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Molecular photovoltaics that mimic photosynthesis*

Michael Grätzel

Ecole Polytechnique Fédéral, CH-1015 Lausanne, Switzerland

Abstract: Learning from the concepts used by green plants, we have developed a photovoltaic cell based on molecular light absorbers and mesoporous electrodes. The sensitized nanocrystalline injection solar cell employs organic dyes or transition-metal complexes for spectral sensitization of oxide semiconductors, such as TiO_2, ZnO, SnO_2, and Nb_2O_5. Mesoporous films of these materials are contacted with redox electrolytes, amorphous organic hole conductors, or conducting polymers, as well as inorganic semiconductors. Light harvesting occurs efficiently over the whole visible and near-IR range due to the very large internal surface area of the films. Judicious molecular engineering allows the photoinduced charge separation to occur quantitatively within femtoseconds. The certified overall power conversion efficiency of the new solar cell for standard air mass 1.5 solar radiation stands presently between 10 and 11. The lecture will highlight recent progress in the development of solar cells for practical use. Advancement in the understanding of the factors that govern photovoltaic performance, as well as improvement of cell components to increase further its conversion efficiency will be discussed.

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 world's energy consumption rate exceeds already the stunning figure of 6000 gigawatts. 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 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. Photochemistry is expected to make important 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.

A way to successfully trap solar radiation is by a 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 the incoming photons to be captured efficiently despite the fact that the oxide is covered only by a monolayer of dye. On a flat support, a monolayer of dye would absorb only a tiny fraction of the incident light. Photoexcitation of the dye initiates two coupled cyclic redox reactions, one involving the dye and the other the iodide/triiodide, Fig. 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 catalysts. Judicious selection of the dye allows to reach turnover numbers as high as 100 million corresponding to about 20 years of operation of the device under natural conditions. The

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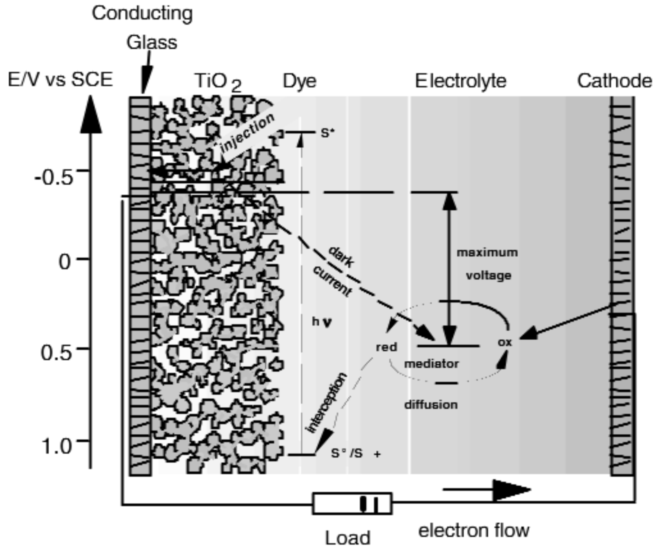

Fig. 1 Biomimetic conversion of light to electricity using two redox catalytic cycles. As in natural photosynthesis, in the artificial analog sunlight sets in action a molecular electron pump. The sensitizer (S) is bound as a monomolecular coating on the surface of a semiconductor oxide, such as TiO_2, 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.

first results of this 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 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 a wealth of groundbreaking results on the new nanocrystalline TiO_2 films, which we learned to produce in a very reproducible fashion. The paper published in *Nature* in 1991 [2] presented the first results on our photovoltaic cell, which showed conversion yields that could already compete with conventional silicon-based photovoltaic devices. Further improvements of this system have been made since then [3,4]. Soon, a whole number of other applications of these nanocrystaline oxide films emerged in the areas of photocatalysis and electrocatalysis, electroluminescent and electrochromic displays, as well as sensors and lithium intercalation batteries. The photoelectrochemical device that resulted from this work does use the same concepts as green plants in order to harvest and convert solar energy. It separates light absorption from the transport of photogenerated carriers. These two functions are assumed simultaneously by silicon in conventional photovoltaic devices leading to the high purity requirements and hence elevated cost of these devices.

IMITATING 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:

$$\sigma = \varepsilon \, 1000/N_A,$$

where N_A is Avogadro's number. 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 multilayers 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 photosensitzation.

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 100–1000 times larger than the apparent one. This allows to capture the incoming photons efficiently despite the fact that the oxide is covered only by a monolayer of dye. 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. As the chlorophyll-containing thylakoids are stacked, visible light is absorbed completely by traversing many superimposed vesicles containing the dye.

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 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

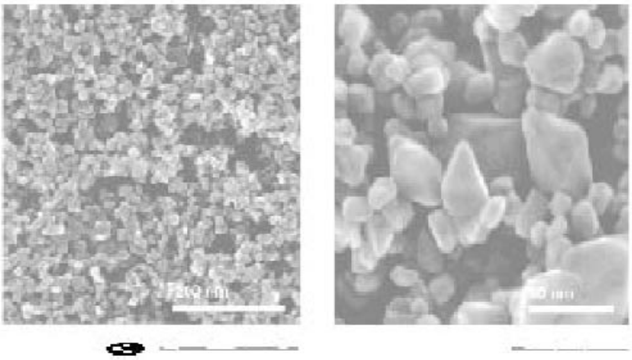

Fig. 2 Scanning electron microscope picture of a nanocrystalline titania (anatase) film.

thickness is typically 5–10 micron and the film mass about 1–2 mg/cm^2. The electronic contact between the particles is produced by a brief sintering process at about 450 °C. A mesoporous structure is thereby formed having a very high effective surface area. Analysis of the layers shows their porosity to be about 60%, the average pore size being 12 nm. Figure 2 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 have a bipyramidal morphology, which is typical for anatase. The exposed surface planes are mostly oriented in the (101) direction. 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 gel-type process used for film preparation.

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 an 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 photoexcited dyes into semiconductors was discovered more than 100 years ago in a famous experiment by James Moser at the University of Vienna [5]. He observed that the photoelectric effect detected first by Becquerel on silver plates [6] was enhanced in the presence of erythrosine. A few years before, Vogel in Berlin had exploited this phenomenon to render silver halide microcrystals sensitive to visible light [7], a process which today has found vast applications in color photography.

For efficient photoconversion of solar energy, 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 [8]. 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 extent of coupling is expressed by the electronic coupling matrix element V which is related to the rate constant for charge injection by the equation:

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

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 [9]. 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 reaction pathways. At least one channel is likely to be barrierless, implying that the driving force of electron transfer compensates the reorganization 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 one 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

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_f 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.

Sensitizers	k_{inj} [s^{-1}]	[V] [cm^{-1}]	t_f [ns]	Quantum yield
$Ru^{II}(bpy)_3$	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_S^{IV}-Alizarin	$>10^{13}$	5×10^3	-	1

transfer sensitizers are shown in Fig. 3. The carboxylate 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 ligand, which is the lowest unoccupied orbital (LUMO) of the complex and the 3d wavefunction manifold of the TiO_2 film. The substitution of the bipyridyl with the carboxylate groups lowers the energy of the LUMO. Since the electronic transition is of MLCT (metal-to-ligand charge transfer) character, optical excitation transfers the electron to a site from which electron injection into the semiconductor can readily occur. With molecules like these, charge injection occurs in the femtosecond time domain, Table 1. By contrast, the recapture of the electrons by the oxidized dye is at least six orders of magnitude slower. The rationale for this behaviour 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 $RuL_2(NCS)_2$ being about 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 rationale 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 [10].

Fig. 3 Structure of *cis*-dithiocyanato-bis(2,2'-bipyridyl-4,44',-dicarboxylate)-ruthenium(II), $RuL_2(SCN)_2$ (left) and the black dye Rutcterpy$(SCN)_3$, tcterpy = 4,4',4"-tricarboxy-2,2':6,2"-terpyridine.

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 no depletion layer is formed 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 carboxylic acid or phosphonic acid anchoring groups of the ruthenium complex to the oxide surface, producing a surface dipole 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 [11], 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.

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 [12]. 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 $5 \times 10^4\ M^{-1}$ 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 [13]. The most likely configuration which is compatible with the results from the adsorption isotherm measurements is shown in Fig. 4. The dye is attached via two of its four carboxylate groups, which straddle one row of titanium ions. The anchoring occurs either through chelation or an ester-type bond to the surface titanium ions. This configuration is supported also by recent infrared absorption studies [14]. The right part of the figure shows a top view of the dye-loaded (101) anatase surface, 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 [15].

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 [16]. The intriguing findings made with these films can be rationalized in terms of a random work of the electron via traps, the trapping and detrapping times being broadly distributed.

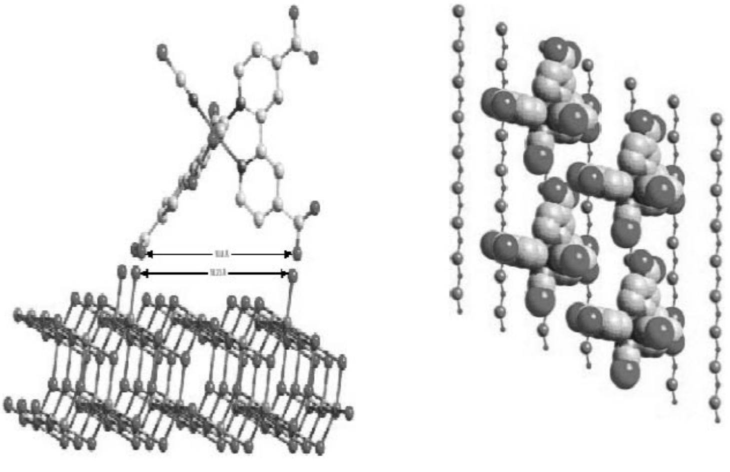

Fig. 4 Structural presentation of the N3 ruthenium complex adsorbed onto the (101) surface of anatase. Left: side view; right: top view.

Back reaction, recapture of the injected electron by the electrolyte

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 dye loaded film under forward bias. The latter should be kept at a minimal level as it determines the voltage of the photovoltaic cell. Engineering the interface to prevent this unwanted heterogeneous redox process will be a challenging task for future development.

ELECTRIC POWER GENERATION FROM LIGHT

A graph that presents the conversion efficiency of incident monochromatic light in electric current is shown for several ruthenium complexes in Fig. 5. 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%. 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 [17]. 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 recently by the discovery of a new black dye $Rutcterpy(SCN)_3$, (tcterpy = 4,4',4"-tricarboxy-2,2':6,2"-terpyridine) [18], having a spectral onset at 900 nm, which is close to the optimum threshold wavelength for the conversion of AM 1.5 solar radiation to electric power in a single junction photovoltaic cell.

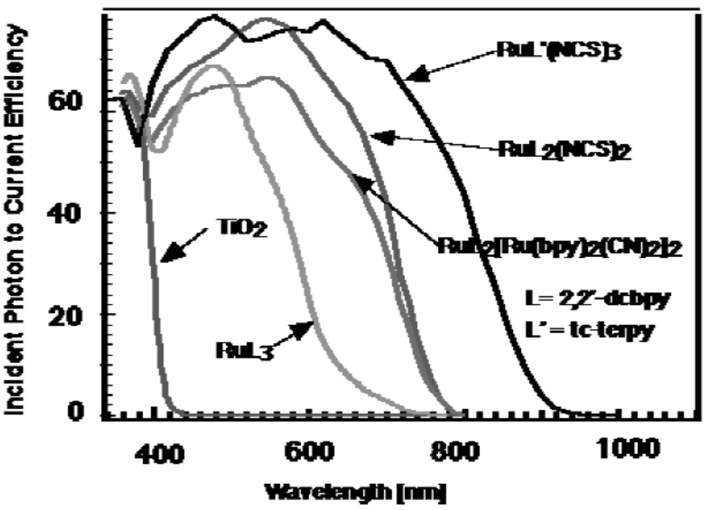

Fig. 5 Photocurrent action spectrum of bare nanocrystalline TiO_2 films and sensitized by various ruthenium complexes, the conversion efficiency of incident photons to electric current is plotted as a function of the excitation wavelength.

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).

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

Current-voltage characteristics for nanocrystalline injection cells based on the black dye sensitizer have been determined in the photovoltaic test laboratory at the National Research and Energy Laboratory in Golden, Colorado, USA. The overall conversion efficiency for standard AM 1.5 sunlight is confirmed as being 10.4%, which is commensurate with the efficiency 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%. Since the temperature of a solar cell will reach readily 50–60 °C under full sunlight this feature of the injection cell is particularly attractive for power generation under natural conditions.

FUTURE OUTLOOK

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. One important issue is to unravel the configuration of the adsorbed sensitizer. 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 photoexcitation 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.

Panchromatic sensitization extending throughout the visible and near IR region is another challenge for the future. Dye cocktails have already been applied to mesoporous TiO_2 films in the form of mixtures of porphyrines and phthalocyanines. The result was encouraging in as much as the optical effects of the two sensitizers were found to be additive, and there was not destructive interference of the dyes. Semiconductor quantum dots are another attractive option for panchromatic sensitizers. These are II–VI- and III–V-type semiconductors particles whose size is small enough to produce quantum confinement effects. Thus, the band gap of materials such as InAs and PbS can be adapted to match the value of 1.35 eV, which is ideal for a single-junction solar quantum converter. During the last decade, a wealth of information has been gathered on the physical properties of these materials, and the research is being pursued very actively.

Development of new material components will be another important aspect of future progress, this being important not only to improve performance but also to be able to compare different material properties with the photoelectrochemical properties. For example, a new process for the preparation of mesoporous films that accomplish directional growth of a metal oxide film on a substrate has recently been developed. Nanostructured films based on, e.g., nanofibers of Fe_2O_3 being oriented perpendicularly towards the substrate have been prepared. Superior photoelectrochemical responses have been achieved with these systems compared to mesoporous films based on spherical particles.

A great advantage of dye-sensitized cells is that they can be used to produce directly high-energy chemicals from sunlight. Such “photosynthetic” devices solve the principal problem of conventional photovoltaic cells, that is the lack of capacity for energy storage. The “Holy Grail” of all photoconversion processes is the splitting of water into hydrogen and oxygen by sunlight, and there is no doubt that this will be one of the primary targets of future research.

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