

Photoelectrochemical cells

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Until now, photovoltaics — the conversion of sunlight to electrical power — has been dominated by solid-state junction devices, often made of silicon. But this dominance is now being challenged by the emergence of a new generation of photovoltaic cells, based, for example, on nanocrystalline materials and conducting polymer films. These offer the prospect of cheap fabrication together with other attractive features, such as flexibility. The phenomenal recent progress in fabricating and characterizing nanocrystalline materials has opened up whole new vistas of opportunity. Contrary to expectation, some of the new devices have strikingly high conversion efficiencies, which compete with those of conventional devices. Here I look into the historical background, and present status and development prospects for this new generation of photoelectrochemical cells.

Ever since the French scientist Edmond Becquerel¹ discovered the photoelectric effect, researchers and engineers have been infatuated with the idea of converting light into electric power or chemical fuels. Their common dream is to capture the energy that is freely available from sunlight and turn it into the valuable and strategically important asset that is electric power, or use it to generate fuels such as hydrogen. Photovoltaics takes advantage of the fact that photons falling on a semiconductor can create

electron–hole pairs, and at a junction between two different materials, this effect can set up an electric potential difference across the interface. So far, the science of solar cells has been dominated by devices in which the junction is between inorganic solid-state materials, usually doped forms of crystalline or amorphous silicon, and profiting from the experience and material availability resulting from the semiconductor industry. Recently, we have seen more use of devices made from compound semiconductors — the III/V compounds for high-efficiency aerospace components and the copper–indium–sulphide/selenide materials for thin-film, low-cost terrestrial cells. But the dominance of the field by inorganic solid-state junction devices faces new challenges in the coming years. Increasingly, there is an awareness of the possible advantages of nanocrystalline and conducting polymer devices, for example, which are relatively cheap to fabricate (the expensive and energy-intensive high-temperature and high-vacuum processes needed for the traditional devices can be avoided), can be used on flexible substrates, and can be shaped or tinted to suit domestic devices or architectural or decorative applications. It is now even possible to depart completely from the classical solid-state junction device, by replacing the phase in contact with the semiconductor by an electrolyte (liquid, gel or organic solid), thereby forming a photoelectrochemical device.

The development of these new types of solar cells is promoted by increasing public awareness that the Earth's oil reserves could run out during this century. As the energy needs of the planet are likely to double within the next 50 years, the stage is set for a major energy shortage, unless renewable energy can cover the substantial deficit left by fossil fuels. Public concern has been heightened by the disastrous environmental pollution arising from all-too-frequent oil spills and the frightening climatic consequences of the greenhouse effect caused by fossil fuel combustion. Fortunately the supply of energy from the Sun to the Earth is gigantic: 3×10^{24} joules a year, or about 10,000 times more than the global population currently consumes. In other words, covering 0.1% of the Earth's surface with solar cells with an efficiency of 10% would satisfy our present needs. But to tap into this huge energy reservoir remains an enormous challenge.

Historical background

Becquerel's pioneering photoelectric experiments in 1839 were done with liquid not solid-state devices — a fact that is often ignored. His research, in which illumination of

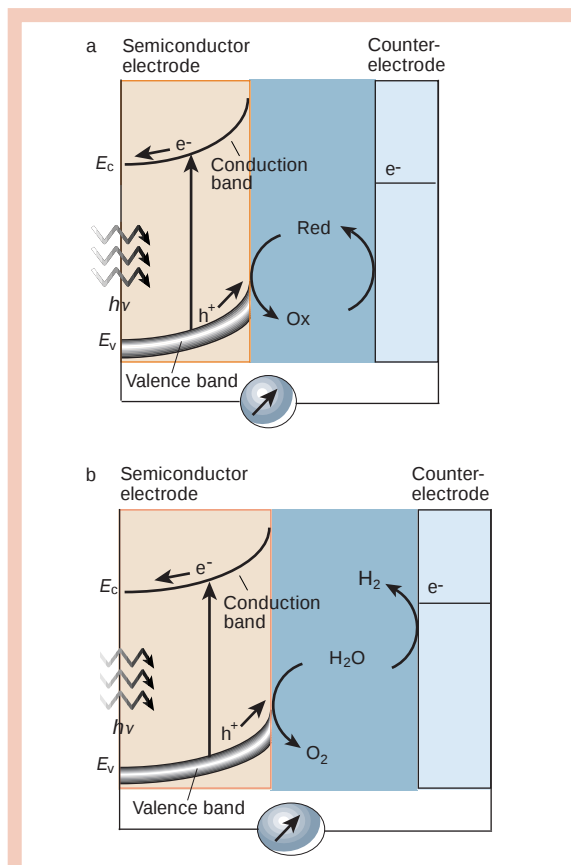
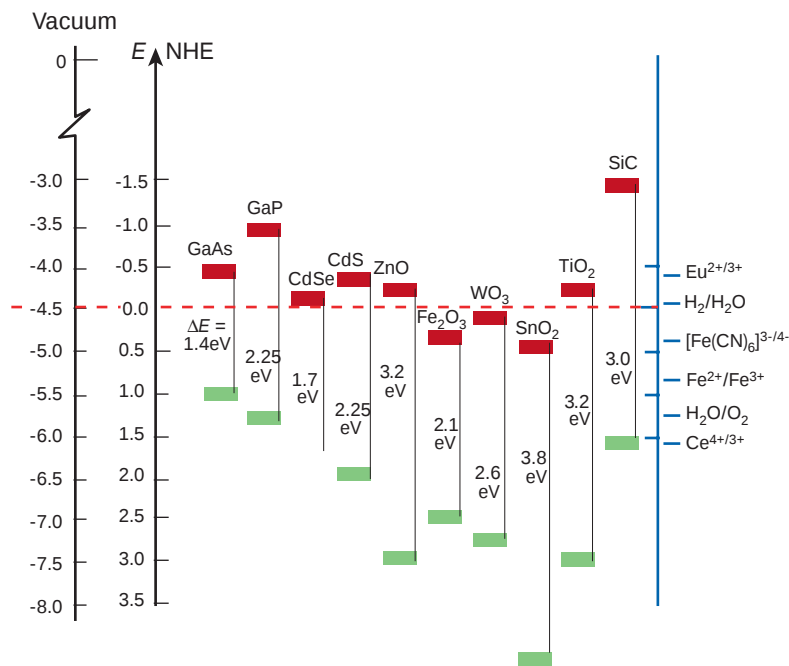


Figure 1 Principle of operation of photoelectrochemical cells based on *n*-type semiconductors. **a**, Regenerative-type cell producing electric current from sunlight; **b**, a cell that generates a chemical fuel, hydrogen, through the photo-cleavage of water.

Figure 2 Band positions of several semiconductors in contact with aqueous electrolyte at pH 1. The lower edge of the conduction band (red colour) and upper edge of the valence band (green colour) are presented along with the band gap in electron volts. The energy scale is indicated in electron volts using either the normal hydrogen electrode (NHE) or the vacuum level as a reference. Note that the ordinate presents internal and not free energy. The free energy of an electron–hole pair is smaller than the band gap energy due to the translational entropy of the electrons and holes in the conduction and valence band, respectively. On the right side the standard potentials of several redox couples are presented against the standard hydrogen electrode potential.



solutions containing a metal halide salt produced a current between two platinum electrodes immersed in the electrolyte, was motivated by photography. Daguerre had made the first photographic images in 1837, and Fox Talbot followed with the silver halide process in 1839. Although the art of formulating emulsions only became a science with the theoretical analysis of the process by Gurney and Mott² in 1938, there was constant empirical progress in the sensitivity of photographic films. Initially, films were particularly insensitive to mid-spectrum and red light. This is now recognized as being due to the semiconductor nature of the silver halide grains: they have a band gap (a gap in the allowed electronic energy levels) which ranges from 2.7 to 3.2 electron volts (eV) and negligible light absorption at wavelengths longer than 460 nm. Vogel's discovery³ in 1883 that silver halide emulsions could be sensitized by adding a dye extended the photosensitivity to longer wavelengths. Four years later, the concept of dye enhancement was carried over by Moser⁴ from photography to photoelectrochemical cells using the dye erythrosine on silver halide electrodes. This parallel between photography and photoelectrochemistry comes as a surprise to many chemists⁵. That the same dyes were particularly effective for both processes was recognized by Namba and Hishiki at the 1964 International Conference on Photosensitization of Solids in Chicago, which was a seminal event in the history of sensitization⁶. It was also recognized that the dye should be adsorbed on the semiconductor electrodes in a closely packed monolayer for maximum efficiency⁷. At this stage it was still debated whether sensitization occurred by transfer of electrons or of energy from the dye to the semiconductor⁸. Subsequent studies, notably by Hauffe⁹, Tributsch and Gerischer¹⁰, showed electron transfer to be the prevalent mechanism both for photographic and for photoelectrochemical sensitization processes.

Photosynthetic and regenerative cells

The foundation of modern photoelectrochemistry, marking its change from a mere support of photography to a thriving research direction on its own, was laid down by the work of Brattain and Garret¹¹ and subsequently Gerischer¹² who undertook the first detailed electrochemical and photoelectrochemical studies of the semiconductor–electrolyte interface. Research on photoelectrochemical cells went through a

frantic period after the oil crisis in 1973, which stimulated a worldwide quest for alternative energy sources. Within a few years well over a thousand publications appeared (see ref. 13 for a list).

Investigations focused on two types of cells whose principle of operation is shown in Fig. 1. The first type is the regenerative cell, which converts light to electric power leaving no net chemical change behind. Photons of energy exceeding that of the band gap generate electron–hole pairs, which are separated by the electric field present in the space-charge layer (see Box 1 for an explanation). The negative charge carriers move through the bulk of the semiconductor to the current collector and the external circuit. The positive holes are driven to the surface where they are scavenged by the reduced form of the redox relay molecule (R), oxidizing it: $h^+ + R \rightarrow O$. The oxidized form O is reduced back to R by the electrons that re-enter the cell from the external circuit. Much of the work on regenerative cells has focused on electron-doped (*n*-type) II/VI or III/V semiconductors using electrolytes based on sulphide/polysulphide, vanadium(II)/vanadium(III) or I_2/I^- redox couples. Conversion efficiencies of up to 19.6% have been reported for multijunction regenerative cells¹⁴.

The second type, photosynthetic cells, operate on a similar principle except that there are two redox systems: one reacting with the holes at the surface of the semiconductor electrode and the second reacting with the electrons entering the counter-electrode. In the example shown, water is oxidized to oxygen at the semiconductor photoanode and reduced to hydrogen at the cathode. The overall reaction is the cleavage of water by sunlight. Titanium dioxide has been the favoured semiconductor for these studies, following its use by Fujishima and Honda for water photolysis¹⁵. Unfortunately, because of its large band gap (3–3.2 eV, as shown in Fig. 2), TiO_2 absorbs only the ultraviolet part of the solar emission and so has low conversion efficiencies. Numerous attempts to shift the spectral response of TiO_2 into the visible, or to develop alternative oxides affording water cleavage by visible light, have so far failed.

In view of these prolonged efforts, disillusionment has grown about the prospects of photoelectrochemical cells being able to give rise to competitive photovoltaic devices, as those semiconductors with band gaps narrow enough for efficient absorption of visible light

Box 1

The semiconductor–electrolyte interface

When a semiconductor is placed in contact with an electrolyte, electric current initially flows across the junction until electronic equilibrium is reached, where the Fermi energy of the electrons in the solid (E_F) is equal to the redox potential of the electrolyte (E_{redox}), as shown in the figure. The transfer of electric charge produces a region on each side of the junction where the charge distribution differs from the bulk material, and this is known as the space-charge layer. On the electrolyte side, this corresponds to the familiar electrolytic double layer, that is, the compact (Helmholtz) layer followed by the diffuse (Gouy–Chapman) layer. On the semiconductor side of the junction the nature of the band bending depends on the position of the Fermi level in the solid. If the Fermi level of the electrode is equal to the flat band potential, there is no excess charge on either side of the junction and the bands are flat. If electrons accumulate at the semiconductor side one obtains an accumulation layer. If, however, they deplete from the solid into the solution, a depletion layer is formed, leaving behind a positive excess charge formed by immobile ionized donor states. Finally, electron depletion can go so far that their concentration at the interface falls below the intrinsic level. As a consequence, the semiconductor is *p*-type at the surface and *n*-type in the bulk, corresponding to an inversion layer. The illustration in the figure refers to *n*-type materials where electrons are the mobile charge carriers. For *p*-type semiconductors, analogous considerations apply. Positive holes are the mobile charge carriers and the immobile negatively charged states of the acceptor dopant form the excess space charge within the depletion layer.

The flat band potential is a very useful quantity in photoelectrochemistry as it facilitates location of the energetic position of the valence and conduction band edge of a given semiconductor material. It is obtained by measuring the capacity of the semiconductor–electrolyte junction. The semiconductor is subjected to reverse bias — that is, a voltage is applied to increase the potential step across the junction — and the differential capacity is determined as a function of the applied potential, V . The space-charge capacity of the semiconductor (C_{sc}) is in series with that of the Helmholtz layer (C_{H}) present at the electrolyte side of the interface. In the depletion regime the condition $C_{\text{H}} > C_{\text{sc}}$ applies, so the measured capacity is that of the space-charge layer. This depends on the applied bias voltage according to the Mott–Schottky equation: $1/(C_{\text{sc}})^2 = 2(\Delta\phi_{\text{sc}}RT/F)/(\epsilon_0\epsilon^1N)$, where $\Delta\phi_{\text{sc}} = V - V_{\text{fb}}$ is the voltage drop in the space-charge layer, R is the gas constant, F the Faraday number, ϵ the dielectric constant of the semiconductor, ϵ_0 the permittivity of vacuum and 1N the ionized donor dopant concentration. A plot of the square of the reciprocal capacity against the applied voltage gives a straight line and this is extrapolated to $1/(C_{\text{sc}})^2 = 0$ to derive the flat band potential V_{fb} .

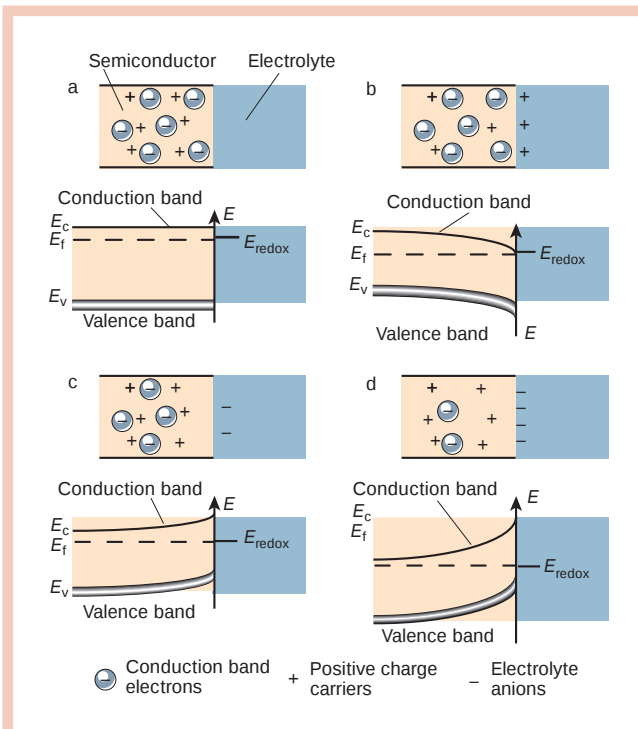
are unstable against photocorrosion. The width of the band gap is a measure of the chemical bond strength. Semiconductors stable under illumination, typically oxides of metals such as titanium or niobium, therefore have a wide band gap, an absorption edge towards the ultra-violet and consequently an insensitivity to the visible spectrum.

The resolution of this dilemma came in the separation of the optical absorption and charge-generating functions, using an electron transfer sensitizer absorbing in the visible to inject charge carriers across the semiconductor–electrolyte junction into a substrate with a wide band gap, and therefore stable. Figure 3 shows the operational principle of such a device.

Nanocrystalline junctions and interpenetrating networks

The need for dye-sensitized solar cells to absorb far more of the incident light was the driving force for the development of

Flat band potentials have been determined for a large number of materials⁴⁹ and some representative examples are shown in Fig. 2. Apart from the type of semiconductor they depend on the nature and composition of the electrolyte. In aqueous solution the flat band potentials of most oxide semiconductors shifts by 0.059 V when the pH is changed by one unit. This is a consequence of the fact that protons are potential-determining ions for these solids.



Box 1 Figure Schematic showing the electronic energy levels at the interface between an *n*-type semiconductor and an electrolyte containing a redox couple. The four cases indicated are: **a**, flat band potential, where no space-charge layer exists in the semiconductor; **b**, accumulation layer, where excess electrons have been injected into the solid producing a downward bending of the conduction and valence band towards the interface; **c**, depletion layer, where electrons have moved from the semiconductor to the electrolyte, producing an upward bending of the bands; and **d**, inversion layer where the electrons have been depleted below their intrinsic level, enhancing the upward band bending and rendering the semiconductor *p*-type at the surface.

mesoscopic semiconductor materials¹⁶ — minutely structured materials with an enormous internal surface area — which have attracted great attention during recent years. Mesoporous oxide films are made up of arrays of tiny crystals measuring a few nanometres across. Oxides such as TiO₂, ZnO, SnO₂ and Nb₂O₅, or chalcogenides such as CdSe, are the preferred compounds. These are interconnected to allow electronic conduction to take place. Between the particles are mesoscopic pores filled with a semiconducting or a conducting medium, such as a *p*-type semiconductor, a polymer, a hole transmitter or an electrolyte. The net result is a junction of extremely large contact area between two interpenetrating, individually continuous networks. Particularly intriguing is the ease with which charge carriers percolate across the mesoscopic particle network, making the huge internal surface area electronically addressable. Charge transport in such mesoporous

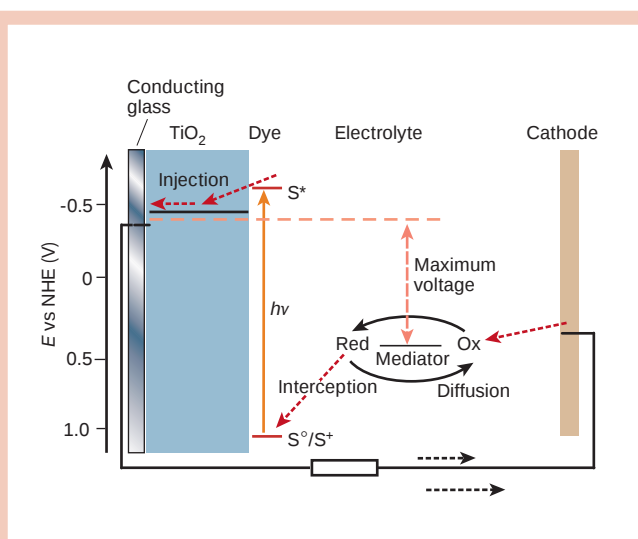


Figure 3 Schematic of operation of the dye-sensitized electrochemical photovoltaic cell. The photoanode, made of a mesoporous dye-sensitized semiconductor, receives electrons from the photo-excited dye which is thereby oxidized, and which in turn oxidizes the mediator, a redox species dissolved in the electrolyte. The mediator is regenerated by reduction at the cathode by the electrons circulated through the external circuit. Figure courtesy of P. Bonhôte/EPFL-LPI.

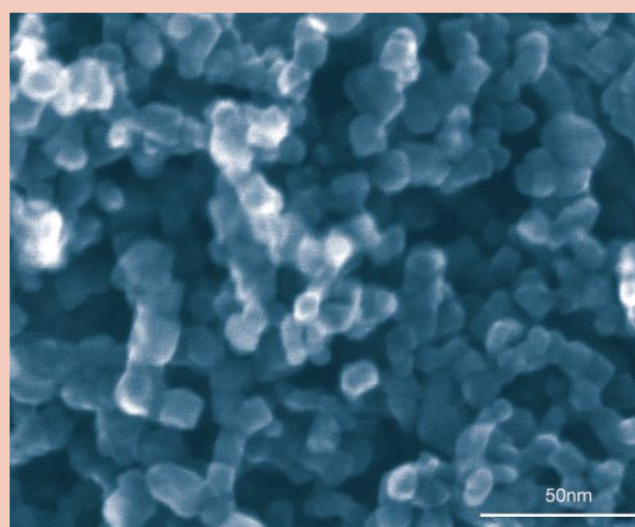


Figure 4 Scanning electron micrograph of the surface of a mesoporous anatase film prepared from a hydrothermally processed TiO_2 colloid. The exposed surface planes have mainly {101} orientation.

systems is under intense investigation today^{17,18} and is best described by a random walk model¹⁹.

The semiconductor structure, typically 10 μm thick and with a porosity of 50%, has a surface area available for dye chemisorption over a thousand times that of a flat, unstructured electrode of the same size. If the dye is chemisorbed as a monomolecular layer, enough can be retained on a given area of electrode to provide absorption of essentially all the incident light. Figure 4 shows an electron micrograph of a nanocrystalline TiO_2 film with a grain size in the range of 10–80 nm. (For details of the hydrothermal deposition procedure, starting with hydrolysis of a titanium isopropoxide precursor and terminating with screen printing and firing of the semiconductor layer on a conductive transparent substrate, see ref. 20.)

The nanostructuring of the semiconductor introduces profound changes in its photoelectrochemical properties. Of great importance is the fact that a depletion layer (see Box 1) cannot be formed in the solid — the particles are simply too small. The voltage drop within the nanocrystals remains small under reverse bias, typically a few millivolts. As a consequence there is no significant local electric field present to assist in the separation of photogenerated electron–hole pairs. The photoresponse of the electrode is determined by the rate of reaction of the positive and negative charge carriers with the redox couple present in the electrolyte. If the transfer of electrons to the electrolyte is faster than that of holes, then a cathodic photocurrent will flow, like in a *p*-type semiconductor/liquid junction. In contrast, if hole transfer to the electrolyte is faster, then anodic photocurrent will flow, as in *n*-type semiconductor photoelectrochemical cells. Striking confirmation of the importance of these kinetic effects came with the demonstration²¹ that the same nanocrystalline film could show alternatively *n*- or *p*-type behaviour, depending on the nature of the hole or electron scavenger present in the electrolyte phase. This came as a great surprise to a field where the traditional thinking was to link the photoresponse to formation of a charge-depletion layer at the semiconductor–electrolyte interface.

What, then, is the true origin of the photovoltage in dye-sensitized solar cells? In the conventional picture, the photovoltage of photoelectrochemical cells does not exceed the potential drop in the space-charge layer (Box 1 Figure). But nanocrystalline cells can

develop photovoltages close to 1 V even though the junction potential is in the millivolt range. It has been suggested that a built-in potential difference at the back contact of the nanocrystalline film with the conducting glass is responsible for the observed photovoltage²². Other evidence²³ suggests that under illumination, electron injection from the sensitizer increases the electron concentration in the nanocrystalline electrode, raising the Fermi level of the oxide and thus shifting its potential²⁴. From recent electrical impedance studies²⁵, it seems that both changes — the potential drop across the back contact and the Fermi level shift of the TiO_2 nanoparticles — contribute to the photovoltage of dye-sensitized solar cells.

Accumulation layers (part b of Box 1 Figure) can be produced in the nanocrystals under forward bias when majority carriers are injected, rendering the film highly conductive. Under reverse bias the carriers are withdrawn, turning it into an insulator. Thus, by changing the applied potential, the film can be switched back and forth from a conducting to an insulating state. Space-charge limitation of the current (arising from limitation of the density of charge carriers because they are repelled by each other's electric field) is not observed as the injected majority carriers are efficiently screened by the electrolyte present in the pores surrounding the nanoparticles. The factors controlling the rate of charge carrier percolation across the nanocrystalline film are under intense scrutiny¹⁷. A technique known as intensity-modulated impedance spectroscopy has proved to be an elegant and powerful tool^{25,26} for addressing these and other important questions related to the characteristic time constants for charge carrier transport and reaction dynamics.

An interesting feature specific to nanocrystalline electrodes is the appearance of quantum confinement effects. These appear when the films are made up of small quantum dots, such as 8-nm-sized CdTe particles²⁷. Such layers have a larger band gap than the bulk material, the band edge position being shifted with respect to the positions indicated in Fig. 2 for macroscopic materials. The conduction band redox potential is lowered and that of the valence band is increased. As a consequence, electrons and holes can perform reduction and oxidation reactions that cannot proceed on bulk semiconductors.

The astounding photoelectrochemical performance of nanocrystalline semiconductor junctions is illustrated in Fig. 5 where we

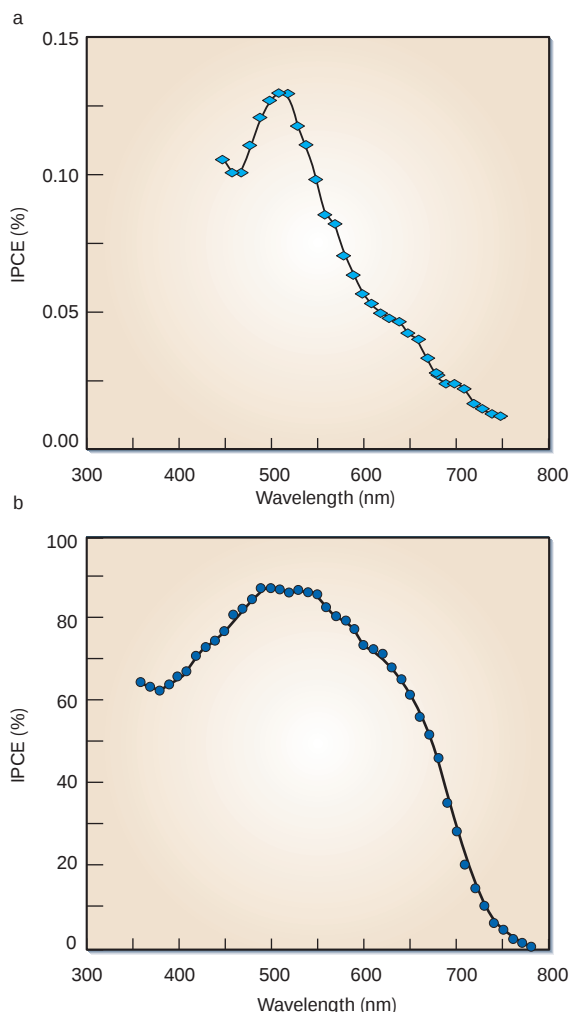


Figure 5 The nanocrystalline effect in dye-sensitized solar cells. In both cases, TiO_2 electrodes are sensitized by the surface-anchored ruthenium complex $\text{cis-RuL}_2(\text{SCN})_2$. The incident-photon-to-current conversion efficiency is plotted as a function of the excitation wavelength. **a**, Single-crystal anatase cut in the (101) plane. **b**, Nanocrystalline anatase film. The electrolyte consisted of a solution of 0.3M LiI and 0.03M I_2 in acetonitrile.

compare the photoresponse of an electrode made of single-crystal anatase, one of the crystal forms of TiO_2 , with that of a mesoporous TiO_2 film. Both electrodes are sensitized by the ruthenium complex $\text{cis-RuL}_2(\text{SCN})_2$ (L is 2,2'-bipyridyl-4,4'-dicarboxylate), which is adsorbed as a monomolecular film at the titania surface. The incident-photon-to-current conversion efficiency (IPCE) is plotted as a function of wavelength. The IPCE value obtained with the single-crystal electrode is only 0.13% near 530 nm, where the sensitizer has an absorption maximum, whereas it reaches 88% with the nanocrystalline electrode²⁸ — more than 600 times as great. The photocurrent in standard sunlight augments 10^3 – 10^4 times when passing from a single crystal to a nanocrystalline electrode (standard, or full, sunlight is defined as having a global intensity (I_s) of $1,000 \text{ W m}^{-2}$, air mass 1.5; air mass is the path length of the solar light relative to a vertical position of the Sun above the terrestrial absorber). This striking improvement is due largely to the far better light harvesting of the dye-sensitized nanocrystalline film as compared with a flat single-crystal electrode, but is also due, at least in part, to the mesoscopic film texture favouring photogeneration and collection of charge carriers²⁹.

The overall conversion efficiency of the dye-sensitized cell is determined by the photocurrent density measured at short circuit (i_{ph}), the open-circuit photo-voltage (V_{oc}), the fill factor of the cell (ff) and the intensity of the incident light (I_s)

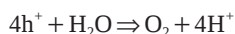
$$\eta_{\text{global}} = i_{\text{ph}} V_{\text{oc}} (\text{ff}/I_s)$$

Under full sunlight, short-circuit photocurrents ranging from 16 to 22 mA cm^{-2} are reached with state-of-the-art ruthenium sensitizers, while V_{oc} is 0.7–0.8 V and the fill factor values are 0.65–0.75. A certified overall power conversion efficiency of 10.4% has been attained at the US National Renewable Energy Laboratory³⁰. Although this efficiency makes dye-sensitized cells fully competitive with the better amorphous silicon devices, an even more significant parameter is the dye lifetime achieved under working conditions. For credible system performance, a dye molecule must sustain at least 10^8 redox cycles of photo-excitation, electron injection and regeneration, to give a device service life of 20 years. The use of solvents such as valeronitrile, or γ -butyrolactone, appropriately purified, in the electrolyte formulation provide a system able to pass the standard stability qualification tests for outdoor applications, including thermal stress for 1,000 h at 85°C , and this has been verified independently³¹.

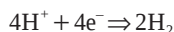
Tandem cells for water cleavage by visible light

The advent of nanocrystalline semiconductor systems has rekindled interest in tandem cells for water cleavage by visible light, which remains a highly prized goal of photoelectrochemical research. The 'brute force' approach to this goal is to use a set of four silicon photovoltaic cells connected in series to generate electricity that is subsequently passed into a commercial-type water electrolyser. Solar-to-chemical conversion efficiencies obtained are about 7%. Much higher efficiencies in the range of 12–20% have been reported for tandem cells based on III/V semiconductors^{14,32}, but these single-crystal materials cost too much for large-scale terrestrial applications.

A low-cost tandem device that achieves direct cleavage of water into hydrogen and oxygen by visible light was developed recently³³. This is based on two photosystems connected in series as shown in the electron flow diagram of Fig. 6. A thin film of nanocrystalline tungsten trioxide, WO_3 (ref. 34), or Fe_2O_3 (ref. 35) serves as the top electrode absorbing the blue part of the solar spectrum. The valence-band holes (h^+) created by band-gap excitation of the film oxidize water to oxygen:



and the conduction-band electrons are fed into the second photosystem consisting of the dye-sensitized nanocrystalline TiO_2 cell discussed above. The latter is placed directly under the WO_3 film, capturing the green and red part of the solar spectrum that is transmitted through the top electrode. The photovoltage generated by the second photosystem enables hydrogen to be generated by the conduction-band electrons.



The overall reaction corresponds to the splitting of water by visible light. There is close analogy to the 'Z-scheme' (named for the shape of the flow diagram) that operates in photosynthesis. In green plants, there are also two photosystems connected in series, one that oxidizes water to oxygen and the other generating the compound NADPH used in fixation of carbon dioxide. As discussed above, the advantage of the tandem approach is that higher efficiencies can be reached than with single junction cells if the two photosystems absorb complementary parts of the solar spectrum. At present, the overall conversion efficiency from standard solar light to chemical

energy achieved with this device stands at 4.5%, and further improvements are being sought.

Dye-sensitized solid heterojunctions and ETA cells

Interest is growing in devices in which both the electron- and hole-carrying materials are solids, but are grown as interpenetrating networks forming a heterojunction of large contact area. From conventional wisdom one would have predicted that solar cells of this kind would work very poorly, if at all. The disordered character of the junction and the presence of the huge interface are features one tries to avoid in conventional photovoltaic cells, because the disruption of the crystal symmetry at the surface produces electronic states in the band gap of the semiconductor, enhancing the recombination of photogenerated carriers. The fact that molecular photovoltaic cells based on the sensitization of nanocrystalline TiO_2 were able to achieve overall conversion efficiencies from solar to electric power of over 10% encouraged work on solid-state analogues, that is, dye-sensitized heterojunctions. The first devices of this type used inorganic *p*-type semiconductors, for example CuI (ref. 36) or CuSCN (ref. 37), as hole conductors replacing the redox electrolyte. Respectable conversion efficiencies exceeding 1% have been reached with such cells. But the lack of photostability of the Cu(I) compounds and the difficulty of realizing a good contact between the two mesoscopic inorganic materials still present considerable practical challenges.

Organic charge-transport materials have advantages in this respect. An amorphous hole conductor can be introduced into the mesoporous TiO_2 film by a simple spin-coating process and readily adapts its form to the highly corrugated oxide surface. Cells based on a spirobisfluorene-connected arylamine hole transmitter³⁸, which fills the pores of a dye-sensitized nanocrystalline TiO_2 film, have reached a conversion efficiency of 2.56% at full sunlight³⁹. The high open-circuit voltage of these devices, exceeding 900 mV, is particularly noteworthy and promising for further substantial improvements in performance. In general, dye-sensitized heterojunction cells offer great flexibility because the light absorber and charge-transport material can be selected independently to obtain optimal solar energy harvesting and high photovoltaic output. The great advantage of such a configuration is that the charge carriers are generated by the dye precisely at the site of the junction where the electric field is greatest, enhancing charge separation.

Extremely thin absorber (ETA) solar cells are conceptually close to dye-sensitized heterojunctions. The molecular dye is replaced by an extremely thin (2–3 nm) layer of a small-band-gap semiconductor, such as CuInS_2 . A hole conductor such as CuSCN is placed on top of the absorber, producing a junction of the PIN type (*p*-type semiconductor/insulator/*n*-type semiconductor)⁴⁰. The structure has the advantage of enhanced light harvesting due to the surface enlargement and multiple scattering. Because photo-induced charge separation occurs on a length scale of a few nanometres, higher levels of defects and impurities can be tolerated than in flat thin-film devices, where the minority carriers are required to diffuse several microns. On the other hand, making PIN-junctions of such high contact area is difficult and this has hampered the performance of these cells. Their conversion efficiency so far has remained below 5%, which is less than one-third of the yield obtained with similar semiconductor materials in a flat junction configuration.

Soft junctions and organic solar cells

Organic materials have the advantage of being cheap and easy to process. They can be deposited on flexible substrates, bending where their inorganic competitors would crack. The choice of materials is practically unlimited, and specific parts of the solar spectrum can be selectively absorbed. Although organic cells are still considerably less efficient than single-crystal gallium arsenide or silicon, progress has been impressive over the past few years. In particular, solar cells based on interpenetrating polymer networks⁴¹, polymer/fullerene blends⁴²,

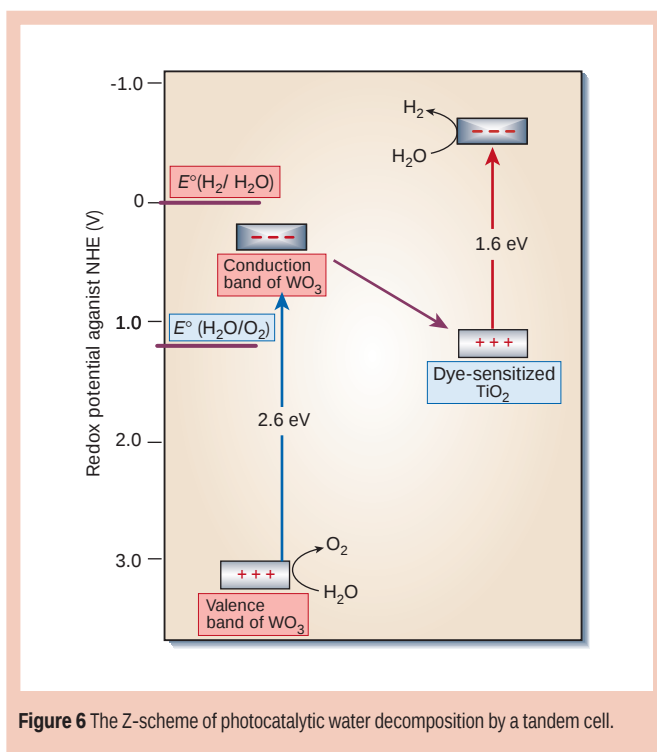


Figure 6 The Z-scheme of photocatalytic water decomposition by a tandem cell.

halogen-doped organic crystals⁴³ and the solid-state dye-sensitized devices mentioned above³⁸ have shown surprisingly high solar conversion efficiencies, currently reaching values of 2–3%.

Conducting polymers, for example poly-(phenylenevinylene) (PPV) derivatives or C_{60} particles, are attracting great interest as photovoltaic materials^{44,49}. Bulk donor–acceptor heterojunctions are formed simply by blending the two organic materials serving as electron donor (*p*-type conductor) and electron acceptor (*n*-type conductor). The advantage of these new structures over the flat-junction organic solar cells investigated earlier⁴⁵ is the interpenetration of the two materials that conduct positive and negative charge carriers, reducing the size of the individual phase domains to the nanometre range. This overcomes one of the problems of the first generation of organic photovoltaic cells: the unfavourable ratio of exciton diffusion length to optical absorption length. An exciton is a bound electron–hole pair produced by absorption of light; to be useful, this pair must reach the junction and there dissociate into two free charge carriers — but excitons typically diffuse only a few nanometres before recombining. Light is absorbed (and generates excitons) throughout the composite material. But in the composite, the distance the exciton has to travel before reaching the interface is at most a few nanometres, which is commensurate with its diffusion length. Hence photo-induced charge separation can occur very efficiently. A conversion efficiency from incident photons to current of over 50% has been achieved with a blend containing PPV and methanofullerene derivatives⁴⁶. The overall conversion efficiency from solar to electric power under full sunlight achieved with this cell was 2.5%. Although these results are impressive, the performance of the cell declined rapidly within hours of exposure to sunlight⁴⁷. In contrast, the output of dye-sensitized solar cells is remarkably stable even under light soaking for more than 10,000 h. Similar long-term stability will be required for large-scale application of polymer solar cells.

Summary

Photovoltaic devices based on interpenetrating mesoscopic networks have emerged as a credible alternative to conventional solar cells. Common to all these cells is an ultrafast initial charge separation step, occurring in femtoseconds, and a much slower back-reaction.

Table 1 Performance of photovoltaic and photoelectrochemical solar cells

Type of cell	Efficiency (%) ^a		Research and technology needs
	Cell	Module	
Crystalline silicon	24	10–15	Higher production yields, lowering of cost and energy content
Multicrystalline silicon	18	9–12	Lower manufacturing cost and complexity
Amorphous silicon	13	7	Lower production costs, increase production volume and stability
CuInSe ₂	19	12	Replace indium (too expensive and limited supply), replace CdS window layer, scale up production
Dye-sensitized nanostructured materials	10–11	7	Improve efficiency and high-temperature stability, scale up production
Bipolar AlGaAs/Si photoelectrochemical cells	19–20	—	Reduce materials cost, scale up
Organic solar cells	2–3	—	Improve stability and efficiency

^aEfficiency defined as conversion efficiency from solar to electrical power.

This allows the charge carriers to be collected as electric current before recombination takes place. Table 1 compares the performance of the new photoelectrochemical systems with conventional devices. Although still of lower efficiency, the nanostructured cells offer several advantages over their competitors. They can be produced more cheaply and at less of a cost in energy than silicon cells, for which 5 GJ have to be spent to make 1 m² of collector area. Unlike silicon, their efficiency increases with temperature, narrowing the efficiency gap under normal operating conditions. They usually have a bifacial configuration, allowing them to capture light from all angles. Transparent versions of different colour can readily be made that could serve as electric power-producing windows in buildings. These and other attractive features⁴⁸ justify the present excitement about these cells and should aid their entry into a tough market. □

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