Photosynthesis: From Natural Towards Artificial *

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Abstract. Photosynthesis, the natural process that yields food, fuel and fibre, spans physical and biological sciences, spatially from atomic scales to the global and temporally from electronic transitions to the evolutionary time frame. Photosynthesis is highly efficient in its primary energy capture, but much less so in terms of conversion to crop yield. The natural photosynthetic system provides fertile ground for exploring and dissecting partial processes that may be mimicked in artificial systems for human needs, perhaps with improved efficiency. Future developments are limited only by the imagination.

1. Oxygenic Photosynthesis in Nature

‘Photosynthesis: the plant miracle that daily gives us bread and wine, the oxygen we breathe, and simply sustains all life as we know it.’

(Theme statement of the 12th International Congress on Photosynthesis, Brisbane, 2001)

1.1. EVOLUTION

The earth was formed about 4.6 billion years ago. The earliest fossil evidence of life on Earth occurs in rocks found in Western Australia, in a place called North Pole. There one finds 3.5 billion-year-old remains of stromatolite reefs built by single-cell blue-green algae. By precipitating lime and trapping silt, these blue-green algae built limestone reef structures in ancient tidal mudflats. Today, living descendants of these blue-green algae are still building stromatolite reefs, as can be seen in Shark Bay, Western Australia.

A notable feature of these blue-green algae, nowadays called cyanobacteria, is that they split water to evolve oxygen and fix CO₂ during photosynthesis. Earlier photosynthetic bacteria during evolution had only used sunlight to combine CO₂ and free hydrogen to make simple sugars. Cyanobacteria were able to use the plentiful water as raw material, evolving oxygen as a by-product. They went even further: by invading multicellular organisms they eventually turned into the green

* Dedicated to the memory of Sir Rutherford (Bob) Robertson

Figure 1. A schematic diagram of the chloroplast, showing a double-membrane envelope enclosing a system of inner membrane sacs (thylakoids). Thylakoids stack together to form grana. The internal aqueous phase of thylakoids (lumen) is continuous, while the external aqueous phase (stroma) contains many photosynthetic enzymes. The thylakoid membranes themselves contain components of the electron transport chain.

chloroplasts in the cells of leaves! As a result of oxygenic photosynthesis, the oxygen concentration in the atmosphere gradually increased to the level today. In turn, the oxygen in the atmosphere gives rise to the ozone layer that protects organisms against harmful ultraviolet radiation.

1.2. THE PHOTOSYNTHETIC APPARATUS

To orient ourselves, we imagine zooming in on the chloroplast: from a tree, to a leaf, to a cell in a leaf, then to the many chloroplasts contained in a single cell. A chloroplast has an envelope enclosing a system of inner membranes where the light-induced reactions take place. These continuous inner membranes stack up in places under the influence of van der Waals attraction, that overcomes the electrostatic repulsion between membrane surfaces that carry net negative charges on proteins, until the inter-membrane distance is determined by a short-range hydration repulsion [1]. The stacking of these membranes, depicted in Figure 1, may also be promoted by the requirement to maximize entropy of the system as a whole [2]. In addition, specific interactions [3] may also contribute to the membrane structure. In any case, membrane stacks are an almost universal feature of chloroplasts of leaves; they may serve to fine tune photosynthetic efficiency [4, 5].

These inner membranes are called thylakoid membranes, from a Greek word meaning sacs, for they are flattened sacs with an inner and an outer aqueous phase. Thylakoid membranes contain bilayer-spanning proteins, some of which provide a scaffold that non-covalently holds the light-harvesting pigments such as chlorophylls and carotenoids, while others carry out some of the enzymic reactions of photosynthesis. The aqueous phase external to the thylakoids is called the stroma.

Figure 2. The time scales of photosynthetic events beginning with light absorption and extending to long-term photosynthetic adaptation to the environment. Depending on the time scale of interest, photosynthesis can be studied from the perspective of a number of scientific disciplines.

It is a space containing many enzymes involved in turning CO_2 into precursors of the final products (carbohydrates), and other enzymes involved in scavenging unwanted, reactive oxygen species. The inner aqueous phase, called the lumen, is continuous among the thylakoids; it too is a space where a great deal of biochemical activity takes place, notably the deposition of protons as a temporary storage of electrochemical energy.

1.3. THE TIME SEQUENCE OF EVENTS IN PHOTOSYNTHESIS

Photosynthesis begins with the absorption of photons by pigment molecules. A number of events occur after photon absorption in a time sequence that is sometimes described as the 'eras of photosynthesis' [6], as shown in Figure 2. In the era of radiation physics (ps to ns after photon absorption), primary charge separation (electron transfer from a primary donor to a primary acceptor) is usually followed by charge stabilization (forward transfer of the electron to a more stable acceptor and replenishment of the electron lost by the primary acceptor). Primary charge separation occurs in competition with other pathways of dissipating the excited states of pigment molecules, such as radiationless de-excitation, and, to a small extent, chlorophyll fluorescence emission. In the era of physical chemistry, secondary

Figure 3. A diagram qualitatively showing energy levels in a chlorophyll molecule. Transition from the ground state to the first or second excited singlet state is induced by red and blue light, respectively. Automatic conversion from the second excited state to the first excited state occurs by emission of heat. From the first excited state useful photochemical conversion takes place, in competition with heat dissipation or fluorescence emission. Occasionally, the long-lived triplet excited state is produced, in which case safe de-excitation of the triplet state is necessary in order to avoid producing harmful singlet oxygen.

electron transfers occur in the realm of oxidation-reduction (redox) reactions (ns to ms). In the era of biochemistry, enzymic reactions occur in the milliseconds to minutes time scale. Finally, plant growth that depends directly on photosynthesis goes on at a slower time scale still. Photosynthesis, by spanning the realms of photophysics, physical chemistry, biochemistry, through to plant physiology and even plant evolution, is truly an interdisciplinary branch of science.

2. Physicochemical Processes in Natural Photosynthesis

2.1. LIGHT ABSORPTION

Of the dual nature of light, it is the particle character that is relevant in electron transfers in photosynthesis. Although absorption of blue light by chlorophyll gives rise to the second excited singlet state, the second excited state soon converts to the first excited state by heat emission (Figure 3). From the first excited state, also induced by absorption of red light, useful photochemical conversion or wasteful heat or fluorescence emission may occur. In this sense, a blue photon is equivalent to a red photon; it is the number of absorbed photons that matters, rather than the original energy of each visible photon.

Absorption of light by chlorophyll is relatively poor at green wavelengths, and enhanced reflection in the green region is the reason for leaves being green. However, even green light is absorbed quite well because multiple scattering within a leaf ensures a long path length and a high probability of absorption. Thus, a leaf typically absorbs 85% or more of incident white light and about 70% of green light.

2.2. EXCITATION ENERGY TRANSFER

Each chlorophyll molecule in a leaf exposed to full sunlight absorbs about 5 photons per second. If each chlorophyll molecule were to have its own set of components to split water, each set would be idle most of the time – not an efficient use of resources. Nature has evolved a mechanism whereby many (about 200) chlorophyll molecules cooperate to funnel any absorbed photons towards a reaction centre where the energy of the photons can be trapped and utilized. These chlorophyll molecules, therefore, act like the antenna of a telescope: a photon absorbed by any pigment molecule initiates excitation energy transfer towards the reaction centre.

In order for the antenna to work, the chlorophyll molecules must be held at an optimal distance apart. When too close together, chlorophyll molecules will form aggregates with additional energy levels that favour de-excitation by heat emission. When too far apart, they cannot efficiently funnel the energy to the reaction centre.

The optimal centre-to-centre distance between the chromophore heads of chlorophyll is achieved using a protein scaffold that non-covalently ligates the pigment molecules in position. Kühlbrandt and Wang [7] have used electron crystallography to determine the three-dimensional structure of the main light-harvesting chlorophyll *a/b*-protein complex of plants; this is the peripheral antenna that contains half of the world's chlorophyll. The single complex (monomer) contains a protein with three membrane-spanning α helices. The protein carries 14 chlorophyll molecules, the centre-to-centre distance between neighbouring chlorophyll molecules being 9–14 Å. It is believed that the native form of this antenna system consists of a trimer of three single complexes. Then there may be four or five trimers serving each Photosystem II (PS II) reaction centre where oxygen is evolved. The entire effective antenna system may consist of about 200 chlorophyll molecules, depending on environmental light conditions.

Energy is thought to be transferred between the chlorophyll molecules by two mechanisms [7]:

1. De-localized exciton coupling. In this mode, effective at distances up to 20 Å, energy oscillates between donor and acceptor pigment molecules without being localized on either. This is the likely mode of transfer within a monomer;
2. Förster transfer. In this mode, still effective at distances much greater than 20 Å, a long-range dipole-dipole interaction occurs in which an acceptor molecule is excited while the donor molecule falls to its ground state. This is the likely mode of transfer between monomers within a trimer and perhaps between adjacent trimers.

Photons absorbed by the antenna are funnelled towards the reaction centre. Pigment molecules that are closer to the reaction centre have excited states of slightly lower energy because of the nature of the local environment in the scaffold, thus tending to give one-way traffic. In this way, excitation energy migrates from the peripheral antenna, via minor light-harvesting chlorophyll-protein complexes, towards the inner antenna surrounding the reaction centre. In the inner antenna of

PS II, chlorophyll *a* molecules are also held in a scaffold with centre-to-centre distance of 8.5–13.5 Å as determined by X-ray crystallography [8]. This range of distances is the same as that (9–14 Å) in the peripheral antenna determined by electron crystallography [7]. This must be the optimal range for excitation energy transfer with minimal thermal losses.

2.3. CHARGE SEPARATION

Since de-excitation by fluorescence emission typically takes about a nanosecond, any useful trapping of the excitation energy must occur in a time much shorter than 1–2 ns. Happily, when an exciton arrives at the PS II reaction centre, the primary charge transfer step in the reaction centre takes only a few picoseconds. The PS II reaction centre contains redox components, including P680 (one chlorophyll *a* molecule in a special pair), pheophytin (Pheo, like a chlorophyll molecule, but without the Mg atom) and the first quinone acceptor of an electron (Q_A). These redox cofactors are bound to the structure of the so-called D1/D2 proteins in PS II. Excitation energy reaching P680 causes primary charge separation.

forming a pair of free radicals $P680^+ \text{ Pheo}^-$. The electron transfer from $P680^*$ to Pheo takes about 3 ps, the speed of electron flow in this primary step being approximately equal to that of a supersonic jet.

The maximum efficiency with which PS II undergoes a charge separation upon excitation can be estimated as follows. Consider the special chlorophyll P680 in the PS II reaction centre with a first excited state energy $E_{680} = hc/\lambda$, where h , c and λ ($= 680$ nm) are Planck's constant, the speed of light and wavelength, respectively. P680 is surrounded by, say, 200 antenna chlorophyll molecules which absorb maximally at a slightly shorter wavelength, say, 670 nm. An exciton in PS II is more likely to reside on P680 than an antenna chlorophyll molecule by a factor of $\exp[(E_{670} - E_{680})/(kT)] = 3.35$ at $T = 300\text{K}$, where k is the Boltzmann constant and T the absolute temperature. That is, the fraction of time that an exciton resides on P680 is $3.35/201 = 0.017$. In the absence of any dissipation of the excited state other than by fluorescence, the mean lifetime of the excited state of chlorophyll is about 15 ns, of which $0.017 \times 15 = 0.25$ ns is available for the reaction centre to initiate charge separation. This is ample time for charge separation which requires only about 10 ps ($k_p \approx 10^{11} \text{ s}^{-1}$) for photochemical conversion. Meanwhile, the residence time of 0.25 ns that an exciton spends at P680 decreases the fluorescence lifetime from 15 ns (in the absence of any other quenching pathways) to 0.25 ns [$k_f = 1/(2.5 \times 10^{-10} \text{ s}) = 4 \times 10^9 \text{ s}^{-1}$]. Therefore, the efficiency of charge separation is $k_p / (k_p + k_f) \approx 96\%$, achieved in low light. However, various losses of photosynthetic efficiency downstream, especially in high light, result in an overall efficiency of 1–2% for the conversion of light into chemical energy stored in harvestable carbohydrates.

2.4. CHARGE STABILIZATION AND CHARGE RECOMBINATION

Following charge separation, the secondary step that stabilizes the charge transfer takes only a further 300 ps or so:

Before charge stabilization, however, there is a good chance that charge recombination will yield the singlet excited state again (sometimes the long-lived triplet state or even the ground state directly):

Because of the reversible nature of trapping excitons and recombination between the redical pair ($\text{P680}^+ \text{Pheo}^-$) to return an excited state, there is said to be an equilibrium between excitons and the radical pair, a model now widely accepted [9].

2.5. SECONDARY ELECTRON TRANSFERS AND PROTON MOVEMENTS

The initial donation of an electron by P680 triggers a series of redox reactions, in which the electron is transferred along a chain of components until it is finally accepted by NADP^+ (oxidised nicotinamide adenine dinucleotide phosphate) to give the reduced form NADPH. Figure 4 shows an arrangement of components of the electron transport chain in a thylakoid membrane. Prior to the reduction of NADP^+ , another photosystem (called PS I) also undergoes a photon-induced charge separation, boosting the free energy of the electron to a level sufficient for the reduction of NADP^+ . Thus, an electron from P680 flows to NADP^+ in two uphill steps in series, one at each photosystem.

Meanwhile, P680^+ extracts an electron from water, with the help of intermediary components. After four cycles, each requiring two photons (one in PS II and one in PS I), one oxygen molecule is evolved for a pair of water molecules split:

Thus, a minimum of eight photons is required to evolve one O_2 molecule; in practice, ~ 9.5 photons are needed in low light.

The protons released in this reaction are not wasted. They, together with other protons released in the inner aqueous phase of thylakoids in downstream redox reactions, drive the synthesis of adenosine triphosphate (ATP), catalyzed by the enzyme ATP synthase, nature's smallest motor. The free energy of NADPH and ATP is then finally stored in carbohydrates. In a nutshell, H_2O is an unlimited raw material, and the useful components from split water are the electrons and protons.

Incidentally, in the zigzag path of electron flow in the thylakoid membrane (Figure 4), there are three places where the electron flows from the inner side towards the outer side of the thylakoid membrane: one at PS II, one at PS I and one at the

Figure 4. A schematic diagram of the electron transport chain in thylakoid membranes. Electrons originating from split water molecules are transported through PS II, the cytochrome *bf* complex, PS I and other carriers before being accepted by NADP^+ to form NADPH. Protons are deposited in the lumen as a result of water oxidation and oxidation of plastoquinol (PQH_2). Protons accumulated in the lumen drive ATP synthesis. The products NADPH and ATP are used in CO_2 fixation in the stroma.

cytochrome *bf* complex, a protein complex that shuttles electrons from PS II to PS I. These steps of 'vectorial' electron transfer are electrogenic, being able to modify the electric field across the thylakoid membrane.

Modifying the electric field distorts the energy of the excited states of membrane-embedded pigment molecules such as chlorophyll *b* and carotenoids, a phenomenon known as electrochromism. The result is a shift of the absorption peak of a pigment and therefore a change in absorbance at a given wavelength, measurable even in a leaf. The very rapid rise in absorbance at 518 nm on firing a laser flash is a prompt response to the establishment of an electric field across the thylakoid membrane (followed by delocalization along each thylakoid surface); this electric field is set up by both photosystems I and II as electrons are transferred from the inner to the outer side of the thylakoid membrane. There is also a delayed rise in absorbance, attributable to electrogenic electron transfer across the membrane at the site of the cytochrome *bf* complex. Signals such as the electrochromic shift, as well as other absorbance changes associated with redox reactions with cytochromes, allow us to monitor electronic transfers *in vivo* [10].

2.6. PHOTOSYNTHETIC REDUCTION OF CO_2

While thylakoids mediate the 'light reactions' of photosynthesis, enzymes in the stroma catalyse the reduction of CO_2 to a triose, then to a hexose sugar, in the so-called Calvin-Benson cycle. Of these enzymes, ribulose 1,5-bisphosphate carboxylase/oxygenase is the most abundant, and is in fact the most abundant protein in the world. In plants in which the first stable product formed from CO_2 has three carbon

atoms, three ATP and two NADPH molecules are required for the reduction of each CO_2 . The light-induced formation of ATP and NADPH is, therefore, responsible for the production of simple sugars that in turn drive the synthesis of more complex molecules.

3. Some Artificial Photosynthetic Systems

3.1. LIGHT-DRIVEN CHARGE SEPARATION IN A CAROTENOPORPHYRIN-QUINONE MOLECULE

The synthesis of a molecule that mimics the reaction centre in natural photosynthesis was reported in 1984 by 12 scientists from three countries [11]. The molecule consists of three parts in a 'triad'. The porphyrin in the middle traps the light, much like P680 in the natural system; the excited porphyrin donates an electron to a quinone group, becoming an electron hole. Before the electron can jump back, a β -carotene at the other end of the molecule speedily donates an electron to the porphyrin. The result is a charge separation that is relatively long-lived, allowing further secondary reactions to be exploited.

3.2. LIGHT-DRIVEN ATP SYNTHESIS IN A PARTIALLY ARTIFICIAL SYSTEM

One reaction that exploits the above triad molecule involves aligning the triad molecules to span the membrane of a liposome (vesicle). A lipophilic quinone in the membrane alternates between its oxidized and reduced forms to couple the charge separation to a proton deposition in the internal aqueous phase of the liposome, which is analogous to the thylakoid lumen. An ATP synthase, purified from spinach chloroplasts, catalyses the production of ATP using the pH gradient (strictly the proton electrochemical gradient) established across the liposome membrane when light is supplied [12] (see also Figure 5).

3.3. SPINNING MINI-HELICOPTER BLADES

A further step is to make use of the ATP that is generated. The ATP synthase is nature's smallest motor. It is known that when it runs in the ATP hydrolysis mode, the 'knob' (F_1) portion of the enzyme rotates, as can be seen at the website <http://www.res.titech.ac.jp/seibutu/nature/flrotate.html>. Montemagno and colleagues anchored this protein rotor on a surface, and fused tiny metal bars to the end of the shaft. When fed ATP exogenously or from the liposome/ATP-generating system described above, the researchers observed the bars spinning [13].

3.4. SYNTHETIC REDOX PROTEIN FOR STUDYING INTRAPROTEIN ELECTRON TRANSFER

Dutton and colleagues [14] have used repeats of the aminoacid sequence (heptad)

Figure 5. Coupling charge separation in a carotenoporphyrin-quinone molecule to redox cycling of a quinone molecule, resulting in the pumping of protons into the inner aqueous phase of a liposome. The accumulated protons are used by the ATP synthase to make ATP. (Re-drawn from [12].)

alanine-glutamate-glutamate-leucine-leucine-lysine-lysine

to construct an amphipathic α -helix of 7 turns, a length comparable to the trans-membrane helices of many natural electron-transfer proteins, with equal numbers of positively-charged lysine and negatively-charged glutamate residues directed towards one face, and non-polar groups of alanine and leucine directed towards the opposite face. These helices self-assemble in aqueous solution to form a 4-helix bundle with a hydrophobic interior. Alternatively, two helix-turn-helix sequences can be assembled into a four-helix bundle. Further, aminoacids (e.g. histidine) can be strategically placed in the interior of a bundle to secure redox components (eg metal porphyrins such as Zn-chlorin [15] and hemes). By bringing such redox partners to within 4–14 Å, rapid electron tunnelling can be studied and compared with electron transfer in natural proteins.

3.5. ELECTRICITY GENERATION IN MICROBIAL FUEL CELLS

A semi-artificial system for generating electricity from glucose has been devised by Park and Zeikus [16]. In one compartment from which oxygen is excluded, a bacterial cell culture (or a mixed culture of anaerobic bacteria in sewage sludge) uses the reducing power of glucose to reduce a dye molecule, neutral red. Reduced neutral red molecules deliver electrons to an anode. In another compartment, separated from the first by a cation-selective membrane, ferricyanide is reduced to ferrocyanide at the cathode; ferrocyanide is then oxidised back to ferricyanide in the presence of oxygen in this compartment. This 0.6 V biofuel cell can deliver up to 17 mA.

Figure 6. A hypothetical electrochemical cell that electrolyses water at the anode and reduces NADP^+ at the cathode. A proton current through ATP synthase completes the circuit, producing ATP in the same compartment as the NADPH. This electrochemical cell produces essentially the same products as a thylakoid, and could be viewed as an artificial thylakoid. However, it is different from its natural counterpart in that light-harvesting and conversion to electricity can be spatially separated from the electrochemical reactions.

3.6. AN ARTIFICIAL THYLAKOID RUNNING ON ELECTRICITY?

The reverse of the above biofuel cell, namely, the synthesis of carbohydrates from electricity will be much more difficult. This does not, however, prevent from us from speculating how such a system may be built one day. A partial system may look something like Figure 6. In one compartment, water is electrolysed at the anode, releasing oxygen and protons, as well as electrons that flow towards the positive terminal of the power source. In the other compartment NADP^+ is reduced to NADPH via suitable redox-coupled reactions at the cathode, at the same time consuming protons. To successfully form NADPH, it will be necessary to minimize undesirable side reactions, particularly those involving oxygen. Possibly, enzymes will need to be used to improve the specificity. Assuming that NADPH can be produced, one then needs to produce ATP as well. A consequence of the reactions in both compartments is that a proton electrochemical gradient is established across the membrane that separates the two compartments. If one places ATP synthase in the membrane in the right orientation, the proton concentration gradient can be harnessed to produce ATP in the same compartment where NADPH is formed.

Such an electrochemical cell is essentially an artificial thylakoid. The difference is that, instead of utilizing light, the electrochemical cell uses electricity to form NADPH and ATP. An important advantage of the electrochemical cell over the thylakoid is that light-harvesting, eg by photovoltaic devices spread over large areas at remote locations, can be spatially separated from the formation of NADPH and ATP which takes place in a confined space. The NADPH and ATP, produced in the

same compartment, may then be used to drive CO₂ fixation into the precursors of carbohydrate synthesis, provided one is able to organize at least 15 other enzymes to cooperate!

4. The Future

In 1969, Rabinowitch and Govindjee [17] remarked that ‘the ultimate possibility of *in vitro* photosynthesis is beckoning’. It is reasonable to assume that the application of *in vitro* photosynthesis will heavily draw upon knowledge gained from natural photosynthesis. In the three decades since, a great deal of progress has certainly been made in understanding the photosynthetic apparatus and its function, including almost atomic-resolution structures of PS II and its light-harvesting complex and of PS I. Also in this period, no fewer than three Nobel prizes have been awarded to discoveries related to photosynthesis. One therefore expects far-reaching advances to be made in the area of artificial systems that mimic the function of natural photosynthetic components. However, as the area is still in its infancy and the territory largely uncharted, it is impossible to predict when artificial photosynthesis will be perfected.

Will artificial photosynthesis bring practical benefits? On the one hand, as Richard Feynman said, science is neither good nor bad, and the same key will open the gates of hell and heaven. On the other, if the dream of the late Rutherford Robertson, an eminent Australian scientist, comes true, a highly significant outcome of photosynthesis research may be, in 50–100 years from now, the artificial production of foods to partly circumvent the problems of shortage of agricultural land and irrigation water. In that case, ‘science can play a vital role, helping us to leave the world a better place for having lived’ [18].

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