Why is photosynthesis interesting?

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Life on the Earth is solar powered. Photosynthesis is the process by which plants use light energy to produce food molecules for all living creatures. Besides light, water and carbon dioxide from the atmosphere are required in green plants photosynthesis.

Life on our planet began about 3.5 billion years ago with the appearance of the first photosynthetic organisms, such as bacteria and primitive algae. At the beginning anaerobic photosynthesis was present, in which H_2S, for example, was used as an external source of electrons and protons. Oxygenic photosynthesis occurred about 2 billion years ago. Cyanobacteria and higher plants are able to extract electrons and protons from water. A by-product of this reaction is oxygen. The occurrence of O_2 in the atmosphere determined the direction of life evolution. Oxygen is essential in the process of respiration by which organic compounds are oxidized back to carbon dioxide and water and at the same time the energy necessary for living organisms is released.

Photosynthesis can be defined as a process utilizing sun energy and converting it into chemical energy by means of complex biophysical and biochemical reactions taking place in plant chloroplasts and in the cells of photosynthetic prokaryotes. The light driven reactions take place in the inner membranes of the chloroplasts called thylakoids (Fig. 1). Photosynthesis consists of a series of reactions starting with the splitting of water molecules into molecular oxygen, protons and electrons, followed by a chain of electron transfer reactions resulting in the production of NADPH and ATP – sources of chemical energy used in cell metabolism (see Frame 1 for details).

FRAME 1

There are three complexes subsequently participating in the electron transport chain in thylakoids: photosystem II (PSII), a cytochrome b6/f complex and photosystem I (PSI). Photosystem II is "heart" of the photosynthetic apparatus. It uses light energy to catalyze water splitting into molecular oxygen, protons and electrons. PS II and PS I are linked by two mobile electron carriers: plastoquinone (PQ) and plastocyanin. The subsequent reactions of the electron transfer through PS II via cytochrome b6/f and through PS I are called a photosynthetic linear electron transfer chain. At the acceptor side of PS I, $NADP^+$ (oxidized form of ***N***icotineamide ***A***denine***D***inucleotide ***P***hosphate) is reduced to NADPH in this reaction: $NADP^+ + H^+ + 2e^- \rightarrow NADPH$. The proton gradient generated by H^+ released from water into the lumen side of thylakoids and by H^+ pumped by PQ through the membrane from the outer to the inner side of thylakoids is a driving force for the ATP formation (***A***denosine ***T***ri***P***hosphate).

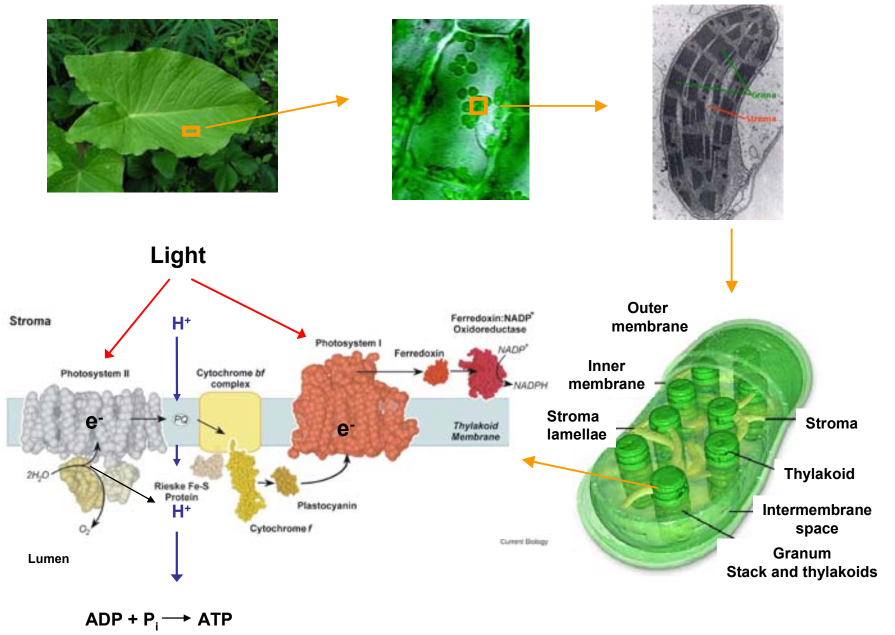

Fig.1. A schematic structure of thylakoids in chloroplasts (green parts of leaves), and a scheme of the linear electron transfer chain in the process of photosynthesis and formation of NADPH and ATP as final products of the light driven photosynthetic reactions

NADPH and ATP produced in photosynthetic light reactions are used in a dark reaction process, known as the Calvin cycle, in which carbohydrates and other organic compounds are synthesized. At this stage of photosynthesis an assimilation of CO_2 occurs. The formation of a six-carbon sugar molecule requires six complete turns of the Calvin cycle, for each of which 3 ATP and 2 NADPH molecules are consumed. The biochemistry of the photosynthetic process can be summarized in the following way:

$$\mathbf{6CO_2 + 12H_2O + 18ATP + 12NADPH \rightarrow}$$
$$\mathbf{\rightarrow C_6H_{12}O_6 + 18ADP + 18P_i + 12NADP^+ + 12H^+ + 6O_2\uparrow}$$

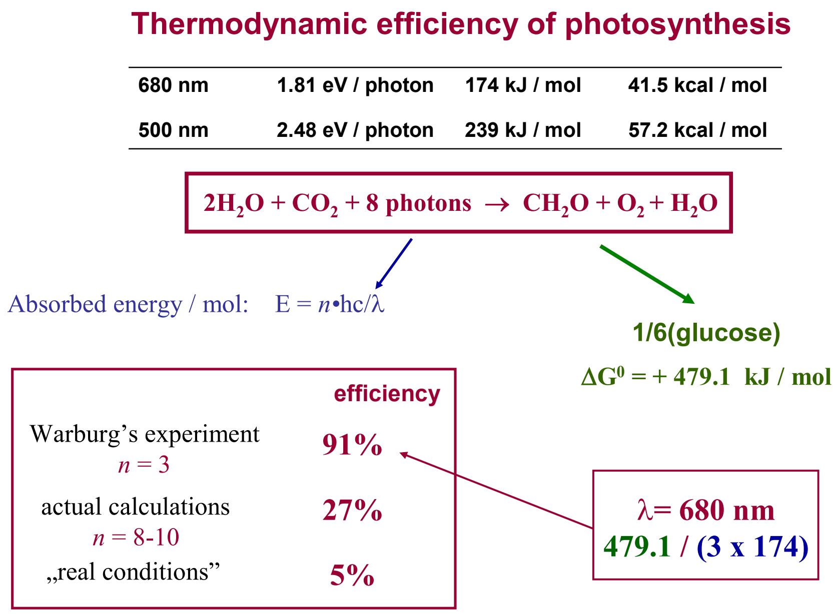

Fig. 2. Thermodynamic efficiency of photosynthesis

In entire scheme 2 it is shown how one can calculate the thermodynamic efficiency of the process of photosynthesis. The final efficiency is only 5% (see Frame 2 for details).

FRAME 2

It is generally accepted that eight moles of photons are required for reduction of each CO_2 mole, it is 8 x 174 kJ/mol, when the wavelength is of 680 nm (the absorption maximum of the PSII reaction center). The free energy of the reaction of the CO_2 reduction to CH_2O (1/6 of a glucose molecule) requires about 479 kJ/mol. Thus, the efficiency of photosynthesis is almost 34% under optimal conditions. In fact, one should consider the higher energy of photons of between 500–680 nm and the requirement of more moles of photons for the reaction of glucose production in natural conditions. The energy of some photons is dissipated and thus not all photons contribute to the reaction. Therefore the efficiency is much lower than 30% and in reality it is only of the order 5%.

The annual flow of sunlight energy toward the surface of the Earth is about 1.4 x 10^{18} kWh but only half of the energy enters the surface. Moreover, only 7 x 10^{14} kWh is utilized by photosynthesis (less than 0.1% of total sunlight energy). However, the "lost portion" of energy can power other processes at the earth's surface such as winds or ocean currents.

Because the current fossil fuel reserve is estimated to be sufficient for only 200 years at the present world annual consumption or even less when the consumption increases with the industrial development of other countries, mankind is searching for new energy sources. They should yield safe, clean and renewable energy. Renewable energy sources can be replenished in a short period of time. The five renewable sources used most often include hydropower (water), solar, wind, geothermal, and biomass. Natural energy sources are shown in Fig. 3.

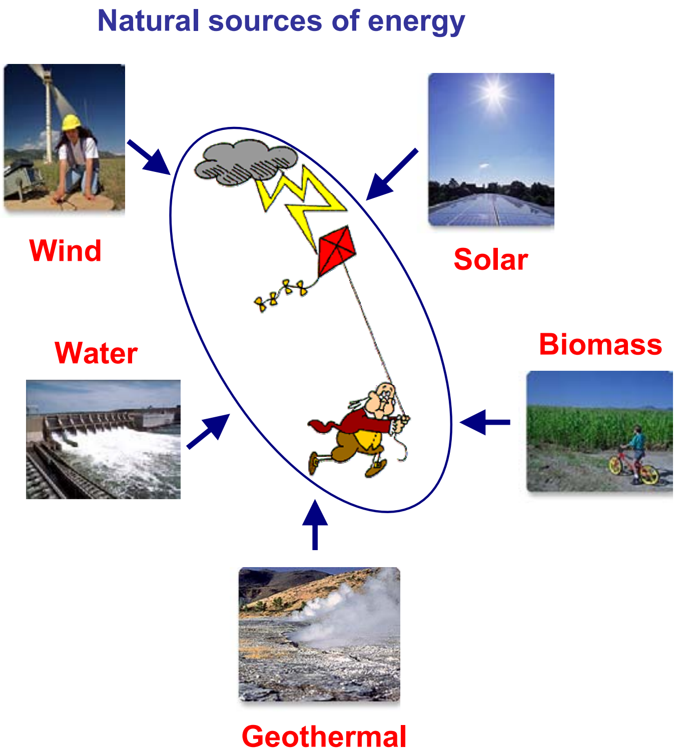

Fig. 3. Natural sources of energy

In view of the energy problems which mankind faces, the issue of biomass and solar energy has attracted recently more and more attention. It is possible to increase the efficiency of the biological energy sources and to decrease the costs of exploatation by genetic modification of photosynthetic organisms which optimally use the photosynthetic process on the molecular level. There are two main directions of genetic and molecular studies: the first one is focused on the selective production of biomass with various fuel source (wood, oil, alcohol) and the second one on the construction of fuel cells based on the combination of processes naturally occurring in photosynthesis.

As an example, we will discuss below hydrogen as biological fuel. Presently it seems to be the best candidate for the fuel in new technological developments. There are many groups of specialists working on that problem including physicists, chemists and biologists. The cleanest way to produce hydrogen is to use sunlight to split water into hydrogen and oxygen. Such photoelectrochemical water splitting is shown in Fig. 4. Fuel cells can work using products of artificial semiconductor systems, which are already on the market, or from natural photosynthetic systems (Fig. 4).

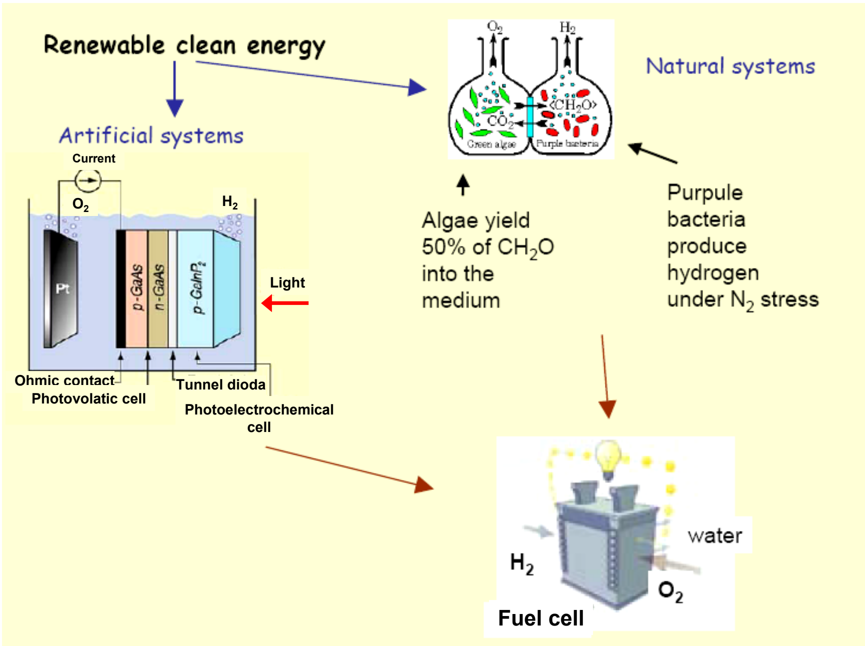

Fig. 4. Natural and artificial systems, which are able to produce H_2

A fuel cell is a device that uses hydrogen or hydrogen-rich fuel and oxygen to create electricity. In the case when H_2 is used, the fuel cell emits only heat and water as byproducts. This means that the energy production is really environment-friendly because it is not related to any air pollution nor greenhouse gases emission. The only problems, but a very important one from the practical point of view, are that the costs of such artificial devices which are too high while their working time is too short. Systems based on photosynthetic organisms could provide a solution to this problem. The present and predicted costs of hydrogen production are shown in Fig. 5. It is clear that the costs and efficiency of natural systems are much better.

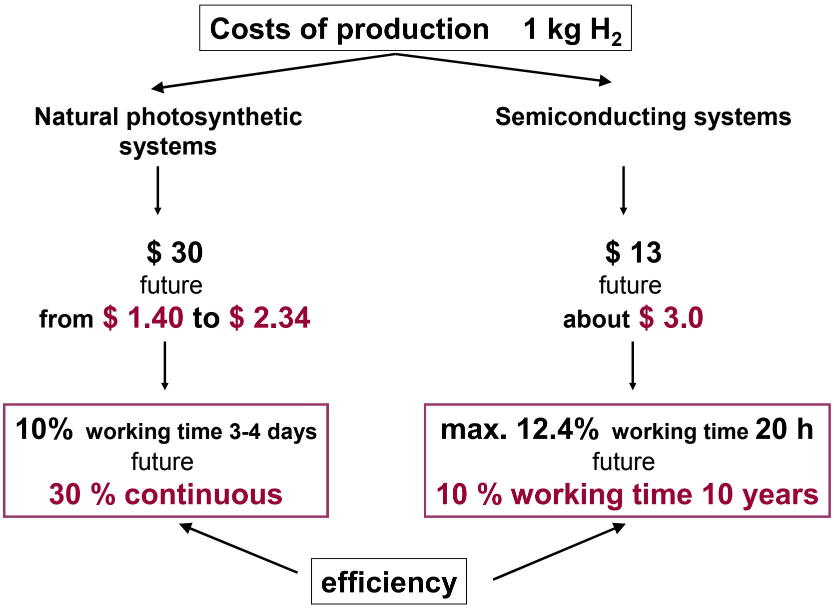

Fig. 5. Efficiency and costs of hydrogen production

In photosynthetic organisms hydrogen is produced along with oxygen. However, the hydrogen producing enzyme called hydrogenase is oxygen sensitive. The presence of O_2 inhibits the formation of H_2. Therefore the efforts of researchers are going in the direction of genetic modification to evolve organisms that can sustain hydrogen production in the presence of oxygen. Another possibility is to manipulate the culture conditions switching metabolism of the natural systems between their photosynthetic growth (an increase of O_2 evolution) and H_2 production phase. It is achievable, for example, in algal cells by controlling sulphur concentration in the medium. Thus, photobiological technology holds – great promise (Fig. 6).

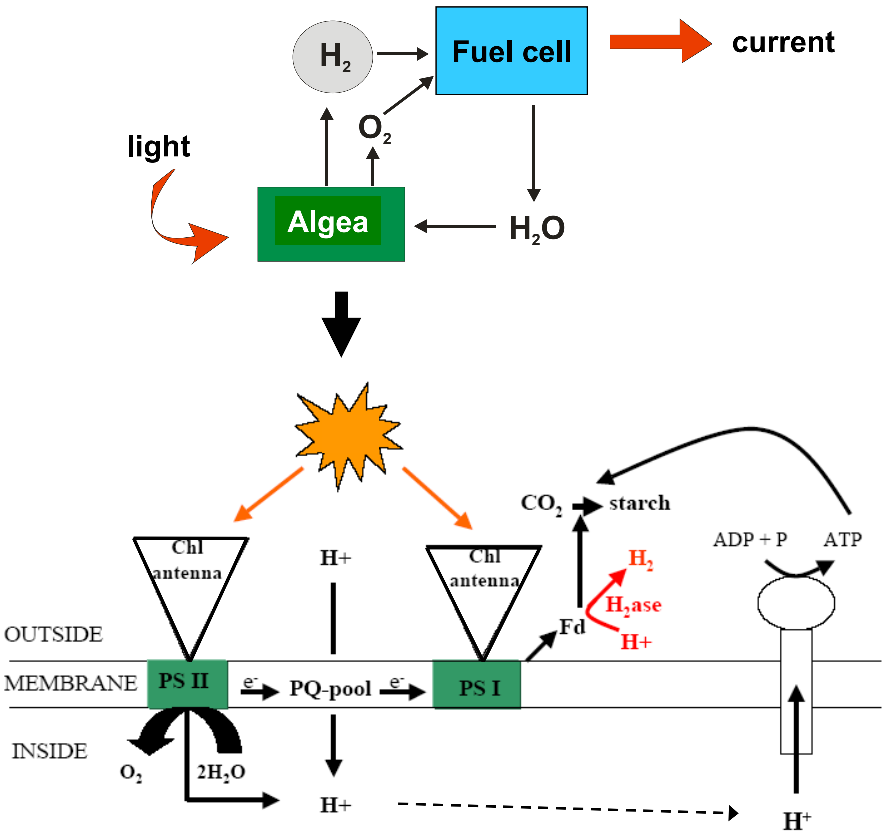

Fig. 6. Algal systems may switch between oxygen and hydrogen production under controlled conditions. The water splitting complex in photosystem II located toward the inner part of photosynthetic membranes is responsible for O_2 evolution. H_2 yield is regulated by hydrogenase (H_2-ase) operating after photosystem I in the outer part of the membranes

There is also another direction of photosynthetic studies. It is concentrated on the recognition of the mechanism of water splitting in the oxygen evolving complex located on the core of photosystem II, which could be a prototype for the biomimicry and formation of new devices with an efficiency of 100% for the light-driven process of water splitting into O_2 and hydrogen ions (H^+). It is known that a manganese cluster containing 4 atoms of Mn and one Ca atom is responsible for water oxidation but the mechanism of H^+ extraction and formation of the O=O bond still remains a puzzle (Fig. 7).

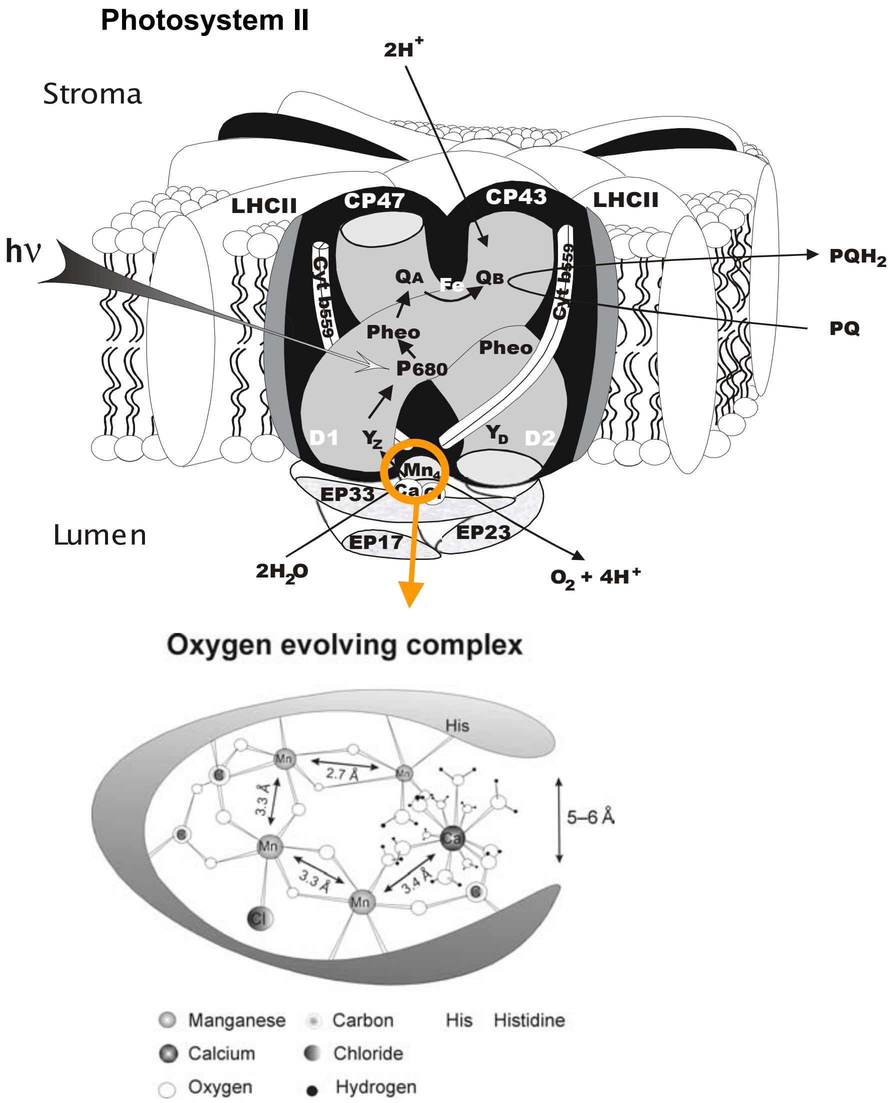

Fig. 7. Scheme of photosystem II with redox active components participating in the linear electron flow within PSII (Tyr – tyrosine, Pheo – pheophytin, QA – plastoquinone bound in site called QA, QB – plastoquinone bound in site called QB, P680 – reaction center of PSII, cyt b559 – cytochrome b559, Fe – an iron atom). A possible arrangement of the oxygen evolving complex containing four Mn atoms and one Ca atom is shown

Physics plays a very important role in this field of investigations. Various physical experimental techniques such as: XANES (X-ray absorption near edge spectroscopy) , EPR (electron paramagnetic resonance), NMR (nuclear magnetic resonance), Mössbauer spectroscopy, fluorescence and absorption spectroscopies, are crucial in studies of the structure of the Mn cluster, spin and valence states of the redox components participating in the electron transfer chain (for example: iron complexes, tyrozines). The interpretation of the data needs a deep understanding of physical phenomena, which allows one to formulate models of photosynthetic energy and electron transfer. Theoretical analysis can certainly be very helpful in the construction of artificial photosynthetic systems.

To summarize, we feel confident that the joint efforts of biologists, chemists, physicists and geneticists will in the nearest future lead to the ultimate goal, which is the discovery of technology for light driven power plants of a high efficiency and low pollution level.

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