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Harnessing Solar Energy for the Production of Clean Fuel

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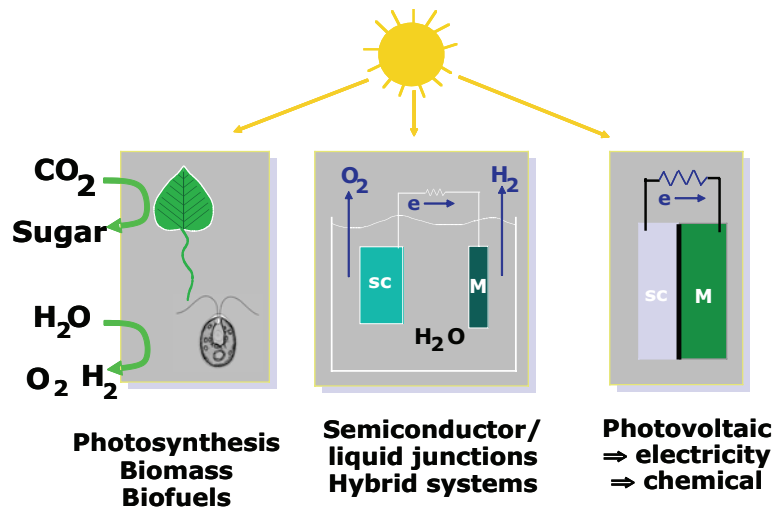
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Harnessing Solar Energy for the Production of Clean Fuels



Foreword

The European Union and its member states are being urged by leading scientists to make a major multi million Euro commitment to solar driven production of environmentally clean electricity, hydrogen and other fuels, as the only sustainable long-term solution for global energy needs. The most promising routes to eventual full-scale commercial solar energy conversion directly into fuels were identified at a recent international meeting in Regensburg, sponsored by the European Science Foundation (ESF). An interdisciplinary task force was established at this meeting to make the case for substantial investments in these technologies to EU and national government decision makers. This report summarizes the outcome of this meeting.

The fundamental issue is that total annual global energy consumption is set at least to double from its current level of 14 TW by 2050, while fossil fuels will start to run out and in any case would produce unacceptable levels of carbon dioxide, bringing global warming accompanied by disastrous effects in many areas, such as food production. Apart from solar energy, the shortfall can only be made up by renewable sources such as wind, along with the other non-fossil, non-renewable fuel source of energy, nuclear. But these will be unable to satisfy the expected increased energy needs, let alone replace fossil fuels entirely, even for electricity production. Another problem is that they will not readily yield stored fuels. Without an unexpected breakthrough in electricity storage, there will be a continued need for fuels for around 70% of total global energy requirements, particularly in transportation, manufacturing, and domestic heating. Electricity only accounts for 30% of global energy consumption at present.

Solar energy, however, is plentiful since enough reaches the Earth's surface every hour to meet the world's annual energy needs. The problem lies in harnessing it, but nature has perfected in photosynthesis a highly efficient and flexible means of doing this across a wide variety of scales from isolated bacterial colonies to large forests. Substantial progress has been made recently, particularly in Europe, to understand and mimic these processes, sufficient for scientists to be confident that it can work to produce fuels on a commercial scale. The focus of research therefore should be on drawing inspiration from biological systems for the creation of both natural and artificial solar energy conversion systems that allow in the long run for a stable and sustainable energy supply. The focus should also be on reducing the ecological footprint of the human economy and thereby increasing the global ecological capacity using technology that is environmentally clean, for instance by conversion of carbon dioxide back into fuels in a cyclic process.

The ESF task force is recommending that three parallel avenues of solar energy research for generating clean fuel cycles should be pursued in Europe:

- 1) Extending and adapting current photovoltaic technology to generate clean fuels directly from solar radiation.
- 2) Constructing artificial chemical and biomimetic devices mimicking photosynthesis to collect, direct, and apply solar radiation, for example to split water, convert atmospheric carbon dioxide and thus produce various forms of environmentally clean fuels.
- 3) Tuning natural systems to produce fuels such as hydrogen and methanol directly rather than carbohydrates that are converted into fuels in an indirect and inefficient process.

These three research themes will overlap, and all will exploit fundamental research elucidating the precise molecular mechanisms involved in the splitting of water into hydrogen and oxygen in photosynthesis by both plants and bacteria. This process, which evolved 2.5 billion years ago, created the conditions for animal life by converting atmospheric carbon dioxide into carbohydrates, and also produced all the fossil fuels, which humans are turning back into carbon dioxide at an increasing rate, threatening catastrophic environmental effects. The same process now holds our salvation again.

Although the principal products of photosynthesis in plants and bacteria are carbohydrates, certain algae and cyanobacteria can produce hydrogen directly from water using sunlight, providing a basis for genetic modification to increase yields, and for the creation of suitable artificial systems. Furthermore, photosynthesis is also capable of generating other chemicals currently made industrially, such as nitrates, and other high value compounds for chemical industry. The European research program will therefore also seek to develop systems for converting solar energy directly into such chemicals with much greater efficiency, offering the prospect not just of producing unlimited energy, but also fixing atmospheric carbon dioxide to bring concentrations back down to pre-industrial levels as part of the overall thrust for clean renewable energy.

There are considerable challenges, with the first being to mimic the functioning of natural photosynthetic systems, particularly photosystem II, the enzyme complex in the leaves of plants that splits water into hydrogen and oxygen via a catalyst comprising four manganese atoms along with some calcium. Significant progress has been made recently on this front. Participants at the ESF's brainstorming conference, describe the solar fuels project as the quest for building the "artificial leaf". There is growing conviction in Europe and elsewhere that by 2050 a large proportion of our fuels will come from such "artificial leaves" and that there is no time to lose starting the crucial enabling research, in order to gain technology leadership in this important future key technology.

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Introduction

The problem

By the year 2050 even the most conservative estimates predict that the world's energy requirements will more than double. Energy is a prerequisite to economic stability and its supply at an affordable cost for the both the developed and developing world can not be guaranteed. For a large part of the global population fulfilling very basic energy intensive needs as food, desalinated water and housing will not be achieved within the current energy scenarios for the coming decades. In addition, improving education and public health critically depends on getting access to affordable energy. Even more important, the current energy system is far from sustainable. This problem is made all the more critical for Europe because its ecological footprint is over double than what the continent can regenerate. In other words, it now takes more than two years to regenerate what we use in a single year, and even on a global scale we have already a serious backlog replacing our current unsustainable linear competitive economy by a sustainable cyclic adaptive economy by about 23%. Most urgently, continued increased use of fossil fuels to satisfy the extra energy demand brings unacceptable environmental consequences with the increased concentrations of CO₂ in the atmosphere that this produces. The biosphere can recycle 4-7 gigaton of CO₂ yearly, and we currently produce around 25 gigaton per year. In addition, energy savings rates in Europe and other developed economies have slowed since 1990, as has the decline in CO₂ emissions relative to GDP. Despite all measures the CO₂ emission will still grow to ~32 gigaton yearly by 2030, mostly from power stations generating electricity and fuels for transportation.

This shows the enormity of the problem: contemplated measures are by far insufficient to reduce the ecological overshoot. How can we provide the energy that mankind requires and at the same time reduce greenhouse gas emissions? **Filling the energy gap without disruptions of the supply while reducing energy poverty in developing countries and without a dangerous continued increase in atmospheric CO₂ destabilizing the climate represents the most serious challenge to the continued existence of man on planet Earth.** It is almost impossible to overemphasize the disastrous combined effects that running out of inexpensive energy supplies and the catastrophic rises in atmospheric CO₂ will have on both the developed and the developing world. Current political problems pale into insignificance by comparison and governments worldwide are pondering about decisive actions to turn the tide.

Solutions

We scientists believe that it is now possible, given sufficient resources, to capitalize on recent excellent scientific progress in the understanding of photosynthesis to learn from Nature how to harness solar energy for sustainable production of primary energy carriers like hydrogen from water or carbon based fuels from CO₂ at an affordable cost. We see here an opportunity for leapfrogging to a new diversified energy system that is scalable and sustainable. When vigorously pursued, this opportunity represents one of the very few major options that mankind has to provide clean energy, provide its security in a humanitarian manner instead of confrontation, and eliminate the 'overshoot' of our footprint that is now maintained by liquidating the planet's ecological resources. It will give Europe a leading role in renewables. Fuel is the predominant primary energy carrier and will continue to dominate the energy

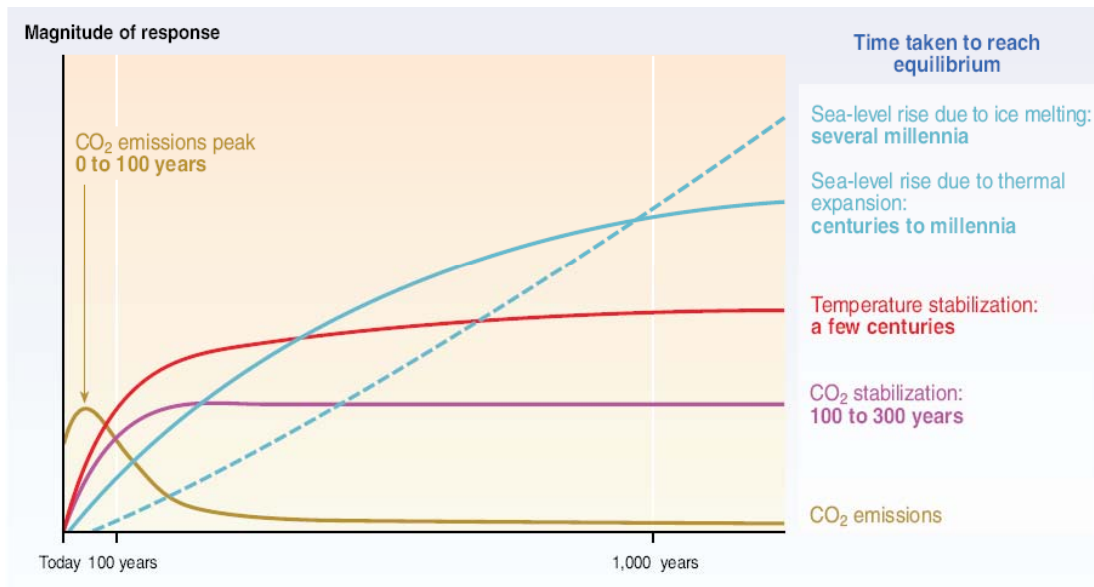


Figure 1. The enormity of the problem is made clear by simulations of the IPCC, which predict that long after CO₂ emissions are reduced atmospheric concentrations will continue to grow for 100-300 years before they stabilize, while the surface air temperature continues to rise slowly for a century or more. Thermal expansion and melting of ice sheets continues to contribute to sea-level rise for many centuries. Adapted from: *Climate Change 2001: Synthesis Report –Summary for Policymakers, Intergovernmental Panel on Climate Change (IPCC)*.

supply in the foreseeable future. The economically developed countries aim for a decline of their emissions after 2020 by actively pursuing efficiency improvements and by shifting towards renewables and nuclear power. However, well over two-thirds of the projected increase in CO₂ emissions will come from developing countries that remain big users of coal, the most carbon-intensive of fuels. Their governments already give it their best effort to obtain efficiency improvements in electricity usage to reduce the use of coal, but this will not prevent the CO₂ emissions from growing further. Responsible consumers of energy are increasingly willing to pay the full cost of energy, including the environmental costs, since they are worried about the burden we put on coming generations. Strongly converging scientific evidence points to a necessity for providing the scientific and technological basis for a major energy revolution moving away from fossil fuels into a new diversified system, in addition to technological improvements such as more efficient and sustainable use of fossil fuels.

Achieving a truly sustainable energy system calls for technological breakthroughs that radically alter how we produce and use energy. Since we cannot dramatically reduce our need for fuel there is only one realistic option, which is to develop new technology to increase the capacity of clean and inexpensive fuels. What are the possible sources of clean energy that can be used to replace presently used fossil fuels? In principle, we have access to two major non-fossil fuel based sources of energy. One is nuclear. Since the energy gap must be filled by the middle of this century we would need to be already building new nuclear power stations at a rate of about 700 per year to satisfy this demand. There seems no possibility of achieving this especially since globally only about 450 exist at present. Moreover, conventional nuclear power stations that consume uranium will, over the same time scale as the loss of oil and gas supplies, run out of inexpensive uranium. This then raises the issue of power generation from

nuclear fusion. This technology may become important in the future, however, it has yet to come to fruition. The other alternative is to use solar energy. Enough solar energy reaches the surface of the Earth every hour to supply the whole world's annual energy requirements. How can we convert enough of this incident solar energy into usable forms so that we can maintain our way of life?

Solar energy represents a continuous and maintenance free clean power source of more than 100,000 TW. Harnessing solar energy for the production of a mix of clean fuels for continuous use without the risk of interruption of the energy supply is a major challenge. There exists at present only a single conversion technology with prospects for long term large-scale use: photovoltaics. In a photovoltaic cell, photons are absorbed and converted to electrical energy. This leads to electric currents that have to be used immediately. The current stops when the light goes out. The advantage of this system is that there are no energy storage losses, but it is insufficient for a continuous and reliable energy supply because of inadequate reserve margins.

For almost 3 billion years, Nature has found fantastic solutions to convert solar energy to produce fuels (See the appendix for the scientific background). In a variety of photosynthetic processes, light energy is dynamically stored as efficient as thermodynamically possible. First, it is stored in a light antenna that allows for rapid transfer of the solar energy to reaction centers that produce electric charges of opposite polarity and then an electrochemical membrane potential. Afterwards, this is fed into a variety of chemical processes that form a dynamic reserve embedded in the energy distribution network of the cell where it is used for maintenance, growth and maturation of organisms (See Figure 2). Plants and green eubacteria use light energy to split water into oxygen and a form of hydrogen in an enzyme complex called photosystem II. Ultimately this hydrogen powers all life on Earth. The main waste product of photosynthesis is oxygen. Together with fuels, this waste product is used to drive cyclic processes that sustain life on Earth in a renewable manner. In recent years structural biology has provided profound insight into the structure and operational mechanisms of the molecular machinery of the photosynthetic apparatus. This sets the stage for a technology push in the coming years.

Now is the time to dedicate ourselves to solving this very important problem. Scientists, energy companies and government organizations are contemplating about how to build up significant research efforts into potentially important directions to fulfill the basic research needs that will lead to the necessary breakthroughs in renewable technologies. The pace of technology development is the key to making the energy system more economically, socially and environmentally sustainable. The financial system has the capacity to fund the required investments, but it will need active steering into the right direction. **Doing nothing is not an option. We require the sort of financial and dedicated commitment to tackle this problem that was shown in sending a man to the moon or in the Manhattan Project.** The clock is already ticking. Action is needed now if there is to be a solution within the next 30-40 years.

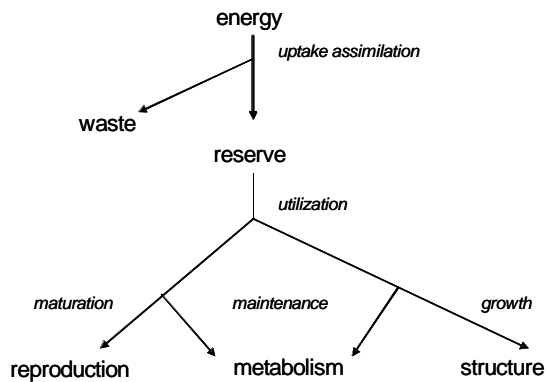


Figure 2. Energy use in the biological steady state

Scalability

Within the traditional energy system it will become increasingly difficult to guarantee supply without disruptions, because it critically depends on import from politically unstable regions over very few and vulnerable supply routes. Sustainable high-end technology based on fossil fuel as a primary energy source will not solve these issues. Since the market power is shifting away from the European countries and other importers, this creates new insecurities with regard to if the necessary large investments in production and upgrading will be done and in time by the producers, in particular in the Middle East and North Africa. In addition, many of the poorest people will still be deprived from modern energy services that they cannot afford.

With solar fuels these problems do not exist since importers become producers at the level of regions, cities, communities and even individual citizens. A crucial element of a new energy system will be to produce a mix of carriers, and to change the way we use them by a dynamic reserve network. In the current energy system, primary carriers are not stored in large amounts. The crude oil in the ground is the reserve while abundant refinery and upgrading capacity secures an uninterrupted flow of primary fuel. Nature provides a paradigm for operating a light-driven energy system very efficiently, close to what is thermodynamically possible by merging a mix of energy carriers and energy reserves in a dynamic network, storing energy no longer than necessary to guarantee uninterrupted supply throughout the network. In the end of an organism's life cycle, even a small amount of the biomass reserve is left for renewable use by other organisms –including mankind. Like in nature, dynamic fuel reserves will be most efficient at a small scale and integrated in the distribution network than at a large scale as separate entities in a distribution network.

With an average energy production at a level of $\sim 25 \text{ W/m}^2$ and a projected energy need in the 20 TW range, around 10^{11} - 10^{12} m^2 will be necessary to collect energy. In natural photosynthesis, ~ 300 chlorophyll dye molecules can sustain a catalytic conversion rate of 10^3 - $10^4/\text{s}$. For hydrogen production through artificial photosynthesis this translates into a target of 1-10 mol H_2/s per mol of dye molecules. On the other hand, 10 TW corresponds with 5×10^7 mol H_2/s . This means that significant energy production translates into $\sim 10^7$ mol of dye molecules and the corresponding devices for producing electric current or fuels. If a porphyrin dye molecule similar to chlorophyll with a molecular weight around 1000 g/mol is used in artificial photosynthesis, around 10 kiloton of dye material needs to be produced and maintained in a sustainable manner. In photosynthesis, the packing of dye molecules is very dense, and for artificial photosynthesis 20-50 kilotons of nanostructure would be sufficient.

Traditional organic chemistry based production methods may not fulfill the requirements with respect to costs and sustainability, in which case the building materials would have to be produced in cell factories.

Because of the large area and quantity needed, the marginal costs involved in collecting the solar energy will be the limiting factor in the end. Nature solves this by self-assembly, self-repair, self-reproduction and by starting from a molecular absorber with a high extinction coefficient. The main technological challenge in artificial photosynthesis is then to learn how to exploit these processes that make photosynthesis affordable and viable in the living world. Considering the massive fundamental research effort that is currently being built up in the life sciences and nanosciences, it is timely to implement a grid-based research program directed towards resolving fundamental research needs and performing technology development for future energy supply and conversion by artificial photosynthesis. With such a concentrated effort, exploration, implementation, validation and up-scaling of artificial photosynthesis can be realized well within the required time scale of 25-30 years, in a bottom-up process guided by clear visions.

Fundamental research requirements for the production of clean fuel: introduction into Priority Research Directions (PRD)

Since achieving a truly sustainable energy system requires technological breakthroughs that radically alter how we produce and use energy, the long-term goal of satisfying global energy needs must be reconciled with the timeframe necessary for the development, dissemination, and exploitation of innovative clean energy sources, all of which must be accomplished in time to secure continued sustainable growth for the planet. Lead candidates for feasible technological solutions are only beginning to emerge, and novel unexplored directions will continue to emerge from basic research. The implementation of photovoltaic technologies, which have accomplished tremendous breakthroughs in recent times remain, for the moment, a most viable solution for the clean production of electricity. At the same time, long-term goals of direct fuel production from solar energy dictate that new approaches must be sought. Three possible directions should be pursued: (a) supplementing current photovoltaic technology to coax clean fuels from photovoltaic modules, (b) construct multi-component devices able to collect, direct, and use solar radiation to produce clean fuels, or (c) harvesting fuel-producing organisms. Regardless of which solutions will ultimately emerge as viable alternatives to fossil fuels, inspiration from natural biological systems will provide invaluable input for the design and construction of functional devices.

An obvious challenge at the present time is to understand the functioning of the natural photosynthetic systems, as outlined in PRD 1. At the same time, current knowledge is definitely good enough to start work on mimicking the individual components. These include antenna systems (PRD 2), reaction centres for charge separation (PRD 3), and catalytic units for multi-electron redox processes (PRD 4). Advances in these areas are crucial for solar energy to fuel conversion devices, regardless of their mode of operation. Clearly, *de-novo* design of artificial photosynthetic architectures will require integration of these processes into a functional assembly, as outlined in Figure 3.

Several types of devices could be sought of that are sound and their development will ultimately lead to important breakthroughs in current knowledge. The underlying principle is that all artificial components can find an analogue in natural systems. For example, a classical photovoltaic cell may combine the light absorbing function, of biological antennae with the charge separation units of biological reaction centres. New directions currently being explored in photovoltaics (3rd generation solar cells) might profit from these processes being separated again (using energetically up- and down-converting front- or backside layers). Here, learning from nature will lead to new solutions as explained in PRD 5. Going for smart materials with functions such as self-adjustment and self-repair (PRD 6) will add immense value in terms of increased life-cycle and performance. The value of current photovoltaic solar to electricity devices can be raised by adding a storage function, as in biological photosynthetic assemblies. This would lead to the development of novel robust photo electrochemical solar batteries (PRDs 7 and 8).

The direct production of clean fuels, the ultimate goal for a self-sustaining society, will be achieved by combining approaches that directly or indirectly rely on natural photosynthetic systems. The most promising approach is to harness green algae and cyanobacteria to produce hydrogen directly from water (PRD 9) but also anaerobic bacteria can be used for hydrogen

production (PRD 10). However, current energy harvesting from biomass has a low efficiency due to intrinsic free energy losses in cellular metabolism. Development of systems and synthetic biology approaches will lead to the engineering of photosynthetic cell factories that are designed for optimal fuel production (PRD 11).

Extraction of the ideas behind the molecular machinery used for the harnessing and converting solar energy in photosynthetic organisms will lead to the engineering of new devices, at the forefront of chemistry, biology and physics (PRD 12). Ultimately, high efficiency can only be obtained through the combination of different energy conversion modules designed to extract all the exploitable energy content of incident solar radiation. This is outlined in PRD 13, where heat by-products of solar-to-fuel conversion devices are used in an integrated solar hydrogen tower. Throughout the research that will lead us to clean fuel, the functioning of integrated devices or components must be tested, requiring novel techniques and methodologies to probe functionalities on a nano- and meso-scale. These new techniques and instruments are summarized in PRD 14. The development of novel systems with the desired solar to fuel conversion properties requires *in silico* evolutionary computational strategies to speed up the design of functionally active superstructures (PRD 15).

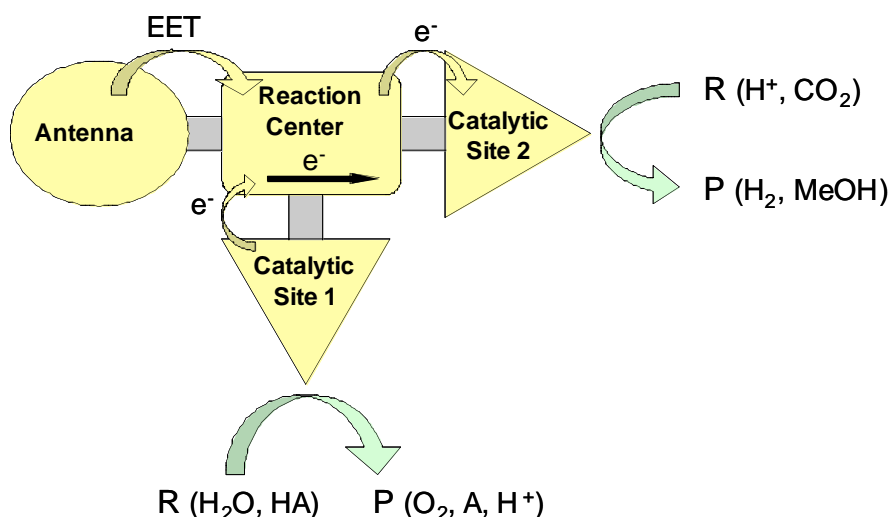


Figure 3. Schematic picture of an integrated artificial device for production of hydrogen and methanol.

1. Biological blueprints for solar hydrogen production from water: Elucidating the biological mechanism of water splitting and hydrogen production

Nature has provided a proof of principle that large-scale water splitting and hydrogen formation can be driven by solar energy. Therefore nature provides a blueprint for the development of new technologies to produce fuels in an environmentally safe way. Deciphering the molecular basis of these reactions is an essential basis for the development of biomimetic and biotechnological systems for solar-driven hydrogen production.

Research Direction

All problems of light-driven water splitting and hydrogen formation have been solved in nature, but crucial aspects of the evolutionary successful solution are not understood. The significant progress obtained in the past still is an insufficient basis for technological developments. This holds in particular for the light-driven water splitting in Photosystem II and dihydrogen formation in hydrogenases. This PRD is aiming at elucidation of the multi-step catalytic processes of water splitting and dihydrogen formation in natural systems.

Potential Impact

Research on the functions of the natural system constitutes the basis for technological systems for solar hydrogen production in two ways:

- 1) Elucidation of the function of natural systems facilitates biomimetic approaches. The natural systems involve a protein matrix carrying organic (*e. g.* pigments) cofactors and catalytic metal complexes. The protein environment also tunes the chemical properties of the functional cofactors and organizes the substrate/products access to/from the active site. The natural systems likely represent suitable blueprint for the catalytic site and the smart matrix of artificial systems. The self-assembly of the biological water-splitting metal site may also serve as a guide for synthesis/assembly in artificial systems.
- 2) Molecular-level understanding of the related enzymology, required for cellular approaches to light-driven fuel formation.

Scientific challenges

1) *Fully elucidate the molecular reactions of the water splitting by PSII.* Structural information at atomic resolution is required in order to follow the catalytic cycle leading to dioxygen formation. Complementary detail of electronic configurations will be required to understand the energetic and quantum mechanical principles for the formation of the intermediate states involving coupled proton/electron transfer and O-O bond formation. Considerable progress has been made in these areas by European scientists but the challenge remains to improve understanding of the molecular and chemical properties of the intermediate states of the water splitting cycle. Higher resolution X-ray structures are required as well as information derived from advanced physical techniques. With these approaches details of the interplay between the catalytic metal centre and its protein environment will be revealed as the chemistry advances from the binding of the two substrate water molecules through to their complete oxidation. The resulting information will provide the basis for quantum mechanical calculations required for the full description of the water splitting chemistry leading to the formation of dioxygen, electrons and protons.

2) *Elucidation of the chemical basis of how biological systems convert electrons and protons to molecular hydrogen.* The structure of some hydrogenases is known to great detail already. Nevertheless the challenge remains to reveal the full mechanism by characterizing the involved intermediates by spectroscopy and crystallography. For future applications in biomimetic systems, it is important to address the following aspects:

(i) By which means some hydrogenases become oxygen insensitive or at least tolerant?

(ii) How can the H₂ production rate be increased and the uptake rate decreased?

Further systematic studies into the structure and function of hydrogenases from organisms living under various conditions is required to fully understand the role of the protein (including channels) and the different active sites during catalysis. Investigations also need to be directed towards coupling of the electron and proton flow from photosynthesis (PSII or PSI) to hydrogenases. Nitrogenases also evolve H₂ and detailed knowledge about this enzyme may also hold important clues for producing H₂ from protons and electrons produced by water splitting.

Timescale

10 years:

- Elucidation of the basic catalytic mechanism of PSII water splitting and hydrogenase function interfaced with research on (i) biomimetic systems and (ii) cellular biological systems.

- Elucidation the role of the protein matrix in directed proton transfer, control of water accessibility and providing stability to the catalytic site.

- Gaining understanding and control of the synthesis/assembly of the active metal site.

Subsequent 10-20 years:

Intensified transfer of the blueprint knowledge to parallel technological initiatives.

2. Self-assembled light-harvesting antennae

Research Direction

Because the intensity of sunlight is dilute, in natural photosynthetic systems ~300 chlorophylls per light-converting unit are needed to have light conversion with an optimal conversion rate. For efficient capture of solar energy in artificial solar devices, the incorporation of a light-harvesting antenna is crucial. Without an antenna, a large surface area should be filled with light-converting units (coupled to catalytic units and further components) that, firstly, do not operate to maximal efficiency and secondly, of which the majority is in an inactive state. Reversely, with incorporation of a light antenna that surrounds the light-conversion units, all light-converting units will be used to a maximal turn-over rate and only the antenna components have to fill a large surface area. The antenna should possess the following properties:

- cover a large spectral range (*i.e.* contain various chromophores)
- possess a high absorption cross section (*i.e.* large number of pigments per light-converting unit and a high extinction coefficient)
- be able to transfer excitation energy sufficiently fast to a light-conversion unit in order to avoid unwanted loss and photodamage processes (*i.e.* short distances between the antenna pigments and directionality of transfer to the light-conversion units)
- have photoprotection (carotenoids), photostability (*i.e.* synthetic photostable chromophores) or a self-repair mechanism (for example, automatic replacement of damaged chromophores)
- have protection against oxidation by the light-converting unit (*i.e.* sufficiently large distance between the antenna and light-conversion unit)
- cover a large surface area

Using Nature's concepts or Nature's units, three routes can be distinguished to create antenna assemblies that can be incorporated into the total light-converting apparatus:

1) *Natural antenna systems.* Promising candidates are purple bacterial antenna proteins. They can be isolated from purple bacteria through standard methods, but also reconstituted in vitro from polypeptides and cofactors. The protein matrix ensures proper positioning of the cofactors and facilitates functional co-assembly with a reaction centre unit. Inherent photoprotection is provided by carotenoids. Methods need to be developed to rebuild these proteins from natural or artificial components produced by inexpensive routes and to incorporate various chromophores for broader spectral absorption. A further challenge is how to functionalize proteins on inorganic substrates for integration in an artificial device.

2) *Self-assembled chromophore nanostructures.* The nanostructures will be based on chlorosomes, antenna units of green bacteria that contain BChl *c* assemblies without a protein matrix. The self-assembly mechanisms of these natural systems are now being elucidated and open the way for design of novel, photostable, artificial chromophores with related self-organization properties. Nanoporous materials or ceramic membranes may be used as templates to control the self-organization process.

3) *Covalent multichromophoric systems.* Alternatively, an artificial antenna could be designed from covalently-linked chromophores. Hereto synthetic chemistry routes need to be optimized for the controlled synthesis of *e.g.* large dendrimer molecules with well-defined structures.

Potential Impact

The incorporation of a stable light antenna will substantially increase the efficiency of fuel-producing solar cells.

Scientific Challenges

The proof of principle of constructing artificial antennae has amply been given. The challenges are to make cost-effective antennae with high absorption cross-section in a broad wavelength region that are easily assembled into the proper size, can be correctly positioned with respect to the other subunits of the solar device, are sufficiently photostable in the presence of oxygen and charge separators and can be (self)repaired or replaced. Furthermore, methods need to be developed to characterize and optimize functioning and organization of a supramolecular antenna on a nanoscale (see PRD 12 and 14).

Timescale

The construction of antennae with a broad absorption cross-section and broad wavelength coverage can be established within 5 years. Being able to repair photodamaged antennae, to assemble these at the proper sizes and co-assemble them with charge-separation units (see PRD 12) should be feasible within 10 years.

3. Charge transfer units with long-lived charge separated states allowing for efficient coupling to catalytic sites

Research direction

The efficient storage of solar energy requires that electronic excitation energy must be efficiently converted into chemical energy by means of a fast electron transfer event leading to a long-lived charge separation. Important issues concern the nature of the donor/acceptor couple (*i.e.* chemical nature of the building blocks, distance, orientation, environment, etc.) and their charge transfer properties. Electronic couplings and reorganization energies must be carefully balanced to optimize fast charge transfer, slow back reaction and minimal energy losses. How rigidity, geometry, electronic structure, strength and type of supramolecular interactions might influence charge transfer and charge transfer dynamics need to be studied in depth.

Two feasible strategies are considerable that should be explored in parallel and complemented whenever profitable at different levels of complexity. The first strategy aims at using nature's conception to achieve long-lived charge separation. The second strategy, on the other hand, implies taking advantage of nature's components, ranging from pigment protein complexes to entire photosystems.

Sequential multi-step relay of charges emerges as an important tool to achieve radical ions pairs that are physically separated by distances greater than 2 nm. Considering an electron tunneling scenario as an operative modus of charge recombination, this ensures retarding this energy wasting step. Implicit is here the design of redox gradients (*i.e.*, avoiding redox traps along the redox chain) to control the unidirectional flow of charges (*i.e.*, both electrons and holes) with high efficiencies and minimal losses of energy. Important is also to avoid charge transfer with the antenna complexes by physically separating the antenna pigments from the cofactors involved in charge separation.

Charge injection into the catalyst should be sufficiently fast, augmented by optimized chemical and electronic couplings. Imperative is in this context the energy matching of the radical ion pair state energetics and the redox energy levels of the catalyst. The redox energy levels of the catalyst should not change upon accepting/donating one or more charges. Each light-induced charge separation reaction is on the single electron level, while catalysis requires two or more electrons/holes. This requires repeated excitation events coupled to the accumulation of several redox equivalents on the catalytic units. This imposes challenges that do not arise on the single electron level, and requires new principles for energetic and kinetic control. The direction of charge transfer must be controlled so that reverse reactions depleting the accumulated redox equivalents are avoided. Accumulation of electrons/holes needs a charge-compensating mechanism to avoid the build-up of charge that would otherwise hinder further accumulation, for instance by coupling proton transfer to electron transfer.

Proteins form the unique electrostatic environment around chromophoric molecules to promote pigment-protein functionalities. It acts like a smart matrix, which dynamically regulates the functions of the cofactors, like color, redox potential, reorganization energy and electronic couplings. These properties must be further addressed in order to search for possibilities to design electrostatic fields around functional pigments and to control their functions and stability.

Potential Impact

Achieving efficient primary conversion of solar energy by fast long-lived charge separation will have a significant impact on the efficiency of energy conversion and storage in solar-to-fuel converting devices.

Scientific Challenges

Fast and long-lived charge separation need to be established in a bio-inspired structure, coupling the charge separating device to an antenna and coupling proton to electron transfer. Furthermore, the role of the protein environment in charge separation processes needs to be elucidated to utilize electrostatic fields for functioning and stability of the artificial charge-separating constructs. Progress will critically depend on novel analysis and theory methods (PRD 14 and 15).

Timescale

5 years: Reaction centres suitable for operation in bio-inspired solar-to-fuel cells.

10 years: Coupling of reaction centres to an antenna (see also PRD 1) and further optimization.

15-20 years: Coupling to catalytic units, and integration in a solar-to-fuel device (see PRD 12).

4. Catalytic reactions involving multi-electron catalysts for clean solar fuel production

The design and synthesis of multielectron catalysts for fuel production from abundant substrates (water, CO₂) involves the discovery of new catalysts for water-splitting, hydrogen production and for CO₂ reduction.

Research Direction

Design principles for the catalysts that are needed are currently lacking, and implementing additional requirements of cost and availability will require radically new concepts. Inspiration from natural systems provides the sole starting point, but it is not necessarily representative of the ideal system from an operational perspective.

The chemical nature of the catalyst should allow a high conversion rate, high turn-over number, and be composed of cheap and environmental friendly materials. Amongst promising candidates are complexes based on first row transition metals and nanoparticles.

Generation of hydrogen-rich fuels based on carbonaceous (CO₂) or nitrous (N₂) feedstock will require the development of alternate catalytic systems. While platinum is an excellent catalyst material for H₂ production, its availability and cost prevent its use on large scale and long term and its usefulness for other systems has not been demonstrated. Alternative molecular catalysts can already be achieved with different systems but the efficiency and durability are low. Theoretical methods allowing novel evolutionary *in silico* design approaches will help to optimize the design prior to experimental implementation.

Potential Impact

A catalytic centre that will exploit the accumulated solar energy to drive a multi-electron reaction is a prerequisite to achieve catalytic fuel production driven by solar energy.

Scientific Challenges

1) Identification, design and preparation of multi-electron catalysts

An important challenge will be the design of biomimetic catalysts inspired by the active sites of natural enzymes. The current strong development of understanding of the water splitting complex in Photosystem II and the hydrogen producing hydrogenases (developed in conjunction with modified biological systems) provides a knowledge platform for the design of the ideal artificial catalyst. The only current molecular systems able to split water with appreciable efficiency and rate is the manganese complex in Photosystem II, and a necessary breakthrough is the realization of water splitting reactions employing artificial systems allowing the production of fuel. A yet to be explored alternative is the use of non-metallic reaction centres, possibly inspired from biological examples of metal-free redox-active enzymes.

2) Catalytic systems for alternative hydrogen carriers

We need to design and realize new materials which can generate the desired intermediates (metal hydrides) at low overpotential, which translates into small energy losses.

Throughout the design process, due consideration to its future integration into a fully operative solar energy conversion device must be given. The electrons or holes (one charge

per photon) needed for the catalytic reaction must be accumulated and stored long enough to allow the completion of the catalytic cycle.

Timescale

H₂ catalysts already exist and will continue to be improved. New catalysts, including metal-free catalysts should become available over the next 10 years. Water-splitting with molecular catalysts requires a breakthrough, which must also occur within the next 5-15 years.

5. Materials for high-efficiency low-cost PV

Today's main way to produce chemical fuels by use of solar energy uses photovoltaic solar cells in combination with electrolyzers. Considerable effort is devoted in classical photovoltaics to develop so-called 3rd generation solar cells achieving either solar efficiencies above 30 % or costs far below those of today. Here principles taken from Nature can lead to new solutions finally even allowing for a combination of the two goals.

Research Direction

Fundamental research in photovoltaics of today follows two directions:

- “Classical” solar cells based on single crystals are achieving today up to about 24% solar efficiency in the lab and about 18% in modules at a very high price. Besides working at reducing the production price scientist are here aiming at the use of nanostructures, optical conversion materials etc. in order to overcome the thermodynamic limit of single band gap photovoltaics of about 30%.
- Organic Solar Cells with its four directions
 - 1) Dye-sensitized Solar Cells (DSCs), in which monolayer of dye absorbs light and injects charges into a nanoporous semiconductor film and gets re-reduced by a redox couple in an electrolyte transporting electrons from a metal-catalyzed counter electrode,
 - 2) Molecular Organic Solar Cells (MOSCs) made from relatively small molecules mostly be evaporation either in the form of classical p/n-type of solar cells of bulk-heterojunctions,
 - 3) Polymer-based Organic Solar Cells (POSCs) produced mostly by printing techniques from mixtures of polymers and mainly C60-Derivatives in the form of bulk-heterojunctions, and
 - 4) Composite Organic Solar Cells (COSCs) produced from mixtures of organic and inorganic materials

are achieving today at most 5-7% module efficiency while being produced by techniques allowing for very low cost ($\ll 0.5 \text{ € /Wp}$). They need to achieve at least 10% module efficiency within the next 5-10 years and maybe 15% thereafter at a price of below 0.2 €/Wp , Even more urgent is to improve the stability of modules which in the case of DSCs might require the replacement of the ion conducting electrolyte by an electron- (or hole-) conducting solid. Here researchers are currently looking for new materials (chemicals and compositions) and the control of (nano)structures achieving stepwise progress with lots of small “breakthroughs”.

Common goals in research are the development and control of nanostructures, the use of self-organization and the control of materials assembly. Here bio-mimetic or even biological approaches should be tested for creating

- biomimetic, organic or biological solutions for optical up- or down-conversion for 3rd generation cells increasing the efficiency of these processes especially if a directed energy transfer could replace the (360°) emission of today's approaches,
- biomimetic, organic or even biological templates (as used in biology also for structuring inorganic structures such as skeletons, shells etc.) in order to create nanostructured solar cells (for Third-generation approaches as well as for Organic Solar Cells),

- sensitizing entities for DSCs in order to extend the charge creating monolayer and thereby allowing for larger electrode structure and/or thinner porous electrodes so that solid hole-conductors can also give the required efficiencies while allowing for more stable modules, and even
- completely new types of multiple band gap solar cells utilizing directional energy transfer into different parts of accordingly structured PV devices.

Solutions are expected to be developed mainly from research on biological self-organization and on photosynthetic antenna-systems and reaction centres. Further down in time even self-adjustment and self-repair might be used in these devices.

Potential Impact

Raising the efficiency in Third Generation Solar Cells to above 30, in multiple band gap cells even close to 50 % might be possible. In DSCs the described solutions could lead to a major improvement in module stability (to above 10 years) and efficiency (above 10 %).

Scientific Challenges

Artificial structures mimicking biological processes or long time stable biologically produced systems need to be developed and introduced into solar cell production schemes. Antenna systems applicable in DSCs need to be found and tested, the control of nanostructures in biology needs to be understood and translated to materials formation for PV application. Also the understanding of directed energy transfer must be improved and artificial, preferably inorganic structures for use in PV need to be developed.

Timescale

In order to introduce such solutions into the production within the next 10 years allowing for a considerable contribution to solving our energy problem within the next 20 years prototypes based on our current knowledge should be available within the next 5 years. Once new structures are produced in larger scale the introduction of improved versions should be possible faster.

6. Smart materials for solar energy conversion

Novel approaches to system assembly of nanoscale components benefit by learning the self-assembly, self-adjustment and self-repair features of biological systems, including fault tolerance.

Research Direction

Rapid development in nanoscience and the revolution in biomedical research combine to create an unusual opportunity for advances in basic materials research for solar energy. The individual microscopic steps of solar energy utilization each take place on the nanometer scale. As a consequence, developing the ability to pattern and control matter on this length scale generates unusual opportunities to create new materials for solar energy. Smart materials is a new area which already has led to the first engineering applications in the development of high-tech applications airplane and automotive sectors on a micro- to meso-scale, while applications on a nanoscale have not yet been realized.

For the development of PV devices, smart materials could include concepts like self-adjustment to various environmental conditions such as light intensities, temperatures etc. In addition such materials could be defect-tolerant and include self-repair for increasing the life time of energy conversion devices.

Potential Impact

The major hurdle for massive implementation of PV is the high production costs, both for established silicon-based PV and emerging DSC technologies. The best way to overcome this hurdle will be to implement self-assembly, self-repair and defect tolerance principles from nature since these will not only reduce the cost but also have an impact on reliability.

Scientific Challenges

The synthesis of complex molecules, macromolecules, and nanoparticles are underlying tools which continue to develop in important ways. However, the key limiting issue now is the assembly of these component building blocks into functional assemblies and ultimately into complete systems. This requires improved understanding of the organic-inorganic soft interface, as well as the ability to harness multiple weak interactions to create and optimize designed patterns. This is how biological materials organize themselves on length scales larger than those of individual macromolecules, yet to reproduce this remains very challenging for chemists and materials scientists working with artificial components. There are many features of biological system assembly that are important to emulate. Chief among these are the ability to create advanced materials despite the presence of disorder and defects, and to not only assemble components, but also to disassemble and reassemble them. These attributes are essential for creating advanced solar converters such as artificial membranes with template function for self-repair and fault tolerance that combine high performance with low cost and long lifetime. The progress critically depends on the development of novel analysis techniques (PRD 14) and evolutionary computation strategies (PRD 15).

A special challenge will be the exploration of artificial life systems concepts for technical applications in smart matrices that dissipate energy for adaptation of properties when in operation in *e.g.* clean solar to fuel applications (PRD 11).

Timescale

5-10 years: Resolving self-assembly principles.

10-15 years: Proof of principle for self-assembling and self-repairing direct solar-to-fuel concepts.

20 years: Prototyping of novel devices using smart materials.

7. Energy storing PV devices

Fast changes either in energy supply (clouds changing the solar intensity) or demand (especially in small decentralized electricity grids) could be buffered by integrated energy storage in PV systems.

Research Direction

Energy storing photoelectrochemical systems have been developed already in the seventies. Overall solar efficiencies of about 10 % were achieved with low stability. Since then there has been little progress and no further breakthroughs. Thus far PV productivity is well below the threshold of ~ 20% that is generally considered an acceptable practical limit for a fluctuating power source. This will change when PV becomes a major source of energy. New concepts could now be explored inspired by biology, combining electrical charge separation with electrochemical storage processes in a smooth and reversible interconversion where energy is temporarily stored in a membrane ion potential. A disadvantage is a water based system and this requires direction of research into dedicated solid nanostructures with low energy barriers and good stability.

Potential Impact

Energy-storing PV devices will reduce the total area necessary to cover a certain electricity demand (higher overall efficiency). Further, they will lead to scalability of the full system.

Scientific Challenges

Photoelectrochemical systems using new PV materials and highly efficient catalysts need to be further developed. Potential redox-couples need to be explored for temporary storage. Nonlinearities in biological system charge separation processes need to be explored for intermediate storage in ion gradients. Further, the possibility to derive a super capacitor concept from here, need to be investigated, as well as the possibility to charge a redox battery by these processes.

Timescale

Development of an ionic or redox couple buffering system will take 5-10 years and prototyping 10-15 years. Practical implementation will be 20 years onward.

8. Photoelectrochemical fuel production

Direct Solar Water Splitting has already in the seventies been “the stuff, that photochemists dreams are made of” (Lord George Porter, 1975). Considerable progress has been made but today’s systems are by far too expensive. Major scientific improvements are needed in order to apply these techniques in commercial systems.

Research Direction

A key problem in electrolyzers in general, and in an even much more pronounced way in photoelectrochemical systems, is the catalysis needed for water splitting, especially for the oxygen production. The current state of the art uses Pt and Pt/Ru catalysts in quite high concentrations which need to be reduced by about a factor of 10 or preferably replaced by non-noble metals in order to become commercially interesting. This requires well-defined catalysts of controlled structures not yet available. Here a biomimetic catalyst or catalyst formation might bring essential breakthroughs. But also for the materials used as semiconductors significant improvements are needed to replace today’s extremely expensive structures. Also here nanostructured devices are already under investigation.

Potential Impact

Direct solar water splitting can in principle be of considerably higher efficiency than an electrolyzer-coupled photovoltaic system. Besides a solar hydrogen formation here also the reduction of nitrogen (N₂) from air would be of great benefit since the formed ammonia would be a very convenient fuel especially for mobile applications. Since the proof of concept (10% efficient photoelectrochemical system were built in the National Renewable Energy Laboratory) was already done, here new materials, structures and catalysts are necessary mainly to improve the price and the life time.

Scientific Challenges

The main challenge is to achieve photoelectrochemical fuel production with efficiencies >10 % at costs of below 2 €/kg. This requires completely new materials, structures and catalysts. Biomimetic approaches might be of great help.

Timescale

2-3 years: Upscaling of existing solid state/electrolysis systems to technical scale and for the use of less expensive preparation techniques.

5-10 years: Proof of concept of direct photoelectrochemical water splitting and to achieve an efficiency of more than 3%.

10-20 years: Achieve an efficiency > 10%.

9. Solar-powered hydrogen and other CO₂ neutral biofuel production by green algae and cyanobacteria

Microalgae and cyanobacteria are the most promising organisms for conversion of solar energy into CO₂ neutral biofuels such as biodiesel and for direct production of H₂ from water. Strong research emphasis should be put on molecular biology, bioinformatics, systems biology as well as on metabolic and bioreactor engineering to select suitable micro-organisms, to improve their capability of biofuel production from sunlight and to design functional and profitable photobioreactor or pond systems.

Research Direction

The rapid development of clean fuels for the future is a critically important global challenge for three main reasons. First, new fuels are needed to supplement and ultimately replace depleting oil reserves. Second, fuels capable of zero-CO₂ emissions are needed to slow the impact of global warming. Third, sunlight must be the ultimate energy source and water as a source of electrons, since both are available in unlimited amounts.

Emphasis will be put on:

- 1) biological CO₂ mitigation processes driven by sunlight and leading to the production of hydrocarbon biofuels and
- 2) solar powered bio-H₂ production processes based on water-splitting photosynthetic micro organisms, green algae and cyanobacteria.

1) CO₂ to hydrocarbons

Research on water-based photosynthetic micro-organisms (primarily microalgae and cyanobacteria) has the potential to meet all of the above goals: microalgae have shown, in experimental plants, photosynthetic efficiencies of up to 5%, in the absence of any genetic optimization. They can accumulate large quantities of triacylglycerols (the starting point for biodiesel).

Unlike land plants, whose CO₂-fixation capacity gets saturated at low CO₂ concentrations, microalgae and cyanobacteria thrive on concentrated CO₂ sources, such as flue gas from power plants. Many can grow on marine water, a plentiful resource and they are able to utilize N- and P-rich wastewater as a nutrient source.

2) Water to H₂

Hydrogen (H₂) is considered to be one of the most promising clean fuels for the future. Advances in hydrogen fuel cell technology and the fact that the oxidation of H₂ produces only H₂O, increase its attractiveness. Yet, despite the many positive aspects of a future hydrogen economy, its viability is completely dependent upon the development of cost-effective sustainable large-scale H₂ production systems, to replace the processes of steam reformation of natural gas, petroleum refining, and coal gasification. Emphasis is made here on direct (H₂O → H₂) methods of solar powered H₂ production using water-splitting micro organisms (microalgae and cyanobacteria).

Potential Impact

Currently the global energy consumption rate is ~13TW-yr and is predicted to increase to 46TW-yr by 2100, suggesting that easily accessible reserves will be largely depleted by the end of the century. Although the rate of fossil fuel depletion is surprisingly fast, a much more rapid switch to zero-CO₂ emissions fuels appears to be needed, to control the effects of global warming. Anthropogenic emissions of CO₂ (total 7gtc p.a.) are only a fraction of the carbon recycled by terrestrial and marine photosynthesis (210 gtc carbon p.a.). Photosynthesis is the only viable alternative to geological sequestration for depleting CO₂ from the atmosphere. CO₂ neutral conversion of light to biofuels like H₂O to H₂ or CO₂ to hydrocarbons will have important impacts on the successful replacement of fossil fuels. This includes a reduction of atmospheric CO₂, the independence from imported energy sources and the development of huge novel markets. Land-derived biofuels are only partially able to meet this demand. In contrast, photosynthetic water splitting micro organisms ideally combine light collection, concentrated CO₂ fixation and biofuel/bioH₂ production in a single highly efficient cell system. In addition, their ability to grow in aquatic environments including sea eliminates potential competition with food producing agriculture.

Scientific challenges

1) CO₂ to hydrocarbons

- Identification and genetic optimization of micro-organisms capable of sustained photosynthetic efficiencies (light to biomass) above 5% and CO₂ fixation at a cost less than 20€ per ton
- Re-direction of the cells metabolism into useful substitutes for petrochemicals (oils, bioplastics etc.)
- Optimization of the resulting biomass for energy uses
- Use of the entire spectrum of sun light for energy conversion

2) H₂O to H₂

- Survey and identification of water-splitting micro organisms capable of producing high amounts of H₂ from sun light and (salt)water under different environmental conditions
- Systems biology-based analysis on water-splitting micro organisms to identify genes and proteins involved in H₂ production
- Construction of micro-organisms capable of simultaneous oxygen evolution and hydrogen production by engineering oxygen tolerant hydrogenases and/or by using nanotechnology based membranes to expel oxygen
- Optimization of energy fluxes to hydrogen production by molecular engineering of the light harvesting antennas and primary metabolic pathways
- Increasing the H₂ production efficiency of water-splitting micro organisms up to a profitable scale (PCE rates of 10% over the entire solar spectrum). At a purity level suitable for use in fuel cells, between 90% and 100%, with a specific focus on the highest possible purity to get the best efficiency.
- Developing photo-bioreactors for centralised and de-centralised production of H₂
- Use of the entire spectrum of sun light for energy conversion

Timescale

For screening of new organisms, 2-5 years is foreseen. Bioengineering of micro organisms (increasing photon conversion efficiency rates) is expected to take 5-10 years. Development of economically and ecologically sustainable photo bioreactor and algal pond designs will take 10-15 years.

10. Solar-powered H₂ production by anaerobic bacteria

Anaerobic photosynthetic bacteria have the capacity to evolve significant amounts of H₂ powered by sunlight. This H₂ can in principle be produced either by hydrogenases or nitrogenases. The bacteria use reductant derived either from solar powered reactions or the oxidation of organic compounds to drive H₂ production. The concept of this work package is to use sunlight and waste organic materials, for example sewage, agricultural or animal wastes, as electron donors to support the growth of bacteria and their subsequent generation of H₂. The procedures/experiments described in this work package will therefore not only produce solar-powered H₂ but have the added environmental benefit of treating and removing waste products in a carbon neutral process.

Research Direction

This research builds on the following observations:

- 1) purple photosynthetic bacteria, when illuminated under N₂ limiting conditions, evolve copious amounts of H₂ using nitrogenase
- 2) purple photosynthetic bacteria, when illuminated under N₂ replete conditions, evolve copious amounts of H₂ using hydrogenase
- 3) since these bacteria are evolving H₂ in the absence of O₂, there are no significant problems of oxygen-sensitivity of the H₂ evolving machinery

In order to develop this concept, we need to

- 1) survey existing species/strains for H₂ production under different conditions
- 2) develop systems which maximize H₂ production by isolated organisms or consortia
- 3) investigate whether robust cell-free systems can be developed for light driven anaerobic H₂ production
- 4) investigate whether H₂ can be efficiently converted into other fuels/energy sources
- 5) develop the use of different sources of organic material to support light-driven H₂ production
- 6) investigate the basic biochemistry of the H₂ evolution enzymes and use this knowledge to optimize H₂ evolution under different environmental conditions
- 7) understand microbial physiology in order to circumvent rate-limiting steps in solar-powered H₂ production

Potential Impact

Successful completion of this work package will allow development of new technologies for solar-powered H₂ production by anaerobic photosynthetic micro-organisms. This will provide significant amounts of solar-derived H₂ as a carbon-neutral replacement for fossil fuels. Since every household, farm and town in Europe continually produces large amounts of sewage or other waste material there are huge reserves of the required feed stocks to support this solar-powered H₂ production concept.

Scientific Challenges

To achieve the goals outlined above, a significant amount of basic research is needed in the following general areas

- 1) selection of microbes or consortia for optimal solar-powered H₂ production
- 2) strategies to maximize activity of the enzymes that evolve H₂ must be developed

- 3) systems to selectively funnel reduction from the solar energy pathways and the oxidation of organic nutrient to the enzymes that produce H₂
- 4) strategies to either recycle or sequester the carbon locked up in the microbial biomass produced during solar-powered H₂ production
- 5) produce a working lab-based prototype for optimization with different microbes and feedstocks

With this knowledge base, we can then take the following steps

- 1) develop platforms to either trap the H₂ for future use or for direct conversion into other fuels
- 2) collaborate with engineers in order to scale up laboratory-based prototypes to the sizes needed to make this a scalable process of use to a range of users from single family farms to large towns

Development of this concept will need the involvement of microbial ecologists, biochemists, biophysicists, system biologists, computational and structural biologists. Once the basic underpinning research has been established, engineers, materials chemists and other physical scientists will be needed to establish the required new technologies to bring the concept of anaerobic solar-powered H₂ production a reality.

Time scale

The basic research underpinning this concept should be complete in 5-10 years. As this basic research comes to fruition, the development of useable systems for anaerobic, solar-powered H₂ production will begin and continue for the following 10 years. We expect these systems will continually be modified as new information on the biology of the process is obtained and more efficient platforms are developed.

11. De novo design of photosynthetic cell factories

Fundamental research into systems biology will lead to novel routes for solar to fuel conversion and direct application in cell factories based on minimal life systems. Photosynthetic cell factories will use sunlight to directly produce fuels or biomass, or high value compounds starting from polysaccharides.

Research Direction

Current energy harvesting from biomass has a low efficiency due to intrinsic free energy losses at various levels in cellular metabolism. Nevertheless, this process has the attractive feature of automatic self-reproduction, so that for the long term energy budget it is not necessary to invest energy in renewing the photosynthetic apparatus. This is in marked contrast to PV cell production. It is a huge but timely scientific challenge to engineer from scratch a self-reproducing biological solar energy converter with maximized efficiency. A combination of systems-biology- and synthetic-biology approaches will be required for this. This should be a long-term concerted effort in which geneticists, physiologists, molecular biologists, biochemists, physicists, and computational experts should join forces to maximize the translation of atomic-level understanding to high yield solar to fuel conversion and coupling it with downstream production processes.

This approach will require understanding of the living cell as a self-regulating, self-ordering, self-maintaining and adaptive entity and will eventually lead to a merger of life science and materials science. Life is based on interplay between diversification at the bottom, through random mutations, and selection from the top (*i.e.* at the organism level). Currently the basic understanding is still lacking regarding how to implement a smart matrix that provides the appropriate selection criteria for development, (genetic) adaptation and evolution into artificial systems with the desired properties. Bacteria generally live in ecosystems where tasks often are distributed over a multitude of species, and the steady state is maintained on a multi-organism level with high metabolic energy cost, in part because of the fluctuating environmental conditions. Alternatively, bacteria have become organelles like chloroplasts, embedded in a host matrix (eukaryotic plant cell) with lower metabolic costs.

Several cyanobacterial genomes have been sequenced already at an early stage in the genomics revolution, since 1996, and the investigation of their systems biology properties is progressing well. *Chlamydomonas reinhardtii*, a recently sequenced single cell green alga, has been put forward as the “cell factory of the future” and biotechnology has produced variants that accumulate high quantities of polysaccharides. Time has come to design an “artificial organism” at the drawing table, including the minimum of pathways that are required to produce an on-board solar energy to fuel system to drive cell-factories in an efficient way. Probably the most suitable fuel is here polysaccharide that can fuel useful chemical conversion pathways taken from a variety of cell factory systems.

Potential Impact

Cell factories with an on-board light-energy conversion system with optimal efficiency and convenience, can produce a wide variety of chemicals and chemical feedstocks in a sustainable manner. In this way efficiency gain and solar energy utilization go hand in hand. Minimally metabolizing units will provide optimal production of desired target compounds including biomass; this includes systems in which biological waste can be converted to nutritious materials with self-reproducing devices containing only a single photosystem.

Scientific Challenges

A major challenge is to provide comprehensive insight into the systems biology of relevant photosynthetic organisms to provide a sound basis for the de novo design of photosynthetic cell factories.

Major hurdles will be to understand and implement: (i) Minimally metabolizing smart matrices and (ii) Proper (genetic) adaptation modules, for guiding development and evolution towards the desired function.

This requires development of methods for de-novo design of minimal life units, including physiological and genetic adaptation for evolutionary optimization strategies, systems design, specification of biological and biophysical mechanisms leading to the desired properties, and analyses of the control and sensitivity in the designed systems. This should lead to the development of minimal self-reproducing units that can be applied in a variety of production processes, including biomass and bioenergy production.

As an alternative, the design of an artificial chloroplast-type entity (*i.e.* without self-reproduction capability) embedded in a host matrix could be considered. This may further improve the efficiency.

The overall success of this approach will also depend on the inclusion of methods that allow for an efficient harvesting of end products, such as spontaneous aggregation of products, self-sedimentation at the end of the (artificial) life cycle and facile drying of sedimented biomass.

Timescale

5 years: photosynthetic cell factory producing polysaccharide reserves;

7 years: proof of principle for optimized minimal organism for biomass and/or fuel production;

10 years: artificial fuel producing organelle in a host matrix and 5 cell factory prototypes;

14 years: prototype minimal organisms;

15 years: implementation of cell factory production schemes and production with minimal organisms;

18 years: prototype artificial organelle in host;

30 years: production with artificial organelles in hosts.

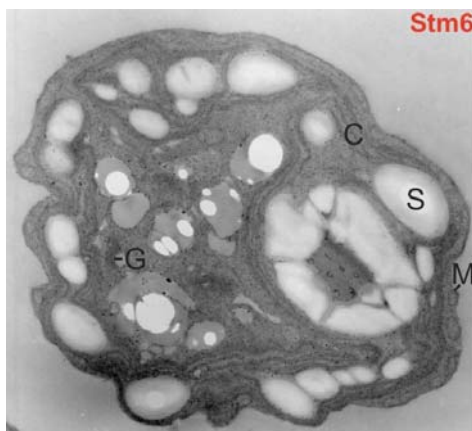


Figure 4. Starch storage.

12. Integration of functional components: Smart matrices for organization and protection of the catalytic devices

Paradigms addressing the integration of functionality at the molecular level are needed to combine independently-developed functional components into operational devices.

Research Direction

1) Organized functional architectures: from nanometers to centimeters

The hierarchical organization of functional components over lengths ranging from the molecular scale to the macroscopic world must be precisely controlled to permit the successful scalability of devices to cover large surface areas without loss of efficiency. At the nanometer level, precise orientation of functional units involved in light-harvesting, directional energy transfer and subsequent charge collection and utilization will be required. Nanoporous materials allow structural organization and confinement on the molecular level. However, much greater control over the final architectures must be obtained if their specific functionalization will enable them to be compatible with multiple compound input-output flow-through.

2) Artificial versus stabilized natural protein or membrane matrices

Compartmentalization of the redox processes in photochemical cells requires spatial distribution of the reactive sites while maintaining adequate chemical transport throughout the system. For this, selective membranes will be required. These “smart” membranes will be sturdy and be based on inorganic, organic, or hybrid systems. Alternatively, bio-inspired systems using modified or natural protein systems can be envisaged. In the latter case, these should be readily available and sufficient stability must be instilled prior to incorporation to achieve good performance over the entire life-cycle of the device.

3) Self-assembly and self-repair

Cross-cutting implementation of directed self-assembly will lead to the spontaneous auto-organization of functional devices from smaller sub-units, each devoted to a specific task. This approach allows the modular assembly of sub-units that are prepared and purified in separate steps, thereby reducing costs and simplifying design. In turn, the molecular disassembly of the spent devices at the end of the life-cycle will allow recovery of the remaining working subunits. Such a recycling scheme greatly widens the opportunity for the use of complex, yet stable, catalytic reaction centres. The implementation of simple, on-site repair or replacement mechanisms within the device can currently be envisaged via targeted molecular or supramolecular repair mechanisms based on known deactivation pathways. Eventually, biologically inspired complex repair mechanisms could be envisaged.

4) Connecting the device to the outside world

Device interfacing is greatly dependent on the device operation: (a) Those devices supplying electrical current, or (b) requiring electrical connection of two or more spatially separated redox processes will require implementation of low-cost large-surface electrodes due to the necessity of collecting diffuse solar radiation. (c) Fuel-producing devices based on nanoscale separation of the redox processes (*e.g.* in ordered nano-architectures) do not require electrodes, but will necessitate separation of the fuel mixture that is produced. The integration of bio-derived functional sub-units within hybrid devices will require the efficient connection of biological material (catalytic centres, proteins, or membranes) to metal electrodes. In the future, nano-structured electrodes will provide a means of achieving large surface area per

unit size, potentially relaxing bottlenecks associated to reduced charge carrier mobility and low absorption cross-section.

Potential Impact

The attainment of the research goals set forth within will enable the construction of next-generation fuel and/or energy producing eco-devices that can be easily prepared and inexpensively assembled. Individual sub-units of end-of-life cycle devices can be recovered and recycled by molecular disassembly. The integration of biological components in hybrid synthetic devices will be possible using tailored nanostructured electrodes or individual molecular connectors.

Scientific Challenges

Wide-based knowledge on the large-scale assembly of molecular units into functional devices is lacking and inspiration from natural systems should be sought. In parallel synthetic methodologies adapted for the preparation of hybrid inorganic-organic and bio-synthetic systems are needed to tackle large, complex architectures. New approaches to nano-structured materials (electrodes and membranes) must be developed for large-scale applications. Theory and modelling is essential to make rapid progress.

Timescale

Suitable nano-structured materials are under development and should be available within a relatively short timeframe (2-5 years). Coupling of antenna systems with functional reaction centres would need to be developed within 8-10 years. This would be necessary to envisage the large-scale integration of operational catalytic assemblies into self-organized nanoscale devices to be completed within 20 years.

13. Solar hydrogen tower

The objective here is to lead the renewable energy market with an innovative technology that does not consume fuel resources or produce greenhouse gas emissions. Glass heliostat antennas will concentrate the light in a macroscopic analogue of the PSI/PSII water splitting enzyme installed in a solar tower and operating at high temperature.

Research Direction

In PV there is a drive towards the 3rd generation to overcome thermalization losses. PV produces electrons in a conductor, and it will be difficult there to thermalize electrons and regain the energy. Therefore PV researchers look for methods to overcome the thermalization losses at the absorber stage. With fuel an opportunity opens up since it is possible to perform the fuel conversion at high temperature with a concentrator and do the thermalization afterwards using the gas that comes out and extract the energy by conventional means. The efficiency of photovoltaics in general decreases with temperature while it increases with concentrating the light intensity. The efficiency of utilizing heat produced by inevitable losses strongly increases with temperature. There exists an interesting temperature range between about 600 and 800 °C which is limited on the lower side by the availability of stable (ceramic) conductors and on the high side by the availability of stable steel parts. In addition there is already a lot of scientific activity exploring the possibility of energy conversion in high temperature fuel cells, while high temperature solar energy conversion in concentrating power stations (solar tower or solar dish systems) also exists. Finally there is already research to produce dye sensitized inorganic mimics of biological water splitting centres at a nanoscale. Very large scale PV solar tower systems have been installed in France and Spain in Europe as well as in Israel, the US and Russia. The price of electricity produced in such plants is currently about tenfold lower than by photovoltaics. Crossing the border between these two research communities will lead to novel concepts for producing both electricity and fuel in a large scale hybrid energy conversion concept by analogy with the organizational principles in photosynthesis.

Potential Impact

Considerable efficiency gain towards 70-80% overall efficiency of one of the cheapest technologies for solar electricity generation already being fully competitive with today's electricity market price. The Solar Hydrogen Tower project can potentially change the world's energy markets forever, and possibly, reduce the effects of global warming. The high efficiency will minimize the land area that will be necessary for solar energy assimilation.

Scientific Challenges

Implementation of a ceramic mimic of PSII/PSI to produce fuel in addition to operating thermal power plants to produce electricity. Since still all waste heat would be available for electricity generation as in a conventional solar thermal plant, the addition of such a system might even double the efficiency of the system directly leading to much lower electricity production costs. To achieve such an improvement is another main challenge.

Timescale

Proof of principle of a macroscopic high temperature solar driven water splitting device can be achieved in 5 years. Implementation and demonstration of an operating prototype in the kW range) will take about 10 years. The first large scale demonstration system (100 MW

range) may take place in 20 years, projecting 30 years for the first commercial system (0.5-2 GW).



Figure 5. Solar Tower plant in Almeria, Spain.

14. Characterization of integrated functional architectures of catalytic devices using novel techniques

To obtain information about geometrical and functional structure of nanoscale solar energy converting devices and related catalysts on various lengths (nm-cm) and time scales (fs-s).

Research Direction

The integration process of the functional components will result in a multitude of nanoscale devices of great variety and displaying a plethora of very different properties. Hence, a detailed characterization of the features of the integrated systems at the fundamental physical level is crucial. We must understand the sequence of molecular events leading from the photon to the fuel, why certain events proceed with a relatively low efficiency, where the losses in the system occur etc. To study such highly complex and dynamic nanoscale structures at the molecular level demands the development of novel and adaptation of existing techniques to reveal information about their functional architecture. This approach includes also new methodologies for modeling, simulation, and quantum chemical calculations.

Next to conventional high-resolution microscopies such as AFM and electron microscopy the development of high-resolution (spatial, temporal) spectroscopies is essential. For example: AFM affinity microscopy, Magnetic Resonance Force Microscopy (MRFM), multi-pulse, multi-resonance NMR and EPR, multi-pulse ultra-fast optical spectroscopy, high-resolution fluorescence microscopy, and surface spectroscopies (SERS, Plasmons, XAS etc.).

Methods have to be developed to manipulate and control the structures by applying chemical and physical techniques to optimise function. Good examples are optical tweezers to manipulate the supramolecular organisation, the exchange of cofactors to tailor specific functions.

Since development of a nanoscale solar energy converting device will require the characterization of many alternatives it is essential to elucidate a small number of principal functional parameters to be used for screening and combinatorial approaches.

Potential Impact

New technologies for characterization of functional architectures and operation of nanoscale solar energy converting devices at the molecular level will enable and facilitate construction, characterisation and manipulation of robust solar energy converting devices.

Scientific Challenges

Understanding the functional architecture and operation of a nanoscale solar energy converting device at the molecular level. Since initially the highly complex materials will be available in small amounts, highly sensitive detection schemes need to be applied that either do not exist or must be adapted from existing technology.

These analytical techniques must be complemented by the further development and innovation of theoretical models, including simulations covering many time- and length scales. In the functional structures the optimization of the microscopic parameters of the active components must be calculated using state-of-the-art quantum chemical methodology (PRD 15).

Timescale

Development and adaptation of new techniques is expected to take 5-10 years and characterization of novel nanoscale solar energy converting devices will take 5-20 years.

15. Evolutionary modeling of bio-inspired nanodevices for artificial photosynthesis

In biology, evolutionary design proceeds in an interplay between diversification at the bottom and selection from the top. The objective is to develop new computational tools able to mimic this process and predict *in silico* the properties and function of nanoscale structures to assist and drive the design of nanodevices for solar energy conversion.

Research Direction

A promising strategy for future breakthroughs in solar energy conversion is the design of highly efficient, artificial, molecular-level energy conversion machines exploiting the principles of natural photosynthesis. Progress in the design and synthesis of nanodevices for artificial photosynthesis needs the concomitant development of computational modeling methods that are able to predict new nanosized materials with specific target properties, with a particular emphasis on nanostructures with desired energy conversion and catalytic properties.

Photosystems I and II, as well as other enzymes can provide inspiration for the development of artificial nanodevices. For instance, the primary photochemistry of photosynthesis, where the chlorophyll molecule is excited by sunlight and the energy produced helps to break down a water molecule resulting in O₂ evolution and release of protons, can be translated into artificial devices of various kinds.

These two examples (as well as most of the organic systems) belong to the “Soft Condensed Matter” category. In other words, their non-bonded energy is comparable to their entropy and thermal fluctuations play an important role in their (inherently) statistical description. The processes that are relevant to solar energy conversion may involve systems with thousands of atoms and different time scales ranging from ps to ms. Hence, even the simplest models must incorporate closely coupled quantum and atomistic/mesosopic/macrosopic levels. It is therefore crucial to extend the size range and time scale of existing methods to deal with these multi-scale processes.

The long-term goal here is to use such hybrid quantum-classical methods (such as Density Functional (DFT) based or QM-MM simulations), as predictive tools, which starting from a wide range of simultaneous desired properties as inputs can yield materials arrangements as outputs. To achieve this goal we need to develop an appropriate interface between these methods and evolutionary algorithms currently used in computer science to find solution to optimization and search problems.

Potential Impact

New computational tools able to predict nanostructures with desired target functions and properties will enable us to enormously focus the search for bio-inspired structures to only those that are potentially active and promising for their high efficiency.

Scientific Challenges

This is a challenging program and requires large-scale computations, as well as theoretical tools that include the quantum-mechanical ingredients needed to properly describe the chemical reactions involved in photosynthesis and multi-scale modeling covering many time- and length scales. This implies:

- 1) Finding the appropriate compromise between the complexity of the biological system and a simplified model structure taking into account the crucial elements of the active site.
- 2) To sample parameter space in an economical way to find the most rapid convergence to desired systems and to overcome the time scale limitations in the simulations.
- 3) Improve the accuracy and efficiency in computing excited-state potential energy surfaces.
- 4) Develop new computational strategies, specifically, grid-based computing methods for they provide seamless and scalable access to wide-area distributed resources and they are particularly suitable in the implementation of evolutionary algorithms.
- 5) Develop a rational compound design technique which would allow to avoid screening of the high-dimensional chemical space spanned by all the possible combinations and configurations of electrons and nuclei and to perform a gradual optimization of the chemical structure of a compound using grand-canonical density functional methods.
- 6) Develop an adaptive technique which would let us study large systems: a part of the system (e.g. next to the electrodes) can be treated quantum mechanically, the nearest layer atomistically, and the bulk of the system has a coarse-grained description.

Timescale

Development of novel computational tools with predictive power in combination with evolutionary modeling is expected to take 5-10 years. In 10-20 years we expect to be able to perform evolutionary modeling of a 10-nm sized macromolecular structure.

Glossary

Aerobic/Anaerobic	Occurring or living only in the presence of oxygen/ occurring or living when oxygen is absent.
Bacteriochlorophyll (BChl)	Photosynthetic pigments that occur in various bacteria.
Biomimetic	Imitating, copying, or learning from biological systems.
Biosphere	Part of a planet's outer shell — including air, land, surface rocks and water — within which life occurs, and which biotic processes alter or transform. From the broadest geophysiological point of view, the biosphere is the global ecological system integrating all living beings and their relationships, including their interaction with the elements of the lithosphere (rocks), hydrosphere (water), and atmosphere (air).
Carbohydrates	Literally “hydrates of carbon,” chemical compounds which act as the primary biological means of storing or consuming energy; other forms being via fat and protein. Relatively complex carbohydrates are known as <i>polysaccharides</i> .
Catalyst	Substance (Greek: καταλύτης, catalytēs) that accelerates the rate or ease of a chemical reaction (called catalysis) without itself being changed at the end of the chemical reaction. Catalysts participate in reactions but are neither reactants nor products of the reaction they catalyse, except for autocatalysis where the reaction product is itself the catalyst for that reaction.
Chlorophyll (Chl)	Green photosynthetic pigment found in plants, algae, and cyanobacteria.
Chloroplast	Organelles found in plant cells and eukaryotic algae that conduct photosynthesis. Chloroplasts capture light energy from the sun to produce the free energy stored in ATP and NADPH.
Desalination	Processes that remove the excess salt and other minerals from water in order to obtain fresh water suitable for consumption or irrigation.
Ecological Footprint	Measure of the 'load' imposed by a given population on nature. It represents the land area necessary to sustain current levels of resource consumption and waste discharge by that population.
Ecological Overshoot	Consumption of resources that goes beyond the surplus resources that can be consumed by humans without damaging the ecosystems.
Electrolyzer	Device in which an electric current splits water into hydrogen and oxygen.

Eubacteria	In modern biological classification, all those bacteria considered to be the true bacteria (Greek: eu = true), characterized by their rigid cell walls. Eubacteria account for most bacteria; they occur in many shapes and sizes and have distinct biochemical and genetic characteristics.
Exciton (photosynthetic)	Electronically excited state of a pigment molecule in a photosynthetic system. Dependent on various parameters, the degree of exciton delocalization can vary from one pigment to many pigment molecules.
Extinction Coefficient	Indicator of how much light it absorbs at a particular wavelength. The <i>molar</i> extinction coefficient is a measure of the amount of light absorbed by a 1 Mole solution in a pathlength of 1 cm at a given wavelength.
GDP	Gross Domestic Product. The GDP of a country is defined as the market value of all final goods and services produced within a country in a given period of time. The most common approach to measuring and understanding GDP is the expenditure method: $GDP = \text{consumption} + \text{investment} + \text{government spending} + (\text{exports} - \text{imports})$.
Gigaton	Metric Unit of mass, equal to 10^9 Metric tons or 10^{12} (1 trillion) kilograms.
Hydrogenase	Enzyme that catalyses the reversible oxidation of molecular hydrogen. Hydrogenases play a vital role in anaerobic metabolism.
<i>In Silico</i>	Literally "within silicon"; refers to modelling research conducted with computers only.
Leapfrogging	A theory of development in which developing countries skip inferior, less efficient, more expensive or more polluting technologies and industries and move directly to more advanced ones.
Light Antenna	Protein or collection of pigments that absorb (sun) light and transfer its energy to a charge-separating unit, where light-to-electrical energy conversion takes place. A supramolecular antenna surrounding a charge-separating unit acts as a sunlight concentrator, because (dilute) sun light striking a large surface area is directionally transferred to the charge-separating unit spot.
Mesoscale	Of the order of 10^{-6} meters (micrometers) to 10^{-3} meters (millimeters) in size.
Mole (M)	SI base unit (symbol: mol) that measures the amount of substance of a system. A Mole is defined as the amount of substance that contains as many elementary entities as there are atoms in exactly 0.012 kilogram of carbon. This quantity

is known as Avogadro's number and is approximately 6.0221415×10^{23} .

Nanoscale	Of the order of 10^{-9} meters (nanometers) in size.
Organelle	Discrete structure of a cell having specialized functions. An organelle is to the cell what an organ is to the body (hence the name organelle, the suffix -elle being a diminutive).
PCE	Photon Conversion Efficiency. Efficiency of converting sunlight into stored energy.
Photovoltaics (PV)	Technology that produces electric power directly from the sunlight. A photovoltaic cell (PV cell) is a specialized semiconductor diode that converts visible light into direct current.
Photosynthesis	Biochemical process in which plants, algae, and bacteria convert the energy of sunlight to chemical energy. The chemical energy is used to drive synthetic reactions such as the formation of sugars or the fixation of nitrogen into amino acids, the building blocks for protein synthesis.
Photosystem I/II (PSI/II)	Interacting photosynthetic units of plants, containing a reaction centre protein surrounded by antenna proteins. Photosystem II is responsible for the conversion of light energy into a redox couple capable of water splitting. When photosystem II absorbs light, electrons in the reaction-centre pigment are excited to a higher energy level and are trapped by the primary electron acceptors. To replenish the deficit of electrons, electrons are extracted from water and supplied to the pigment. Photoexcited electrons travel to photosystem I through an electron transport chain. Photosystem I functions to produce NADPH that is used to reduce carbon dioxide.
Porphyrin	Pigment consisting of a heterocyclic macrocycle made from 4 pyrrole subunits. If one of the three pyrrole subunits is reduced to pyrroline, a chlorin is produced, the ring structure found in <i>chlorophyll</i> .
Reaction Centre (RC)	Photosynthetic charge-separating unit consisting of a light-absorbing protein that uses light energy to reduce an electron acceptor, creating a charge separated state.
Redox Reaction	Complementary chemical reactions characterized by the loss or gain, respectively, of one or more electrons by an atom or molecule. Originally the term <i>oxidation</i> was used to refer to a reaction in which oxygen combined with an element or compound. Similarly, <i>reduction</i> referred to a decrease in the amount of oxygen in a substance or its complete removal.
Renewables	Resources used to generate electricity that are capable of being replaced naturally. Includes technologies such as solar

photovoltaic energy, solar thermal energy, wind power, low-head hydro power, geothermal energy, landfill and mine-based methane gas, energy from waste and sustainable biomass energy.

Self-Assembly

The process where components spontaneously organize or assemble into more complex objects without a central control mechanism or external assistance. The process takes place through random movements of the molecules and formation of weak chemical bonds between surfaces with complementary shapes.

Supramolecular

Any chemical system that exists at a higher level of complexity than individual molecules (for example, multi-enzyme complexes, organelles and membranes).

Tera Watt (TW)

10^{12} Watt.

URL Links

International Energy Agency (IEA)

World Energy Outlook 2005

<http://www.iea.org/Textbase/npsum/WEO2005SUM.pdf>

World Energy Outlook 2004

<http://www.iea.org/Textbase/npsum/WEO2004SUM.pdf>

Oil Crises & Climate Challenges- 30 Years of Energy Use in IEA Countries

<http://www.iea.org/Textbase/npsum/30YearsSUM.pdf>

Intergovernmental Panel on Climate Change (IPCC)

Climate change 2001 – Synthesis report

<http://www.ipcc.ch/pub/un/syrenng/spm.pdf>

http://www.grida.no/climate/ipcc_tar/wg1/index.htm

The Ecological Footprint Network

The Ecological Footprint Europe 2005 (WWF Report)

<http://assets.panda.org/downloads/europe2005ecologicalfootprint.pdf>

The Ecological Footprint Asia-Pacific 2005 (WWF Report)

<http://assets.panda.org/downloads/asialpr2005.pdf>

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Appendix: scientific background

Natural photosynthesis

Photosynthetic organisms are ubiquitous on the surface of the Earth and, in fact, responsible for the development and sustenance of all life on the planet. Among these many different classes of photosynthetic organisms many varied types of light-harvesting and electron transport systems are used. However, they all use the same basic pattern whereby the light energy is initially absorbed (and concentrated) by an antenna system and this energy is then transferred to a specialized reaction centre, where that captured energy is transduced into useful chemical energy. This allows photosynthesis to operate efficiently over a wide dynamic range of light intensities.

Photosynthesis can be divided into oxygenic (O_2 producing) photosynthesis carried out by cyanobacteria and plants, and non-oxygenic photosynthesis (e.g. purple bacteria, green-sulphur bacteria). Oxygenic organisms harness solar energy to extract the H^+ and e^- from H_2O , required for CO_2 fixation. Non-oxygenic organisms cannot generate the necessary oxidizing potential, to oxidize H_2O and therefore extract H^+ and e^- from alternative substrates (e.g. H_2S). Under normal conditions both processes use the derived H^+ and e^- for synthesis of ATP, NAD(P)H and ultimately CO_2 fixation, to produce carbohydrates such as starch and glycogen which can be considered to be H^+ and e^- 'stores' that can be used for the CO_2 neutral production of fuels.

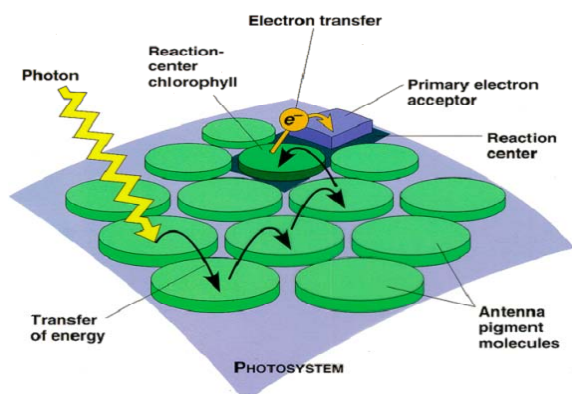


Figure 1. Compartmentalization of light harvesting and charge separation (schematic).

Purple non-sulphur bacteria contain the most studied photosynthetic apparatus. It consists of two light-harvesting pigment-protein complexes (LH1 and LH2) and a single type of reaction centre (RC). Both of these pigment-protein complexes are membrane bound and utilize bacteriochlorins and carotenoids.^{4,5} Green sulphur bacteria use large aggregates (up to 10,000) of Chl *c* molecules that are contained in specialized vesicles called chlorosomes. The energy harvested by these chlorosomes is transferred via the FMO complex to the membrane bound reaction center.⁶ Cyanobacteria use large peripheral phycobilisomes as their major light-harvesting system. The phycobilisomes funnel absorbed energy down into the membrane and supply excitation energy to both photosystem I (PSI) or the photosystem II (PSII).⁷ Photosystem I (PSI) contains ~100 chlorophyll *a* and 12-16 β -carotene molecules. PSI couples electron transport to an electrochemical membrane potential and produces NADPH for carbon fixation.⁸ In contrast, PSII contains 36 Chl *a*, two pheophytin *a* and about seven β -carotene molecules. Uniquely, the PSII reaction centre can split water to produce oxygen. The next section will focus on the structure and dynamics of light harvesting and photoconversion within the purple bacterial photosynthetic apparatus and within PSI and PSII of plants and cyanobacteria where we have detailed X-ray crystal structures.

Light Harvesting

Natural light-harvesting antennae permit an organism to increase greatly the absorption cross section for light without having to build an entire reaction centre (RC) and associated electron transfer system for each pigment, which would be very costly in terms of biosynthesis and cellular resources. In addition, the antenna proteins increase the absorption cross-section by containing densely-packed dye molecules, as they are assemblies of transmembrane polypeptides with many pigment binding sites. The antenna system is organized to collect and deliver excited-state energy to the RC complexes where charge separation takes place. The intensity of sunlight is dilute so that any given pigment molecule absorbs at most a few photons per second. By incorporating many pigments into a single antenna unit and creating supramolecular assemblies of antenna units, large photosynthetic membrane surfaces are covered, ensuring that photons striking any spot on the surface will be absorbed. The antenna units are inter-connected to carry light energy through exciton migration over long distances to the RC's. They surround the RC's, optimizing the energy transfer efficiency by multiple antenna-RC connections.

The excitation energy is transferred primarily via Coulomb dipole-dipole Coulomb interactions in a Förster mechanism according to

$$k_{EET} = k_f \left(\frac{r_0}{r} \right)^6 \quad (1)$$

with k_f the radiative constant and r_0 the half-radius of the Förster process. Since the length scale of exciton migration in the antenna is large, the exciton lifetimes should be long enough to allow for photons striking any part of the antenna to reach the RC.

Once excitons are trapped in the RC, the process of charge separation should take place faster than back-transfer to the antenna units. This is achieved by a relatively large antenna-RC distance versus a short distance for the redox pigments in the RC. Furthermore, surrounding of the RC's by assemblies of antenna pigments gives a spatial arrangement in which energy transfer is optimized by multiple entries to the RC. The combination of constraints (spatial distance antenna-RC and multiple entries) is achieved by circular-like arrangements of antenna pigments around the RC's.

Electron Transfer

In the RC electron transport via multiple steps is necessary because transfer across the membrane in a single step would be too slow to compete with decay of P* to the ground state and dissipation of the energy into useless heat, according to the principles outlined in the preceding section. If the electron and hole can be further separated before charge recombination occurs, the electronic coupling and therefore the rate constant for recombination is drastically reduced. The use of multiple cofactors separated by an edge-to-edge distance less than 0.6 nm ensures a rapid tunneling time of ~10 ps or less for every step. The dependence of the rates of electron transfer reactions within covalently-linked donor-acceptor molecules on the free energy of reaction and the electronic interaction between the donor and the acceptor are described well by theory.⁹⁻¹³ Equation 2 shows how the rate depends on these quantities:

$$k_{ET} = \frac{2\pi}{\hbar} V_{DA}^2 \left(\frac{1}{(4\pi\lambda kT)^{1/2}} \right) e^{-(\Delta G_0 + \lambda)^2 / 4\lambda kT} \quad (2)$$

where ΔG_0 is the free energy of reaction, V_{DA} is the electronic coupling between the donor and acceptor, and λ is the total energy of the nuclear reorganization (structural change) within the donor, acceptor and solvent required for the reaction to occur. One of the key features of eqn. 2 is that it

predicts that the rate of an electron transfer reaction will slow down when the free energy of reaction becomes very large. This is the so-called "inverted region", which has been proven experimentally.^{13,14} This fact has proven critical to the design of long-lived charge separation systems. The total reorganization energy λ is usually divided into contributions from nuclear motions within the donor and acceptor molecules, λ_i , and solvent molecules, λ_s . The value of λ_i may be calculated from the force constants for all the molecular vibrations in both the reactant and product, while λ_s can be determined by application of the dielectric continuum model of a solvent.⁹

Photoprotection

An extremely important design feature of the photosynthetic complexes is their built-in mechanism against photo-oxidative damage. In shade, light is efficiently harvested in photosynthesis. However, in full sunlight, much of the energy absorbed is not needed and there are vitally important switches to specific antenna states, which safely dissipate the excess energy as heat. This way protection is given against the potential photo-damage of the photosynthetic membrane. Carotenoids (Car) have a key-role in this photo-protective mechanism. They are highly unsaturated long-chain polyenes that function in a photoprotective capacity by directly quenching the chlorophyll excited triplet state, which could otherwise sensitize formation of singlet oxygen. Furthermore, they act as accessory light-harvesting pigments by absorbing light energy in the visible spectrum unavailable to chlorophylls and stabilize the (non-covalently assembled) structures of the photocomplex assemblies. Carotenoids have a strong excitonic coupling with the light-harvesting pigments to achieve efficient energy transfer. In plants –with a ratio Car:Chl about 1:6– the carotenoids are capable of 100% quenching of the Chl triplets. This means that each Car is capable to quench on average six Chls, requiring a very specific positioning of the carotenoids in the photocomplexes, which has been optimized by the protein environment.

Self-repair

Splitting of water into protons and oxygen is energetically demanding and chemically difficult. The manganese-containing, water splitting catalytic site in natural photosystem II (PSII) complexes performs this reaction at close to thermodynamically limited efficiency (< 0.2 V overvoltage), at a high turnover rate ($\sim 10^3$ s⁻¹), and under mild external but low effective internal pH conditions. The catalytic reaction involves highly oxidative chemistry. The D1-protein binds the majority of the cofactors involved in light-driven charge transfer reactions of PSII, including the primary electron donor P680 and the Mn cluster at which the water-splitting reaction occurs. During operation the D1-protein is damaged, most likely due to singlet oxygen and/or oxygen radicals formed during the water-splitting process. As a consequence, the reaction centre of PSII has the most dramatic self-repairing system within photosynthesis. The vulnerable D1 protein is removed from the complex from time to time (about 30-60 minutes in an illuminated leaf!) and replaced by a newly synthesized D1-protein. The operational details of this self-repair process are not yet fully resolved.

Light harvesting and charge transport in purple bacteria

The structures of the purple bacterial light-harvesting and reaction centre proteins reveal elegant symmetries that are intimately related to their functions. LH2 consists of a circular nonamer of alpha-helical $\alpha\beta$ -apoproteins that bind 9 monomeric bacteriochlorophyll *a* (BChl *a*) cofactors (B800) that are positioned parallel to the membrane plane, and 18 tightly coupled BChl *a* molecules (B850) that are arranged perpendicular to the membrane plane (See Figs. 2a and b).¹⁵⁻¹⁷ Optical excitation within B800 is localized on a single chromophore and moves by Förster-type electronic energy transfer (EET) to B850 in ~ 0.7 ps (See Figure 2b). In contrast, the BChl *a* molecules of B850 are strongly coupled. This gives rise to strong excitonic interactions that distribute excitations across several chromophores.² The "hopping time" of the excitons within the B850 ring is ~ 100 fs. The energy can be transferred from B850 to the B875 molecules in LH1 in ~ 3 ps.¹⁸ Carotenoids enhance light-harvesting capability in the blue-green spectrum. They are located in van der Waals contact with both the B800 and B850 molecules. This proximity allows efficient and rapid energy transfer from both of the carotenoid's two

lowest excited singlet electronic states.¹⁹ The carotenoids also protect LH2 from photooxidative damage from by rapidly quenching potentially harmful BChl triplet states.¹⁹

LH1 is elliptical and contains 15 or 16 $\alpha\beta$ -apoproteins. These apoproteins bind 30-32 strongly coupled BChl *a* molecules (B875) that lie perpendicular to the membrane plane in a similar orientation to the B850 chromophores in LH2 (See Figure 2a).^{4, 20, 21} As in the B850 manifold, the B875 BChl *a* molecules are strongly exciton coupled and when they are excited that excitation is shared by several chromophores.² Again, as in the LH2, excitation hopping within B875 takes place on the femtosecond time scale. The LH1 ellipse surrounds the bacterial reaction centre. Energy transfer from LH1 into the reaction centre takes place in ~ 35 ps.¹⁸

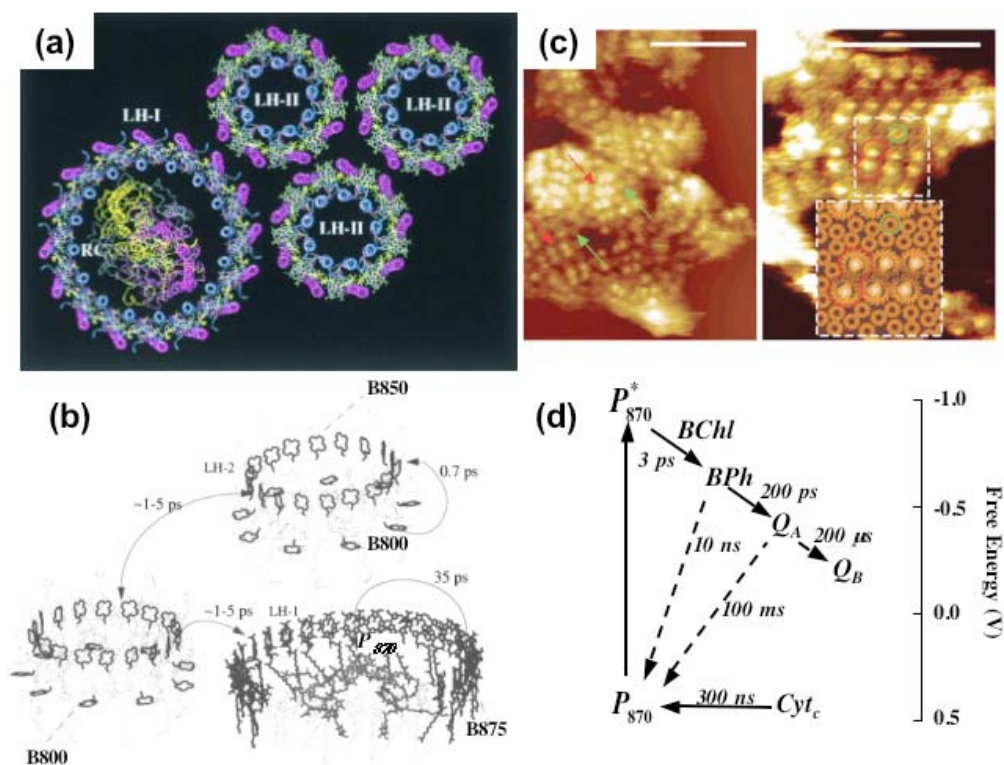


Figure 2. Photosynthetic unit of purple bacteria. (a) Modeled structure of light harvesting units 1 and 2 (LHI and LHII) and the reaction center (RC). The structures of LH-II and the RC are from the crystal structures, and LHI is simulated by analogy to LHII. (from Hu et al., 1998) (b) Dynamics of energy transfer processes between bacteriochlorophylls B50 and B800 in LH2, B875 in LH1, and the special pair P870 in the RC. ² (c) AFM image of arrangement of LH2 (highlighted in green) and LH1-RC (red) complexes in the bacterial membrane. The bright spots are the LH1-RC complex and the inset in the second panel is a model using the known crystal structures to reproduce the image.³ (d) Energies and time-scales of electron transfer within the reaction center.

The bacterial reaction centre consists of two membrane spanning proteins. These two proteins have an intriguing pseudo 2-fold symmetry and organize the pigments into two parallel electron transfer pathways, termed the A-side and B-side, from the primary electron donor (P870) to either quinone A (Q_A) or (Q_B). However, the RC only utilizes the A-side cofactors for electron transfer. Excitation of the special pair produces the P870* excited state species that quickly charge separates by electron transfer to the P870⁽⁺⁾BPheo *a*⁽⁻⁾ species in ~ 3 ps, a process mediated by the adjacent accessory BChl *a*,

which may participate as either a direct or “virtual” intermediate state in the electron transfer (see Figure 2d). The electron then moves to Q_A in ~ 200 ps and is subsequently transferred to Q_B in ~ 200 μ s.²² Following a second photochemical reduction, $Q_B H_2$ moves away from the RC through a break in the LH1 ring, a process likely regulated by a small alpha-helical protein, PufX.²⁰ As observed by atomic force microscopy (AFM), the LH1-RC complexes form small linear arrays that are interconnected by groups of 10-20 LH2 complexes (Figure 2c).³ This architecture allows for efficient EET between LH2 complexes and from any LH2 to several LH1-RC complexes. Once deposited in an LH1 complex, the close proximity of other LH1s allows for efficient migration of the excitation should the initially associated RC be already in use.

Photosystem I

Photosystem I (PSI) functions to produce NADPH that is used to reduce carbon dioxide in the reactions of the Calvin cycle. When cooperating with PSII, it uses the energy of light to transfer electrons from plastocyanin or soluble cytochrome c_6 to ferredoxin and eventually to $NADP^+$.²³ In an alternative pathway, the electrons from ferredoxin are transferred back to plastocyanin via the cytochrome b_6/f complex. This cyclic electron transport, which does not require the input of free energy by PSII, results in a transmembrane electrochemical gradient that can be used to produce ATP. NADPH and ATP are used to reduce CO_2 to carbohydrates in the subsequent dark reactions.²⁴ An X-ray structure of PSI has been obtained at 2.5 Å resolution²⁵ (see Figure 3a). The PSI core is a large pigment-protein complex consisting of 11-13 protein subunits. The largest two subunits, PsaA and PsaB, comprise a heterodimer which binds the majority of the reaction centre co-factors and core antenna pigments. The reaction centre is bound in between PsaA and PsaB along the local pseudo- C_2 axis. The components of the reaction centre are as follows: P700 (a dimer containing one Chl a and one Chl a' molecule⁸) where charge separation is initiated, A_0 (a Chl a molecule), A_1 (a phylloquinone), and the three [4Fe4S] clusters F_x , F_A , and F_B (see Figure 3b). While the exact electronic structure of the P700 special pair is still unknown, the redox potential of P700* of ~ -1.2 V makes it the one of the most powerful reducing agents found in Nature. After photoexcitation, P700 transfers an electron to A_0 within 1-3 ps. Subsequent electron transfer from $A_0^{\cdot -}$ to A_1 occurs within 20-50 ps.²⁵ Reoxidation of $A_1^{\cdot -}$ via F_x shows biphasic kinetics with $\tau_{1/2} = 20$ ns and 150 ns and is the source of much debate. The kinetics of electron transfer from F_x to the terminal iron sulphur clusters F_A and F_B are also under review since the rates are faster than for electron transfer from A_1 to F_x . Once the electron is transferred from F_x , through F_A , to the terminal iron sulphur cluster F_B , it reaches the soluble electron carrier ferredoxin ($\tau_{1/2} = 500$ ns) and leaves the site for use in the reduction of $NADP^+$.

Photosystem I contains an integral antenna system consisting of about 90 Chl a molecules and 22 carotenoids. The antenna pigments can be divided into three regions, one where the antenna pigments surround the inner core, and two peripheral regions where chlorophylls form layers on the stromal and luminal sides of the membrane. The average RC Chl to antenna Chl distance is larger than 20 Å, however two antenna Chl molecules are located within 14 Å of the closest RC pigment and may serve as a functional bridge between other antenna and the RC. Included in the peripheral regions are the chlorophylls which absorb at longer wavelength than P700 (so called ‘red’ chlorophylls). The red-shifted absorption is caused by exciton interactions, electronic interactions with polypeptides and changes in the dielectric constant of the surrounding protein environment. Excitation on the antenna pigments results in a rapid equilibrium distribution of the energy among the antenna chlorophylls with a 4–8 ps lifetime.²⁵ The rate of energy transfer from the antenna system to P700 or ‘trapping time’ varies between (20 and 35 ps)⁻¹ and depends on the organism and the antenna size.

Photosystem II

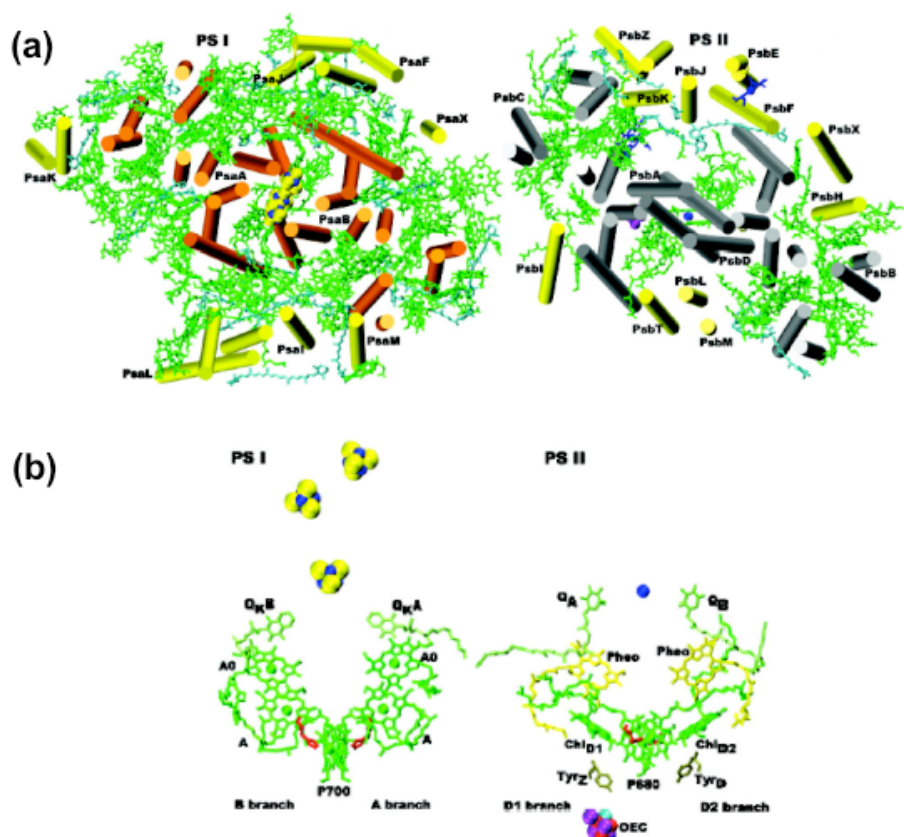


Figure 3. Photosystems I (PSI) and II (PSII) (from Grotjohann et al., 2004). (a) Comparison of the protein structures and cofactor arrangement of each photosystem. The major proteins that flank the reaction centers are shown in orange (PSI) and silver (PSII). Smaller protein subunits are depicted in yellow. (b) Arrangement of the redox cofactors within the reaction center of each photosystem. Chlorophylls are shown in green; pheophytins in yellow; plastoquinones in lime; coordinating histidines in red. The 4Fe4S clusters are shown above the PSI quinines in yellow and blue and the oxygen evolving complex is shown in purple and red below the tyrosine in PSII.

Photosystem II (PSII) catalyzes one of the most thermodynamically demanding reactions in biology: the conversion of light energy into a redox couple capable of oxidizing water.²⁶ As a by-product, O_2 is released into the atmosphere. The crystal structure of PSII reveals details with a resolution of 3.5 Å. The PSII core complexes consist of 19 proteins. The central region shows striking similarities to the protein structure of the bacterial reaction centre (see Figure 3a).²⁷ The RC complex of PSII contains 6 Chl *a* molecules, 2 β -carotene molecules and 2 pheophytin *a* molecules and is bound to a heterodimeric protein core formed by subunits D1 (a.k.a. PsbA) and D2 (a.k.a. PsbD, see Figure 3b). Unlike the photosystem I P700 analogue, P680 is not a ‘special pair’ of strongly interacting molecules as the exciton coupling of P680 is far weaker.²⁸ Instead, the four inner-most chlorophyll *a* molecules are coupled so that the initially local excited state becomes delocalized over the reaction centre chlorophylls in 100-500 fs. The intermediate charge transfer state, formed with an intrinsic rate constant of 1.5 ps, is attributed uniquely to $Chl_1^{+*}Pheo_1^{-*}$.²⁹ Electron transfer proceeds further to the first plastoquinone Q_A within 200 ps. Q_A^{-} then doubly reduces the secondary quinone acceptor, Q_B , with the possible involvement of a non-heme iron located on the pseudo-C2 axis with time constant of 0.2-0.4 ms and 0.6-0.8 ms for the first and second reductions respectively. After receiving two protons, Q_B^{-} then leaves its binding pocket as a plastoquinol molecule. The plastoquinol then diffuses out of the protein to be oxidized by cytochrome *b₆f*.

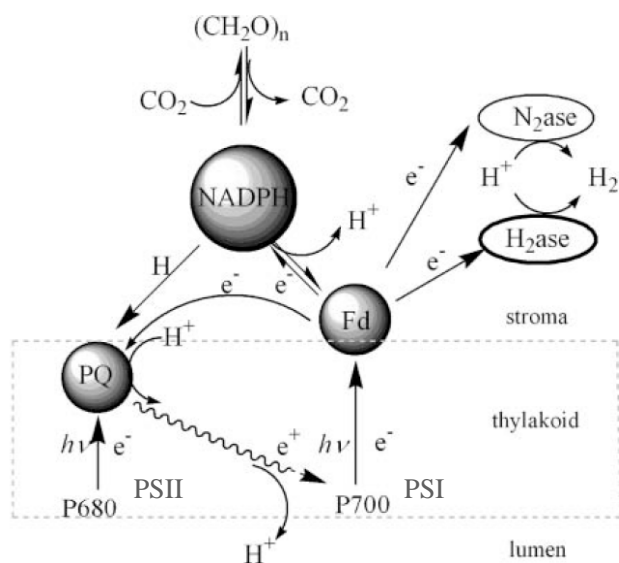


Figure 4. Electron storage and fuel production using oxygenic photosynthesis. Two consecutive light-driven reactions ($h\nu$) in the photosystems PS I and PS II transfer electrons via plastoquinon(PQ) to ferredoxin (Fd). Subsequently the electrons can be used to reduce protons (H^+) and produce fuel, either by CO_2 fixation via NADPH into starch or by hydrogenase/nitrogenase into H_2 (adapted from ¹).

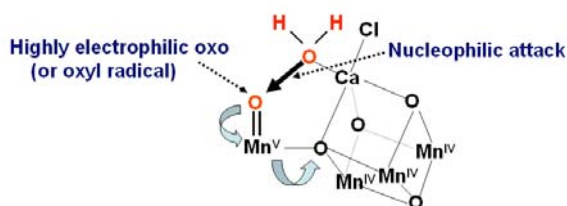


Figure 5. A proposed mechanism for the final step of the state cycle when the dioxygen bond of O_2 is formed that is of possible interest for design of artificial photosynthesis components. The very high oxidation state of the Mn-cluster, particularly the Mn ion outside the $Mn_3Ca^{2+}O_4$ cubane, leads to a high electron deficient oxo ($=O$) after deprotonation of water molecules during the S-state cycle or oxyl radical ($-O\cdot$) which facilitates a nucleophilic attack on an oxygen of a second water molecule located in the coordination sphere of Ca^{2+} . The arrows indicate direction of movement of electrons (Barber 2006).

The oxidized primary donor $P680^{+*}$ is among the strongest oxidants generated in biological systems and has a redox potential estimated to be 1.3 V versus the standard hydrogen electrode. The first $P680^{+*}$ reduction by a redox-active tyrosine residue occurs on a time scale of 20-40 ns. The tyrosine residue then oxidizes one of the Mn ions contained within a cluster of four in the oxygen evolving center (OEC). For each reduction of $P680^{+*}$ to P680 one oxidizing equivalent is generated. As P680 undergoes further photoinduced oxidation cycles, the $(Mn)_4$ cluster accumulates oxidizing equivalents and the time for re-reduction of P680 increases from tens of ns to hundreds of ns. After four oxidizing equivalents are accumulated by the $(Mn)_4$ cluster, one oxygen molecule is produced, and the cycle begins again. The recently determined structure of PSII has provided insights into the organization of the 4 Mn ions and Ca^{2+} which make up the catalytic center of the oxygen evolving complex and the protein side chains which surround it including those involved in directly in ligating the metals (see Figure 5).

The structural model of the OEC shown in Figure 5 is providing a frame work for describing the water splitting chemistry of PSII and therefore is of major importance for designing artificial catalytic systems for reproducing this chemistry.

The quenching of ^3Chl by carotenoids occurs in all types of chlorophyll-binding light-harvesting complexes and in all reaction centres of oxygenic photosynthetic organisms except PSII. As a result, triplet P680 can produce singlet oxygen which oxidizes the D1 protein. If the β -carotene molecules within the PSII reaction centre were sufficiently close to P680 to facilitate triplet energy transfer, they would be quickly oxidized by the $\text{P680}^{+\ast}$. The RC's of PSII in green plants and algae compensate for the oxidative damage by regularly replacing the D1 protein every hour.³⁰ Another consequence of the oxidizing ability of $\text{P680}^{+\ast}$ is the almost complete lack of central core antenna in the pigment-protein complex. While there are an additional 32 Chls bound by the protein, the average antenna Chl to RC Chl distance is 25 Å. In order to prevent oxidation of the antenna Chl molecules, the efficiency of energy transfer from those antenna chromophores to the RC is reduced relative to that in PSI.²⁸

Photochemical thermodynamics of energy storage

The photosynthetic apparatus is connected to the steady state network of catalytic conversion reactions in the organism that is continuously dissipating energy. If there is a shortage at one spot, it can be smoothly compensated from other dynamic reservoirs in the network. The storage of energy is dynamic in the sense that it is continuously redistributed to prevent depletion of the complete network of the reserves in the organism.³¹ The carbohydrate pool in green plants allows the organism to survive during low light periods and the Calvin cycle is the metabolic pathway found in the stroma of the chloroplast in which carbon enters in the form of CO_2 and leaves in the form of sugar. For 680 nm light, the energy conversion efficiency into the chemical energy of the primary products of photosynthesis is about 50%; the maximum conversion energy of solar energy into carbohydrates is about 27%.

The storage and downstream utilization can be described as a single step conversion of solar energy into Gibbs free energy. In its simplest form the photosynthetic solar cell is a heat engine that produces charge separation (see Figure 6). Inside the engine a molecular absorber is excited that produces charge separation. There are three basic conversion processes in the primary mechanism of the photosynthetic solar cell:³²

- 1) Excitation of a molecular chlorophyll absorber with rate g
- 2) Energy conversion by charge separation with rate I into an electron and hole in dynamic equilibrium with the absorber
- 3) Back reaction with rate $1/\tau$ from the excited chlorophyll state into the ground state

These three processes form an “elementary steady state” that drives the living state by coupling into the chemical conversion network. Photosynthesis researchers have realized the importance of an intimate connection between energy conversion and storage already at an early stage.³¹ First, excitation of a molecular Chl absorber in exchange with the field of solar irradiation leads to a difference in chemical potential

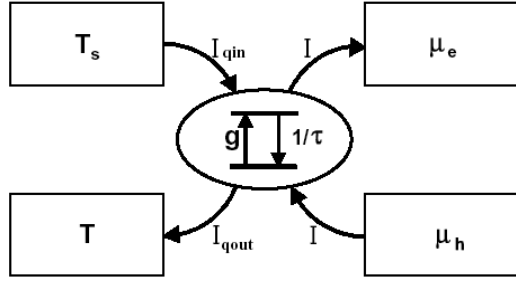


Figure 6. The basic mechanisms of the photosynthetic solar cell. A chlorophyll molecule is connected to a reservoir at ambient temperature $T \sim 300$ K, and emitting heat at a rate I_{qout} , is excited due to the heat flow I_{qin} from the solar reservoir at temperature T 5800 K with a rate g to an excited state separated by an energy $h\nu$ from the ground state. The excited chlorophyll state either decays with loss rate $1/\tau$ or produces an electron-hole pair with net charge separation rate I and free energy $\Delta\mu = \mu_e - \mu_h$.

$$\Delta\mu_{abs} = h\nu_0 + k_B T \ln\left(\frac{p}{p_0}\right) \quad (3)$$

with p, p_0 the populations of the excited and ground state of the absorber. In the dark the excited and ground state are in equilibrium and $\Delta\mu_{abs} = 0$, leading to $p/p_0 = \exp(-h\nu_0/k_B T)$, the Boltzmann distribution. For Chl a in the plant $h\nu_0 = 1.8$ eV. The upper limit at the absorber stage is $\eta = 1 - 4T/3T_S = 93\%$ efficiency due to entropic losses originating from the different temperatures of the incoming radiation and of the heat reservoir.

A PV solar cell produces electricity, while a photosynthetic reaction centre produces a photochemical steady state with a voltage over the membrane and charge separation in dynamic equilibrium with the absorber. When the light is switched on and the absorber is coupled to a storage reservoir, a steady state is produced, where the formation of the excited state is balanced by its decay due to the limited life time and the net flow of energy into the charge separated state. The

$$\Delta\mu_{e-h} = e\Delta\psi + k_B T \ln\left(\frac{p'q'}{p_0'q_0'}\right) \quad (4)$$

represents the difference in chemical potential or free energy produced by light-induced charge separation and contains an electronic and a photochemical term that measures the concentration $p'q'$ of the charge separated state in the light relative to the concentration p_0q_0 in the dark and is proportional to the temperature.³³

In a diverse energy conversion and storage network the initial assimilation is intimately connected with conversions and fuel reservoirs further downstream. Biochemically it is very difficult to maintain a membrane potential, which is rapidly converted in a ΔpH that is used to produce ATP, an intermediate energy carrier that is present in catalytic amounts and drives the Calvin cycle. When a storage reservoir is connected to the absorber, energy flows can be forward from the absorber into the reserve, and backward, from the reserve back into the absorber, where it can be emitted. In this way assimilation has to compete against depletion of the reserve by backward reaction coupled to radiative loss in the absorber. The entire system has to operate linearly and close to the thermodynamic limit to minimize losses. The net production rate of charge separation and energy extraction can be described by the solar cell equation

$$I = I_f - I_b \left(e^{\Delta\mu/k_B T} - 1 \right) \quad (5)$$

with I_f , I_b the forward and backward reaction rates.

The energy storage from an elementary steady state process can be generalized according to

$$\Delta\mu_{st} = \Delta\mu_{max} + k_B T \ln(\delta) \quad (6)$$

The quantum yield is³¹

$$\eta_{st} = \left[I_f / (\tau^{-1} + I_f) \right] \cdot (1 - \delta) \quad (7)$$

Here the first factor is due to the kinetics of the steady state, while δ measures the thermodynamic activity of the trap. In order to favor the forward reaction over the backward process, the energy of the combined products is lower than for the excited state by at least $k_B T \ln(\delta)$. The maximum power is generated for $\delta \sim k_B T / \mu_{max}$, a compromise between a high conversion efficiency and a high storage efficiency. For plant photosystems I and II under operational conditions $\Delta\mu_{st} \sim 1.2$ eV and $\Delta\mu_{max} \sim 1.3$ eV.³¹

Eq.4 can be generalized to storage processes further downstream and longer time scales, where the entire system is in Boltzmann equilibrium with the initial excited state. $\Delta\mu_{st}$ should be sufficiently low to maintain the steady state against back reactions and represents the work that can be obtained, *e.g.* from sugar or biomass.

When the solar radiation is interrupted, the unavoidable back-reaction causes gradual depletion of the accumulated energy. For instance, a plant in the dark produces a small flux of photons (luminescence) from its reserve that was stored during illumination periods. This leads to a generalized expression for the thermodynamic limit of energy storage in a steady state reserve at all time and length scales, starting from the initial free energy stored in the solar energy assimilation $h\nu_0$, according to

$$\Delta\mu_{st}(t) = h\nu_0 - k_B T \ln(t/\tau) \quad (6)$$

with t the storage time.³⁴

For instance, in the PSII reaction centre light excitation energy localizes on one or several chlorophyll molecules P*, Chl* (See Figure 3). The enzyme is able to keep its overall catalytic turnover efficiency at > 90% yield in a cascade of reversible electron transfer reactions. The overall time scale is set by the initial fluorescence life time of the P* of $\sim 10^{-9}$ s and charge separation gets gradually slower as the probability for recombination becomes smaller for the later intermediates. In this way energy dissipation is used to optimize catalytic turnover with a maximum rate of 10^3 - 10^4 s⁻¹. Almost nothing is wasted since the dissipating enzyme operates very close to the thermodynamic limit imposed by the second law of thermodynamics for linear non-equilibrium processes.

The highest yields and efficiencies are attainable when energy is used as soon as it is assimilated, avoiding intermediate storage, for instance by generating and using electricity, by running catalytic converters at a nanoscale directly from the photoconverter, and storing the energy in a redox couple, by coupling a chemical cycle directly to a photoconverter like in the chloroplast, by connecting the chloroplast directly to respiration like in the plant, or by using light driven cell factories for production of food and chemical feedstock.

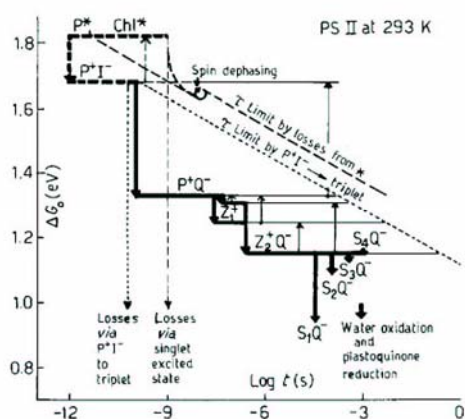


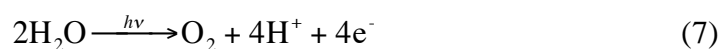
Figure 7. Thermodynamic scheme for the reaction centre of PSII. The stabilization required to allow the reactions with water and with plastoquinone is obtained by a large energy dissipation in the form of heat and by the high energy level of the primary radical pair, P⁺ I⁻.

Energy is not only stored but also used in growth, reproduction and maintenance in a variety of nonlinear irreversible events that produce entropy.³⁵ Reported crop yields of <1% originate from the fact that the products of photosynthesis are often used by plants for other purposes than production of biomass. Similarly an algal species producing fuel by growing has to compromise. It has the advantage of being entirely self-organizing, self-repairing and self-reproducing. In addition, the efficiency of (artificial) photosynthesis decreases underwater in the sea, where the solar radiation levels are less intense and the balance between repletion and depletion of the reserve is less favourable compared to a system exposed to full sunlight on the land. Recent progress in biotechnology offers novel routes for improvement. For instance, experiments with genetically modified *Chlamydomonas reinhardtii* have shown sustained production of hydrogen at > 98% purity over 14 days at levels that correspond with 5 times the production of the wild type species. There is general consensus among researchers that an energy storage efficiency of 10% over the entire solar spectrum is a realistic target for biological fuel production.³⁶

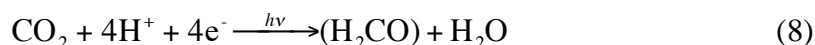
Table 1 Thermodynamic limits for a dynamic reserve. In practice molecular dyes have an excited state life time of ~10⁻⁹ s, the theoretical maximum storage time is thirty orders of magnitude longer and the efficiency limit for storage on human time scales is 0.5-0.4.

time scale	$\eta(t)$
Chlorophyll excited state	1
charge separation	0.868
water oxidation	0.802
A night	0.552
A bacterial life span	0.538
A weekend (Fri-Mo)	0.526
10 cloudy days in a row	0.505
A winter season	0.467
An agricultural season	0.458
A year	0.454
A decade	0.421
A human lifespan	0.393
A century	0.388
Fossil reserve time span	0.379
A millennium	0.355

Business dilemmas between cost and benefit will be central to artificial photosynthesis. A very nice example of how this business dilemma is solved in nature is the chloroplast. This organelle derives from a photosynthetic cyanobacterium and is stripped down to perform light driven water splitting



and light-driven CO₂ reduction



with high efficiency. Each half reaction requires four photons and together they lead to the net production of solid (i.e. without back pressure) carbohydrate fuel. This task is performed by the Calvin cycle that runs in the chloroplast organelle, which relies for its maintenance and reproduction on its embedding in the higher organism environment of the green plant. In general chemical cycles perform optimally when they run in a small compartment.

In vivo 9–10 photons are required for reactions (9) and (8), under the most favourable conditions, with low irradiation flux. An energy input of 1760 kJ is required per mole of O₂ produced, which is approximately four times more than the standard free energy change of 467 kJ/mol, and corresponds with a maximum efficiency of 27% of absorbed light at 700 nm.³⁷ This reduces by 700/400 for 400 nm illumination, to 15%. The mean optimal efficiency between 400 nm and 700 nm thus reduces to ca. 21% of the absorbed light. This is equal to a conversion efficiency of 9% of the total solar spectrum, assuming only the spectrum between 400–700 nm is used. In comparison, commercial multi-junction Silicon photovoltaic cells absorb above 1.1 eV from the visible through to the near infrared region and are rated at ~14% over the entire solar spectrum, but without storage of the electrons that are produced. In photosynthesis, much of the energy that is stored is subsequently used to support cellular processes and therefore only a very minor fraction is stored as biomass.^{38,39}

The starting point for all biological solar driven H₂ production methods is the water splitting process (7). Algal H₂ production was reported as early as the 1930s.⁴⁰ H₂ production rates can be increased by temporally separating the water oxidation from the H₂ production process, catalyzed by hydrogenase.⁴¹ However, this process has the down side that H₂ is only produced ~50% of the time and it uses 6 quanta of light per H₂ produced. It would therefore be more efficient to use a direct H₂O → H₂ continuous conversion process using 4 quanta at low sulphur concentrations, in which PSII generates O₂ at a rate just below that at which it is consumed by respiration. For comparison, typically four Si PV cells can be connected in series to an electrolyzer to produce hydrogen in an operational configuration with overvoltage, and around 16 photons are used to drive the four-electron water splitting reaction. However, since the Si cells operate with a band gap of 1100 nm they collect ~40% more photons than photosynthesizers and this contributes to the overall efficiency of the device.

The energy produced in photosynthesis has to be sufficient to drive the desired catalytic reaction for maintaining the chemical (fuel) reserve and its downstream utilization. Photosynthesis is able to produce intermediate solid fuel with very good quantum yield, since ~10 photons are needed in practice to drive reactions (7) and (8) at low light intensity. An isolated photosynthetic system can sustain a catalytic conversion rate of 10³-10⁴ s⁻¹ with ~300 chlorophyll molecules in the spectrum of solar irradiance.⁴² Catalysis occurs on the time scale of self-diffusion of molecules, ~10⁻³ s. Fe-catalysts derived from hydrogenases may be attractive for use in bulk catalytic converters since the proton diffusion is very rapid and the natural enzyme can catalyze the reduction of protons to form hydrogen at a rate of more than 25,000 s⁻¹, among the highest of any known enzyme.

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