Artificial Photosynthesis: Solar Splitting of Water to Hydrogen and Oxygen

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Water Splitting

The maintenance of life on earth, our food, oxygen, and fossil fuels depend upon the conversion of solar energy into chemical energy by biological photosynthesis carried out by green plants and photosynthetic bacteria. In this process sunlight and available abundant raw materials (water, carbon dioxide) are converted to oxygen and the reduced organic species that serve as food and fuel. A long-standing challenge has been the development of a practical artificial photosynthetic system that can roughly mimic the biological one, not by duplicating the self-organization and reproduction of the biological system nor the aesthetic beauty of trees and plants, but rather by being able to use sunlight to drive a thermodynamically uphill reaction of an abundant materials to produce a fuel. In this Account we focus on "water splitting", the photodriven conversion of liquid water to gaseous hydrogen and oxygen:

$$H_2O(l) \xrightarrow{\text{sunlight}} H_2(g, 1 \text{ atm}) + \tfrac{1}{2}O_2(g, 1 \text{ atm}) \quad (1)$$
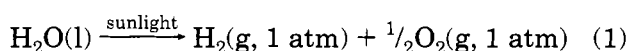
Beyond the intellectual challenge of designing and fabricating such a system, there are several practical implications. H_2 could serve directly as a fuel, e.g., for transportation or for the production of electricity in fuel cells, without producing pollutants or greenhouse gases upon combustion. For some purposes, however, it might be useful to use the H_2 as a reactant to produce a different fuel, such as one that is liquid at the usual temperatures and pressures. Thus, we seek as a "Holy Grail" a renewable energy source driven by solar energy that produces a clean and storable fuel.

Let us define this Holy Grail more specifically. We want an efficient and long-lived system for splitting water to H_2 and O_2 with light in the terrestrial (AM1.5) solar spectrum at an intensity of one sun. For a practical system, an energy efficiency of at least 10% appears to be necessary. This means that the H_2 and O_2 produced in the system have a fuel value of at least 10% of the solar energy incident on the system. In the southern United States, the instantaneous maximum intensity is of the order of 1 kW/m^2 and the average 24-h intensity throughout a year is about 250 W/m^2. Thus, the system should produce H_2 at a rate of about 0.7 g/s or 7.8 L(STP)/s per m^2 of collector at maximum solar intensity. Long-lived implies that the

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sensitizers and catalysts, as well as the materials of construction, will not be consumed or degraded under irradiation for at least 10 years. The solar spectrum at sea level extends from the near infrared through the visible to the near ultraviolet with photon energies up to 3.0 eV. This region is not absorbed by water itself, so photochemical reactions are only possible in the presence of some recyclable absorbing sensitizer. Finally, for practical applications, the cost of H_2 produced by the system (on an energy equivalent basis) should be competitive with that of fossil fuels.

Although we have defined our Holy Grail in terms of the water-splitting reaction, other chemical solar energy conversions are possible and have been investigated. For example, there are semiconductor liquid junction systems that, when irradiated with visible light, carry out the reactions $2HBr \rightarrow H_2 + Br_2$ and $2HI \rightarrow H_2 + I_2$. Indeed, the "brine splitting" or "photochloralkali" reaction,

$$2H_2O + 2Cl^- \xrightarrow{h\nu} 2OH^- + Cl_2 + H_2 \quad (2)$$

would probably be more useful than water splitting, but has so far not been achieved without applying an additional external potential.

Many investigations in this field have involved sacrificial donors, which are reduced materials that are oxidized more easily than water, for example, ethylenediamine tetraacetic acid or triethanolamine. The use of such compounds usually greatly improves the efficiency of the solar process, but clearly is not of interest in practical systems, especially if the sacrificial donors are more expensive than the H_2 produced. It might be possible to use reduced waste materials in this role, but is it unlikely that this approach will be practical in large-scale fuel production.

Photoelectrochemical approaches may be useful, however, as a means of water treatment, destroying organic wastes and removing metals. There are also a number of chemical schemes for converting solar energy to electrical energy, e.g., in liquid junction photovoltaic cells. Indeed, devices with single-crystal semiconductors have been constructed which show solar efficiencies of above 10%. It remains to be seen whether such chemical photovoltaic systems will be practically competitive with solid state ones based, for example, on single-crystal or amorphous Si. Although many of these alternative chemical solar energy systems are interesting, we focus here on the water-splitting reaction, because it effectively represents the scientific challenges typical of all such efforts.

History and Progress

A. Efficiency. The free energy change for reaction 1 is $\Delta G° = 237.2$ kJ/mol or 2.46 eV/molecule of H_2O.

Since two electrons are involved in the reaction as written ($n = 2$), this corresponds to 1.23 eV/e, which is also the standard emf for the reaction. The photons in the solar spectrum provide sufficient energy to drive this reaction, but the efficiency of the reaction depends upon how the reaction is carried out. It is possible to cause water splitting thermally with light via concentrators and a solar furnace by heating water to 1500–2500 K.[1] However, the efficiency of this process is typically below 2%, and the cost of the capital equipment and material stability problems suggest that this approach to solar water splitting is not a promising one.

Since water itself does not absorb appreciable radiation within the solar spectrum, one or more light-absorbing species (photoconverters or sensitizers) must be used to transduce the radiant energy to chemical (or electrical) energy in the form of electron/hole pairs, i.e., to the oxidizing and reducing potential needed to drive the reaction. The maximum efficiency for photochemical solar converters has been considered in a number of papers[2] and depends upon the band gap (or threshold energy), E_g, of the photoconverter. Radiation of energy below E_g is not absorbed while that above E_g is partly lost as heat by internal conversion or intraband thermalization processes. Additional thermodynamic losses occur because the excited state concentration is only a fraction of that of the ground state and because some excited states are lost through radiative decay.[2] When these factors are taken into account, the threshold photon energy and the maximum efficiency can be calculated. For a single photoconverter system, wavelengths below 770 nm (or energies above 1.6 eV) are required to yield a maximum efficiency of about 30%. Lower photon energies and higher efficiencies are attainable if one employs two photoconverters. Thus for a system with two photoconverters with two different, optimized E_g values, one finds a maximum solar efficiency of 41%.[2] These calculations show that, in principle, the desired efficiency for water splitting is attainable, even with a system involving a single photoconverter.

B. Semiconductor Solid State Photovoltaic-Based Systems. A number of different approaches are possible with semiconductors as the photoconverter. The most direct, brute force, approach employs a solid state photovoltaic solar cell to generate electricity that is then passed into a commercial-type water electrolyzer (Figure 1A). The maximum theoretical efficiency for a Si photovoltaic cell is 33%, and the efficiencies of the best laboratory cells have been reported to be about 24%. Commercial single-crystal Si solar cells generally have efficiencies in the 12–16% range. The electrolysis of water at a reasonable rate in a practical cell requires applied voltages significantly larger than the theoretical value (1.23 V at 25 °C), and electrolysis energy efficiencies of about 60% are typical. Thus, the efficiency of the combined solar/electrolyzer system using commercially available components is close to the desired 10% defined for solar hydrogen generation. Moreover, the components are rugged and should be long-lived. The problem with such a system is its cost. Solar photovoltaics cannot currently produce electricity at competitive
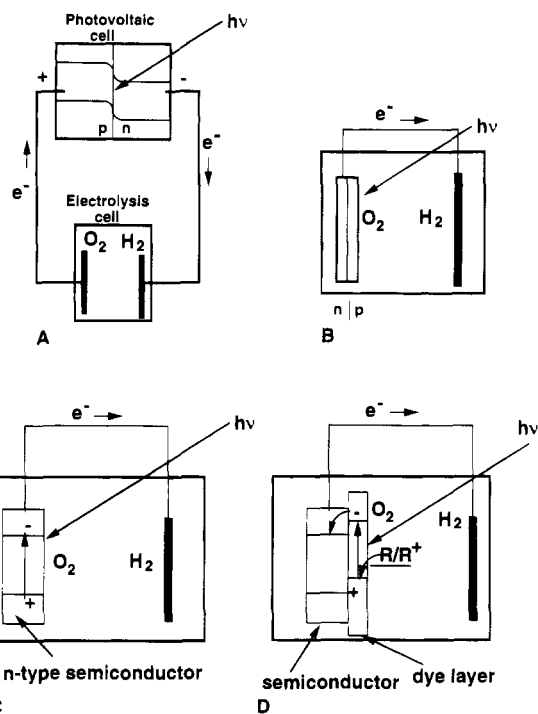

Figure 1. Schematic diagrams of different types of semiconductor-based systems proposed for solar water splitting: (A) solid state photovoltaic cell driving a water electrolyzer; (B) cell with immersed semiconductor p/n junction (or metal/semiconductor Schottky junction) as one electrode; (C) liquid junction semiconductor electrode cell; (D) cell with dye-sensitized semiconductor electrode.

prices, and hydrogen from water electrolyzers is significantly more expensive than that produced chemically from coal or natural gas. Lower cost solar cells are possible, e.g., through the use of polycrystalline or amorphous Si or other semiconductors (CdS, CdTe, $CuInSe_2$), and some improvements in water electrolyzer efficiency through better configurations and catalysts and the use of higher temperatures are possible. However, it probably will be difficult to bring the overall cost down to levels that make such a configuration practical in the foreseeable future.

An alternative system involves the semiconductor photovoltaic cell immersed directly in the aqueous system (Figure 1B). At the least this eliminates the costs and mechanical difficulties associated with separate construction and interconnection of solar and electrochemical cells. In one such system, the electrodes are composed of single or multiple semiconductor p/n junctions that are irradiated while they are within the cell. This simpler apparatus is attained at the cost of encapsulating and coating the semiconductors to protect them from the liquid environment and probably with a more limited choice of electrocatalyst for O_2 or H_2 evolution. Moreover, the open-circuit photovoltage of a single Si p/n junction is only 0.55 V, so at least three of these in series would be needed to generate the necessary potential for water splitting. For example, in a system developed at Texas Instruments[3] (TI) p-Si/n-Si junctions were produced on small (0.2 mm diameter) Si spheres embedded in glass and backed by a conductive layer to form an

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array. Each sphere behaved as a photovoltaic cell and produced about 0.55 V. The use of two arrays, protected with noble metal catalysts (M), i.e., M/p-Si/n-Si and M/n-Si/p-Si, connected in series and in contact with HBr, allowed H_2 and Br_2 to be generated with about an 8% efficiency. Multiple TI photoarray cells to carry out water splitting and other reactions requiring higher potentials are possible[4] at a considerable sacrifice in efficiency. Note that, in addition to p/n semiconductor junctions, those between a metal and semiconductor (Schottky barriers) can be used to produce a photopotential, e.g., in electrodes such as Au/n-GaP, PtSi/n-Si, and Pt/n-GaAs.

C. Semiconductor Electrode (Liquid Junction) Systems.

Of more interest to chemists are systems in which the photopotential to drive the water-splitting reaction is generated directly at the semiconductor/liquid interface (Figure 1C). In 1839 Becquerel noted small photoeffects when metal electrodes were irradiated in electrochemical cells.[5] Rather extensive research was carried out on various metal electrodes, sometimes covered with oxide or other films, and immersed in a variety of solutions, including some containing fluorescent dyes.[6] The effects seen were usually small, and given the state of electrochemistry and knowledge of the electronic properties of solids, the results were generally poorly understood. The discovery of the transistor and interest by chemists and physicists in semiconductor materials, notably Si and Ge, led to more extensive electrochemical and photoelectrochemical studies, usually with the goal of characterizing the semiconductor.[7,8]

The modern era of semiconductor electrodes and interest in these in photoelectrochemical devices for energy conversion, especially via the water-splitting reaction, can be traced to the work of Honda and Fujishima on single-crystal TiO_2 electrodes.[9] Indeed, water splitting in TiO_2-based cells can be accomplished, but only with an additional electrical bias. The problem with TiO_2 is that the conduction band is too low (i.e., at an insufficiently negative potential) to generate hydrogen at a useful rate. Moreover, because the TiO_2 band gap is large (3.0 eV for rutile), only a small fraction of the solar light is absorbed and the efficiency of TiO_2-based cells can never attain the specified 10% level. Cells with TiO_2 electrodes of various types (e.g., single crystal, polycrystalline, thin film) have nevertheless been heavily investigated, largely because TiO_2 is very stable and is a good model for understanding the semiconductor/liquid interface.

The stability of the semiconductor in contact with a liquid and under irradiation is an important factor. To generate oxygen, rather energetic photogenerated holes are required, and these tend to cause decomposition of the semiconductor. Thus, a key requirement in cells of this type, involving a single photojunction, is the discovery of a semiconductor with an appropriate band gap (< about 2.5 eV), with the conduction

band sufficiently negative for hydrogen evolution and the valence band sufficiently positive for oxygen evolution, so that it remains stable under irradiation. This single-junction semiconductor electrode has not yet been discovered. Indeed, it is only with materials with band gaps even larger than that of TiO_2, like $SrTiO_3$, that water splitting can be carried out without an additional electrical bias. The solar efficiency of such cells is very small.

D. Semiconductor Particle Systems.

A considerable simplification of the apparatus is possible if the electrochemical cell can be replaced by simple dispersions of semiconductor particles. In such dispersions, the semiconductor particles can be coated with islands of metals that behave as catalytic sites, with each particle behaving as a microelectrochemical cell.[10] TiO_2 has been a favorite material, although other compounds, such as CdS and ZnO, have also been studied. While a number of interesting photoreactions have been carried out, including the use of particles to destroy organics and to plate metals from waste water[11] and for synthetic purposes,[12] reports on the use of particulate systems for water splitting remain controversial. At best the solar efficiencies of processes reported to date have been very small (<1%). An extension of this approach is the use of colloidal-sized particles down to nanoparticles (or Q- or quantum-particles) with band gaps larger than that of the bulk material and a function of particle size. Such small particles also have very high surface areas that, in principle, allow faster capture of the photogenerated charges by solution species and with less bulk recombination. To prevent agglomeration of these particles, they are usually capped with polymers or immobilized on an inert support.

E. Sensitized Semiconductor Systems.

To overcome the problems of a large band gap and inefficient utilization of the solar spectrum, e.g., with TiO_2, dye sensitizers can be adsorbed on the surface of the electrode or particle.[13] The photon absorbed in the dye creates an electron which passes into the semiconductor, eventually causing a reduction reaction, and the hole is filled by an electron from an adsorbed or solution species in an oxidation reaction (Figure 1D). With a thin film of dye, the quantum efficiency, i.e., the number of electrons injected into the semiconductor per photon *absorbed*, can be very high. However, with a thin dye layer, even in dyes with high extinction coefficients, only a small fraction of the incident photons are absorbed, so the overall solar efficiency tends to be small (usually <1% and more often <0.1%). The total absorbance by the dye layer can be increased by increasing its thickness, but in that case, since most of the photons are absorbed away from the interface between semiconductor and solution and must diffuse and migrate to that site before reaction, the quantum efficiency decreases sharply. A recent advance has been the use of highly porous TiO_2 electrodes with very large surface areas ("fractal electrodes") as substrates for the dye sensitizer.[14] These apparently absorb a

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large fraction of the incident light while still maintaining a high quantum efficiency. A photoelectrochemical cell based on a ruthenium complex sensitizer adsorbed on TiO_2 showed an efficiency above 7% in direct sunlight for conversion of light to electricity. In this example, iodine was generated at the dye-coated electrode and was reduced at the counter electrode.[15] For water splitting, the oxidation reaction at the dye/liquid interface would have to generate oxygen, a considerably more difficult process. Indeed, a fundamental problem with dye-sensitized systems may be the photochemical instability of the sensitizer, especially when holes sufficiently energetic to liberate oxygen are produced during irradiation.

F. Homogeneous and Microheterogeneous Systems. An alternative to these electrochemical methods is to employ multicomponent solutions or dispersions as complex arrays for multistep water splitting. Such a system would typically combine an efficient sensitizer, one or more relays or charge accumulation sites, and one or more gas evolution catalysts. Much effort has been devoted to understanding and optimizing the function of each constituent of these arrays, but their combination (even of the best single components) has so far not produced the desired synergism needed to attain the high solar conversion efficiency that is the goal of this quest.

The most thoroughly studied systems employ microheterogeneous arrays, with either the oxidation ($H_2O \rightarrow O_2$) or the reduction ($H_2O \rightarrow H_2$) half-reactions being the targeted goal. In such arrays, the excited state of the sensitizer is quenched either reductively or oxidatively, and most require a sacrificial electron donor or acceptor. A major disadvantage of most systems studied so far is that they do not accomplish true water splitting; rather, they focus on either hydrogen generation in the presence of a sacrificial electron donor or oxygen production in the presence of a sacrificial electron acceptor. Even when optimized, a successful melding of these half-reactions into a simple composite array remains elusive. Furthermore, the consumption of a sacrificial reagent in the optimized half-reactions obviates the economic advantages of simple water splitting and mars its environmental attractiveness as a means for chemical production of fuel by solar energy conversion. Including a sacrificial reagent also often completely reverses the net thermodynamics, converting an inherently uphill (photosynthetic) reaction such as water splitting into a net energetically downhill (photocatalytic) transformation by coupling the endothermic steps with other highly exothermic ones.

In the half-reaction involving the production of hydrogen, the following coupled sequence is typically followed. The key photochemically-driven step is the oxidation of the excited sensitizer S, which is accomplished by transferring an electron to a molecule R that acts as a relay to a proton source, usually in the presence of a catalyst Cat. The singly oxidized sensitizer is then reconverted to its original neutral state by interaction with a sacrificial electron donor D, which is consumed in a sequence of one or more chemical steps initiated by irreversible electron donation. The radical anion produced upon oxidation of the sensitizer acts as a relay reagent, transferring its
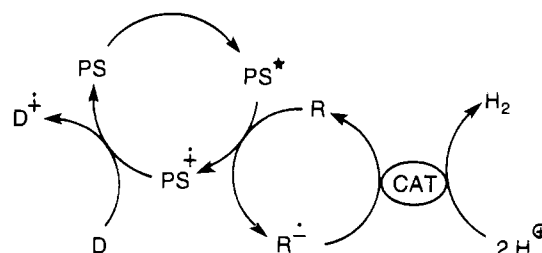
extra electron, usually in the presence of a catalyst, to water, thus producing hydrogen gas. The catalyst thus functions both to accumulate electrons to provide the necessary electrochemical potential and the number of electrons for the reduction of water and to serve as a gas evolution site.

For efficient hydrogen evolution, several features are necessary: (1) the oxidative trapping must occur faster than radiative or nonradiative relaxation of the sensitizer excited state; (2) each of the intermediate charge relays must be stable in both the oxidized and reduced states so that the sensitizing dye can be multiply recycled; (3) a robust catalyst for efficient evolution of hydrogen must be effective in trapping the reduced relay; (4) the sacrificial donor must be inexpensive and readily available; and (5) each of the components of the array must be chemically and optically compatible. In operation, these requirements are often structurally contradictory, and even when a high quantum efficiency (production of fuel per absorbed photon) is observed, low solar efficiency (production of fuel over the entire range of incident photons) is commonly encountered.

Lehn and co-workers have provided an early example of one such ensemble, using a metal complex $Ru(bpy)_3Cl_2$, as sensitizer, triethanolamine as the sacrificial donor, and colloidal platinum generated *in situ* from K_2PtCl_6 as the gas evolution catalyst.[16] Numerous other variants of these studies were undertaken in the subsequent decade,[17] with sensitizers including metal complexes, metalated porphyrins and phthalocyanines, organic dyes, (e.g., xanthines or cyanines), or organic polymers [e.g., poly(vinylpyridines)]. In such studies, a range of relays (e.g., viologens, phenanthroline complexes, multivalent cations like V^{3+} or Cr^{3+}, or redox enzymes like cytochrome c_3) and catalysts (e.g., metal alloys, enzymes, supported metal oxides, colloidal metals, etc.) were employed.

In a typical optimized system [with $Ru(bpy)_3Cl_2$ as sensitizer and methyl viologen as relay for hydrogen evolution on colloidal platinum or gold in the presence of sacrificial ethylenediamine tetraacetic acid (EDTA)], hydrogen evolves efficiently, with catalytic turnover (about 100) limited by competing hydrogenation of the methyl viologen relay.[18] Turnover efficiency could be substantially improved by substituting a family of newly synthesized viologens that are resistant to catalytic hydrogenation[19] and by replacing the hydrogen evolution catalyst with colloidal platinum. Most studies with these artificial arrays, however, have

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focused on forward- and back-electron-transfer rates and on structural improvement of photophysical properties: for example, with a complex five-component antenna system, Sasse and co-workers have reported a quantum efficiency of 93% for hydrogen evolution from an array containing 9-anthracenecarboxylate in acetate buffered to pH 5 in a solution containing EDTA and methyl viologen.[20]

Similarly, oxygen evolution could be induced by irradiation with redox catalysts that act as pools of oxidative equivalents.[15,21,22] In a recent variant, Calzaferri has employed Ag$^+$-loaded zeolites toward this objective, with self-sensitization by O$_2$ being demonstrated to improve O$_2$ evolution efficiency.[23] In general, much lower efficiencies are observed for the evolution of oxygen than of hydrogen, mainly because of the difficulty in accumulating the necessary four oxidative equivalents required to convert water to oxygen.

Self-assembling arrays have also been constructed in media in which one or more of the components is confined within a fixed matrix, either a sol–gel or a zeolite. In functionalized zeolites, for example, Mallouk and co-workers have shown that a substantially extended charge separation lifetime of 37 μs can lead to a quantum efficiency for charge separation of about 17% from flash photolysis measurements,[24] although a quantum efficiency for hydrogen evolution of only 0.05% has been reported by Dutta and co-workers for a similarly constructed array.[25] Given that very long charge carrier lifetimes (from excitation of pyrene to a viologen confined to a silicate matrix in the presence of a mobile electron relay[26]) have been reported, one might expect high efficiencies for hydrogen production in analogous sol–gels if mass transport limitations can be overcome.

Another option to a self-assembling, multicomponent, microheterogeneous array is using a covalent supramolecular assembly to accomplish long-term electron–hole pair separation. Such arrays containing three, four, or five absorbers, relays, or traps have been described by a number of groups as capable of relatively long distance (tens of angstroms) charge separation with high quantum efficiency and long lifetimes (83% for an electron-transfer pentad with a charge separation lifetime of 55 μs in chloroform[27]),

with the rate of forward electron transfer favored by a factor substantially greater than 10^3 over the energy dissipative back electron transfer.

Despite the inherent difficulties encountered in attempts to optimize the oxidative and reductive half-reactions in solution phase systems, it is clear that impressive progress has been made. Nonetheless, combinations of such half-reactions to a more complex array capable of water splitting (with concomitant hydrogen and oxygen evolution) have proven to be difficult. To our knowledge, no truly homogeneous nonsacrificial system for water splitting has yet been reported. Even so, compartmentalized tandem oxidation–reduction does take place on several nonelectroactive spatially confined solids, although the catalytic turnover numbers remain small (turnover number of about 5 for a Ru(bpy)$_3^{2+}$/clay/Eu^{3+} array[28]), the reactions oscillatory, and the net quantum efficiencies low [4% upon excitation of tris[1-(4-methoxyphenyl)-2-phenyl-1,2-ethylenedithiolenic] tungsten in the visible[29] (400–500 nm)].

Prospects for the Future

These scientific difficulties continue to pose tantalizing challenges to scientists bent on devising commercially viable means for solar energy conversion, especially as it relates to chemical fuel production and its contribution to a hydrogen-based economy. Although we claim no special insight into the ultimate solutions to these problems, we can speculate on those research directions that may seem most promising. Given the difficulties associated with homogeneous routes employed so far, it is a fair bet that heterogeneous arrays will be needed for high-efficiency solar energy conversion. The problem of accumulating multiple redox equivalents for the oxidation and reduction half-reactions also suggests that these systems will require multifunctional components. One possibility is the use of multijunction devices, such as the bipolar CdSe/CoS semiconductor photoelectrode panel array on which unassisted water photodecomposition can be stoichiometrically attained with an equivalent solar energy efficiency of about 1%.[30] It is also likely that new semiconductor materials and multielectron catalysts will be key components of such heterogeneous arrays, perhaps with small metal clusters or films to protect the semiconductor surface, for example, as noble metal silicides[31] or microscopically discontinuous metal overlayers.[32] Dramatically new families of photosensitizers might also overcome some of the practical barriers still encountered in attempts to utilize the whole solar spectrum: the use of nanoparticles of one semiconductor on a highly porous film of TiO$_2$[33] seems a very interesting possibility. In any case, it seems clear that a creative breakthrough, probably focused within the boundaries defined by intriguing basic research conducted over the last decade, is needed to reach this "Grail".

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