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THE ARTIFICIAL LEAF, MOLECULAR PHOTOVOLTAICS ACHIEVE EFFICIENT GENERATION OF ELECTRICITY FROM SUNLIGHT

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Abstract

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 day light and 7% under direct (AM1.5) solar irradiation.

1) Introduction

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 juntion must diffuse to the p-n contact were the local electrostatic field separates 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 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.

2) Molecular Photovoltaics and Artificial Photosynthesis

Our newly developed photovoltaic cell replicates the most important principles of its prototype, photosynthesis. The 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 significant 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 complexes1) mainly of the elements osmium and ruthenium which are exceptionnally 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 noticable 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 sensitizer is to 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 3eV) 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 production 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 grm. of titanium dioxide is used per square meter of solar collector surface, representing an investment of only 1 cent per square meter.

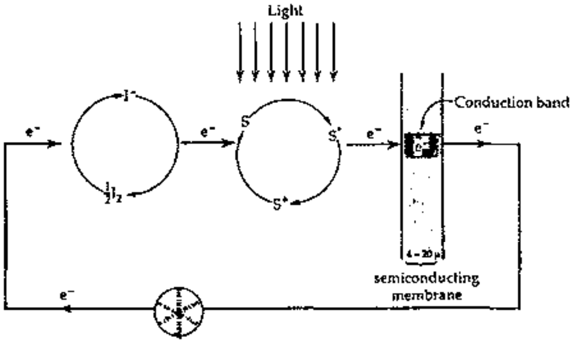
The role of the titanium dioxide film is to provide a support for the sensitizer which must be applied to the surface of the membrane as a monomolecular layer. Furthermore, the conduction band of the titanium dioxide accepts the electrons from the electronically excited sensitizer. The electron injected 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 for 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 trans-membrane electron movement. The charge transfer across the photosysnthetic membrane is less rapid since it takes about 100μs to displace the electron across the 50 A 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 -0.3V 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.

ARTIFICIAL PHOTOSYTHESIS

⇒ The sensitizer S replaces chlorophyll

⇒ The semiconducting membrane replaces the biological membrane



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

Fig. 1: The principles of the artificial leaf: the chlorophyll in plants is replaced by a transition metal sensitizer while the phospholipid membrane is exchanged for a ceramic semiconducitng membrane made of TiO_2. As in photosynthesis, the new solar converter constitutes a molecular electron pump driven by sunlight.

As in natural photosynthesis, in the new photovoltaic device sunlight sets in action a molecular electron pump, whose principle is schematically represented in Fig. 1 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 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 oxidised 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.

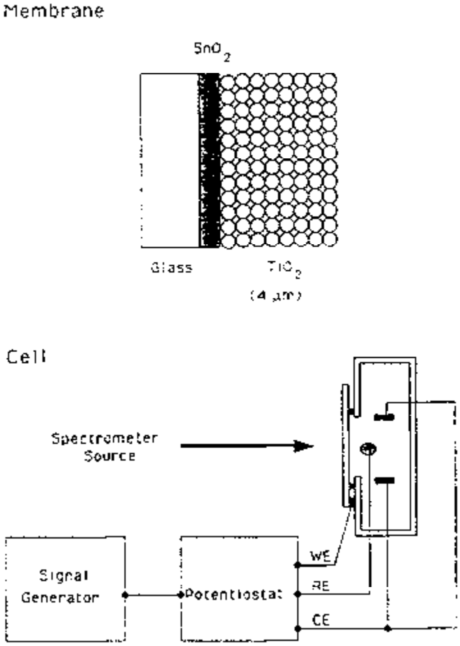


Fig. 2: Experimental set-up for steady state and real-time spectroscopy of electronic processes in nano-structured TiO_2 membranes.

3) Real-time Spectroscopy of Conduction Band Electrons in TiO2 Membranes

We have initiated fundamental studies of electronic processes in the transparent titanium dioxide membranes. The experimental set-up allowing for investigations of steady state and real time spectroscopy of charge carrier reactions in nanostructured TiO_2 films is shown in Figure 2. The colloidal particles (size ca 15 nm) are deposited as a 10 micron thick film on the conducting glass support and electronic contact is established between the particles by brief sintering. The supported film is incorporated as the working electrode (WE) in an electrochemical cell which contains also a Pt counterelectrode (CE) and a saturated calomel reference electrode (CE). Potentiostatic control of the Fermi level within the particles is possible in this way. Thus, the nano-sized particles can be driven into the depletion, accumulation or flat band regime allowing for the exploration of the effect of the electric potential on the dynamics of electron transfer processes [2)]. In addition, these optical studies have povided a wealth of information on a variety of important electronic phenomena, such as the effect of pH on the nature of the cations on the flatband potential of the film, the dynamics of space charge limited charge carrier injection as well as the role of surface states in charge carrier trapping processes [3)].

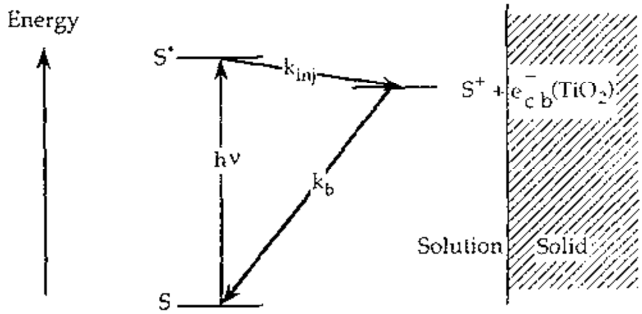
4) Light-induced charge separation and current yield

As an important step of the conversion of light into electrical current, 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 characterisation 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 behaviour is 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 semicondcutor membrane is an extremely rapid process. By constrast, 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. Expressing by LHE the light harvesting efficienbcy, by ϕ_{inj} the quantum yield for charge injection and 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:

PHOTO – INITIATED ELECTRON TRANSFER CYCLE



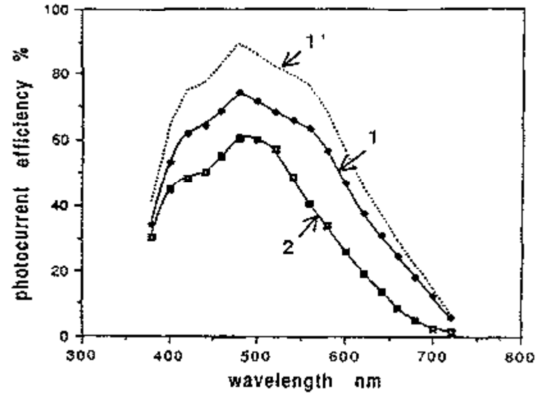
k_{inj} rate constant for charge injection [s^{-1}]
k_b rate constant for recombination

Fig. 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.

$$\eta_i(\lambda) = \text{LHE}(\lambda) \times \phi_{inj} \times \eta_e \tag{1}$$

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 equation (1) 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 4). The dotted line I' 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.



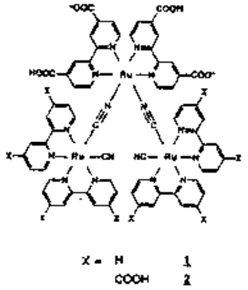


Fig. 4: Photocurrent action spectrum of titanium dioxide films with the trinuclear sensitizers 1 and 2 observe in a thin film cell with lithium iodide/iodine solution in ethanol as electrolyte The incident photon to current conversion efficiency is plotted as a function of the wavelength of the exciting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

5. Cell voltage and overall conversion efficiency

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).

(2) $\eta_{global} = i_{ph} \times V_{oc} \times ff/I_s$

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.

(3) $$i_{ph} = \int_0^{\infty} I_s(\lambda)\, \eta_t(\lambda) d\lambda$$

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}, 0.85V, 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 between 7% and 8% in good agreement with the expectations 5).

Acknowledgment

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