

REVIEW

Learning from photosynthesis: how to use solar energy to make fuels

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This short review describes how the basic reactions of photosynthesis can be broken down into four distinct steps. The current understanding of the molecular mechanisms of these steps, within light-harvesting complexes and reaction centres, in this process is discussed as a framework for the construction of artificial systems capable of using solar energy to make fuels.

Keywords: photosynthesis; solar energy; artificial photosynthesis; light-harvesting; reaction centres; solar fuel

1. Introduction

One of the major challenges in the area of renewable energy is to devise sustainable systems capable of using solar energy to produce dense, portable fuels, especially for flying or shipping. There are already many ways to produce electricity renewably: the big issue is how to make fuels.

There is, however, one major chemical process on Earth that does already use solar energy to make fuel and that is photosynthesis [1]. This biological process ultimately provides most of the ‘fuel’ that powers all life on Earth and even, as a by-product, produces all the oxygen that we breathe. It is possible to analyse the reactions that take place during photosynthesis and to use this information to devise novel ways to harness solar energy for fuel production.

This paper summarizes the basic reactions of photosynthesis and presents a framework of how to think about replicating its reactions. A basic fundamental property of the biological process is that it self-assembles and self-repairs. At present, reproducing these special features in an artificial system is a long way off. A major hurdle to be overcome, therefore, is to be able to build enough robustness into any proposed artificial system capable of mimicking the essential features of photosynthesis so that it will survive long enough to be both practical and, of course, affordable.

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Table 1. Breakdown of the overall process of photosynthesis into four distinct steps.

| | what reaction? | location | function |
|--------|-------------------------------|--|---|
| step 1 | harvesting solar energy | light-harvesting complexes | efficient collection of solar energy and its transfer to the reaction centre |
| step 2 | light-induced redox reactions | photosynthetic reaction centres | transmembrane charge separation: positive charge on one side of the membrane and negative charge on the other |
| step 3 | oxidation of water | oxidizing side of the photosystem II reaction centre | to use water as a ubiquitous source of electrons |
| step 4 | reductive synthesis of fuels | either in the chloroplast stroma for CO ₂ fixation, or the reducing side of photosystem I for hydrogen production | to produce a fuel that can be used as an energy store |

2. Brief summary of photosynthesis

Photosynthesis is the process by which plants, algae and some bacteria are able to use light energy to reduce atmospheric carbon dioxide to carbohydrate. In oxygenic plant photosynthesis, the reductant used in the process comes from water and as a result oxygen is produced. Classically, photosynthesis can be thought of as the continuation of two partial processes called ‘light’ and ‘dark’ reactions [2,3]. In the light-reaction, solar energy is absorbed and used to produce ATP and reduce NADP. In the dark-reaction, these two products are consumed by the Calvin–Benson–Bassham cycle to reduce CO₂ to carbohydrate. The light-reactions take place in, on and across the thylakoid membrane in plant chloroplasts, while the dark reactions are confined to the stromal phase inside the chloroplast.

However, for the purpose of this study, it is more useful to break down the photosynthetic reactions into four steps [4] (table 1). The first is light harvesting. The second is using this harvested light energy to drive a charge separation reaction. This takes place in photosynthetic reaction centres. Then the positive charges are used to extract electrons from water (the third step), and the negative charges are used to reduce CO₂ to a fuel (the fourth step). By thinking about photosynthesis in these four stages, it allows each one to be separately considered. It is far easier to try to devise ways of replicating each stage independently than to try to reproduce the whole process at once. It should be noted that in the native process in plants and algae, there are actually two types of reaction centres.

3. Light-harvesting

In the past few years, there has been a great deal of progress in our understanding of photosynthetic light-harvesting. There are high-resolution X-ray crystal structures for a wide range of different types of antenna complexes and their

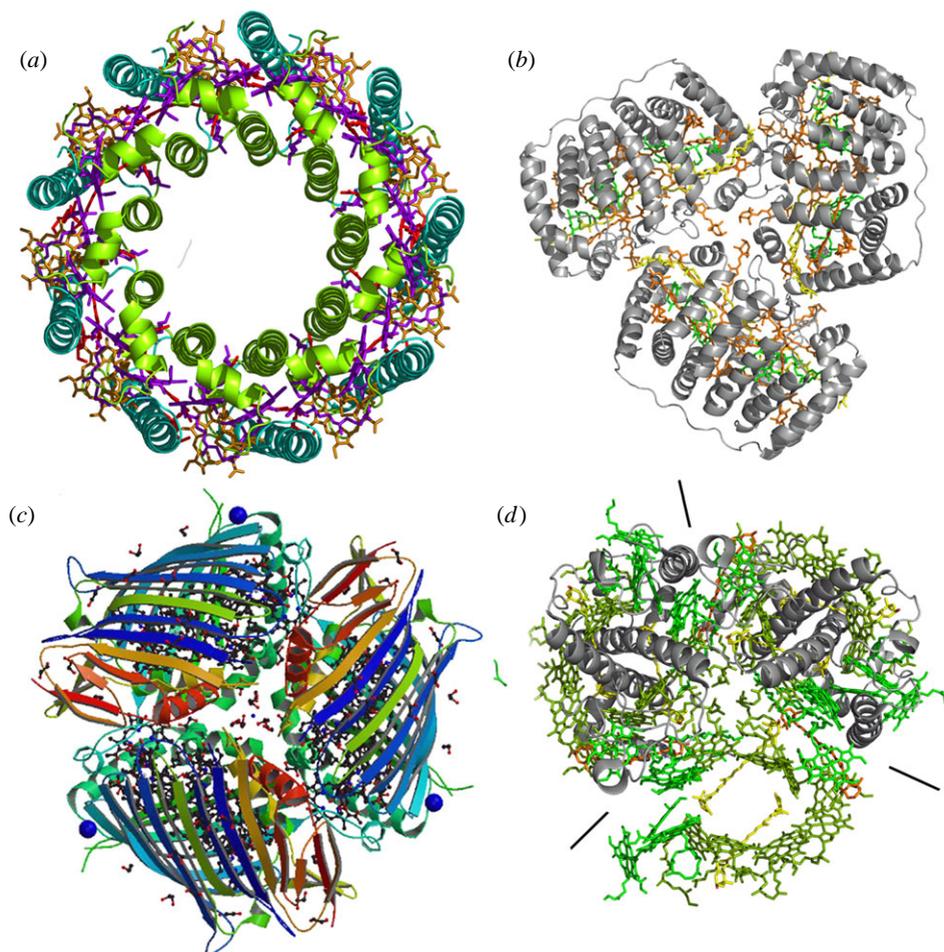


Figure 1. X-ray crystal structures of four different light-harvesting complexes. (a) The LH2 complex from *Rhodospseudomonas acidophila* strain 10050 [5], pdb 1KZU. (b) The peridinin-chlorophyll protein (PCP) from *Amphidinium carterae* [6], pdb 1PPR. (c) The Fenna-Matthews-Olson protein from *Prosthecochloris aestuarii* [7], pdb 3EOJ. (d) The light-harvesting complex II (LHCII) from spinach [8], pdb 1RWT. Note that the protein scaffold has been removed from one of the trimer subunits to reveal the pigment organization.

energy transfer reactions have been time-resolved from a few femtoseconds out to much longer times. A range of these structures is shown in figure 1. Often in biology, a comparative study of a family of proteins that carry out a similar reaction will reveal important general features. When this approach is carried out with light-harvesting complexes, few, if any, general structural features can be seen. The different types of antenna structures have very different protein structures and very different arrangements of their light-harvesting pigments. Indeed, in the case of the chlorosomes (figure 2) from green sulphur bacteria, no protein is actually involved in the light-harvesting complex at all. Why should this be? The reason is that the physics of energy transfer is rather tolerant. For example, when a molecule of chlorophyll is excited by light the first excited

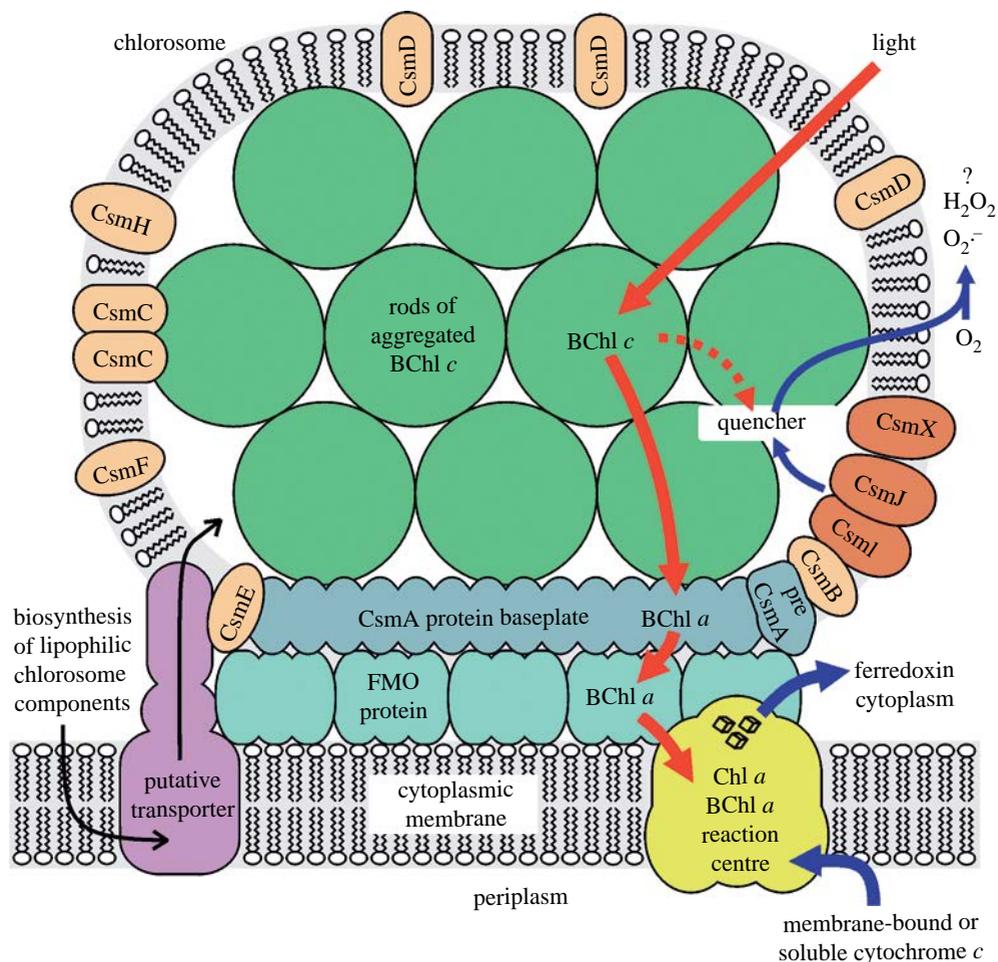


Figure 2. Schematic of the photosynthetic apparatus in *Chlorobium tepidum*. Excitation energy transfer is shown by red lines and electron transfer is shown by blue lines. Adapted from Frigaard & Bryant [9].

singlet state lasts for 1–2 ns and if the productive energy transfer reactions take place significantly faster than this, then the light-harvesting process can be very efficient. Once a photon is absorbed, a ‘clock’ starts ‘ticking’ and then energy transfer must outcompete this clock. As long as the chlorophyll molecules in an antenna complex are positioned sufficiently close to each other, with the transition dipoles of the first excited singlet state sufficiently well aligned relative to each other, the light-harvesting process can outcompete the natural radiative lifetime of the excited singlet state. This is encouraging for people wishing to make artificial light-harvesting systems, because there will be a great deal of structural flexibility and, therefore, there will be many possible solutions.

It is also worth pointing out that a great deal of the biological variation in the structures of the native light-harvesting complexes comes from the need that each different type of photosynthetic organism has to be able to absorb solar energy in the region of the solar spectrum that is related to the precise

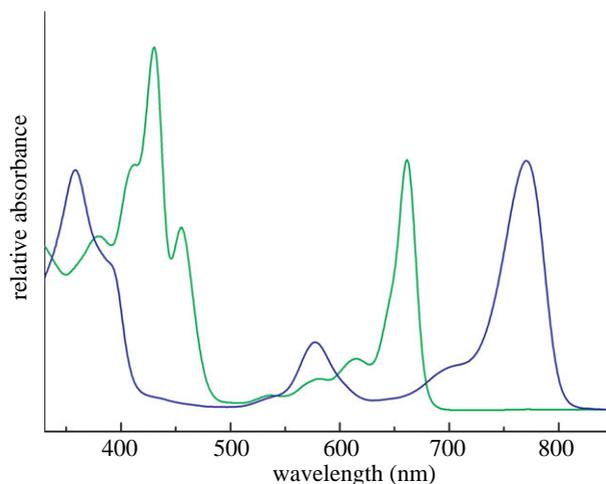


Figure 3. A comparison of the absorption spectra of chlorophyll *a* (green curve) and bacteriochlorophyll *a* (blue curve).

ecological niche in which they grow [10]. For example, the purple bacteria, which grow photosynthetically in the absence of oxygen, live in the water column below the oxygenic chlorophyll containing phototrophs. Therefore, they use bacteriochlorophyll rather than chlorophyll, and are thus able to survive photosynthetically on the light that is available to the ‘red’ of where chlorophyll stops absorbing (figure 3).

4. Reaction centres

The function of antenna complexes is to deliver excitation energy to the reaction centres. There are now rather good X-ray crystal structures of purple bacterial reaction centres and reaction centres from photosystem I (PS I) and photosystem II (PS II) [11–13]. In this case, a comparison of their structures reveals that they are all highly homologous, both on the basis of their protein folds and on the arrangement of their redox cofactors. This is clearly because the physics of electron transfer is much more stringent than that of energy transfer [14]. Each reaction centre lies across the photosynthetic membrane and the redox reaction separates charge across the membrane. The redox carriers are arranged in a short chain that enables the forward, productive reactions to successfully outcompete the potential, energy-wasting back reactions. In general, each forward jump slows the back reactions by a factor of 10^3 . Previously, the photosynthetic reactions were presented as four steps for the sake of simplicity. However, as mentioned earlier, oxygenic photosynthesis actually uses two types of reaction centres, PS I and PS II. This allows light energy to be ‘used’ twice in the overall process. Once to extract electrons from water (PS II) and once to produce the strong reductant, NADPH, required for CO_2 reduction (PS I).

The redox reactions taking place in the reaction centres are now well understood and there have been many successful attempts to replicate their reactions in synthetic analogues [4].

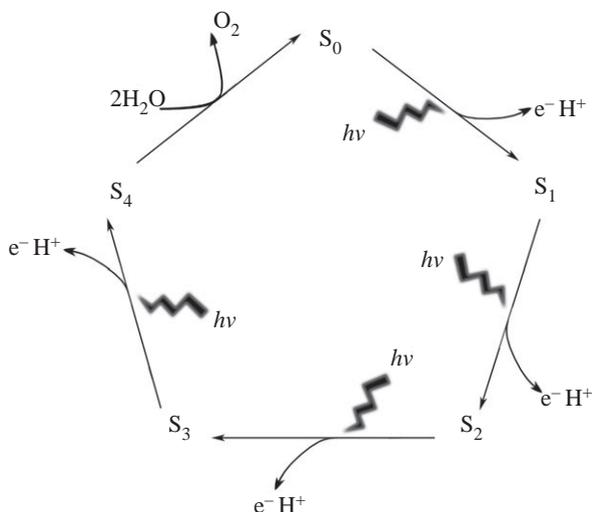


Figure 4. A schematic, called the Kok cycle [16], of the photochemistry within the manganese cluster of photosystem II. Four positive charges are sequentially stored from four single one photon-induced turnovers and these result in the oxidation of two molecules of water.

5. Oxidation of water

Water can be oxidized by electrolysis. However, this process requires rare earth catalysts and significant over-potentials. Photosynthesis accomplishes this with Earth-abundant catalysts (Mn) all with minimal over-potentials at ambient temperature. Even though there is now a much improved X-ray crystal structure for PS II [15], the precise details of the mechanism of oxygen evolution remain to be elucidated. The overall reaction can be summarized as in figure 4 [16]. The ‘S’ states refer to different charge accumulation states of the PS II Mn₄ cluster. Each time a photon is absorbed, the ‘S’ state is advanced by one. At S₄, there is a fast, concentrated four-electron reaction where two molecules of water are split into oxygen, four electrons and four protons.

The reaction centres are one electron/one photon devices. Oxygen evolution requires four turnovers of the reaction centre. This is difficult and dangerous chemistry. Charge accumulation is difficult and the requirement for highly oxidized species to be able to oxidize water is very dangerous. Indeed, during normal photosynthesis, PS II is regularly damaged by these highly oxidizing species and turns over approximately once every 30 min [17].

A great deal of effort is now being dedicated to trying to produce novel catalysts for water splitting that use Earth-abundant metals. This is essential if any overall process is to be scalable.

6. Reduction/production of fuel

Conceptually, the simplest fuel to make from the electrons produced by reaction centres is hydrogen. This process requires the accumulation of two electrons. There are a range of hydrogenase enzymes that can do this but they are, in

general, oxygen-sensitive [18]. This is a major problem because water splitting naturally produces oxygen that can potentially destroy the hydrogenase enzymes. How can the oxidation reactions be kept sufficiently separate from the reduction reactions? This is a hurdle that remains to be overcome. Maybe a two 'pot' system could work.

Hydrogen, however, is not a good target as a fuel for transport. Transportation requires a dense, portable fuel. There is a need, therefore, to investigate the possibility of using the electrons produced on the reductive side of the 'reaction centres' to make alternative fuels—for example, terpenoids. This may well be possible using techniques of synthetic biology.

Different species of bacteria have very many different metabolic capabilities, such as being able to synthesize terpenoids. The idea here would be to try to move such enzyme systems that can do this into other species that can use solar energy to provide reductants and ATP required to drive these reductive syntheses.

There is also a need to try to develop novel catalysts that can carry out such reactions aimed at fuel production in a fully chemical system. At this time, the goals are clear. Mankind urgently needs these aims to be achieved before oil and gas run out. However, though we know where we want to get to, the roadmap required to achieve this is far from clear. Notwithstanding this, the problem is so important that this type of research must be strongly promoted, and the very best young scientists should be actively encouraged to tackle it.

7. Final remarks

Photosynthesis clearly provides a model paradigm for how to use solar energy to make fuel. It is, however, inherently inefficient. Efficiency is a key issue since any scalable system to harness solar energy will require large areas of land over which solar energy can be collected. The lower the efficiency the larger the area of land required. Land is not an infinite resource. We need land for growing food, for living on and for allowing natural biodiversity to flourish. Any scalable system for using solar energy to make fuel must, therefore, be sufficiently efficient that the land requirements will be socially acceptable. Finally, the costs of such fuel production must also be economically viable.

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