U.S. Department of Energy

Genomics:GTL

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Photosynthetic Production of Hydrogen from Water

Although microorganisms are capable of carrying out different types of photosynthesis, that found in plants, algae, and cyanobacteria is best understood. Photosynthesis in these organisms is a complex series of reactions that use light energy to drive electron transfer from water to carbon dioxide to yield carbohydrates.

Instead of using electrons harvested from water to synthesize carbohydrates from CO_2, under certain conditions green algae and cyanobacteria can use them to reduce protons and produce hydrogen gas (H_2). Molecular complexes involved in mediating electron flow from water to carbon-fixing or hydrogen-production reactions make up the photosynthetic electron-transport chain found in the thylakoid membranes of cyanobacteria and green algae. In eukaryotic green algae, thylakoid membranes are housed within a cellular organelle known as the chloroplast; in prokaryotic cyanobacteria, thylakoids are found in the cytoplasm as an intracellular membrane system (see Fig. A).

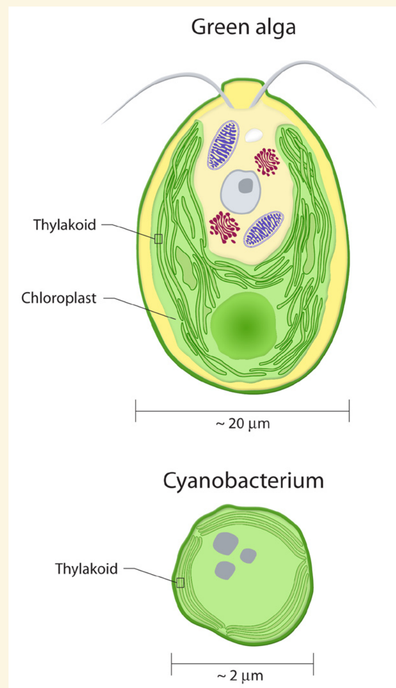

Fig. A. Thylakoids in Green Algae and Cyanobacteria.

An overview of steps involved in using light energy to produce carbohydrates or hydrogen is depicted in Fig. B and described below.

1. **Light Absorption by Photosystem II (PSII) Initiates the Photosynthetic Pathway.** PSII is a large molecular complex that contains several proteins and light-absorbing pigment molecules. The primary pigment molecules are chlorophylls and carotenoids, but cyanobacteria also have other pigments called phycobilins that absorb light at different wavelengths. The pigments are bound to proteins to form antenna complexes that absorb photons and transfer the resultant excitation energy to the reaction center of PSII, where energized electrons move to a small electron-carrier molecule. This molecule shuttles the excited electrons to the next complex in the photosynthetic electron-transport chain. To replace electrons lost in the transfer, the reaction center strips low-energy electrons from two water molecules, releasing four protons and an oxygen (O_2) molecule into the thylakoid space.

2. **Electron Transport Through the Cytochrome Complex Generates a Proton Gradient.** The electron carrier from PSII passes through the thylakoid membrane and transfers its electrons to the cytochrome complex, which consists of several subunits including cytochrome *f* and cytochrome b_6. A series of redox reactions within the complex ultimately transfer the electrons to a second electron carrier that acts as a shuttle to photosystem I (PSI). As electrons are transported through the complex, protons (H^+) outside the thylakoid are carried to the inner thylakoid space. The increase in proton concentration inside the thylakoid space creates a proton gradient across the thylakoid membrane.

3. **Light Absorption by PSI Excites Electrons and Facilitates Electron Transfer to an Electron Acceptor Outside the Thylakoid Membrane.** PSI is another large protein-pigment complex that contains light-absorbing antenna molecules and a reaction center. Light absorbed by the PSI reaction center energizes an electron that is transferred to ferredoxin (Fd), a molecule that carries electrons to other reaction pathways outside the thylakoid. The reaction center replaces the electron transferred to ferredoxin by accepting an electron from the electron-carrier molecule that moves between the cytochrome complex and PSI.

4. **Under Certain Conditions, Ferredoxin can Carry Electrons to Hydrogenase.** Normally, ferredoxin shuttles electrons to an enzyme that reduces NADP+ to NADPH, an important source of electrons needed to convert CO_2 to carbohydrates in the carbon-fixing reactions. Under anaerobic conditions, hydrogenase can accept electrons from reduced ferredoxin molecules and use them to reduce protons to molecular hydrogen (H_2).

5. **Dissipation of Proton Gradient is Used to Synthesize Adenosine Triphosphate (ATP).** ATP synthase couples the dissipation of the proton gradient generated in step 2 to the synthesis of ATP. Translocation of protons from a region of high concentration (thylakoid space) to a region of low concentration (outside thylakoid) releases energy that can be used to drive the synthesis of ATP from adenosine diphosphate (ADP) and phosphate (P). ATP is a high-energy molecule used to convert CO_2 to carbohydrates in the carbon-fixing reactions.

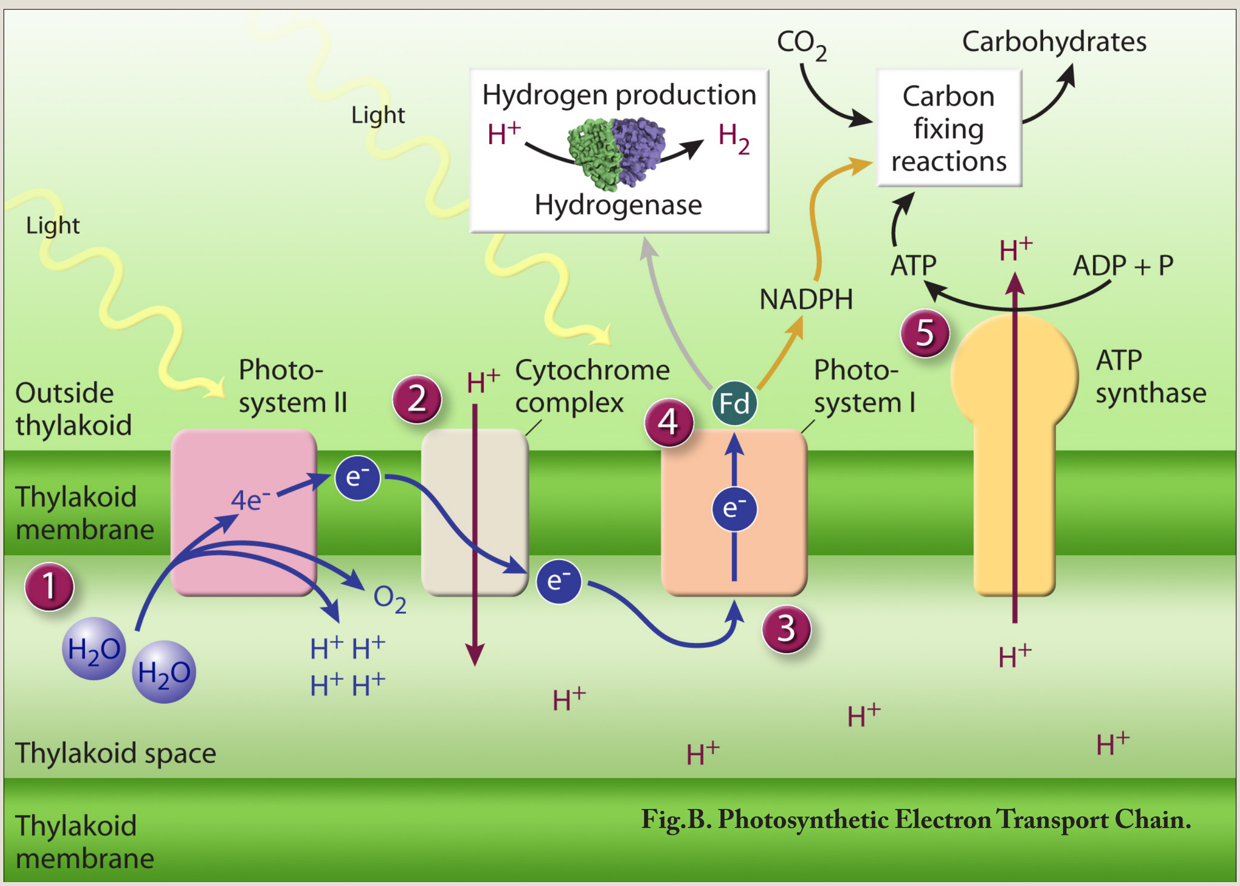

Fig.B. Photosynthetic Electron Transport Chain.