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The Light Reactions of Photosynthesis as a Paradigm for Solar Fuel Production

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Abstract

The overall process of photosynthesis can be deconstructed into four distinct stages, each of which can be mimicked as a first step towards developing robust, integrated, supra-molecular systems or devices capable of using solar energy to produce a reduced product, fuel. This process is necessary because natural photosynthesis is rather inefficient. In this short review we outline the steps that would be required to produce systems capable of using solar energy to make fuels more efficiently. It is emphasised that these aims will require an extended multi-disciplinary effort that will undoubtedly involve close collaboration between academic and industrial scientists.

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1. Introduction

Developing clean and sustainable sources of energy is no longer just a global issue. It has also become a major regional imperative. In Indonesia, the total energy demand under a business-as-usual (BAU) assumption has been

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recently projected to reach 305 Mtoe (3546 TWh) in 2035 [1]. Therefore, the fact that 120000 TW of solar energy irradiates the surface of the Earth every year means harvesting even only a fraction of this sunlight offers the tantalizing possibility of providing a clean and green solution to mankind's, and Indonesia's, energy requirements. However sunlight is a relatively weak and diffuse form of energy that must be collected and concentrated before being able to be put to use. The efficiency of solar energy conversion into electricity through the use of photovoltaic (PV) cells is currently of the order of 10 to 28% [2] with a theoretical limit of around 30% [3]. A great deal of research effort is being expanded to increase the efficiency of this as well as simplifying and economising production of current PV technology. Nonetheless electricity generation from solar energy will always be hostage to the twin realities of variable supply (the sun does not shine at night) and the inability of electricity to be effectively stored for long periods of time. These drawbacks could be circumvented if a sustainable system capable of harvesting solar energy to produce a dense, portable liquid fuel is devised. Fuel, which effectively provides energy available on demand, could then be used to buffer fluctuations in electricity supply provided from renewable sources.

Fuel in this context can be thought of as a reduced molecule that can be oxidised, usually with molecular oxygen, to produce energy as required. Natural photosynthesis converts sunlight into carbohydrate and recent research has unraveled almost all of the molecular details of this conversion and enabled us to begin to use this information as a guide towards using solar energy to produce fuel. 'Photosynthesis' is already being used by man directly in the conversion of the photosynthetic product sucrose into ethanol (first generation biofuels), yet the overall conversion of incident solar energy into bioethanol is low [4]. This efficiency is the key issue [5]. The amount of solar energy arriving at the surface of the planet is high, however the average amount per square meter is only about 200W [6]. This means that in order to meet the energy demand of Indonesia alone an unfeasibly large area of land must be set aside for bioethanol and this would certainly compromise both food production and rain forest biodiversity. Is it possible, therefore, to use the design principles of photosynthesis and produce an artificial system that is more efficient? This article deconstructs the natural photosynthetic process into its key steps and considers how this long term but important goal might be achieved. The hurdles that need to be overcome before such a system can be realised will also be discussed.

2. Four-step model in an artificial photosynthetic reaction

Photosynthesis is the process by which plants, algae and some bacteria use light energy to split water and to use the electrons and hydrogen ions produced for the reduction of carbon dioxide to sugar. Photosynthesis can be divided into two separate reactions, the light and the dark reactions. In the light reactions, light energy is absorbed and used to power the synthesis of ATP and reduction of NADP. The subsequent dark reactions then consume these two to reduce carbon dioxide into carbohydrate. The natural photosynthetic process stores energy in chemical bonds. This is the key point! The theoretical maximal efficiency of conversion of solar energy into total biomass has been estimated to be 4.6% for C3 and 6% for C4 plants [7]. These values are for total full spectrum incident solar radiation. The maximum photosynthetic efficiency is higher (5-7%) for microalgae grown in enclosed outdoor bioreactors [8]. In comparison, the maximum theoretical limit of solar energy conversion into electricity by first-generation PV is about 30% [3].

Although the general reaction of photosynthesis appears to be relatively simple, its replication in any artificial analogue is a daunting challenge [9]. However, this challenge can be rendered more manageable when the overall process is separated into four distinct sequential, partial reactions. These can then be developed into modules that could then be combined to regenerate the whole process (Fig. 1). The first reaction is light harvesting, in which photons are collected in an antenna. The antenna complexes concentrate and direct the absorbed energy to the reaction centres where the second step, charge separation, takes place. The third reaction involves using the positive cation 'hole' produced by the charge separation in the reaction centre to oxidise a suitable electron donor molecule. Ideally this donor molecule would be water as it is abundant, cheap and clean. However the oxidation of water brings its own difficulties that will be detailed later. In the fourth step the electrons, again produced in the charge separation reactions, are used for reductive chemistry to produce the desired fuel. Thus by conceptualising 'artificial photosynthesis' as this four-step modular process, it is easier to construct devices that are able to replicate each of

the stages independently. It should not be overlooked, however, that in the natural process two distinct types of reaction centres are involved.

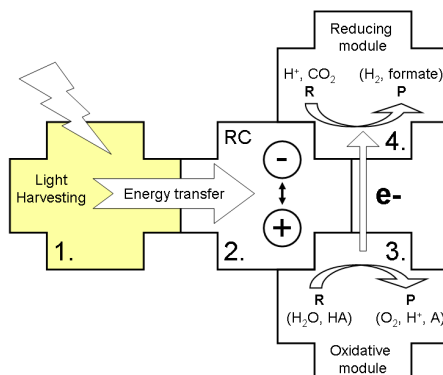


Fig. 1. Schematic for the decomposition of photosynthesis into four working modules, each of which can be used in turn as the basis for construction of artificial systems capable of photosynthesis. Module 1 (shaded yellow for reference) is a light-harvesting device (concentrator) that funnels energy into the reaction center. In natural photosynthetic organisms, this module is equivalent to the antenna proteins. Module 2 is equivalent to the reaction center and uses this incoming energy to separate charge across a membrane. The separated positive and negative charges can then be made to do work. Module 3 is the oxidative part of the system as the positive charge from the reaction center is used to remove electrons from a suitable substrate, hopefully water. In plants, this function is performed by the Oxygen Evolving Complex present in Photosystem II. The electrons are then carried to Module 4 where reduction of a suitable substrate occurs, which can be either protons to form hydrogen gas or carbon dioxide to form formate and then methanol. If all four modules can be combined in a functional system then the goal of synthesising a working, artificial photosynthetic device will be achieved.

3. The light-harvesting module

In Nature the pigment-protein complexes that harvest photons, prior to this energy being used to separate charges across the photosynthetic membrane, are called antenna complexes. Antenna complexes from many different organisms have been studied using the full panoply of biochemical, biophysical and spectroscopic techniques available. In addition there are already several high-resolution X-ray crystal structures of light-harvesting, antenna complexes from different photosynthetic organisms [10–14] and some examples of these are shown in Fig. 2. The fundamental structure of antenna complexes is that they are composed of pigments as the photosensitiser and proteins as their smart matrix. The protein provides a scaffold for the pigment for stable attachment and holds the pigments at the right orientations and distances for efficient energy transfer to occur. The protein is not just an inert structure correctly positioning the pigments. It also controls the photochemical properties of these pigments, such as modulating where they absorb [15]. The striking feature when these structures are compared is that the different types of light-harvesting complexes have very different protein folds and quite different arrangements of their pigments. When a chlorophyll molecule is excited by a photon the first excited singlet state lasts for about 1–2 ns and the process of energy transfer must then occur on a faster timescale than this to be efficient. In general though the physics of energy transfer is rather tolerant and so many different combinations and orientations of pigments within proteins are still able to be transfer energy well within the lifetime of the first excited singlet state and with high efficiency [16]. The results of this structural variation leads to the pigments, often within each individual molecule, experiencing different protein environments, resulting in pigment molecules with a range of site-energies and this leads to pigments with different absorption bands in the spectrum (Fig. 3). This is of functional importance as pigments with different absorbance bands provide energy gradients that funnel energy from the blue, shorter wavelength, higher energy, pigments to red, longer wavelength, lower energy molecules and on to the reaction centres.

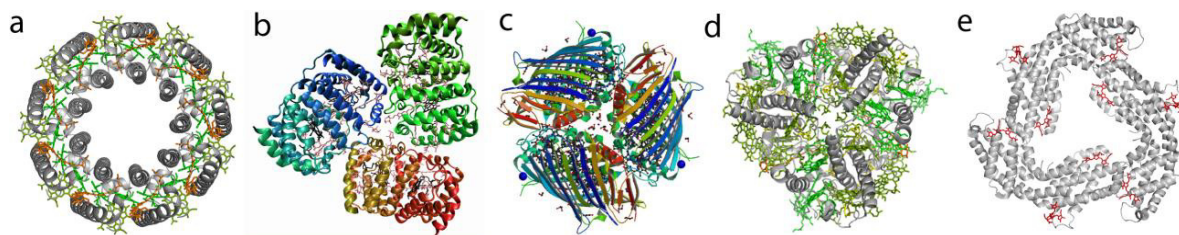


Fig. 2. X-ray crystal structures of five different light-harvesting antenna complexes. (a) The LH2 complex from *Rhodospseudomonas acidophila* strain 10050 [10], pdb 1KZU. (b) The Fenna-Matthews-Olson protein (FMO) from *Prosthecochloris aestuarii* [11], pdb 3EOJ. (c) The peridinin-chlorophyll-protein (PCP) from *Amphidinium carterae* [12], pdb 1PPR. (d) The light-harvesting complex II (LHCII) from spinach [13], pdb 1RWT. (e) The phycocyanin hexameric rod structure from the cyanobacteria *Thermosynechococcus vulcanus* phycobilliprotein antenna [14], pdb 3O18.

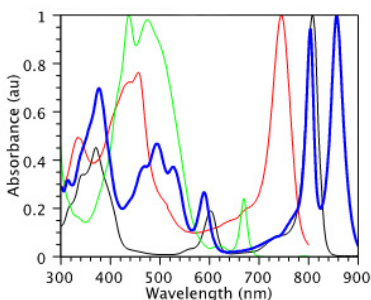


Fig. 3. Absorption spectra of the Fenna-Matthews-Olson protein (black line) [11], the chlorosome (red line) from *Chlorobaculum tepidum*, the light-harvesting (LH2) complex from *Rhodospseudomonas palustris* (blue line) [similar to 10] and the peridinin-chlorophyll protein from *Amphidinium carterae* (green line) [12].

However natural pigment-protein antenna complexes are too labile ever to be usefully used in an artificial light-harvesting module that should be robust and last for years. They do however provide working modules that can be used to test design in artificial light harvesting devices. Efforts are underway to use our pre-existing knowledge of the structure and function of antenna complexes to produce robust analogues that will be stable in an artificial context. As part of this process experiments are already producing multi-helix bundled maquettes containing pigments that are providing a wealth of information on how to control the inter- and intramolecular interactions of these molecules *in vitro* [17].

4. The charge separating, reaction centre module

A comparison of the x-ray crystal structure of different types photosynthetic reaction centers reveals that they are all highly homologous, both on the arrangement of the cofactors, their edge-to-edge and the protein folds [18-21]. This is because the physics of efficient, uni-directional electron transfer is rather strict. The reaction centre contains a short chain of redox carriers that are positioned in such way as to enable the forward reaction and prevent energy-wasting back recombination reactions. In Nature the first molecules that receive the incoming harvested light are generally two chlorophyll molecules, called ‘the special pair’. This energy is used to promote an electron to the first excited singlet state. Electron transport takes place from this excited state and the electron then travels down the

arrangement of co-factors to finally reduce the so-called primary electron acceptor. Each forward step in the chain reduces the back reaction by three orders of magnitude and so a stable separation of charge is achieved. This charge separation event is the first committed stage in photosynthesis and the energy stored in the separation event is then used to drive the subsequent chemical reactions. The energy levels of the various pigments involved are obviously of crucial importance for the system, e.g., if water is to be used as the electron donor, then photons with energy lower than 700 nm cannot be used as they do not contain sufficient energy to drive the water splitting reaction [22].

Attempts to produce artificial charge separating donor-acceptor dyads date back to the 1970s. However triad molecules then appeared that were able to separate and stabilise charge separated states for long enough so that they were able to perform subsequent redox reactions. Many such molecules and variations thereof have now appeared as well as more complicated, promising molecules that contain their own antenna systems [23]. No functioning chromophoric molecule has yet been produced that comes close to mimicking a natural photosynthetic reaction centre. The major hurdle is to produce robust chemical systems that can stabilize the charge separation reactions for long enough so that they can be coupled into systems capable of catalyzing the subsequent chemical reactions, such as water splitting and fuel production. One extra issue is that the reaction centres are one photon/one electron devices and the subsequent chemical reactions all require the concerted use of multiple charges. Nobody has yet produced any artificial charge accumulators equivalent to the Oxygen Evolving Complex (OEC) in Photosystem II.

5. The oxidizing module

The third step in the reduced model of photosynthesis is the use of the oxidizing equivalents produced by the reaction centre to split water.

All oxygenic photosynthetic organisms use water as their electron donor. An intricate Mn₄-oxo-Ca²⁺ cluster and a Cl⁻ ion on the thylakoid luminal side of Photosystem II forms the oxygen evolving complex (OEC) [21]. The OEC splits water into molecular oxygen, protons and electrons through a series of one electron steps known as the Kok cycle [24]. This process overcomes the high thermodynamic barrier required to oxidise water and simultaneously breaks four hydrogen-oxygen bonds, forms two oxygen-oxygen bonds and successfully juggles the storage of charge necessary to accomplish this. However this is highly corrosive reaction and Photosystem II in high light is turned over every 30 min due to continual damage by oxidising species.

Recent high-resolution X-ray structures of PSII have provided unprecedented insight into the geometry of the OEC [21]. Unfortunately this is only a static picture and the reaction cycle clearly involves conformational changes. Further work is still needed to understand the full molecular details of this reaction. Recently there have been exciting indications that serial femtosecond crystallography (SFX) using an x-ray free-electron laser (XFEL) may be able to resolve the changes in the OEC as it proceeds through the reaction cycle. Nevertheless, the high resolution structural data obtained so far combined with biophysical measurements (e.g. XAFS) and advanced computational modeling has resulted in a fairly complete picture of the OEC. However, attempts thus far to construct an artificial bioinspired organometallic analogue capable of water splitting have not been successful. Ironically, water can relatively easily be split in an electrolysis cell to produce hydrogen and oxygen. However, this reaction generally has a rather high over-potential, relies on platinum catalysts and any attempt to reproduce the function of the OEC that can be scalable must use cheaper Earth abundant metals [25, 26]. Recent work using a polyoxymetalate complex has shown how it may be possible to couple an efficient solar cell to a water electrolysis cell and to produce hydrogen more efficiently by separating oxygen and hydrogen evolution temporally [9, 27, 28].

6. The reducing module

The last step in the photosynthetic process involves using the electrons produced by the reaction centres for reductive chemistry to produce a fuel. Although not a liquid fuel hydrogen can be produced by the reduction of protons using the enzyme hydrogenase [29] and, therefore, there is a great deal of interest in using this enzyme both in algal bioreactors *in vivo* and in biohybrid systems to produce hydrogen. Hydrogenases generally have high turnover numbers but, unfortunately, operate at equilibrium constants close to one and are strongly inhibited by even small amounts of oxygen, not ideal if one wishes to employ analogues in a continuously operating oxygenic

bioinspired photosynthetic device. Nevertheless the recent discovery of some small bacterial hydrogenases that are somewhat oxygen tolerant offers some hope for their future use [30].

Other enzymes such as fumarate reductase [31] and formate dehydrogenase [32] have also been considered as the base molecule for a reducing module. The former utilizes electrons to reduce fumarate to succinate [33] and the latter uses electrons to reduce carbon dioxide to produce formate [34]. The formate can then be converted to methanol, a very appealing outcome as a carbon-based fuel is very important if we are, for example, to still use current combustion engines. Moreover such a system could be carbon neutral.

So far any fuel that is being contemplated involves using enzymes as we are a long way from having chemical catalysts capable of activating carbon dioxide under ambient atmospheric conditions.

7. Conclusion

At first reading the challenges ahead to produce a scalable, bioinspired device capable of solar fuel generation may appear rather daunting. Nevertheless, with the current, rapid advances in synthetic biology and nanomaterials coupled with the ever present external driving force to produce a green fuel, the goal of constructing an artificial device that uses solar energy to produce a usable fuel may be ambitious but it is certainly achievable over the medium term. Indeed, it could well be argued that it must be achieved!

The deconstruction of photosynthesis into four conceptual, discreet steps allows a complicated overall process to be simplified into separate modules that can be mimicked individually and then integrated to reproduce the overall reaction but with a product (fuel) that can be, within limits, tailored as required. As more understanding develops of what is required to make the system work it may well be that the modular outline described above may need to be adapted, for example the introduction of compartmentalisation may be required [27] or coupling established PV technology or emerging organic PV technology that produces solar current that can be used by redox modules to produce fuel.

The pressure to discover new methods of scaling up solar fuel production will require innovative thinking and demand input not just from the scientific community but will rely on working hand-in-hand with government and industry as well. In our laboratories, we are working towards artificial photosynthesis and beginning by using biological photosynthetic complexes as working units [35-37]. Our aim is to gain more inside on the interplay between working modules and nanoparticles, and to explore design possibilities that can give an added value and enhance the properties for the fabrication of small-scale system capable of making solar fuels.

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