Feature

ENET
9802626-1

The artificial leaf, bio-mimetic photocatalysis

Michael Grätzel
Institute of Physical Chemistry
Swiss Federal Institute of Technology
Lausanne
Switzerland, CH 1015

Learning from the concepts used by green plants, an efficient and stable molecular photovoltaic cell based on the dye sensitization of mesoporous oxide films has been developed. The discovery of this photocatalytic device has opened up a realm of other applications, including spin-offs in the field of redox catalysis, intercalation batteries, nanocrystalline electronic junctions, and display technology.

Introduction

There can be no question that the quality of human life is intimately associated with the ready availability of energy resources. At present, the worlds' energy consumption rate exceeds already the stunning figure of 6000 Gigawatt. This is expected to grow rapidly in the next decades due to the increase in demand from the developing countries. The overwhelming part of our energy supply arises from the chemical energy stored in the fossil fuels. These reserves are being rapidly depleted and their combustion has led to unacceptable levels of pollution of our environment. Further acceleration of this process would lead to disastrous climatic consequences. It is evident that the well being of mankind is threatened unless renewable energy resources can be developed in the near future. Catalysis is expected to make decisive contributions to identify environmentally friendly solutions to the energy problem. One attractive strategy discussed below is the development of systems that mimic natural photosynthesis in the conversion and storage of solar energy.

I became infatuated with light and photo-induced redox reactions already as a graduate student. Working as a postdoctoral fellow with Prof. Kerry Thomas at the University of Notre Dame in the early seventies I was fortunate to be given a topic that related to artificial photosynthesis. My task was to study light induced electron transfer reactions in micelles which served as simple model systems for biological membranes. Those experiments showed beautifully how molecular self-assembly may be used to achieve photo-induced charge separation. I became very excited by the prospect of developing biomimetic photocatalytic systems and embarked with great enthousiasm on a research project to realize what was then called an "artificial leaf". However, during the following years my coworkers and I wondered sometimes - in view of the many frustrations and setbacks we encountered - whether it had been a good idea to take up such a challenging task. Finally, after a decade of hard work we were rewarded. We had found a way to successfully trap solar radiation by a

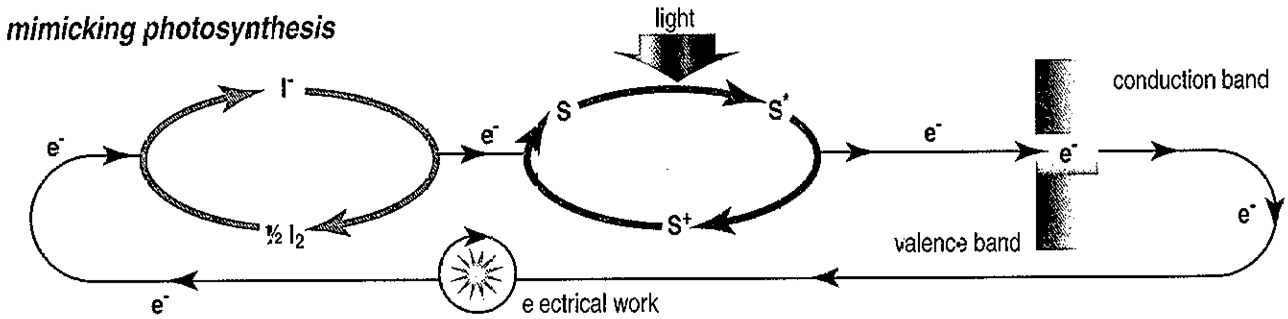


Figure 1. Biomimetic conversion of light to electricity using two redox catalytic cycles. As in natural photosynthesis, in the artificial analog sunlight sets in action a molecular electron pump. The sensitizer (S) is bound as a monomolecular coating on the surface of a semiconductor oxide, such as TiO_2, ZnO, SnO_2 or Nb_2O_5. 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 oxide. The conduction band electrons then cross the film 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 oxide 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 triiodide to iodide ions which diffuse from the counter electrode to the nanocrystalline film surface where they regenerate the sensitizer by electron transfer to the sensitizer cations, while simultaneously the iodide is oxidized back to iodine or triiodide. The redox catalytic cycle leading to the conversion of light into electrical current is thereby closed.

The Magazine of Catalysis Sciences, Technology and Innovation

CATTECH

SUBSCRIPTION

BULK
BULK
BULK
BULK

CATTECH now offers *bulk subscriptions* to academic and non-commercial institutions for *educational purposes*. The issues of CATTECH received as part of bulk subscriptions are for *personal use* of faculty staff and students *only* and are not to be made available to non-affiliated individuals or libraries.

The minimum number of copies to be ordered is 25. Bulk subscription applications can only be ordered directly from Baltzer Science Publishers.

If your institute is interested in an *educational bulk subscription*, please make use of the application form below.

Price: Sfr 20.- /US$ 14.- per copy (excluding postage)

One 'copy' refers to one annual volume of two issues.

CATTECH Volume 3, 1999, ISSN 1384-6566

Yes, we are interested and we would like to order a bulk subscription

Please indicate payment method:

○ Check enclosed
○ Please send invoice
○ Please charge to our credit card
  ○ Euro/MasterCard ○ VISA
  Card no.: .... Cardholder: ....
  Expiry date: ....

Name (please print): ....
Address: ....
City: ....
Postal code: ....
Country: ....
E-mail address: ....
Date: .... Signature: ....

Number of copies .... (minium order 25 copies)

Baltzer Science Publishers
P.O. Box 221 — 1400 AE Bussum — The Netherlands — E-mail: publish@baltzer.nl — Tel. +31 35 6954 250 — Fax +31 35 6954

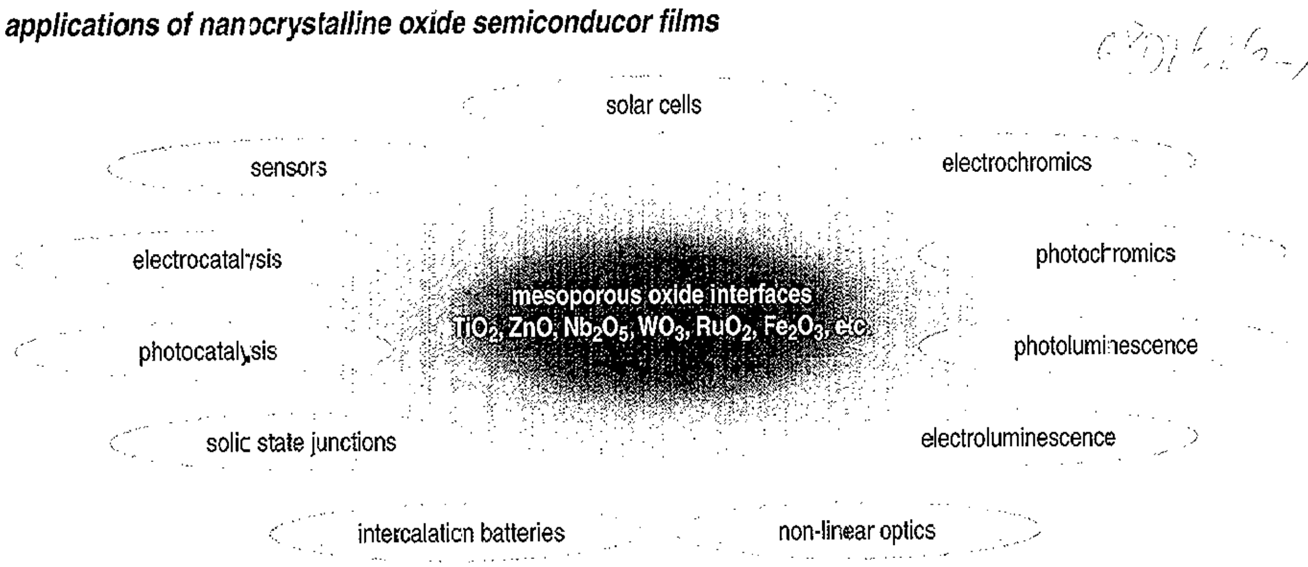

applications of nanocrystalline oxide semiconducor films

Figure 2. Applications of mesoporous oxide films.

sensitizer anchored as a monolayer on a rough titania surface. The mesoporous morphology of the support plays a crucial role in the harvesting of sunlight. It allows to capture the incoming photons efficiently despite of the fact that the oxide is covered only by a monolayer of dye. On a flat support this would absorb only a tiny fraction of the incident light. Photo-excitation of the dye initiates two coupled cyclic redox reactions, one involving the dye and the other the iodide/triiodide, Figure 1. As a result, electric power is produced from light in a catalytic fashion, i.e. without permanent chemical change. Both the dye and the iodide function as molecular redox catalyts. Judicious selection of the dye is able to reach turnover numbers as high as 100 million corresponding to about 20 years of operation of the device under natural conditions. The first results on this photocatalytic system were published in 1988[1] and in the same year I presented them during a lecture at an international congress in Chicago. After my talk I was approached by Brian O'Regan, a brilliant young graduate student working with Mark Anderson in the Water Department of the University of Wisconsin, who invited me for a seminar to Madison. It had occurred to Brian that the mesoporous TiO_2 membranes developed at Wisconsin for filtration purposes might present an advantage for our photoconversion systems. The quick experiment we carried out together during my visit looked so promising that Brian decided to join me for a few days during my sabbatical stay in Heinz Frei's laboratory at the University of California in Berkeley and later as a coworker at the Swiss Federal Institute of Technology in Lausanne. This collaboration produced groundbreaking results on the nanocrystalline TiO_2 films which we learned to prepare in a simple and reproducible fashion. In 1991 we announced a sensitized electrochemical photovoltaic device with a conversion efficiency at that time of 7.1% under solar illumination[2]. Progress since then has been incremental, a synergy of structure, substrate roughness and morphology, dye photophysics and electrolyte redox chemistry, the certified efficiency for conversion of air mass 1.5 solar radiation to electric power being now over 10%[3,4] under standard reporting conditions, i.e. 1000 W/m^2 incident solar power and 25°C.

Other catalytic and optoelectronic applications of these nanocrystalline oxide films emerged soon, in particular in photocatalysis and electrocatalysis, electroluminescent and electrochromic displays as well as sensors and lithium intercalation batteries. An overview of the different areas of current research and development is summarized in Figure 2. The photocatalytic device that resulted from this work uses similar concepts as green plants in order to harvest and convert solar energy. Therefore it is useful to briefly review the salient features of its natural analogue.

How does the green leaf operate ?

Green plants, algae and cyanobacteria make use of sunlight to drive a thermodynamically uphill reaction, the reduction of carbon dioxide to carbohydrates by water.

$$CO_2 + H_2O \rightarrow \tfrac{1}{6}C_6H_{12}O_6 + O_2 \qquad \Delta G = 522\ \text{kJ/mol}$$

ΔG = Gibbs free energy
per mole of reaction

The input chemicals are carbon dioxide and water while the output is oxygen and carbohydrates. The latter serve as a feed stock for other organic products such as wood, coal, oil and gas constituting the worlds' fossil fuel reserves, Figure 3. The amount of energy trapped by this natural photocatalytic process is enormous. About 100 billion tons of carbon dioxide are assimilated annually by plants on earth, whereby $3x10^{18}$ kJ of solar energy are harvested corresponding to the continuous generation of 90,000 gigawatt of electrical power.

Photosynthesis is comprised of a light and a dark reaction. The first, called photophosphorylation, involves the two-electron reduction of nicotinamide adenine di-

the photosynthesis of plants

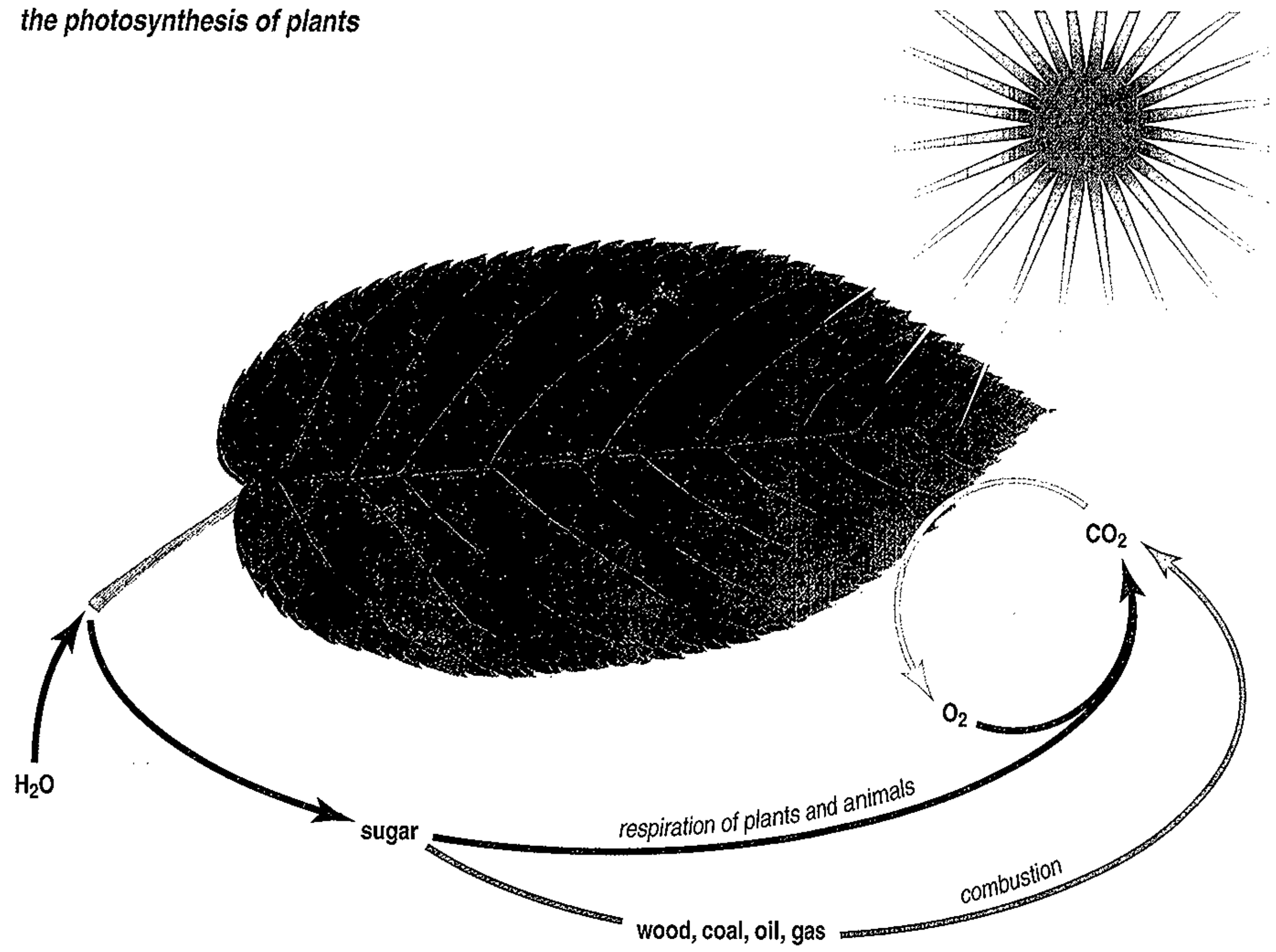


Figure 3. Photocatalytic carbon dioxide assimilation by green plants. The input chemicals for the green leaf are CO$_2$ and water while the output are oxygen and carbohydrates. The latter serve as a feed stock for other chemicals including our natural reserves of fossil fuels. The overall reaction of carbon dioxide assimilation is thermodynamically uphill by 522 kJ/mole. The free energy is supplied by sunlight which provides the driving force for the light reaction of photosynthesis.

nucleotide phosphate (NADP$^+$) by water, to produce NADPH and oxygen. The redox reaction is coupled to the generation of adenosine triphosphate (ATP) from adenosine diphosphate (ADP):

$$2H_2O + 2NADP^+ + 3ADP + 3P \rightarrow 2NADPH + H^+ + 3\,ATP + O_2$$

where P stands for the phosphate anion. This light-driven reaction takes place in the thylakoid membranes located in the interior of the chloroplasts of plant cells. The photosynthetic unit assembled in these membranes is composed of antenna pigments for light energy harvesting, i.e. chlorophyll and carotinoids, as well as a reaction center consisting of two photosystems. The photons absorbed by the antenna pigments are first transferred to a chlorophyll dimer that is part of the reaction center. The electronic excitation causes electrons to be ejected from the chlorophyll dimer and then passed on to various electron-transferring mediators. The judicious spatial arrangement of these components allows the electrons to be transferred in a vectorial fashion from the inner to the outer part of the membrane, Figure 4. The positive charges left behind produce oxygen and protons from water while the electrons reduce NADP$^+$ to NADPH. The latter is nothing else but a hydride, i.e. a stored form of hydrogen. The pH gradient generated across the membrane is used to store additional energy via the phosphorylation of ADP to ATP.

The dark reaction, known as Calvin cycle, uses the reducing power of NADPH as well as the free energy stored in the ATP to assimilate carbon dioxide in the form of carbohydrates. The way by which nature achieves carbon fixation is via the reaction of CO$_2$ with ribulosebiphosphate (RuBP) to give two molecules of 3-phosphoglycerate, a process which is catalyzed by the enzyme RuBP carboxylase. The phosphoglycerate is converted further to fructose 6-phosphate, the final product of the Calvin cycle. The overall reaction, despite its complex mechanism corresponds to the simple equation above.

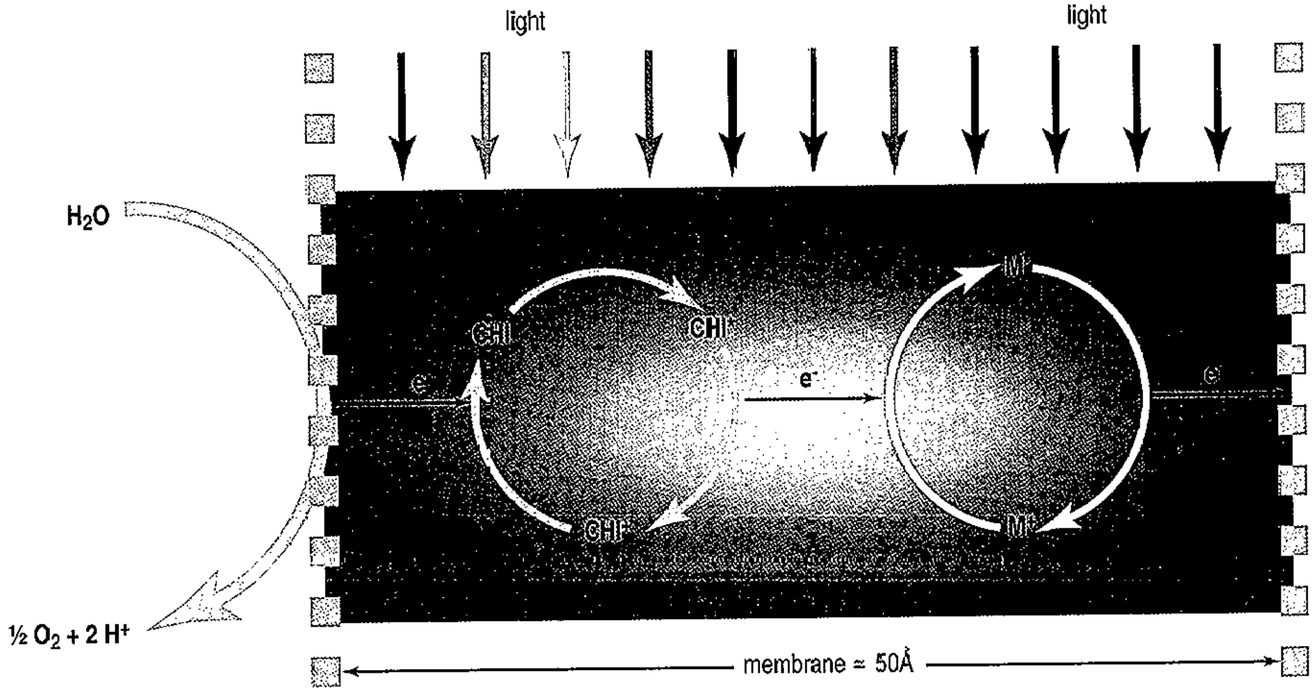


Figure 4. Schematic presentation of the cyclic redox reactions occurring during the light reaction in the green plants. Light serves as electron pump which is set in action by the excitation of chlorophyll molecules which serve as electron transfer sensitizer. The electrons are transferred through a series of redox mediators M from the inner part to the outer part of the membrane, resulting in charge separation. During the light reaction, the photon energy is converted to the electrochemical potential of the products oxygen, ATP and NADPH.

Mimicking the light reaction of natural photosynthesis

Light harvesting by monomolecular layers

For the absorption of solar rays by a sensitizer attached as a monolayer to the surface of an oxide film, there is a fundamental problem of the limited light capture cross section of the dye molecule. The cross section σ is related to the molar extinction coefficient ε by the formula:

$$\sigma = \varepsilon \times 1000/N_A,$$
$$N_A = \text{Avogadro's number} = 6 \times 10^{23} \text{ molecules / mole}$$

Typical ε-values for dyes lie between 10^4 and 5×10^5 M^{-1} cm^{-1} yielding for the light capture cross section values between 0.0016 and 0.08 nm^2. The area the sensitizer molecule occupies on the surface of the supporting oxide is much larger, e.g. about 1-2 nm^2. Hence at most a few percent of the incident light can be absorbed. One could naturally think, then, of depositing a multilayer of dye on the oxide in order to increase its 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 photocatalysis.

A successful strategy to solve the problem of light absorption through such molecular layers is found in the application of high surface area films consisting of nanocrystalline oxide particles with a diameter of 10-20 nm. The mesoporous morphology of the layer plays a crucial role in the harvesting of sunlight. Depending on film thickness, their real surface area can easily be made 1000 times larger than the apparent one. This is able to capture the incoming photons efficiently: when light penetrates the dye covered oxide "sponge", it crosses hundreds of adsorbed dye monolayers. Thereby photons whose energy is close to the absorption maximum of the dye are completely absorbed. The mesoporous structure thus mimics the light absorption by green leaves. The chlorophyll containing thylakoids are stacked and visible light is absorbed completely by traversing the superimposed vesicles.

Consider the case of a 3 micron thick mesoporous film whose effective surface is about 300 times greater than that of a compact oxide and that the film is covered by a monolayer of dye molecules each of which occupies an area of 1 nm. On the geometric projection of such a rough surface a dye coverage of $\Gamma = 3 \times 10^{16}$ molecules cm^{-2} is reached. Its absorbance A is given by the equation:

$$A = \Gamma \times \sigma$$

Suppose that the dye molecule at the wavelength of its absorption maximum has a light capture cross section of 0.005 nm^2 = 0.5×10^{-16} cm^2. As a result the absorbance of the film would be 1.5. Neglecting light scattering by the film its light harvesting efficiency (LHE) is given by:

$$\text{LHE} = 1 - 10^{-A}$$

For A = 1.5, LHE is 0.97 implying that 97% of the incident photons are absorbed.

Preparation and morphology of mesoscopic oxide semiconductor films

Mesoporous oxide films are commonly produced via a sol-gel type process involving a hydrothermal step. The procedure is illustrated for TiO_2 in Figure 5. The precipitation process involves controlled hydrolysis of a Ti(IV) salt, usually an alkoxide such as Ti-isopropoxide or a chloride, followed by peptization. Autoclaving of these sols (heating at 200-250°C for 12 h) allows for controlled growth of the primary particles and improves their crystallinity. During this hydrothermal growth smaller particles dissolve and fuse to large particles by a process known as "Ostwald ripening". After removal of solvent and addition of a binder the sol is now ready for deposition on the substrate. For the latter a conducting glass (sheet resistance = 8-10 Ohm/square) is often used. The sol is deposited by doctor blading or screen printing and fired in air for sintering. The film thickness is typically 5-10 μm and the film mass about 1-2 mg/cm². The electronic contact between the particles is produced by brief sintering at about 500°C. A mesoporous structure with a very high effective surface area is thereby formed. Analysis of the layers shows their porosity to be about 60 % the average pore size being 12 nm. Figure 6 illustrates the morphology of such a nanocrystalline TiO_2 (anatase) layer deposited on a transparent conducting oxide (TCO) glass. A large fraction of the particles has a bipyramidal morphology which is typical for anatase. The exposed surface facettes are mostly oriented in the (101) direction[5]. The mean particle diameter of the oxide is 20 nm in this case. Their size and morphology can be adjusted by varying the conditions of the sol-geltype process used for film preparation. Films of self-assembled rod-like particles have been obtained if the hydrothermal treatment of the TiO_2 colloid is done in the presence of tetramethylammonium hydroxide at 190 - 230°C. SEM micrographs illustrating the self-ordering of the nanoparticles are shown in Figure 7. The rod-like particles were observed to have (100) faces terminated from the (001) side. The pores diameter of the film is 4 nm with a very narrow size distribution[6].

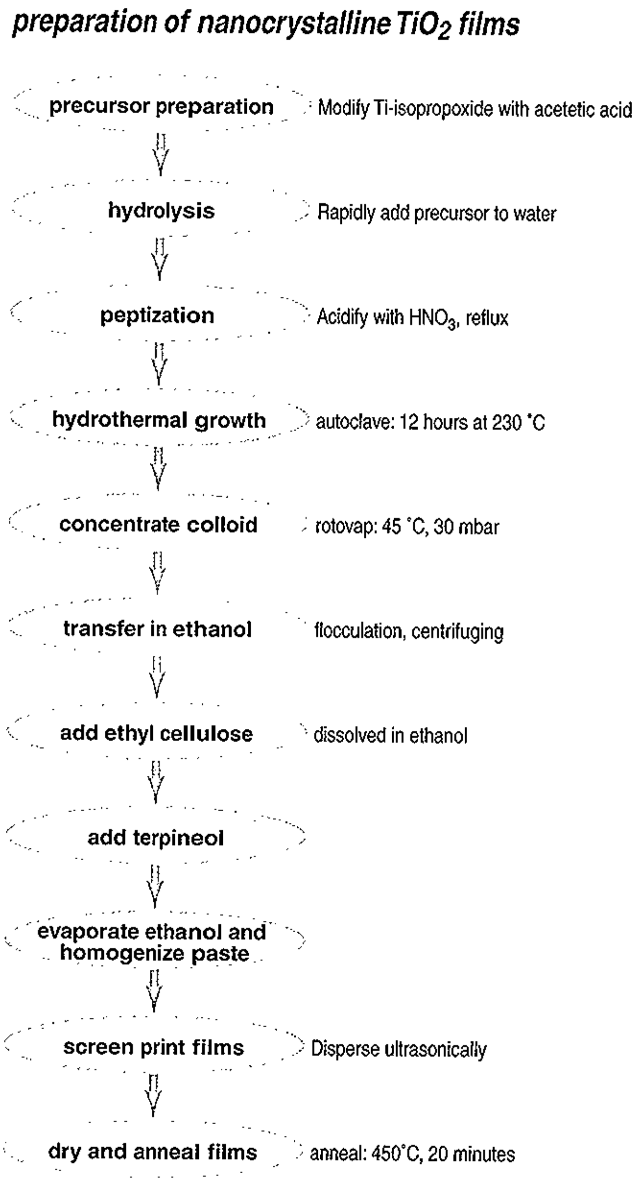
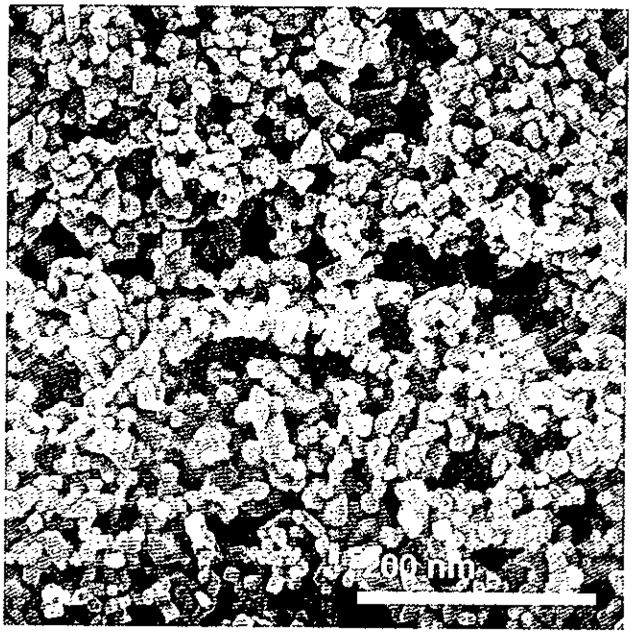
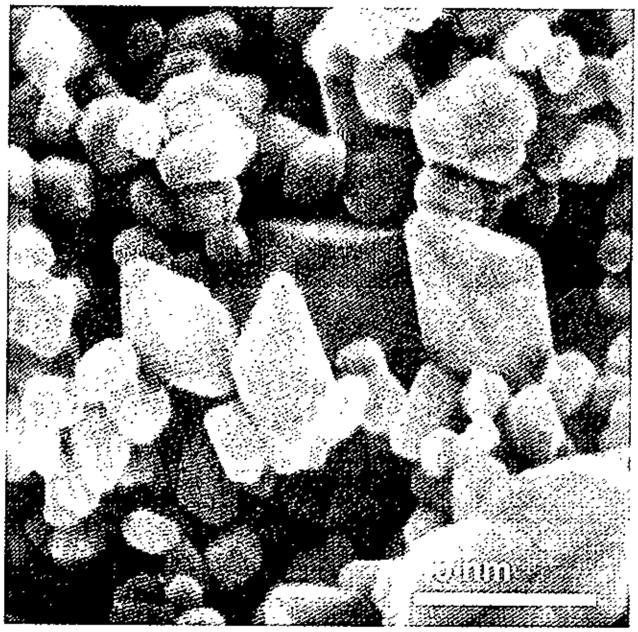
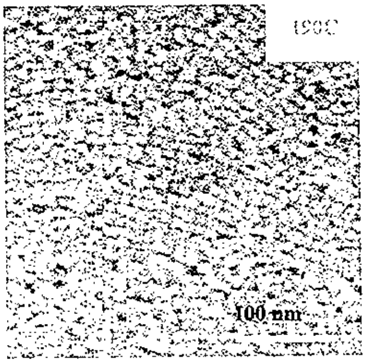
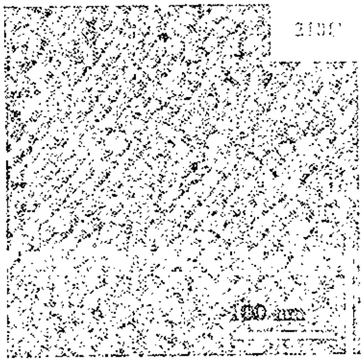


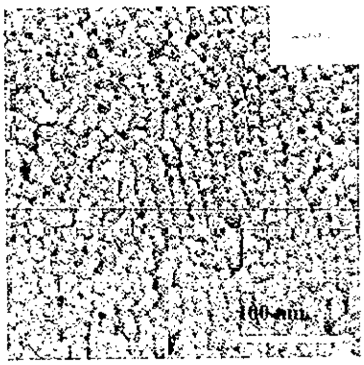
Figure 5. (above) Outline of the steps involved in the preparation of mesoporous TiO_2 films.

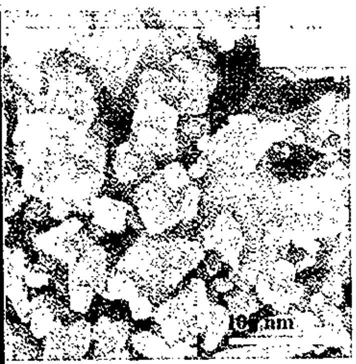












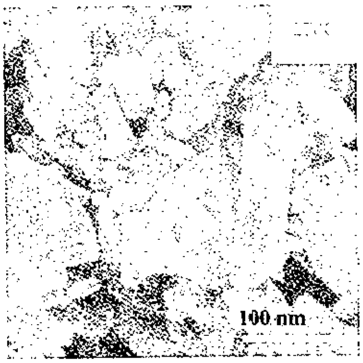
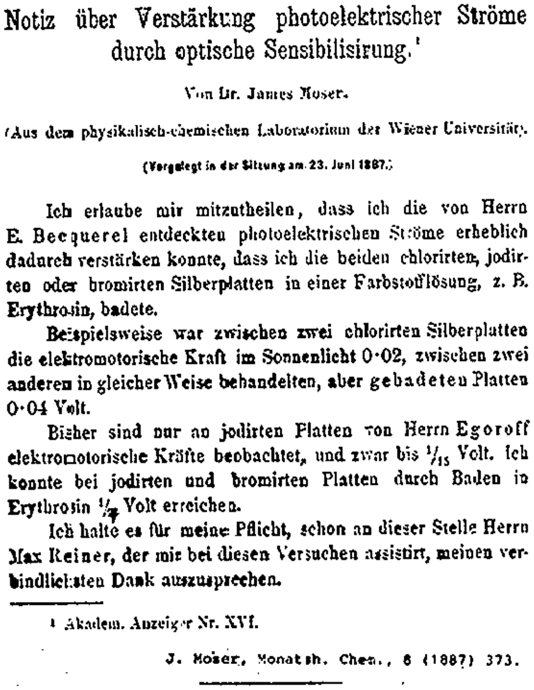


Figure 7. (above) SEM micrographs of thin films deposited from TiO_2 colloids autoclaved at different temperatures.

igure 6. (left below) Scanning electron micrograph of a mesoporous TiO_2 films upported on conducting glass. The predominant facets of the anatase crystals ave (101) orientation.

Photoinduced charge separation at the dye/oxide interface

The use of mesoporous oxide films as a substrate to anchor the dye molecules allows sunlight to be harvested over a broad spectral range in the visible region. Similarly to chlorophyll in the green leaf, the dye acts as a in electron transfer sensitizer. Upon excitation by light it injects electrons in the conduction band of the oxide resulting in separation of positive and negative charges. Charge transfer from photo-excited dyes into semiconductors was discovered more than 100 years ago in a famous experiment by James Moser at the University of Vienna[7]. He observed that the photoelectric effect detected first by Becquerel on silver plates[8] was enhanced in the presence of erythrosine. The one-page publication describing his observations is shown in Figure 8. A few years before, Vogel in Berlin had associated dyes with the halide semiconductor grains to make them sensitive to visible light[9].This led to the first panchromatic film, able to render the image of a scene realistically into black and white[10]. However, the clear recognition of the parallelism between the two procedures, a realization that the same dyes in principle can function in both systems[11] and a verification that their operating mechanism is by injection of electrons from photo-excited dye molecules into the conduction band of the n-type semiconductor substrates[12] date to the 1960's. In subsequent years the idea developed that the dye could function most efficiently if chemisorbed on the surface of semiconductor[13,14]. The concept emerged to use dispersed particles to provide a sufficient interface[15], then photo-electrodes were employed[16] Titanium dioxide became the semiconductor of choice. The material has many advantages for sensitized photochemistry and photo-electrochemistry: it is a low cost, widely available, non-toxic and biocompatible substance, and as such is even used in health care products as well as domestic applications such as paint pigmentation.



Notiz über Verstärkung photoelektrischer Ströme durch optische Sensibilisirung.[1]

Von Dr. James Moser.

(Aus dem physikalisch-chemischen Laboratorium der Wiener Universität.)

(Vorgelegt in der Sitzung am 23. Juni 1887.)

Ich erlaube mir mitzutheilen, dass ich die von Herrn E. Becquerel entdeckten photoelektrischen Ströme erheblich dadurch verstärken konnte, dass ich die beiden chlorirten, jodirten oder bromirten Silberplatten in einer Farbstofflösung, z. B. Erythrosin, badete.

Beispielsweise war zwischen zwei chlorirten Silberplatten die elektromotorische Kraft im Sonnenlicht 0·02, zwischen zwei anderen in gleicher Weise behandelten, aber gebadeten Platten 0·04 Volt.

Bisher sind nur an jodirten Platten von Herrn Egoroff elektromotorische Kräfte beobachtet, und zwar bis $^{1}/_{15}$ Volt. Ich konnte bei jodirten und bromirten Platten durch Baden in Erythrosin $^{1}/_{4}$ Volt erreichen.

Ich halte es für meine Pflicht, schon an dieser Stelle Herrn Max Reiner, der mir bei diesen Versuchen assistirt, meinen verbindlichsten Dank auszusprechen.

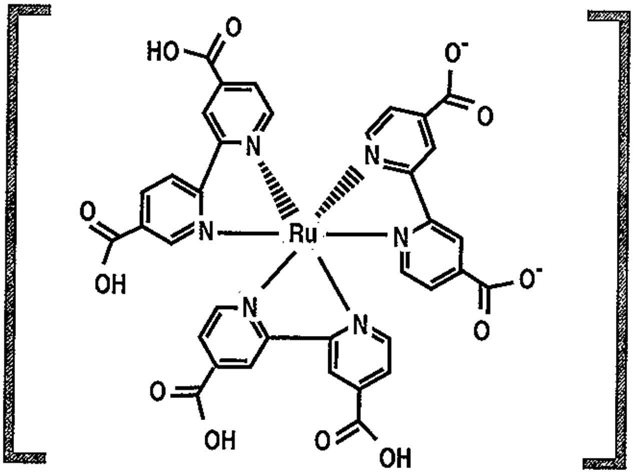
---

[1] Akadem. Anzeiger Nr. XVI.

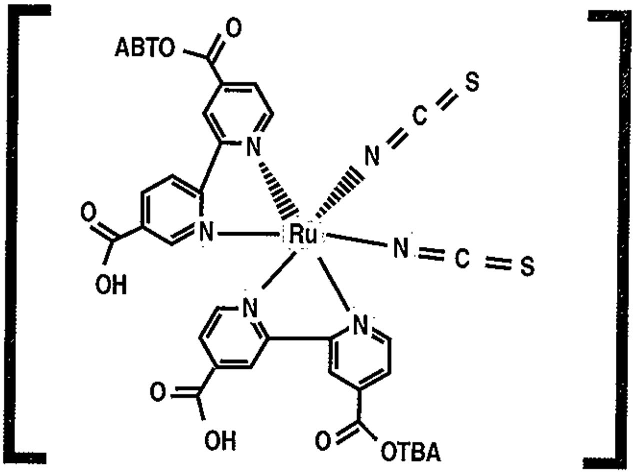
J. Moser, Monatsh. Chem., 8 (1887) 373.

Figure 8. (right) A copy of the 1887 publication by James Moser on the amplification of photoelectric currents by optical sensitization.

RuL_3



$RuL_2(NCS)_2$



$RuL'(NCS)_3$

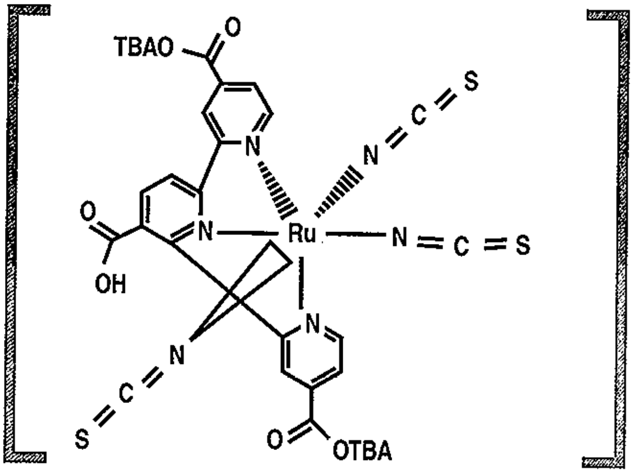


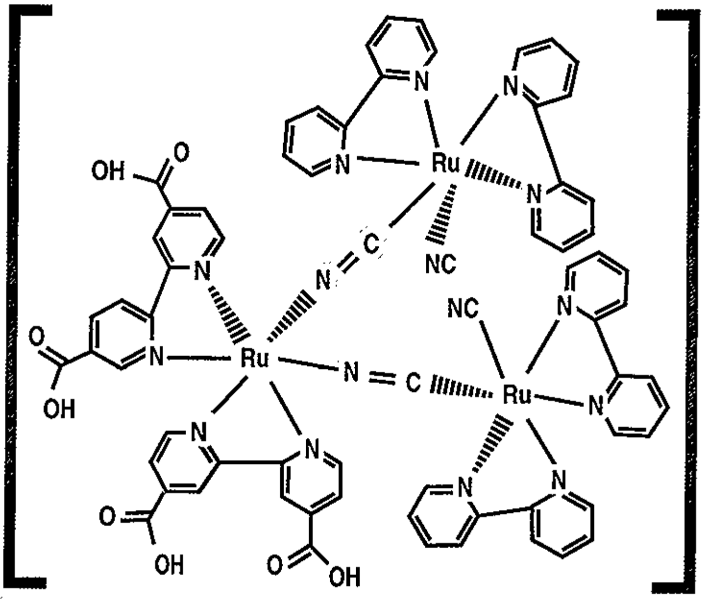
Figure 9. Molecular structures of ruthenium complexes used as charge transfer sensitizers.

For efficient photo-conversion, the charge injection must occur with unit quantum yield. Rate constants for electron transfer from excited dyes into TiO_2 have been determined by time resolved laser photolysis experiments and some representative examples are shown in Table 1[17]. The rates vary over 8 orders of magnitude depending on the type of dye employed, the fastest injection times being in the femtosecond domain. The key to obtain such rapid electron transfer is to endow the dye with a suitable anchoring group, such as a carboxylate or phosphonate substituent or a catechol moiety, through which the sensitizer is firmly grafted onto the surface of the titania. The role of these groups is to provide good overlap between the dye molecule's excited state orbital and the empty acceptor levels, i.e. the Ti^{IV}-3d orbital manifold forming the conduction band of TiO_2. Alizarin is a special case as it produces a strongly colored complex by reacting directly with titanium ions present at the surface of TiO_2. The extend of coupling is expressed by the electronic coupling matrix element V which is related to the rate constant for charge injection by the equation

$$k_{inj} = (2\pi / h) \cdot |V|^2 \cdot \rho$$

here h is Planck's constant, |V| is the electron coupling matrix element and ρ is the density of electronic acceptor states in the conduction band of the semiconductor. The equation assumes that electron transfer from the excited dye molecules into the semiconductors is activationless and hence exhibits a temperature independent rate. This has been confirmed experimentally. For example the charge injection from excited perylene dye was found to be temperature independent from 4 to 300 K[18]. The explanation for this is that there is a continuum of electronic states in the conduction band accessible to the injected electron which combined with the different vibrational levels of the other reaction product, i.e. the oxidized dye, yields a multitude of possible

$RuL_2\{(NC)_2Ru(bpy)_2\}_2$



reaction pathways. At least one channel is likely to be barrierless implying that the driving force of electron transfer compensates the reorganisation energy, i.e. the free energy necessary to rearrange the nuclear coordinates of the dye/solvent system accompanying electron transfer. The activationless channel is the fastest and hence will be the preferred mechanism for the reaction.

The most promising results have so far been obtained with ruthenium complexes where at least one of the ligands was 4,4'-dicarboxy-2,2'-bipyridyl. A few typical structures for this kind of charge transfer sensitizers are shown in Figure 9. The carboxylates groups serve to attach the Ru complex to the surface of the oxide and to establish good electronic coupling between the π^* orbital of the electronically excited complex and the 3d wavefunction manifold of the TiO_2 film, Figure 10. The substitution of the bipyridyl with the carboxylate groups lowers also 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, i.e. the one from which electron injection into the semiconductor takes place. With molecules like these, charge injection occurs in the femtosecond time domaine, Table 1. By contrast, the recapture of the electrons by the oxidized dye is at least six orders of magnitude slower. The rational for this behavior is that the back reaction 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 weakens further the electronic coupling. A second very important contribution to the kinetic retardation of charge recombination arises from the fact that this process is characterized by a large driving force and small reorganization energy, the respective values for RuL2(NCS)2 being 1.5 and 0.3 eV, respectively. This places the electron recapture clearly in the inverted Markus region reducing its rate by several orders of magnitude. This provides also a rational for the observation that this interfacial redox process is almost independent of temperature and is surprisingly insensitive to the ambient that is in contact with the film[19].

Of significance for the inhibition of charge recombination is the existence of a local electric field at the surface of the titanium dioxide film. While there is practically no depletion layer within the oxide due to the small size of the particles and their low doping level, a surface field is established spontaneously by proton transfer from the protonated carboxylate or phophonate groups of the ruthenium complex to the oxide surface producing a surface dipol layer. If the film is placed in contact with a protic solvent the latter can also act as proton donor. In aprotic media, Li^+ or Mg^{2+} are potential determining ions for TiO_2[20] and they may be used to charge the surface positively. The local potential gradient from the negatively charged sensitizer to the positively charged oxide drives the injection in the desired direction. The same field inhibits also the electrons from exiting the solid after injection has taken place.

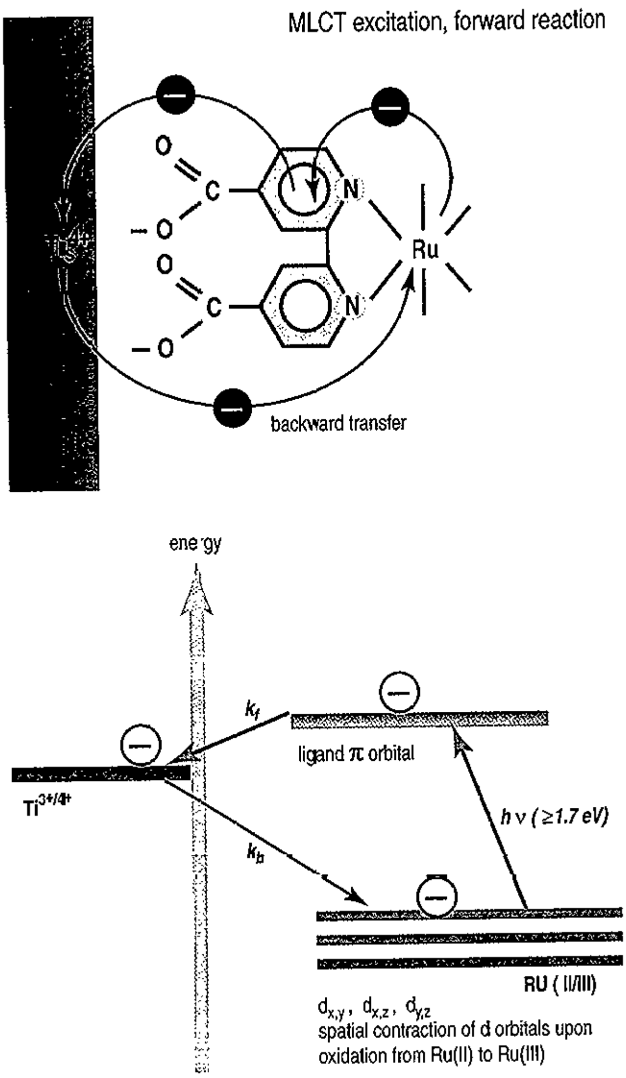


photo induced heterogeneous electrons transfer cycle

Figure 10. Interfacial electron transfer reactions involving ruthenium complexes anchored to the oxide through a carboxylated bipyridyl group. Molecular configuration of the adsorbed dye and orbital energy diagram.

Sensitizers	k_{inj} [s^{-1}]	[V] [cm^{-1}]	t_r [ns]	Φ_{inj}
$Ru^{II}(bpy)_3$	2 ¥ 10^5	0.04	600	0.1
$Ru^{II}L_3(H_2O)$	3 ¥ 10^7	0.3	600	0.6
Eosin-Y	9 ¥ 10^8	2	1	0.4
$Ru^{II}L_3(EtOH)$	4 ¥ 10^{12}	90	600	1
Coumarin-343	5 ¥ 10^{12}	100	10	1
$Ru^{II}L_2(NCS)_2$	10^{13}	130	50	1
Ti_i^{IV}-Alizarin	> 10^{13}	5 ¥ 10^3	-	1

Table 1. Electron injection rate constants k_{inj} and electronic coupling matrix elements |V| measured by laser flash photolysis for various sensitizers adsorbed onto nanocrystalline TiO_2. t_r and Φ_{inj} are the excited state lifetime and the injection quantum yield, respectively. In the sensitizers column, L stands for the 4,4'-dicarboxy-2,2'-bipyridyl ligand and bipy for 2,2'-bipyridyl.

Investigations have centered so far largely on *cis*-dithiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylate)-ruthenium(II), $RuL_2(SCN)_2$ which displays extraordinary properties as a charge transfer sensitizer[21]. The adsorption of this complex onto mesoporous TiO_2 (anatase) from an acetonitrile/tert.butanol solvent mixture follows a Langmuir isotherm. The binding constant and the area occupied by the dye at the surface were determined as $5x10^4 M^{-1}$ and 1.6 nm^2/molecule, respectively. Molecular dynamics calculations have been used to model the interaction of this sensitizer with the (101) surface plane of anatase[22]. The most likely configuration which is compatible with the results from the adsorption isotherm measurements is shown in Figure 11a. The dye is attached via two of its four carboxylate groups. The anchoring of the carboxylate occurs either through bridging of two surface titanium ions from adjacent rows or through hydrogen bonding to Ti-OH groups. This configuration is supported also by recent infrared absorption studies[23]. Figure 11b shows a top view of the dye loaded (101) anatase surface of the RuL_2SCN_2-molecules being presented with their contacting van der Waals surfaces. Surface reconstruction is not taken into account here. Relaxation effects have however been quantified in the context of recent density functional calculation of water adsorption on anatase[24].

Charge carrier percolation and collection
The migration of electrons within the TiO_2 conduction band to the current collector involves charge carrier percolation over the mesoscopic particle network. This important process which leads to nearly quantitative collection of injected electrons is presently attracting a great deal of attention[25-30]. For example, the elegant experiments conceived by Rensmo et al.[26] have given useful keys to rationalize the intriguing findings made with these films under band gap illumination.

It should be noted that apart from recapture of the electrons by the oxidized dye there is an additional loss channel in the nanocrystalline injection cell which involves reduction of triiodide ions in the electrolyte present within the mesoporous network.

$$I_3^- + 2e^-_{cb}(TiO_2) \rightarrow 3I^-$$

This reaction can be directly followed by measuring the dark current of the photovoltaic cell. The latter should be kept at a minimal level as it determines the photovoltage of the cell. Engineering the interface to prevent this unwanted heterogeneous redox process will be a challenging task for future development. The high contact area of the junction nanocrystalline solar cells renders mandatory the grasp and control of interfacial effects for future improvement of cell performance. The nature of the exposed surface planes of the oxide and the mode of interaction with the dye is the first important information to gather. Synthetic efforts will focus on the molecular engineering of sensitizers that enhance the charge separation at the oxide solution interface. The structural features of the dye should match the requirements for current rectification: in analogy to the photo-field effect in transistors, the gate for unidirectional electron flow from the electrolyte through the junction and into the oxide is opened by the photo-excitation of the sensitizer. The reverse charge flow, i.e. recapture of the electron by the electrolyte could be impaired by judicious design of the sensitizer. The latter should form a tightly packed insulating monolayer blocking the dark current to yield higher cell voltage.

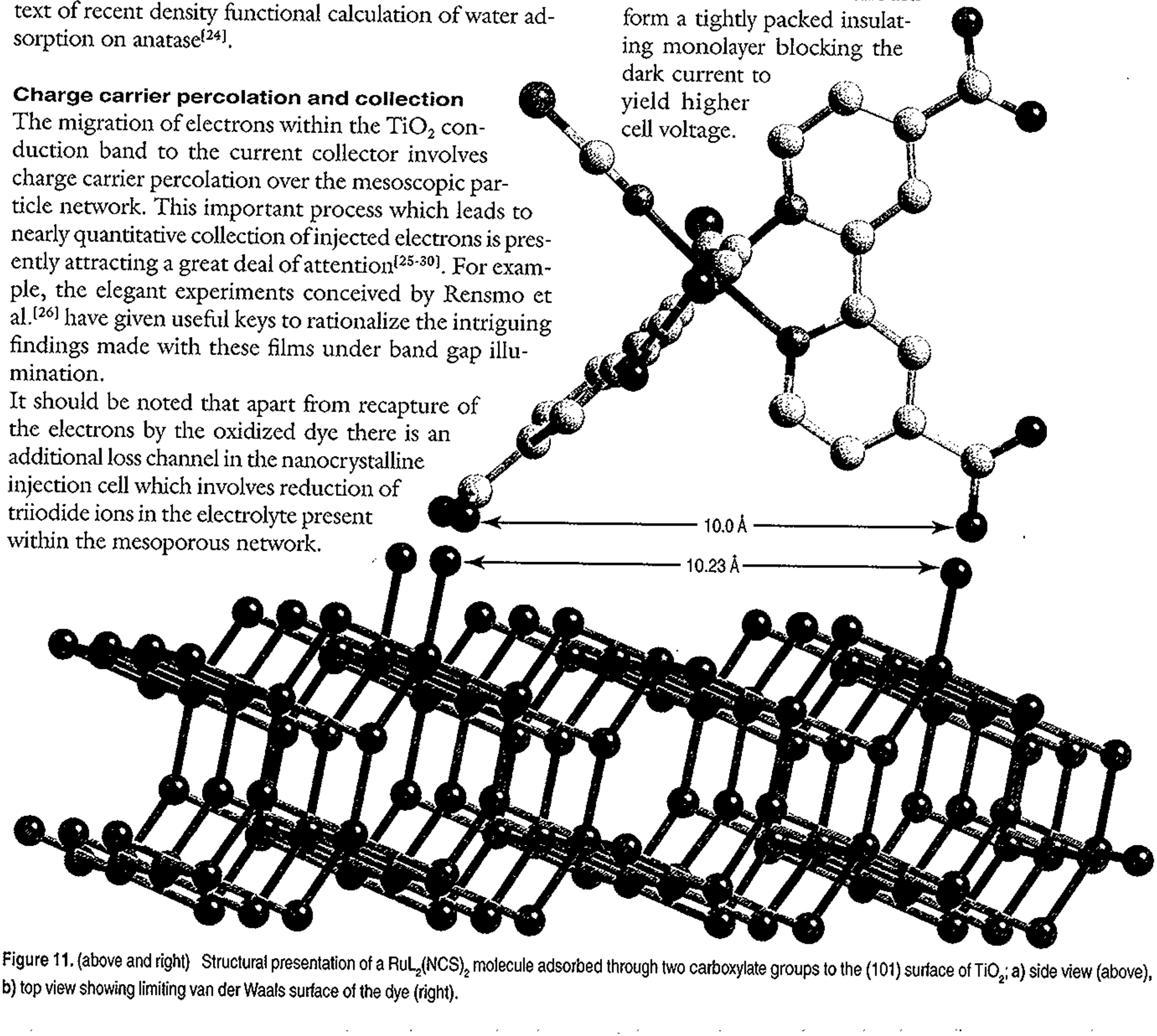


Figure 11. (above and right) Structural presentation of a $RuL_2(NCS)_2$ molecule adsorbed through two carboxylate groups to the (101) surface of TiO_2; a) side view (above), b) top view showing limiting van der Waals surface of the dye (right).

Photocatalysis and electric power generation from light

A scheme of the photocatalytic device used in the generation of electric power from light is shown in Figure 12. The mesoporous semiconductor oxide films is sandwiched between two conducting glass plates, its pore space being filled with a redox electrolyte or a hole conductor. We have shown above how the molecular properties of the sensitizer are chemically engineered to ascertain efficient electron injection from the excited state (S*) into the conduction band of the titanium dioxide. We also discussed how the recapture of the electrons by the oxidized dye (S^+) is intercepted by transferring the positive charge to a redox mediator R/R^+, i.e the iodide/triiodide couple, present in the electrolyte and thence to the counter electrode. Via this last charge transfer, in which the mediator is returned to its reduced state, the circuit is closed. The system converts light into electricity in a catalytic fashion, i.e. without permanent chemical transformation. The maximum voltage ΔV that such a device could deliver corresponds to the difference between the redox potential of the mediator and the conduction band position of the semiconductor.

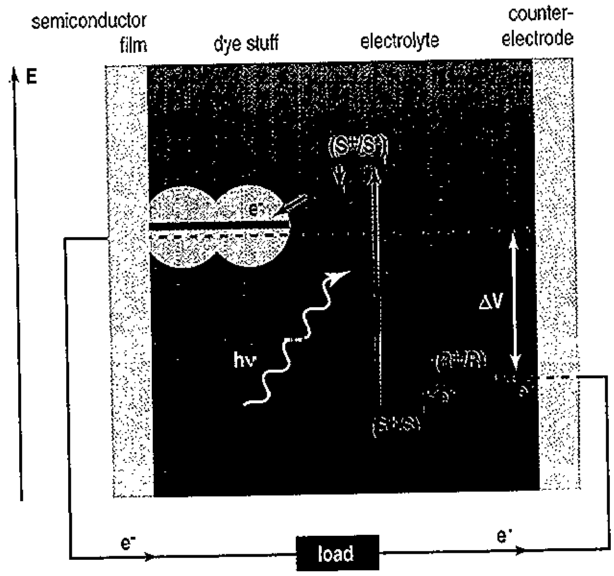


Figure 12. (above) Schematic representation of the principle of the nanocrystalline injection cell to indicate the energy level in the different phases. The cell voltage observed under illumination corresponds to the difference in the quasi-Fermi level of the TiO_2 under illumination and the electrochemical 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.

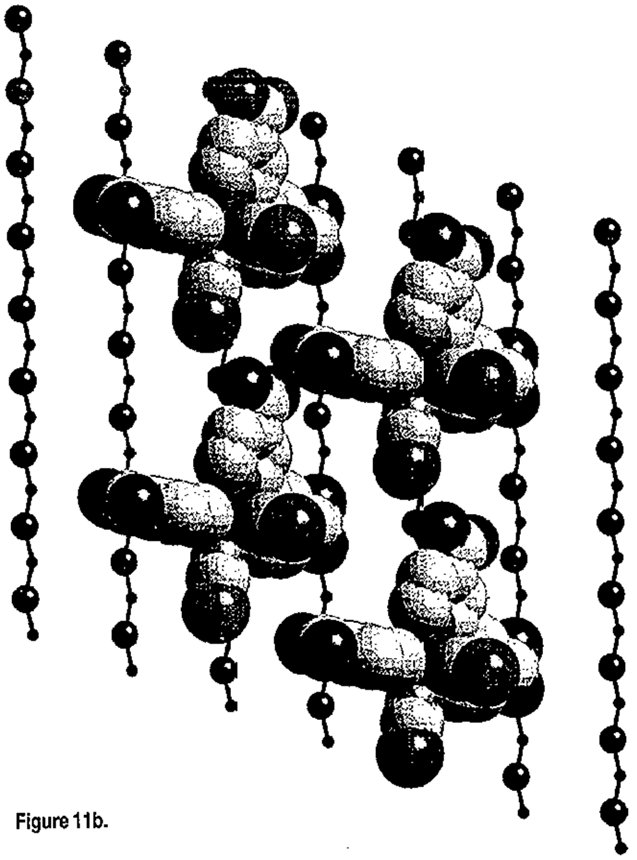
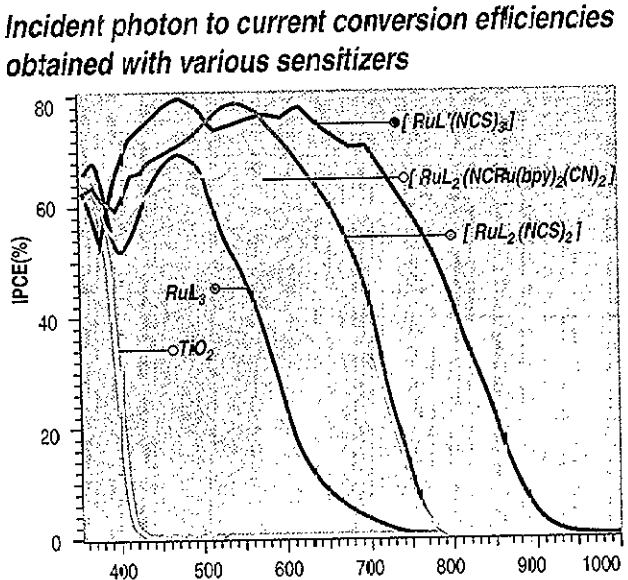


Figure 11b.

A graph which presents the conversion efficiency of incident monochromatic light in electric current is shown for several ruthenium complexes in Figure 13. Very high efficiencies of current generation, exceeding 80%, were obtained. When corrected for the inevitable reflection and absorption losses in the conducting glass serving to support the nanocrystalline film the yields are practically 100 percent. Historically, RuL_3 (L = 2,2'-bipyridyl-4,4'-dicarboxylate) was the first efficient and stable charge transfer sensitizer to be used in conjunction with high surface area TiO_2 films. However, its visible light absorption is insufficient for solar light conversion. A significant enhancement of the light harvesting was achieved in 1990 with the trimeric complex of ruthenium whose two peripheral ruthenium moieties were designed to serve as antennas[31]. The advent of $RuL_2(NCS)_2$ in 1991 marked a further improvement since it extended the light absorption over a broad range in the visible[3]. Its performance was only superseded


Incident photon to current conversion efficiencies obtained with various sensitizers

L' = 4, 4', 4'' - tricarboxy - 2,2' : 6', 2'' - terpyridine
L = 4, 4' - dicarboxy - 2, 2' - bipyridine

Figure 13. Photocurrent action spectrum obtained with four different ruthenium complexes attached to the nanocrystalline TiO_2 film. The blank spectrum obtained with the bare TiO_2 surface is shown for comparison. The incident photon to current conversion efficiency is plotted as a function of the wavelength of the exciting light.

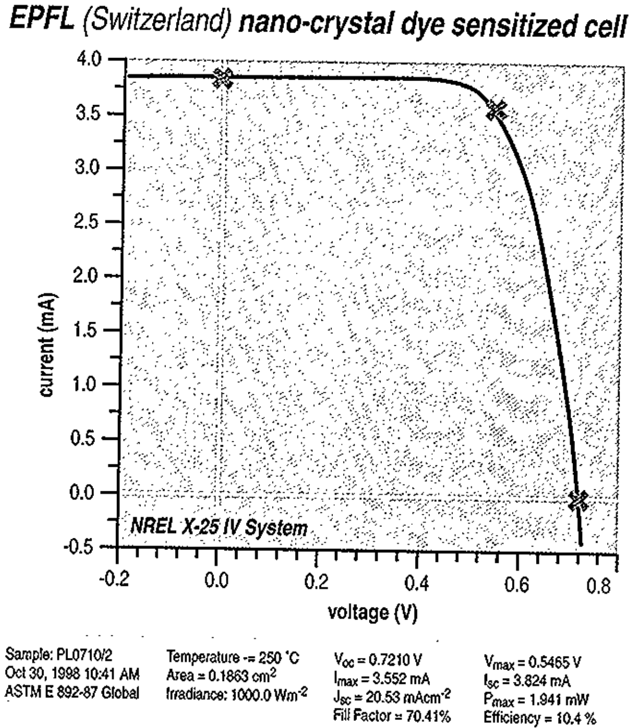


Figure 14. Photocurrent voltage curve for a nanocrystalline photovoltaic cell based on black dye as a sensitizer.

recently by the discovery of a new black dye[32] tri(cyanato)-2.2'2"-terpyridyl-4,4'4"-tricarboxylate)-ruthenium(II) having a spectral onset at 900 nm which is optimal for the conversion of AM 1.5 solar radiation to electric power in a single junction photovoltaic cell. 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).

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

Figure 14 gives an example for the current-voltage characteristics of a nanocrystalline injection solar cell based on the black dye sensitizer as measured in the photovoltaic test laboratory at the National Research and Energy Laboratory in Golden Colorado, USA. The overall solar to electric conversion efficiency air mass 1.5 -type sunlight for under standard reporting conditions, i.e. 1000 W/m² incident light intensity 25°C is confirmed as 10.4% which is commensurate with the performance of conventional photovoltaic devices. An advantage of the nanocrystalline solar cell with respect to competing technologies is that its performance is remarkably insensitive to temperature change. Thus, raising the temperature from 20 to 60°C has practically no effect on the power conversion efficiency. In contrast, conventional silicon cells exhibit a significant decline over the same temperature range amounting to ca. 20 percent. Since the temperature of a solar cell will reach readily 60°C under full sunlight this feature of the injection cell is particularly attractive for power generation under natural conditions.

The "Holy Grail" of photocatalysis: water cleavage by visible light

As pointed out by Allen Bard and Marye Anne Fox in a recent review[33], the photo driven conversion of liquid water to gaseous hydrogen and oxygen:

$$H_2O \rightarrow H_2 + 0.5\,O_2 \quad \Delta G° = 237.7\ \text{kJ/mol}$$

$\Delta G°$ = standard Gibbs free energy per mole of reaction

is the "Holy Grail" of all photocatalytic reactions. It has been a long standing challenge of practical artificial photosynthetic systems. The hydrogen produced from sunlight and water can be subsequently employed in the catalytic reduction of carbon dioxide to produce fuels such as methane or methanol. The latter could also be used as feed stock for the production of organic chemicals. Alternatively, hydrogen could serve directly as a fuel for transportation or for the production of electricity in fuel cells, without producing pollutants and green house gases upon combustion. For a practical system, a conversion efficiency of at least 10% is required, implying that the hydrogen and oxygen produced have a fuel value of at least 10% of the solar energy incident on the system. As the peak solar power incident on earth is about 1 kW/m² this corresponds to a hydrogen production rate of 0.7 mg/s or 7.8 mL(STP)/s per m² of collector surface at maximum solar intensity.

As water is transparent to sunlight, a sensitizer is required in order to absorb the solar photons and transduce their radiant energy to generate the chemical potential required to split the H_2O molecules. The optimal absorption threshold for a single photoconverter has been calculated to be at an energy of 1.6 eV[34] implying that all solar photons below 770 nm are absorbed. Such a system could split water with an efficiency of up to 30%. Higher efficiencies of up to 41% can be obtained by using a tandem device where two photosystems operate in series.

The "brute force" approach to achieve this goal is to employ a solid state photovoltaic cell to generate electricity that is subsequently passed into a commercial-type water electrolyzer. Although efficiencies obtained are high, i.e. close to 12%[35], these devices are very expensive. Hence the price of hydrogen produced this way cannot compete with conventional sources.

Photocatalytic water cleavage systems based on aqueous dispersions of semiconductor particles are much cheaper but their efficiency is generally below 1%[36]. They have the additional drawback that hydrogen and oxygen are produced simultaneously. Apart from the problem of gas separation this produces a slow down of the photoreaction as the two gases accumulate and back react with each other. A way to avoid the latter problem is to separate the hydrogen and oxygen generating half reactions as reported recently by Arakawa et al.[37].

We have developed a tandem device that achieves the direct cleavage of water into hydrogen and oxygen by visible light developed in collaboration with two partner groups from the University of Geneva and Bern[38]. This is based on the sseries connection of two photo-

Circuit diagram of the tandem cell for water photolysis

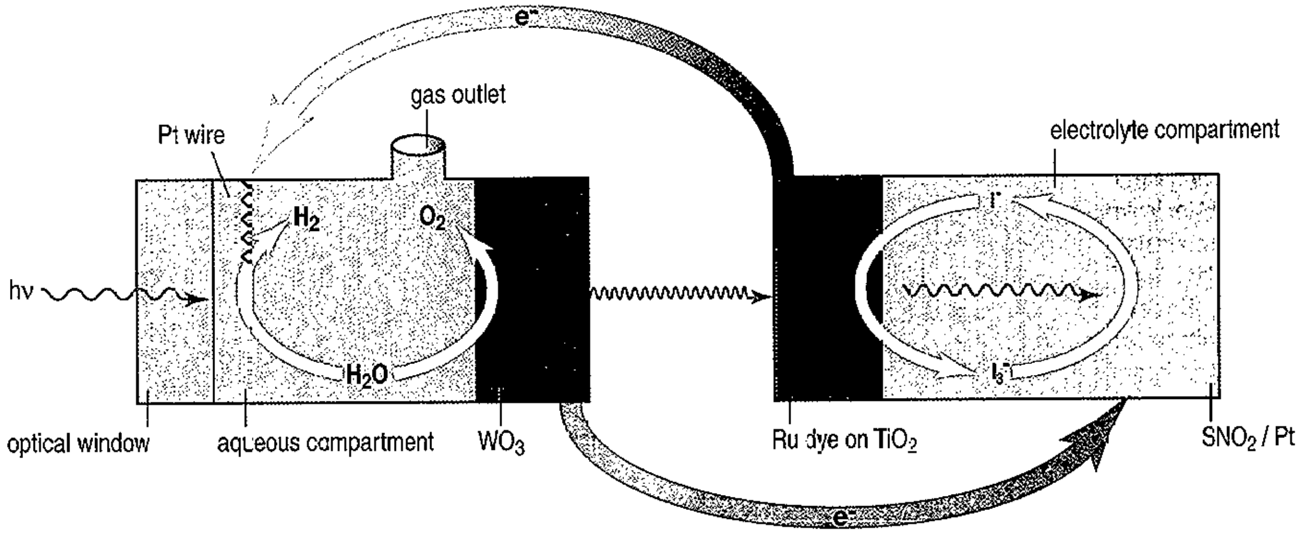


Figure 15. Circuit diagram of the tandem cell for water cleavage by visible light.

systems. A thin film of nanocrystalline tungsten trioxide absorbs the blue part of the solar spectrum.

$$WO_3 + h\nu \rightarrow WO_3(e^-, h^+)$$

The valence band holes (h^+) created by band gap excitation of the WO_3 serve to oxidize water to oxygen:

$$4h^+ + H_2O \rightarrow O_2 + 4H^+$$

while the conduction band electrons are fed into the second photosystem. It consists of the dye sensitized nanocrystalline TiO_2 film. The latter is placed directly behind the WO_3 film capturing the green and red part of the solar spectrum that is transmitted through the top electrode, Figure 15. The photovoltage generated by the second photosystem enables the generation of hydrogen by the conduction band electrons.

$$4H^+ + 4e^- \rightarrow 2H_2$$

The overall reaction corresponds to the splitting of water by visible light.

There is close analogy to the Z-scheme operative in the light reaction of photosynthesis in green plants. This is illustrated by the electron flow diagram shown in Figure 16. In green plants, there are also two photosystems connected in series, one affording water oxidation to oxygen and the other generating the NADPH used in carbon dioxide fixation. As discussed above, the advantage of the tandem approach is that higher efficiencies than with single junction cells can be reached if the two photosystems absorb complimentary parts of the solar spectrum. At present the overall AM 1.5 solar light to chemical conversion efficiency achieved with this device stands at 4.5%. Figure 17 shows a photograph of such a cell producing hydrogen and oxygen bubbles vigorously under visible light illumination. Present endeavors aim at further improving the efficiency of the device.

The Z scheme of biphotonic water photolysis

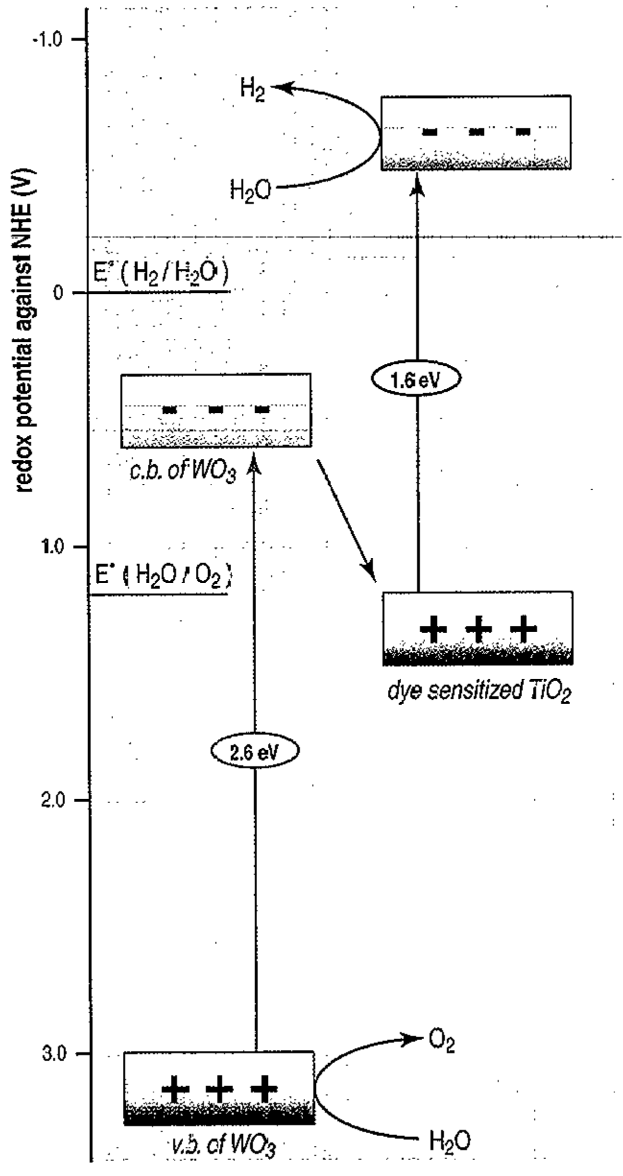


Figure 16. The Z-scheme of biphotonic water photolysis.

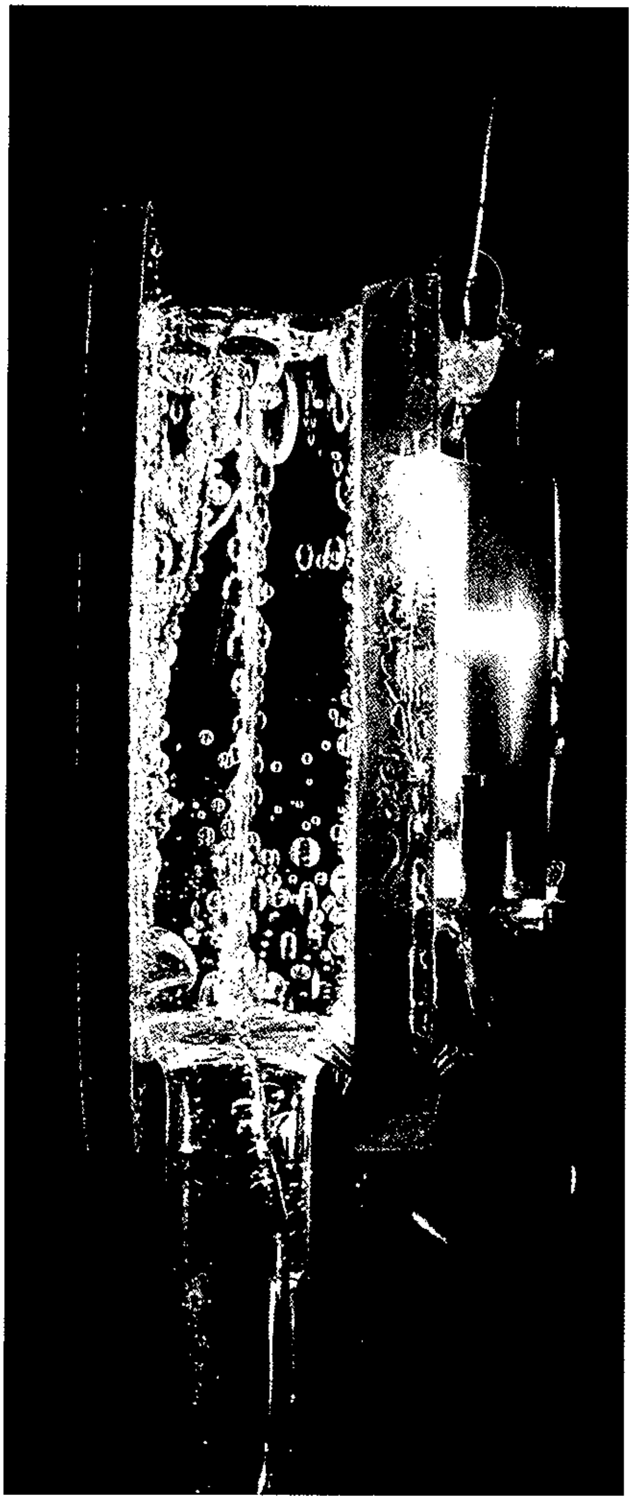


Figure 17. Photograph showing the decomposition of water by visible light using a tandem cell consisting of a mesoporous WO_3 film and a mesoporous dye sensitized TiO_2 which are superimposed.

Outlook

Intensive research is presently carried out around the world focusing on the following issues:

i) the molecular design and synthesis of new sensitizers having enhanced near infrared light response, examples being phthalocyanines or the black dye discussed above;

ii) a better understanding of the interface, including experimental and theoretical work on dye adsorption processes;

iii) the analysis of the dynamics of interfacial electron transfer processes down to the femtosecond time domain;

iv) the unraveling of the factors that control electron transport in nanocrystalline oxide semiconductor films;

v) the replacement of the liquid electrolyte by solid materials;

vi) the development of tandem cells and their use for the cleavage of water by visible light.

Rapid progress is expected in these areas as an impressive number of competent teams around the world are actively pursuing this research. These systems will undoubtedly promote the acceptance of renewable energy technologies, not least by setting new standards of convenience and economy.

questions and answers

What is the turnover frequency of the dye in the mesoporous solar cell?

Typically the dye loading of the mesoporous TiO_2 film is 10^{-7} moles per cm^2. In direct sunshine the photocurrent density reaches 20 mA/cm^2. Hence each sensitizer molecule undergoes the injection/regeneration cycle described in Figure 1 about 2 times per second. This is ten times less than the turnover frequency of the chlorophyll molecule in the green leaf which in full sunshine is 20 s^{-1}.

Which turnover number must be reached by the photocatalyst to render the photovoltaic cell stable for 20 years of operation?

This number depends on the region of the earth where the cell is placed. For our latitude the solar power per square meter collector surface, averaged over day and night and all seasons is about 130 W/m^2 as compared to 1000 W/m^2 in full sunlight. The charge passed through one square centimeter of the dye loaded mesoporous film during 20 years of operation is therefore 1.64 million coulombs which corresponds to a turnover number of 100 million for the dye. Such high turnover number has indeed been reached in accelerated testing with the $RuL_2(NCS)_2$ dye without loss of performance.

curriculum vitae

Michael Grätzel has been Professor at the Swiss Federal Institute of Technology in Lausanne, Switzerland since 1977, where he directs the Institute of Photonics and Interfaces. His laboratory initiated studies in the domain of nanocrystalline semiconductors and mesoporous oxide semiconductor films. Investigations focus on photo catalytic and redox catalytic properties and applications of these systems. He is the inventor of the new dye-sensitized nanocrystalline solar cell, which is being developed presently on a worldwide scale. Professor Grätzel, who is the author of over 400 publications, two books and 10 patents, has been a visiting professor at several foreign universities, including the University of California at Berkeley, the University of Tokyo and the Ecole National Superieur de Cachan in Paris. He has received numerous awards and honorary lectureships. In 1996 the University of Uppsala, Sweden, conferred to him an honorary doctor degree in recognition of his scientific achievements. He is a member of several editorial boards and acts as a consultant to international industrial corporations.

keywords

- renewable energy\photocatalysis
- redox catalysis
- mesoscopic oxides
- nanocrystalline junctions
- photovoltaic cells
- water cleavage

references

[1] N. Vlachopoulos, P. Liska, J. Augustynski and M. Grätzel, *J. Am. Chem. Soc.* 110 (1988) 1216.

[2] B. O'Regan and M. Grätzel, *Nature,* London 353 (1991).

[3] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.* 115 (1993) 6382.

[4] M.K. Nazeeruddin, P. Péchy, M. Grätzel, U. Bach, D. Lupo, P. Comte, J.-E. Moser, F. Weissörtel, J. Salbeck, H. Spreitzer and M. Grätzel, *Nature* 395 (1998) 583.

[5] Ch.J. Barbe, F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover, and M. Grätzel, *J. Am. Ceram. Soc.* 80 (1997) 3157.

[6] S.D. Burnside, V. Shklover, Ch. Barbé, P. Comte, F. Arendse, K. Brooks, and M. Grätzel, *Chem. Mater.* 10 (1998) 2419.

[7] J. Moser, *Monatsh. Chem.* 8 (1887) 373.

[8] E. Bequerel, *Comptes Rendues* 9 (1839) 561.

[9] H.W. Vogel, *Ber. Dtsch. Chem. Ges.* 6 (1873) 1730.

[10] W. West, Proc. Vogel Centennial Symp., *Photogr. Sci. Eng.* 18, (1974) 35.

[11] S. Namba, Y. Hishiki *J. Phys. Chem.* 69 (1965) 774.

[12] H. Gerischer, H. Tributsch, *Ber. Bunsenges. Phys. Chem.* 72 (1968) 437.

[13] M.P. Dare-Edwards, J.B Goodenough, A. Hamnet, K.R. Seddon, R.D. Wright, *Faraday Disc. Chem. Soc.* 70 (1980) 285.

[14] H. Tsubomura, M. Matsumura, Y. Noyamaura, T. Amamyiya, *Nature* 261 (1976) 402.

[15] D. Duonghong, N. Serpone, M. Grätzel, *Helv. Chim. Acta* 67 (1984) 1012.

[16] J. DeSilvestro, M. Grätzel, L. Kavan, J. Moser, J. Augustynski, *J. Am. Chem. Soc.* 107 (1988) 2988.

[17] J.M. Moser, P. Bonhôte and M. Grätzel, *Coord. Chem Rev.* 245 (1998) 1171.

[18] B. Burnfeind, T. Hanappel, W. Storck, and F. Willig, *J. Phys. Chem.* 100 (1996) 16436.

[19] J.E. Moser, and M. Grätzel, *Chem. Phys.* 176 (1993) 493.

[20] G. Redmond, and D.J. Fitzmaurice, *J. Phys. Chem.* 97 (1993) 11001.

[21] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphrey-Baker, E. Müller, P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.* 115 (1993) 6382.

[22] V. Shklover, Yu.E. Ovchinnikov, L.S. Braginsky, S.M. Zakeeruddin and M. Grätzel, *Chem. Mater.* 10 (1998) 2533.

[23] K.S. Finnie, J.R. Bartlett and J.L. Woolfrey, Langmuir 14 (1998) 2744.

[24] A. Vittadini, A. Seloni, F.P. Rotzinger and M. Grätzel. Phys. Rev. Lett. 81 (1998) 2954.

[25] A. Wahl and J. Augustynski *J. Phys. Chem. B*, 102 (1998) 7820.

[26] H. Rensmo, H. Lindström, S. Södergren, A.-K. Willsted, A. Solbrand, A. Hagfeldt, and S.-E. Lindquist, *J. Electrochem Soc.* 1996, 3173-3178.

[27] F. Cao, G. Oskam, G.J. Meyer, and P.C. Searson, ; *J. Phys. Chem.* 100, (1996) 17021.

[28] L. Dloczik, O. Ileperuma, I. Lauermann, L.M. Peter, E. A. Ponomarev, G. Redmond, N.J. Shaw, I. Uhlendorf . *J. Phys. Chem. B* 101 (1997) 10281.

[29] Nelson, J.; *Phys. Rev. B* 1999,

[30] A. Hagfeldt and M. Grätzel, *Chem. Rev.* 95 (1995) 4.

[31] R. Amadelli R. Argazzi, C. A. Bignozzi, and F. Scandola, *J. Am. Chem. Soc.* 112 (1990), 70293.

[32] Md. K. Nazeeruddin, P. Pechy, and M. Grätzel, *Chem. Commun.,* 1997, 1705.

[33] A.J. Bard and M.A Fox, Accounts Chem. Res. 28 (1995) 28.

[34] M.D. Archer, and J.R. Bolton, J. Phys. Chem. 94 (1990) 8028.

[35] O. Khaselev and J. Turner, Science 280, 1998, 455.

[36] K. Kalyanasundaram, M Grätzel, and E. Pelizzetti, Coord. Chem. Rev. 69 (1986) 57.

[37] K. Hara, K. Samaya and H. Arakawa, Chem. Lett. 1998, 387.

[38] J. Augustynski, G. Calzaferri, J.C Courvoisier, M. Grätzel, M. Ulmann, Proc. 10th International Conference Photochem. Stor. Sol. Energy, Interlaken, Switzerland, 1994, pp. 229.

Terminal oxidation of alkanes: a radically new approach?

Jay A. Labinger
Beckman Institute
California Institute of Technology
Pasadena, CA 91125, USA
email: jal@its.caltech.edu
phone: 626-395-6520
fax: 626-449-4159

While there have been many advances in the field of selective alkane functionalization over the last decade or two, one important target that has remained frustratingly elusive is selective oxidation at a terminal methyl position. A number of potential applications might be made practical if such methodology were available; the obvious one would be the production of linear terminal alcohols from alkane feedstock, rather than from olefins (via hydroformylation) as currently practiced. The late Derek Barton proclaimed selective methyl oxidation to be among the major unsolved problems of organic chemistry. In response to this challenge J. D. Roberts has put up a prize: $5000 for the first to achieve oxidation (chemical or biochemical) of n-hexane to adipic acid with 85% selectivity[1].

Very recently, J. M. Thomas and coworkers found that reaction of linear alkanes with molecular oxygen, catalyzed by transition metal-substituted molecular sieves, can give unexpectedly high selectivity for terminal oxidation[2]*. While the report does not appear to present any* immediate *threat to Jack Roberts' pocketbook, it does offer considerable encouragement. Perhaps most intriguingly, it takes a quite different approach from what previous common wisdom would seem to suggest. In the following perspective, I will give some background on the terminal oxidation problem, summarize the findings reported, and offer some mechanistic speculation which may indicate some potentially profitable directions for further research.*

Background

I will consider three categories of catalytic oxidation (an admittedly incomplete classification scheme, as we shall see): heterogeneous, organometallic, and biological/biomimetic. Alkane oxidation over heterogeneous catalysts — metal oxides in particular — most often (always?) begins with homolytic C-H bond cleavage. The relative reactivity of a given C-H bond in such a radical-based mechanism is largely governed by C-H bond strength. This has a major adverse consequence for selective alkane oxidation *in general*: many desired oxidation products (alcohols, aldehydes, etc.) will have one or more C-H bonds considerably weaker than any of those in the starting alkane and will hence be more reactive, thus placing severe constraints on attainable yield. This consideration alone can be used for semi-quantitative explanations of performance ceilings, as we showed some years ago for methane oxidative coupling and oxidation to methanol[3], and has since been extended to a wide range of hydrocarbon oxidations[4]. But as difficult as it is to make *any* oxidation product selectively from alkanes, it will be harder still to achieve selective terminal oxidation, as primary C-H bonds are stronger than secondary or tertiary ones. Hence this approach does not appear too promising.

In the realm of organometallic chemistry of alkanes, the situation is quite different. A large number of systems have been found, over the last 20 years or so, to activate C-H bonds in alkanes under remarkably mild conditions[5]. While we still lack full mechanistic understanding, it seems certain that something quite different from C-H homolysis is involved, and bond strengths have little if any effect on reactivity, as shown (*inter alia*) by the fact that aromatic C-H bonds are almost always more reactive than aliphatic. For alkanes, reaction at terminal positions is generally favored, sometimes exclusively so. Table 1 shows a few representative examples. As noted, the origin of terminal selectivity remains to be worked out. It is not even known with certainty in every case whether selectivity is a consequence of kinetic or thermodynamic factors, as rearrangements have been shown to be extremely facile in many systems. (For example, the difference between the entries involving Rh and Ir is clearly due to the former being under thermodynamic control, the latter, kinetic.) But it is clear that we do have the means to turn an alkane into a terminal alkyl-metal complex, under mild conditions and with good to excellent selectivity.

The problem is, having gotten that far, what do we do next? Virtually all attempts to incorporate reactions of the sort shown in Table 1 into useful catalytic cycles have failed. In many cases the organometallic systems are instantly destroyed by oxygen or other strong oxidants. A few examples of catalytic alkane oxidation that appear to proceed via organometallic activation have been demonstrated, most prominently the Shilov system (last entry in Table 1, and Scheme 1)[9,10] and the