Biological solar energy

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Through the process of photosynthesis, the energy of sunlight has been harnessed, not only to create the biomass on our planet today, but also the fossil fuels. The overall efficiency of biomass formation, however, is low and despite being a valuable source of energy, it cannot replace fossil fuels on a global scale and provide the huge amount of power needed to sustain the technological aspirations of the world population now and in the future. However, at the heart of the photosynthetic process is the highly efficient chemical reaction of water splitting, leading to the production of hydrogen equivalents and molecular oxygen. This reaction takes place in an enzyme known as photosystem II, and the recent determination of its structure has given strong hints of how nature uses solar energy to generate hydrogen and oxygen from water. This new information provides a blueprint for scientists to seriously consider constructing catalysts that mimic the natural system and thus stimulate new technologies to address the energy/CO₂ problem that humankind must solve. After all, there is no shortage of water for this non-polluting reaction and the energy content of sunlight falling on our planet well exceeds our needs.

Keywords: photosynthesis; solar energy; biomass; water splitting; photosystem II; efficiency

1. Introduction

More than 3 billion years ago biology developed the capacity to efficiently capture solar energy and use it to power the synthesis of organic molecules. This photosynthetic process set into motion an unprecedented explosion in biological activity, allowing life to prosper and diversify on an enormous scale as witnessed by the fossil records and by the extent and diversity of living organisms on our planet today. Indeed, it has been the process of photosynthesis over eras of time, which has provided us with the oil, gas and coal needed to power our technologies, heat our homes and produce the wide range of chemicals and materials that support everyday life.

Today, it is estimated that photosynthesis produces more than 100 billion tons of dry biomass annually, which would be equivalent to a hundred times the weight of the total human population on our planet at the present time and equivalent to a mean annual rate of energy storage of approximately 100 TW. The success of this energy generating and storage system stems from the fact that the raw materials and energy needed to drive the synthesis of biomass are available in almost...
unlimited amounts, i.e. sunlight, water and carbon dioxide. At the heart of the reaction is the splitting of water by sunlight into oxygen and hydrogen. The oxygen is released into the atmosphere, where it is available for us to breathe and to use for burning our fuels. The ‘hydrogen’ is not normally released into the atmosphere, but instead is combined with carbon dioxide to make organic molecules of various types. When we burn fuels, we combine the ‘stored hydrogen’ of these organic molecules with oxygen. Similarly, energy is also released from organic molecules when they are metabolized within our bodies by the process of respiration. Thus, in the biological world, photosynthesis brings about the splitting of water into oxygen and hydrogen, respiration being the reverse, combining oxygen and hydrogen in a carefully controlled and highly efficient way so as to create metabolic energy. It is important to appreciate that all energy derived from the products of photosynthesis (food, biomass and fossil fuels) originates from the energy falling on our planet in the form of sunlight (figure 1).

2. Energy available and photosynthetic efficiency

The Sun provides solar energy to our planet on an annual basis at an average rate of 100 000 TW, exceeding our current rate of demand of approximately 14 TW a year by 7000 times. In other words, the energy of 1 h of sunlight falling on our planet is approximately equal to the total amount of energy used by humankind in a year. The overall efficiency by which photosynthesis converts this enormous energy source to biomass is rather low. To appreciate why this is, several factors must be considered.

(i) Although photosynthetic organisms can efficiently trap light energy at all wavelengths of visible solar radiation, the energy used for splitting water and fixing carbon dioxide is only equivalent to the red region of the...
spectrum. Higher energy photons are degraded to heat by internal conversion within the light-harvesting pigments to the energy level of ‘red’ photons.

(ii) For every electron/proton extracted from water and used to reduce CO₂, the energy of two red photons is required. This is accomplished by linking together, in series, two different photosystems, i.e. photosystem II (PSII), which uses light to extract electrons/protons from water, and photosystem I (PSI), which uses light to give additional energy to the ‘PSII-energized’ electrons/protons so as to drive the CO₂ fixation process (figure 2). Therefore, photosynthesis uses the energy of at least eight red photons per O₂ molecule released or CO₂ molecule fixed. A typical product of carbon fixation is glucose (C₆H₁₂O₆), whose energy content is 672 kcal per mole if burnt in a calorimeter. To make a glucose molecule, the energy of 48 red photons is required and assuming a wavelength of 680 nm, corresponding to 42 kcal per quantum mole, the efficiency of conversion is 33%. Although this is an impressive number, in reality, the overall conversion of solar energy to organic matter is lower. Energy is lost in degrading higher energy light to the energy of red photons and in driving the enormous number of reactions that occur in photosynthetic organisms to maintain their organization, metabolism and survival.

Figure 2. A simplified scheme of the light reactions of photosynthesis. For every electron extracted from water and transferred to CO₂, the energy of two photons of light is required. One is absorbed by photosystem II (PSII), which generates a strong oxidizing species (P680⁺), able to drive the water-splitting reaction and a reductant, plastoquinol (PQH₂). The other generates a strong reducing species, NADPH₂ (reduced nicotinamide adenine dinucleotide phosphate), which donates ‘hydrogen’ to CO₂ to produce sugars and other organic molecules, symbolized as (CH₂O) and a weak oxidant P700⁺. Electron and proton flow from PQH₂ to P700⁺ results in the release of energy to convert ADP (adenosine diphosphate) to ATP (adenosine triphosphate). In biology, ATP acts as a ‘universal energy currency’ and is needed, along with NADPH₂, to fix CO₂. Since the production of O₂ involves the splitting of two water molecules, the overall process requires eight photons of light.
There are a host of ways to define and calculate photosynthetic efficiencies, but the approach adopted by Thorndike (1976) is attractive, since it engulfs the whole range of definitions. He considered the following free energy stored per photon, $F$:

$$F = \eta_T \eta_R \eta_S \eta_L \eta_O h \nu_O,$$

where $h \nu_O$ is the energy of a photon at the optimum frequency for conversion (i.e. red light); $\eta_O$ is the thermodynamic efficiency (conversion from energy to free energy produces an explicit entropy $T \eta_S$ loss); $\eta_L$ is a factor accounting for irreversibility in energy losses in photochemical and biochemical pathways; $\eta_S$ is a factor accounting for the spectral distribution of light and the fact that there is a minimum usable photon energy (close to $h \nu_O$); $\eta_R$ is a correction factor for leaf reflectivity; and $\eta_T$ is a correction factor for saturation effects. Taking $h \nu_O$ as 680 nm and adopting reasonable values for the various coefficients ($\eta_O = 0.73$, $\eta_L = 0.50$, $\eta_S = 0.32$, $\eta_R = 0.80$, $\eta_T = 0.5$), Thorndike calculated a maximum efficiency for the conversion of light to stored chemical energy (dry carbon matter) of approximately 4.5%. A similar value was calculated by Walker (1979), Archer & Barber (2004) and by others (see Bolton 1977, 1979).

In fact, this value is rarely reached. Only in exceptional cases will dry matter yield exceed 1 or 2%, as in the case of intense cultivation of sugar cane in tropical climates. Normally, agricultural crops yield biomass at efficiencies less than 1%, even when pampered with ample supplies of fertilizer and water. Environmental conditions, degree of light interception, availability of nutrients and water are key factors in reducing the efficiency below the maximum, while intrinsic genetics of particular plant species also dictates growth rates and maximum biomass.

On a global basis, the efficiency of photosynthesis is significantly lower than for optimal agricultural crops owing to seasonal changes and the existence of large areas of land on our planet, which do not sustain vegetation. Thus, the rate of energy stored annually by photosynthesis, estimated to be 100 TW, represents just 0.1% conversion, given that over the same time period, solar energy incident on our planet averages at a rate of 100,000 TW. This energy is stored mainly in wood and fibres of terrestrial trees and plants. A similar amount of photosynthetic activity occurs in the oceans, but most of the fixed carbon is rapidly recycled into the food chain (Falkowsky & Raven 1997). Therefore, overall, an approximate efficiency of global photosynthesis is 0.2%. The fixed carbon provides biomass, which was the traditional source of energy for humankind prior to the exploitation of fossil fuels. It is not surprising therefore that there is now a growing interest in returning to the use of biomass as an alternative to fossil fuels, since its production and use is carbon dioxide neutral.

3. Biomass

Wood and other forms of biomass can be used to generate heat, electricity, biogas (mainly methane and carbon dioxide), syngas (hydrogen and carbon monoxide) and other biofuels (mainly ethanol) (Slesser & Lewis 1979; Spath & Drayton 2003; Bridgewater & Maniatis 2004; Bullard 2004; Parika 2004). Biomass is the end product of photosynthesis and represents energy conversion from solar of 0.1 to 1.0% efficiency depending on its origin. Many organizations consider ‘biomass power’ as an increasingly attractive option to partially replace fossil fuels,
including the European Union, US Department of Energy (USDOE) and many national government departments and agencies, major companies and utilities in countries like Brazil, Finland, Sweden, Austria, the UK and elsewhere. Currently, the global use of biomass is equivalent to an energy consumption rate of approximately 1.4 TW on an annual basis. In the USA, biomass surpasses hydroelectric power as a source of renewable energy in providing over 3% of the country’s energy requirements, corresponding to a mean annual production rate of approximately 0.1 TW. However, a recent joint report from the US Departments of Energy (USDOE) and Agriculture (USDA; 2005) has concluded that biomass could provide the USA with approximately 30% of its present total energy needs. This would be achieved by using non-food producing agricultural land and maximizing on forestry products to generate 1.3 billion tons of dry biomass annually, corresponding to an energy production of approximately 1 TW year. This optimistic projection also relies on plant breeding and genetic engineering strategies to produce new cultivars for high yields of biomass, requiring minimum input of fertilizers, water and pesticides. Moreover, improved technologies will be required to maximize the use of biomass, including those for producing liquid biofuels to replace gasoline. Also, such calculations must take into consideration the energy costs of maintaining ‘energy farms’, harvesting the biomass and transporting to a central location for use.

The USA and many other countries, such as Brazil, are blessed with large land masses and good conditions for growing biomass crops and trees. In contrast, the UK has very little spare land available for large-scale biomass production for energy. Despite this, the current estimate is that biomass contributes 1.4% to the total energy consumption in the UK, although some of this includes burning domestic waste or using methane gas generated at land fill sites. Recent reports from the UK Carbon Trust (2005) and the UK Biomass Task Force (2005) suggest that this figure could be significantly improved upon and that biomass could contribute more to energy demands of the UK. It was concluded that in the future, the UK could use biomass to satisfy approximately 4.5% of its present total energy needs and that this energy was best extracted by combustion, possibly by co-firing with coal in power stations. Much of this biomass is part of a cascade of usage, reuse and recycling of biomass materials, including residues generated on farms and from forestry (Oogwijk et al. 2001). However, specific crops for energy such as cereals (Bullion 2003), oilseed rape (Martini & Schell 1998), sugar cane (Goldemberg et al. 2004) and soybeans (Wu et al. 2004) are considered to be crops with the potential to supply the expanding biofuels market.

The major biomass-derived fuel is ethanol produced from the fermentation of sugars or starches. Three countries, Brazil, the USA and India, produce 90% of the world’s ethanol from biomass, with the total ethanol production being equivalent to an average annual rate of production of 0.02 TW. Brazil has invested significantly in producing ethanol from sugar cane, which is used as a substitute or an additive to gasoline (Geller 1985). Although the production and use of this bio-ethanol has been heavily subsidized, improved technologies and the rising cost of petroleum imply that ethanol fuels are now competing favourably with gasoline in Brazil and are having an impact in some parts of the USA and Canada, as well as in India and the Far East.
For millennia, biomass was the only primary energy source available to humankind. For the last two centuries, however, energy demand has outpaced biomass production. Although biomass can still contribute to this demand in several different ways and to different extents depending on climate and available landmass, it is hard to see how it could match the present level of global fossil fuel consumption or to cope with increasing demands for energy in the future. Using the best-known crops for biomass production to provide a supply of energy at an annual rate of 20 TW would require covering approximately 30% of the land mass of Earth, which corresponds to almost three times all the cultivatable land currently used for agriculture. To reduce this to a reasonable level so as not to seriously compete with global food production would require the biomass crops to have solar energy conversion efficiencies close to the theoretical maximum of approximately 4.5%. Nevertheless, if a new generation of energy crops could be produced by plant breeding or genetic engineering, which are environmentally robust requiring minimal inputs of water and fertilizer and can convert solar energy at efficiencies well above 1%, biomass could make a significant contribution to global energy demand. New and improved technologies to extract this energy will also have to emerge as this source of energy comes on stream.

Finally, we should remind ourselves that plant biomass is not just a store of energy, but also a source of complex molecules that constitute our food, which provides us with a wide range of valuable materials, such as timber, linen, cotton, oils, rubbers, sugars, starches, etc. The increased use of ‘designer’ plants to produce high-value compounds for chemical and pharmaceutical industries should not be underestimated (Ragauskas et al. 2006). Moreover, new methodologies will emerge to release the valuable molecular building blocks of cellulose, lignin and other polymers, which constitute plant cell walls and fibres (Somerville et al. 2004). In these various ways, plant biomass will also contribute to the energy requirements of modern industrialized society.

Although it may be possible to engineer plants and other types of photosynthetic organisms as energy-converting ‘machines’ and ‘chemical factories’, the overall efficiency will rarely exceed 1% and will usually be much less. Moreover, the growing of energy crops on a very large scale will compete with cultivatable land used for food production. However, there is an alternative and complementary approach for using solar energy. It may be possible to develop a highly efficient, all-artificial, molecular-level energy-converting technology, which exploits the principles of natural photosynthesis.

4. Photosynthesis and the water-splitting reaction

Photosynthetic solar energy conversion has produced most of the energy that fuels human society and sustains life on our planet. As explained in §2, the process is underpinned by the light-driven water-splitting reaction that occurs in an enzyme found in plants, algae and cyanobacteria known as PSII (Barber 2003, 2006). Solar energy is absorbed by chlorophyll and other pigments and is transferred efficiently to the PSII reaction centre where charge separation takes place. This initial conversion of light energy into electrical energy occurs at the maximum thermodynamic efficiency of greater than 70% and generates a radical pair state P680\(^+\)Pheo\(^-\), where P680 is a chlorophyll \(a\) molecule and Pheo is a
pheophytin \(a\) molecule (chlorophyll molecule without a Mg ion ligated into its tetrapyrrole head group). The redox potential of \(P680^+\) is very oxidizing, estimated to be more than +1 V, while that of \(\text{Pheo}^-\) is approximately \(-0.5\) V. The latter is sufficiently negative that, in principle, it could drive the formation of hydrogen. Instead, the reducing equivalent is passed along an electron transport chain to PSI (figure 2), where it is excited by the energy of a second red photon absorbed by a chlorophyll molecule, known as P700, to give a redox potential of \(-0.7\) V or more. In this way, sufficient energy is accumulated to drive the fixation of carbon dioxide, which not only requires the generation of the reduced 'hydrogen carrier', nicotinamide adenine dinucleotide phosphate (NADPH\(_2\)), but also the energy-rich molecule adenosine triphosphate (ATP), formed by the release of some energy during electron transfer from PSII to PSI (in the form of an electrochemical potential gradient of protons; Blankenship 2002). The \(P680^+\) species generated in PSII drives the splitting of water. It does so by extracting electrons from a catalytic centre composed of a cluster of four manganese (Mn) ions and a calcium ion (Ca\(^{2+}\)). The splitting of water into dioxygen and reducing equivalents is a four-electron process and therefore PSII must absorb four photons (4\(h\nu\)) to drive this reaction,

\[
2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 4e^-.
\]

The reducing equivalents leave PSII in the form of plastoquinol (PQH\(_2\)), while the dioxygen is released into the atmosphere,

\[
2\text{H}_2\text{O} + 2\text{PQ} \rightarrow \text{O}_2 + 2\text{PQH}_2.
\]

The efficiency of this reaction is high being almost 50% when driven by the energy of red photons, but decreases to approximately 30% when taking into account the fact that light is absorbed across the whole solar spectrum. Of course, in photosynthetic organisms, the reaction can only proceed continuously when the PQH\(_2\) molecules are oxidized by the light absorbed by PSI, thus allowing the hydrogen to be transferred to carbon dioxide.

In many ways, the photosynthetic reaction centre of PSII and also those of PSI and anoxygenic photosynthetic bacteria (organisms that do not split water) are highly efficient molecular photovoltaic nanomachines, in that they use light energy to bring about electrical charge separation. The organization of the electron carriers in these nanomolecular devices is optimized to facilitate forward energy-storing reactions and minimizing backward energy-releasing reaction. There is considerable information about these photosynthetic reaction centres that indicates that they are structurally and functionally very similar. Indeed, there are aspects of their design that could be incorporated into an ‘artificial photosynthetic’ device and are similar to certain types of existing photovoltaic systems (Graetzel 2005).

Similarly, the light-harvesting systems of different photosynthetic organisms have common principles for facilitating energy capture across the whole of the visible spectrum and aiding efficient energy transfer to the associated reaction centres with minimum losses of energy. Again, detailed spectroscopic and structural studies have revealed the molecular basis of these systems, details which could also be adopted for designing light-concentrating systems for a new generation of solar energy-converting technologies.
However, it is the water-splitting reaction of PSII that holds the greatest promise for developing new technologies for converting solar radiation into usable energy, particularly in generating hydrogen. The invention of the photosynthetic water-splitting reaction occurred approximately 2.5 billion years ago and was the ‘big bang of evolution’ since, for the first time, living organisms had available an inexhaustible supply of hydrogen (in the form of reducing equivalents) to convert carbon dioxide into organic molecules. In a nutshell, biology had solved its energy problem.

Clearly, using solar energy to split water to produce hydrogen is also the perfect solution for humankind. In principle, the technology exists today to do this.

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Electricity can be generated by photovoltaic solar cells and used to carry out the electrolysis of water. With a solar cell efficiency of 10 and 65% efficiency for the electrolyser system, the overall efficiency would be 6.5%. Electrolysis relies on platinum or other catalysts for gas evolution, which are in limited supply. At present, very little hydrogen is generated by conventional electrolysis, owing to the lower price of electricity generated by conventional means. Similarly, the cost of photovoltaic solar cells marginalizes this route for using solar energy to produce hydrogen. But perhaps a bio-inspired water-splitting catalyst can be devised, which works along similar chemical principles used by PSII.

Owing to the importance of understanding the chemistry of the water-splitting reaction of PSII, there has been an arsenal of techniques employed to probe the molecular mechanisms involved and to investigate the structure of the catalytic centre. Recently, the crystal structure of PSII has been obtained by X-ray diffraction analysis, revealing for the first time the organization of the Mn cluster and details of its protein environment (Barber et al. 2004; Ferreira et al. 2004; Barber 2006). The PSII complex used was isolated from a cyanobacterium called

Figure 4. Organization of the electron transfer cofactors that make up the reaction centre of photosystem II as revealed by X-ray crystallography (Barber et al. 2004; Ferreira et al. 2004). Excitation of the reaction centre via the chlorophylls (Chl) shown in green leads to electron transfer from the special chlorophylls called P_{D1} and P_{D2} to the pheophytin (Pheo) acceptor leading to the radical pair P680^{+}Pheo^{-}. The radical cation of P680 is localized on P_{D1}, while the radical anion is located on Pheo_{D1}. The electron on Pheo_{D1} is rapidly donated to a firmly bound plastoquinone Q_{A} (shown in purple) and then transferred to a second plastoquinone Q_{B} (also shown in purple). This electron transfer is aided by the presence of a non-haem iron located mid-way between them. When the Q_{B} plastoquinone accepts two electrons, it is protonated to plastoquinol (PQH_{2}), which then diffuses from the Q_{B}-binding site into the lipid matrix of the membrane, P680^{+} is reduced by a redox active tyrosine (Tyr_{Z}), which then extracts electrons from the Mn_{3}Ca^{2+}O_{4} cluster that constitutes the oxygen-evolving centre (OEC). These electron transfer processes occur mainly on the D1-side of the reaction centre and the symmetrically related cofactors located on the D1-side are non-functional. Other cofactors shown including the haem of cytochrome b_{559} (Cyt b_{559} shown in red) and the β-carotene molecule (shown in brown) play a role in protecting PSII against photoinduced damage.
**Thermosynechococcus elongatus.** It contained 19 different protein subunits, with the reaction centre, composed of the D1 and D2 proteins, at its heart (figure 3). The crystal structure of PSII revealed the organization of the cofactors involved in primary charge separation in the reaction centre (figure 4). However, the most important outcome of this structural study was the conclusion that three Mn ions of the water-splitting centre seemed to form a cubane-like structure with a Ca\(^{2+}\), where the metals are probably linked by oxo bridges. It was suggested that a fourth Mn ion is linked to the cubane by a mono-\(\mu\)-oxo bridge (figure 3, inset). The precise arrangement of these metal ions will emerge, as higher resolution structures of PSII are elucidated. Surrounding the Mn\(_4\)Ca\(^{2+}\)O\(_4\) cluster are a number of amino acid residues that either provide ligands to the metal ions or act to facilitate hydrogen-bonding networks, which almost certainly play a key role in deprotonation of the substrate molecules (McEvoy *et al.* 2005). A nearby tyrosine Tyr\(_Z\) (residue 161 of the D1 protein) functions as an intermediate electron carrier between the Mn\(_4\)Ca\(^{2+}\)O\(_4\) cluster and P680\(^{+}\). Most of the key amino acids identified in the water-splitting site belong to the D1 protein, although another PSII protein, known as CP43, also provides key residues. All these amino acids are fully conserved in all known amino acid sequences of the D1 protein and CP43, whether they are from prokaryotic cyanobacteria or eukaryotic algae and higher plants. We can therefore assume that there is no variation on a theme for this catalytic centre, which is able to carry out one of the most oxidative and thermodynamically difficult reactions of biology.

With this information, realistic chemical schemes are being proposed for the water-splitting reaction. It has been known for some time that there are at least five intermediate states leading to the formation of dioxygen, known as S-states. The sequential advancement from S\(_0\) to S\(_4\) is driven by each photochemical turnover of the PSII reaction centre, as depicted in the S-state cycle (figure 5).

The progression through the S-states to S\(_4\) results in the storing of four oxidizing equivalents, which are reduced in the final step (S\(_4\) to S\(_0\)) by four electrons derived from two substrate water molecules with the concomitant formation of dioxygen.

Deprotonation of one of the substrate molecules occurs prior to the formation of the S\(_4\)-state. The crystal structure strongly suggests that the water-oxidizing chemistry specifically involves the bimetal site composed of the Mn ion not contained within the cubane (Mn4 in the inset of figure 3) and the Ca\(^{2+}\). It is possible that by the S\(_4\)-state, this catalytic Mn ion has been oxidized to Mn(V) and that the substrate water bound to it has been deprotonated to an oxo. Given that this Mn(V) = O, or possibly Mn(IV)-oxyl radical, is already very oxidizing and is also linked to three other Mn ions poised in high oxidation states (probably all Mn(IV)), the oxo will be highly electron deficient and therefore very electrophilic. This is an excellent situation for a nucleophilic attack by the oxygen of the second substrate water molecule bound within the coordination sphere of Ca\(^{2+}\) to form the O=O bond of molecular oxygen (figure 6). The distance between the two metal ions of approximately 4 Å is compatible with this mechanism. More details of how this reaction is likely to occur have been formulated by McEvoy & Brudvig (2004), McEvoy *et al.* (2005) and, more recently, by Siegbahn (2006) and Sproviero *et al.* (2006).
5. Artificial photosynthesis

While some progress has been made in mimicking photosynthesis in artificial systems, researchers have not yet developed components that are both efficient and robust for incorporation into a working system for solar fuel production.

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To date, the main focus of research has been to design and synthesize molecular systems consisting of electron donors and acceptors and mimic light-driven charge separation, which occurs in photosynthetic reaction centres. These studies have allowed in-depth analyses of the dependencies of electron transfer efficiency on the physical and chemical properties (donor/acceptor distance and orientation, free energy of the reaction and electronic interactions) of the system, thus providing basic rules for their construction, including the desirability for multi-step charge separation (Moser et al. 1992, 2005; Gust et al. 2001; Imahori et al. 2003).

The bio-inspired systems employ chromophores to absorb light energy analogous with the photosynthetic pigments, such as chlorophyll. Often, however, the chromophores are directly engaged in the electron transfer processes and, in this way, act like the redox active chlorophylls within the photosynthetic reaction centres, e.g. P680 and P700. Having an antenna, or light-harvesting array, without carrying out charge separation itself, is an engineering design adopted by natural photosynthesis to maximize on solar energy absorption. Covalently linked arrays of light-harvesting chromophores that funnel energy to a central site where charge separation can occur have been demonstrated in artificial systems (Liddell et al. 2004). However, the synthesis of such arrays requires significant effort, and it would be desirable to create self-assembly, functional antenna arrays using robust dyes, such as those used as pigments in industrial paints.

Despite the fact that PSII contains the chemical machinery to split water into oxygen and hydrogen, no artificial photochemical system has yet been constructed to mimic this reaction. However, the insights gleaned from the recent structural determination of PSII have major implications for the design of an artificial catalytic system for using solar energy to release hydrogen from water (Heyduk & Nocera 2001; Lewis & Nocera 2006). The hydrogen produced could be used directly as a source of energy, but could also be used, as it is in photosynthesis, to reduce carbon dioxide to other types of fuels, such as methane (Hirose et al. 2003). Artificial catalysts designed to reproduce the reactions of PSII may also have to incorporate other bio-inspired features, particularly the employment of light-harvesting systems that can capture the energy of all the colours of the visible solar spectrum and efficiently use this energy to drive the chemistry of water splitting. Our understanding of the nature of photosynthetic light harvesting and how they are coupled to reaction centres is at an advanced level, such that the basic principles of their construction and operation are now well established.

The challenge is to have a molecular arrangement in the artificial catalyst that will allow the dioxygen bond to form. Recently, it has been demonstrated that catalysts based on Mn are capable of water splitting and the generation of dioxygen occurs when a strong oxidant is used to drive the Mn into high oxidation states (believed to be Mn(V); Pecoraro et al. 1998; Limberg et al. 1999). Light-driven water splitting can, however, be accomplished using semiconductor-based photocatalysis, as first demonstrated by Fujishima & Honda (1972). These workers initially used TiO₂, but it was necessary to replace TiO₂ by SrTiO₃ in order to produce both hydrogen and oxygen. Since these reactions are driven by high-energy UV radiation, they are of limited use for fuel generation. Current efforts are being made to dope these types of semiconductors with organic or inorganic compounds so that they can carry out photo-driven redox reactions using visible light (Kato et al. 2003; Graetzel 2005). Similar types of semiconductor technologies are being developed to catalyse the photoelectrocatalytic reduction of carbon dioxide.
6. Conclusions

It is anticipated that the global demand for energy will be more than double by the mid-century and perhaps more than triple by the end of the century. Satisfying this demand will be necessary in order to achieve vibrant technological progress, economic growth and, most importantly, political stability over the coming decades. Already we are faced with the prospect of catastrophic climate change due to the release of carbon dioxide into the atmosphere brought about by the burning of fossil fuels (Climate Change 2005). In the short term, we must exploit all technologies known to us to produce energy, while at the same time reduce carbon dioxide emission. The nature of the mix of various technologies will vary between different countries depending on their resources with some dominating (e.g. geothermal in Iceland, biomass in Brazil, etc.). Coupled with this challenge is the need to use energy more efficiently. Here again, we can learn from nature. In biology, the ‘combustion’ of fuel (food) is accomplished isothermally by highly efficient and subtle biological reactions, involving a host of clever catalysis (enzymes). For example, when the hydrogen of glucose is combined with oxygen during the process of respiration to produce water and carbon dioxide, 38 ATP molecules are produced. ATP is the energy currency of cells. Since ATP stores 12 kcal per mol of usable energy and the energy content of glucose is 672 kcal per mol, the efficiency of energy conversion is 68%. It therefore seems to me that humankind should follow biology’s example and strive to develop new technologies that have efficiencies which match those achieved in biology.

For the long term, we will have very few options to replace fossil fuels and satisfy the increased energy demands of a global population approaching 10 billion. Renewables such as hydropower, wind, wave, geothermal and biomass will not be able to supply energy at a mean annual rate of 20 TW, even when taken together (Lewis 2005; Lewis & Nocera 2006). Our Sun is the champion of energy sources, i.e. delivering energy to Earth far in excess of humankind’s needs.

The enormous untapped potential of solar energy is an opportunity that should be addressed with urgency. Biology chose this energy source and there is no reason why those chemical reactions devised by photosynthetic organisms cannot be mimicked by ingenuity of humans. We already have a considerable knowledge base to start from and the emerging nanotechnologies to exploit. With a concerted input of motivated scientists trained in different disciplines, it should be possible to move the technologies of solar energy cells forward. The recognition of a Manhattan- or Apollo-like initiative to develop new sustainable energy technologies in response to the CO$_2$ problem, as suggested by Hoffert et al. (1998) (also see Hoffert et al. 2002 and Lewis 2005), was the driver of a recent US DOE-sponsored report (2005). This report detailed areas of solar energy research that need to be urgently explored and which has generated substantial funding in the USA.

7. Recommendations

Photosynthesis is the most successful solar energy converter on Earth. It provides energy for all life on our planet and is the source of the fossil fuels that drive our technologies. The time has come to exploit our considerable knowledge
of the molecular processes of photosynthesis and plant molecular biology to attack the challenge of providing non-polluting renewable energy for the future benefit of humankind. There are two avenues that must, in my opinion, be explored with vigour, which are as follows.

**Biomass.** To continue to improve our knowledge of the molecular genetics that underlie plant metabolism, growth and survival, with the view to engineering designer crops with high solar energy conversion efficiencies, but having minimum requirements for fertilizer, insecticides and water. Genetic manipulation of the chemical composition of these robust energy plants will facilitate their use in a variety of ways ranging from the production of liquid biofuels and biogas to high-value chemicals for the chemical and pharmaceutical industries. Coupled with these objectives, there must be improvements of appropriate technologies to exploit biomass in a range of different ways. These developments will in part be driven by market forces and in part by the policies of world governments and organizations to reducing CO₂ emissions with the purpose of minimizing human-made global climate change.

**Artificial photosynthesis.** To establish, as a matter of urgency, a multidisciplinary effort to construct robust artificial systems able to efficiently use solar energy to split water and have the capacity to either release the hydrogen or use it to reduce carbon dioxide to liquid fuels. In recent years, there have been significant developments in understanding the molecular processes of photosynthetic energy conversion and water splitting. This knowledge base can now be combined with that of photovoltaics and nanotechnology to construct an ‘artificial water-splitting’ system with a solar energy conversion efficiency of at least 10%. If this artificial system, or related photovoltaic system, converts solar energy at 10% efficiency, then it would cover in total 0.16% of the Earth’s surface to satisfy a global energy consumption rate of 20 TW (Lewis 2005). Unlike a biological leaf, this artificial equivalent could, for example, be placed in the arid...
desert areas of our planet, whose total capacity well exceeds that required. Owing to this, the ‘artificial leaf’ will not compete for cultivatable land in the way that massive biomass production will. Since this is a long-term goal with benefit to all, it will need investment by the international community in a way similar to that which nuclear fusion research enjoys through the recent ITER initiative (2005; http://www.iter.org/).

Finally, I refer the reader to figure 7 and quotes from Jules Verne’s novel L’Ile Mysterieuse written in 1875:

I believe that water will one day be used as a fuel, because the hydrogen and oxygen which constitute it, used separately or together, will furnish an inexhaustible source of heat and light. I therefore believe that, when coal deposits are oxidised, we will heat ourselves by means of water. Water is the coal of the future.

and from Professor Giacomo Ciamian (1912) of the University of Bologna published in Science:

On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and humankind is.

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