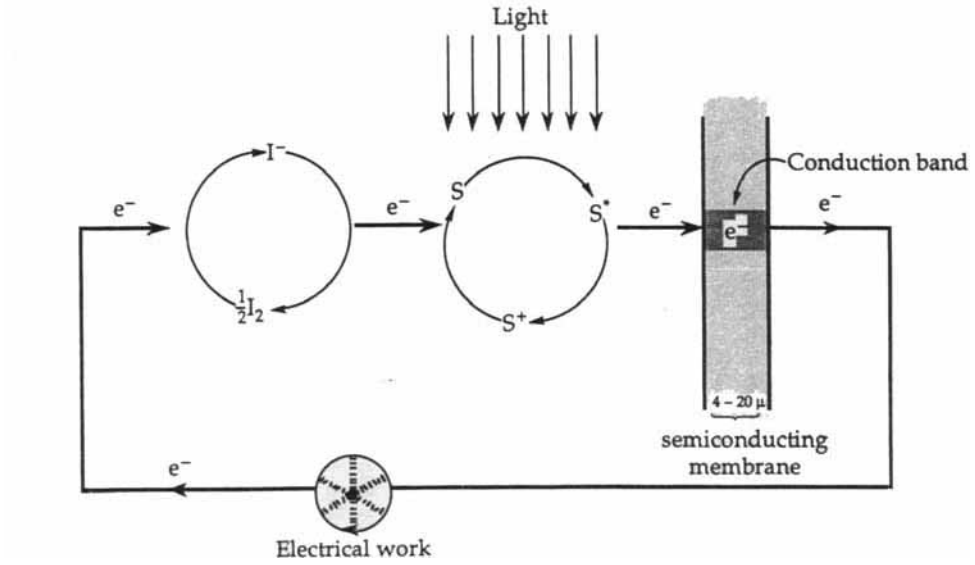
It is important to note that minority carriers, i.e., holes in the case of an n-type conductor such as TiO_2, do not participate in the photoconversion process. This is a great advantage in comparison to conventional photovoltaic devices, where, without exception, the generation and transport of minority carriers is required. The performance characteristics of the conventional device are strongly influenced by the minority carrier diffusion length, which is very sensitive to the presence of imperfections and impurities in the semiconductor lattice. Our cell operates entirely on majority carriers whose transport is not subjected to these limitations and hence will be much less sensitive to lattice defects.

As in natural photosynthesis, in the new photovoltaic device sunlight sets in action a molecular electron pump, whose principle is schematically represented in Fig. 2. The sensitizer (S) is bound as a monomolecular coating on the surface of the titanium dioxide membrane. It absorbs the incident solar rays, and is thereby raised to the electronically excited state S^*. From this state it injects an electron into the conduction band of the titanium dioxide. The conduction band electrons then cross the membrane and are directed through a charge collector into the external current circuit where electrical work is done. The electrons are then returned to

ARTIFICIAL PHOTOSYNTHESIS

⇒ The sensitizer S replaces chlorophyll

⇒ The semiconducting membrane replaces the biological membrane



The new molecular machine constitutes an electron pump, driven by sunlight

FIGURE 2 The principles of the artificial leaf: the chlorophyll is replaced by a transition metal sensitizer while the phospholipid membrane is exchanged for a ceramic semiconducting membrane made of TiO_2. As in photosynthesis, the new solar converter constitutes a molecular electron pump driven by sunlight.

the cell through a counter electrode. Between this counter electrode and the titanium dioxide membrane is an electrolyte containing a redox couple, i.e., iodine and iodide. This redox electrolyte allows for the transport of electrical charge between the two electrodes. The electrons reduce iodine to iodide ions which diffuse from the counter electrode to the titanium dioxide membrane, where they regenerate the sensitizer by electron transfer to the sensitizer cations, while simultaneously the iodide is oxidized back to iodine. The redox cycle leading to the conversion of light into electrical current is thereby closed. In direct sunshine each sensitizer molecule follows this cycle about twenty times per second. The molecular machine runs therefore at 1200 rpm.

2.1 Light Harvesting by Monomolecular Layers

For the absorption of solar rays by sensitizers attached as monolayers to the surface of a titanium dioxide membrane, there is a fundamental problem of the limited light capture cross section of the dye molecule. The cross section σ is related to the decadic molar extinction coefficient $\epsilon(\lambda)$ by the formula:

$$\sigma(\lambda) = \epsilon(\lambda) \times 1000/N_A, \quad \text{where } N_A = 6 \times 10^{23}. \qquad (2)$$

Typical values for the decadic extinction coefficient of transition metal complexes lie between 10^4 and 5×10^5 M^{-1} cm^{-1}. This implies a light capture cross section between 0.16 and 0.8 $Å^2$. In contrast, the sensitizer molecule occupies an area of about 100 $Å^2$ on the surface of the membrane. It is clear from this comparison that the surface area requirement of the sensitizer is at least 125 times larger than its light capture cross section. That signifies that a monomolecular layer of the sensitizer on a smooth surface absorbs less than 1% of the incident light in the wavelength range of maximum absorption. One could naturally think, then, of depositing several molecular layers of sensitizer on the semiconductor membrane in order to increase the light absorption. This would however be a mistaken tactic, since the outer dye layers would act only as a light filter, with no contribution to electrical current generation. The application of a monomolecular layer of sensitizer is therefore unavoidable.

A successful strategy to solve the problem of light absorption through such extremely thin molecular layers is found in the application of textured titanium dioxide membranes. It is possible using the sol-gel method to produce transparent membranes consisting of colloidal titanium dioxide particles with diameters of 10–20 nm. The electronic contact between the particles is produced by a brief sintering at about 500°C.[3] A microporous structure with a very high effective surface area is thereby formed. For example the effective surface of a 5 micron thick film of such a colloidal structure is at least 300 times greater than that of a smooth membrane. On the geometric projection of such a surface a sensitizer concentration of $\Gamma = 3 \times 10^{16}$ molecules cm^{-2} is reached when colloidal membranes are used. The optical density

$$OD(\lambda) = \Gamma \times \sigma(\lambda) \tag{3}$$

calculated for this coating level and a light capture cross section per sensitizer molecule of 0.5 $Å^2 = 10^{-16}$ cm^2 is 1.5. The light harvesting efficiency of the device LHE(λ) is then given by:

$$LHE(\lambda) = 1-10^{-\Gamma \times \sigma(\lambda)} = 1-10^{OD(\lambda)}. \tag{4}$$

With an optical density of 1.5, 97% of the light is absorbed by the membrane loaded with sensitizer.

2.2 The Quantum Yield of Charge Injection

The quantum yield of charge injection (ϕ_{inj}) is the fraction of the absorbed photons which are converted into electrons injected in the conduction band. Charge injection from electronically excited sensitizer into the conduction band of the semiconductor is in competition with other radiative or radiationless deactivation channels. Taking the sum of the rate constants of these nonproductive channels together as k_{eff} results in:

$$(\phi_{inj}) = k_{inj}/(k_{eff} + k_{inj}). \tag{5}$$

One should remain aware that the deactivation of the electronically excited state of the sensitizer is generally very rapid. Typical k_{eff}

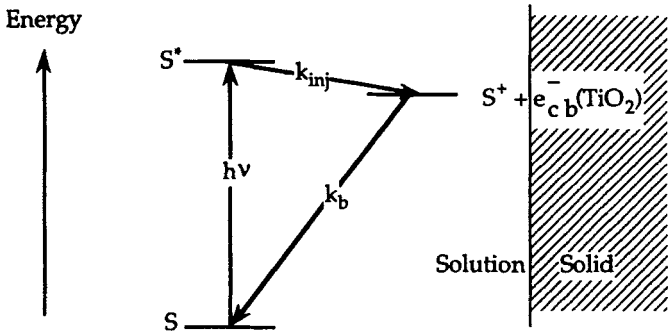
values lie in the range from 10^6 to 10^{10} sec^{-1}. To achieve a good quantum yield the rate constant for charge injection should be at least 100 times higher than k_{eff}. That means that injection rates up to 10^{12} sec^{-1} must be attained. In fact, in recent years sensitizers have been developed that satisfy these requirements. These dyes should incorporate functional groups ("interlocking groups") as for example carboxylates or chelating groups, which besides bonding to the titanium dioxide surface, also effect an enhanced electronic coupling of the sensitizer with the conduction band of the semiconductor.

Very promising results have so far been obtained with ruthenium complexes where at least one of the ligands was 4,4′-dicarboxy-2,2′-bipyridyl. The two carboxylate groups serve to attach the Ru complex to the surface of the TiO_2 and to establish good electronic coupling between the π^* orbital of the electronically excited complex and the 3d wavefunction manyfold of the TiO_2 film. The substitution of the bipyridyl with the carboxylate groups also lowers the energy of the π^* orbital of the ligand. Since the electronic transition is of MLCT (metal to ligand charge transfer) character, this serves to channel the excitation energy into the right ligand, that is, the one from which electron injection into the semiconductor takes place. With molecules like these the quantum yield of charge injection generally exceeds 90%.[3,4]

2.3 Light-Induced Charge Separation and Current Yield

As the last step of the conversion of light into electrical current, a complete charge separation must be achieved. On thermodynamic grounds, the preferred process for the electron injected into the conduction band of the titanium dioxide membrane is the back reaction with the sensitizer cation (Fig. 3). Naturally this reaction is undesirable, since instead of electrical current it merely generates heat.

For the characterization of the recombination rate an important kinetic parameter is the rate constant k_b. It is of great interest to develop sensitizer systems for which the value of k_{inj} is high and that of k_b low. Fortunately, for the transition metal complexes we use, the ratio k_{inj}/k_b is often greater than 10^3, which significantly facilitates the charge separation. The reason for this behavior is



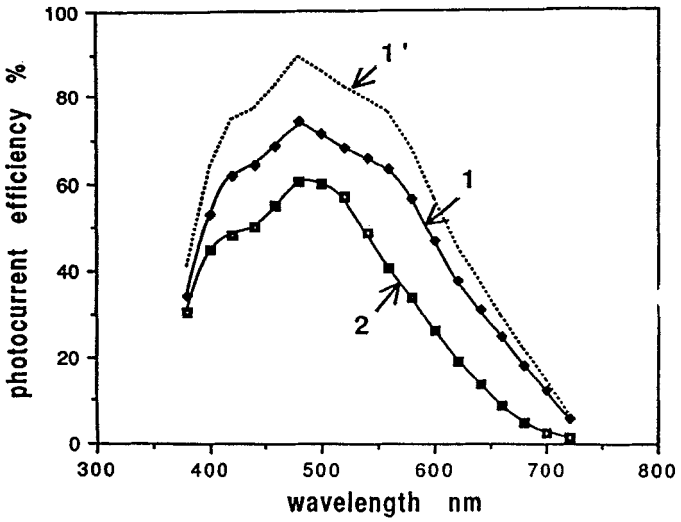
k_{inj} rate constant for charge injection [s^{-1}]
k_b rate constant for recombination

FIGURE 3 Photoinduced charge separation on the surface of titanium dioxide; k_{inj} and k_b represent the rate constants for electron injection and recombination, respectively.

that the molecular orbitals involved in the back reaction overlap less favorably with the wavefunction of the conduction band electron than those involved in the forward process. For example, for our Ru-complexes bound to the titanium dioxide membrane, the injecting orbital is the π^* wavefunction of the carboxylated bipyridyl ligand since the excited state of this sensitizer has a metal to ligand charge transfer character. The carboxylate groups interact directly with the surface Ti(IV) ions resulting in good electronic coupling of the π^* wavefunction with the 3d orbital manifold of the conduction band of the TiO_2. As a result, the electron injection from the excited sensitizer into the semiconductor membrane is an extremely rapid process. By contrast, the back reaction of the electrons with the oxidized ruthenium complex involves a d-orbital localized on the ruthenium metal whose electronic overlap with the TiO_2 conduction band is small. The spatial contraction of the wavefunction upon oxidation of the Ru(II) to the Ru(III) state further reduces this electronic coupling and this explains the large

difference between the forward and backward electron transfer rates.

Of great significance for the inhibition of charge recombination is the existence of an electric field in the titanium dioxide mem-



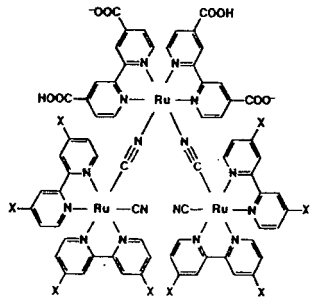


FIGURE 4 Photocurrent action spectrum of titanium dioxide films with the trinuclear sensitizers **1** and **2** observed in a thin film cell with lithium iodide/iodine solution in ethanol as electrolyte. The incident photon to current conversion efficiency is plotted as a function of the wavelength of the exciting light. The dashed curve 1′ was calculated from the experimentally observed curve 1 by correcting for the light absorption in the conducting glass used as support for the TiO_2 film.

brane. This field is established spontaneously by electron flow from the semiconductor to the redox electrolyte when these are brought into contact. This charge transfer is driven by the difference between the Fermi level in the titanium dixode and the redox potential of the solution. It will stop once the electrochemical potentials on both sides of the junction are equal. The depletion of majority charge carriers leads to the establishment within the titanium dioxide of a space charge layer.[5] Within this layer the conduction band is curved towards the interior of the semiconductor. On injection of electrons from an excited sensitizer, the band bending acts to draw them from the surface to the interior of the membrane. This effect in addition depresses the rate of recombination further, by a factor of the order of 1000.[3] Expressing by η_e the proportion of photoinduced electrons which avoid recombination and pass into the external current circuit, the monochromatic current yield is given by

$$\eta_i(\lambda) = \text{LHE}(\lambda) \times \phi_{inj} \times \eta_e \qquad (6)$$

This current yield expresses the ratio of the measured electric current to the incident photon flux for a given wavelength. By development of appropriate sensitizers and systematic improvement of the electronic properties of the titanium dioxide membrane, systems are now available for which all three factors in Eq. (6) are close to unity. Thereupon, within the wavelength range of the sensitizer absorption band a quantitative conversion of incident photons to electrons is obtained.

A graph which presents the monochromatic current output as a function of the wavelength of the incident light is called the "photocurrent action spectrum." An action spectrum of this type for two trinuclear ruthenium complexes as sensitizers appears as Fig. 4.[6] The dotted line 1′ applies to complex 1 and is derived from curve 1 by correction for light losses in the conducting glass which serves as substrate for the titanium dioxide film. It establishes the very high efficiency of current generation, exceeding 75% over a wide range of wavelengths with these complexes.

2.4 Cell Voltage and Overall Conversion Efficiency

The photovoltage of our cell represents the difference between the Fermi level of titanium dioxide under illumination and the redox

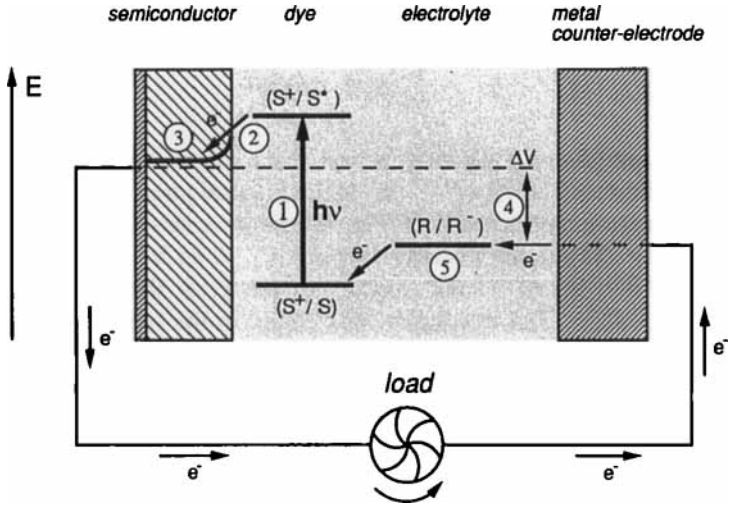


FIGURE 5 Schematic representation of the principle of the new photovoltaic cell to indicate the electron energy level in the different phases. The cell voltage observed under illumination corresponds to the difference in the quasi-Fermi level of the TiO_2 under illumination and the electrochemical potential of the electrolyte. The latter is equal to the Nernst potential of the redox couple (R/R^-) used to mediate charge transfer between the electrodes.

potential of the electrolyte (Fig. 5). Using an alcoholic iodine–iodide solution under full sunlight an open-circuit cell voltage of 0.7 to 1.0 V can be measured. Under a 1000-fold lower intensity the cell voltage is about 200 mV lower, a relative change of cell voltage of only 20–30%. For the conventional silicon cell the cell voltage decreases by a factor of 3 for a comparable change of light intensity. This shows that the photovoltage of our cells is significantly less sensitive to light intensity variations than in conventional photovoltaic devices.

The overall efficiency (η_{global}) of the photovoltaic cell can easily be calculated from the integral photocurrent density (i_{ph}), the open-circuit photovoltage (V_{oc}), the fill factor of the cell (ff) and the intensity of the incident light (I_S).

$$\eta_{global} = i_{ph} \times V_{oc} \times \text{ff}/I_s. \tag{7}$$

The integral photocurrent density is given in turn by the overlap integral of the solar spectral emission $I_s(\lambda)$ and the monochromatic current yield:

$$i_{ph} = \int_0^\infty I_s(\lambda)\, \eta_i(\lambda) d\lambda. \tag{8}$$

For example, for an AMI distribution of the solar spectral emission (overall intensity 88.92 mW · cm^{-2}) the integral photocurrent density for action spectrum 1 in Fig. 4 can be calculated as 11.09 mA · cm^{-2}. Using the average value of V_{oc}, 0.85 V, and for a fill factor of 0.7, the predicted overall efficiency for the cell has the value of 7.45%. This prediction was tested in the laboratory with small cells (area 1.5 cm^2) under simulated AMI light. The measured conversion efficiency was 6% in good agreement with the expectations, the decrease in the efficiency being due to a lower fill factor at high light levels.

3. DEVELOPMENT AND TESTING OF THE FIRST CELL MODULE

Meanwhile, the development and testing of the first cell module for practical applications has begun. The assembly of the module is presented in Fig. 6. The cell consists of two glass plates **1**, **7**, which are coated with a thin electrically conducting tin oxide layer. The colloidal titanium dioxide film deposited on one plate by the sol-gel procedure is notable for its high roughness factor and functions as a light trap. Visible light is absorbed by a monomolecular layer of an appropriate transition metal complex **4**, which functions as sensitizer. On illumination this injects an electron into the titanium dioxide conduction band. With such a system it is possible to convert 80% of the incident photons into the wavelength range of the sensitizer absorption maximum into electric current. The electrons pass over the collector electrode **6** into the external current where they do work. They are then returned to the cell via the counter electrode **2**. The sensitizer film is separated from the counter electrode by the electrolyte **3**. In the electrolyte there is a redox system, for example iodine/iodide, whose function is to transport electrons from the counter electrode to the sensitizer

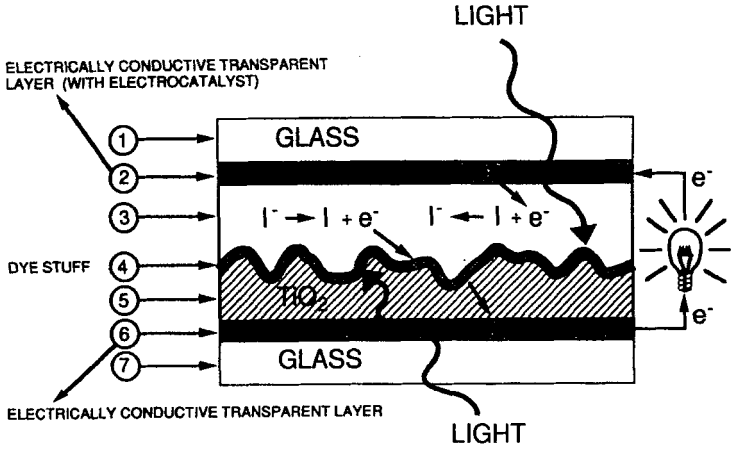


FIGURE 6 Construction of a cell module with transparent glass electrodes. **1** and **7**: glass sheets; **2** and **6**: transparent conductive layer of fluorine doped tin oxide; **5**: colloidal TiO_2 membrane (thickness ca. 5 microns), **3**: electrolyte containing the I_2/I^- redox couple.

layer, which had been left positively charged as a result of the electron injection. The area of this module is between 20 and 100 cm^2.

In Fig. 7 there is a comparison of the characteristics of a 20 cm^2 module with those of a conventional silicon cell under diffuse daylight (cloudy sky). Our cell has a current density lower by a factor of 2, which is, however, compensated by a higher voltage and a significantly better fill factor, so that a final efficiency of 11% is obtained, against 6% for the conventional silicon cell.

In direct sunlight the conversion efficiency of the silicon cell rises to 12.5%, while that of the module drops to ca. 6%. The efficiency reduction under high light intensity is attributable to a shift of the spectral distribution of the light, as well as ohmic losses in the conducting glass. A further cause is the kinetic limitation of the current on the counter electrode (iodine reduction). In dealing with this relatively trivial technical problem, no serious technical obstacles to improvement are evident. The short term laboratory goal is to increase the overall efficiency to 10%. Very

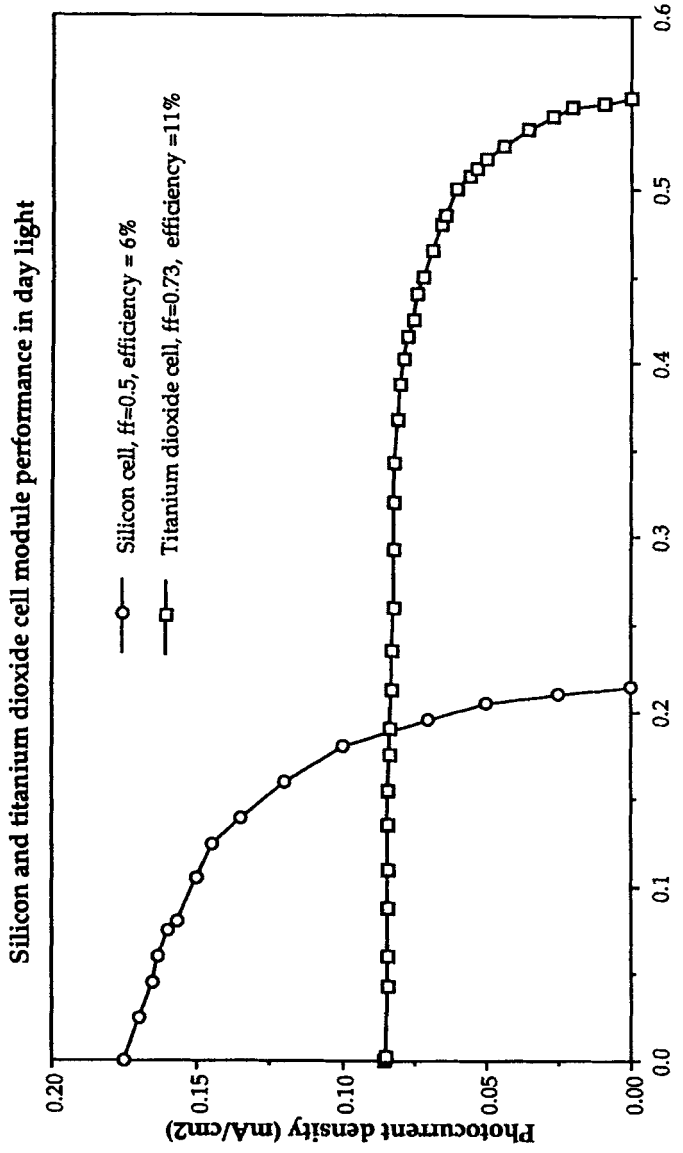


FIGURE 7 Comparison of the current/voltage characteristics of the titanium dioxide module and of a normal silicon cell under cloudy sky.

recently, photocurrent densities of up to 25 mA · cm^{-2} have been obtained without problems with sensitized colloidal TiO_2 membranes.

In summary, then, it can be stated that in the present stage of development the overall efficiency of the module in AMI sunlight is 6%. This should be further increased in the near future. For this the principal line of attack is the improvement of the spectral matching of the sensitizer absorption and the solar emission. In diffuse light or under a cloudy sky the efficiency of the cell is suprisingly high, already largely exceeding that of normal silicon cells. These new photovoltaic cells should be attractive in particular for decentralized applications, i.e., for domestic use where they could make an important contribution to the supply of electrical energy. Furthermore, the excellent performance of these cells under diffuse daylight would predestine them for utilization in countries where cloudy weather conditions prevail. Their price is expected to be significantly lower than that of the conventional silicon device.

Acknowledgments

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References

1. J. Deisenhofer, H. Michel, and R. Huber, Trends Biochem. Sci. **10**, 243 (1985).
2. A. Juris, V. Balzani, F. Barigiletti, S. Campagna, P. Belzer and A. V. Zelewski, Coord. Chem. Rev. **84**, 85 (1988).
3. B. O'Regan, J. Moser, M. Anderson and M. Grätzel, J. Phys. Chem. **94**, 8720 (1990).
4. N. Vlachopoulos, P. Liska, J. Augustynski and M. Grätzel, J. Am. Chem. Soc. **110**, 1216 (1988).
5. H. Gerischer, Electrochim. Acta **35**, 1677 (1990).
6. M. K. Nazeeruddin, P. Liska, J. Moser, N. Vlachopoulos and M. Grätzel, Helv. Chim. Acta **73**, 1788 (1990).