Fundamentals of Photosynthesis for Energy Storage

Z.-Y. Wang-Otomo

Abstract Photosynthesis is the most fundamentally important energy-converting process on Earth. It converts solar energy to chemical energy and provides all the food we eat, the fossil fuels we consume and the oxygen we breathe. The basic concepts underlying photosynthesis have been well established and a brief introduction is given in this chapter. The principles, especially those obtained from primitive photosynthetic organisms, are considered to serve as a guide for the development of artificial photosynthesis today.

1 Introduction

The sunlight reaching the earth's surface every year is estimated to bring about energy of some 2.5×10^{24} J. Only about 0.2 % is utilized by photosynthesis to produce organic matter [1]. This is partly because the sunlight has a broad spectrum and only the visible range of wavelength from 400 to 700 nm, called photosynthetically active radiation and comprising about 40 % of the solar irradiance, can be used by most photosynthesis. Despite the low efficiency, the amount of energy stored by photosynthesis each year in the biosphere is still roughly four times that of the annual consumption by humans [1].

The fossil fuels we use today are all made from ancient photosynthesis. Coal, petroleum, and natural gas are decomposition products of plants and animals. The energy stored in these organisms was harnessed from the solar radiation millions of years ago. Total resources of the fossil fuel stored under the earth's surface is equivalent to about 60 years of net photosynthesis [2].

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M. Sugiyama et al. (eds.), *Solar to Chemical Energy Conversion*,
Lecture Notes in Energy 32, DOI 10.1007/978-3-319-25400-5_21

2 The Energy Flow, Electron Sources and Carbon Circle

The solar energy captured through photosynthesis is stored in the form of chemical bonds, i.e., the formation of new C–C bonds. This process is also called carbon-fixation that converts atmospheric CO_2 into organic molecules (Fig. 1). The photosynthesizing reaction requires electrons provided from external sources. For primitive photosynthesis, as occurred in sulfur bacteria, the electron donor is the reduced sulfur compounds [3]:

$$n\mathrm{CO_2} + 2n\mathrm{H_2S} \xrightarrow{\text{light}} (\mathrm{CH_2O})_\mathrm{n} + 2n\mathrm{S} + n\mathrm{H_2O} \quad (1)$$

where $(CH_2O)_n$ represents a carbohydrate, typically the glucose ($C_6H_{12}O_6$). The S^{2-} in H_2S loses 2 electrons to become elemental S^0. This reaction has a midpoint redox potential $E_m^{'}$ of −0.23 V which is much lower than +0.64 V ($BChl^+ + e^- \rightleftharpoons BChl$, BChl stands for bacteriochlorophyll) of the special pair (see below) in the reaction center (RC) of purple bacteria (Fig. 2, left scheme). The green plants, algae and cyanobacteria, which developed much later, have evolved to acquire the ability to extract electrons from water molecules, but in essentially the same way as that of sulfur bacteria (Fig. 2, middle scheme):

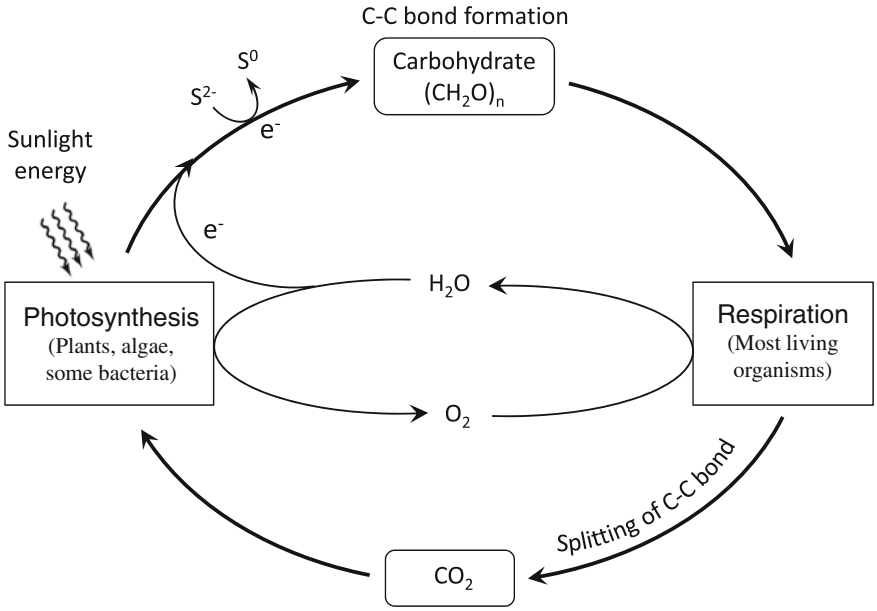


Fig. 1 A schematic diagram showing the relationship between photosynthesis and respiration. The energy storage by photosynthesis requires external electron sources. CO_2 and O_2 are circulated in the atmosphere and cells

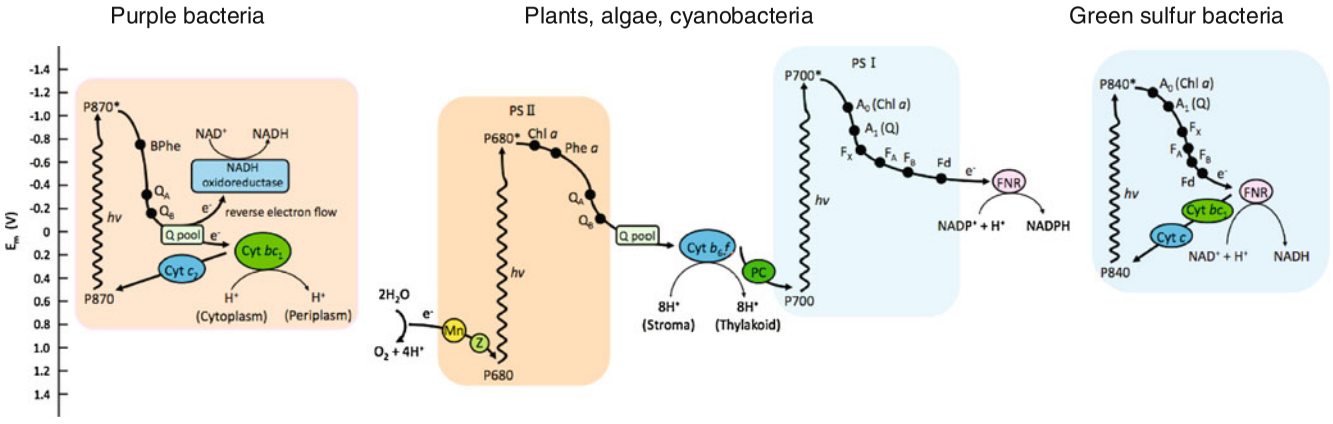


Fig. 2 Comparison of the electron transport chains between the photosynthetic bacteria (*left* and *right* schemes) and green plants (*middle* scheme). P870 and P870*: ground and excited states of the special pair in purple bacteria, respectively; *Q* quinone; *BPhe* bacteriopheophytin; *Cyt* cytochrome; *ATP* adenosine triphosphate; *NADH* nicotinamide adenine dinucleotide; *NADPH* nicotinamide adenine dinucleotide phosphate; P680 and P680*: ground and excited states of the special pair in photosystem II, respectively; *Chl* chlorophyll; *Phe* pheophytin; *PC* plastocyanin; P700 and P700*: ground and excited states of the special pair in photosystem I, respectively; *F* Fe-S cluster: *Fd* ferredoxin; *FNR* ferredoxin-NADP reductase; P840 and P840*: ground and excited states of the special pair in green sulfur bacteria, respectively; Q_A quinone-binding site A; Q_B quinone-binding site B

$$n\mathrm{CO_2} + n\mathrm{H_2O} \xrightarrow{\text{light}} (\mathrm{CH_2O})_n + n\mathrm{O_2} \quad (2)$$

If we use glucose to represent the carbohydrate, the overall photosynthetic reaction can be written as follows:

$$6\mathrm{CO_2} + 6\mathrm{H_2O} \rightarrow \mathrm{C_6H_{12}O_6} + 6\mathrm{O_2} \quad (3)$$

The reaction (2) is actually composed of two reactions, in which the water molecule is first split by light (photolyzed) and then the released electrons are used for carbohydrate synthesis:

$$2\mathrm{H_2O} \rightarrow 4\mathrm{H^+} + \mathrm{O_2} + 4\mathrm{e^-} \quad (4)$$

$$\mathrm{CO_2} + 4\mathrm{H^+} + 4\mathrm{e^-} \rightarrow (\mathrm{CH_2O}) + \mathrm{H_2O} \quad (5)$$

Therefore, the photosynthesis can also be viewed as a two-stage process in which the light energy is utilized to gain electrons from H_2S or H_2O and these electrons are subsequently used to build C–C bonds with CO_2 as a substrate.

The photosynthesized organic compounds are consumed by animals through a process called "respiration" (Fig. 1). It is a reverse reaction of photosynthesis that use molecular oxygen, also released by photosynthesis, to burn (oxidize) the organic molecules into CO_2 and waters. This is also a decomposition process that splits the C–C chemical bonds. The photosynthesis and respiration are complementary processes.

3 Four Steps for the Energy Storage

The whole photosynthesis process can be divided into four steps as shown in Fig. 3: (1) light absorption and energy transfer; (2) energy conversion by charge separation; (3) electron transfer for producing adenosine triphosphate (ATP) and nicotinamide adenine dinucleotide phosphate (NADPH) and (4) CO_2 assimilation.

For the photosynthesis to occur, any photosynthetic organism needs first to collect sunlight energy. These organisms developed to contain a large amount of pigment molecules, typically the chlorophylls (Chl) for eukaryotes and cyanobacteria, and the bacteriochlorophylls (BChl) for photosynthetic bacteria. Both Chl and BChl are squarish planar molecules with a Mg atom at the center of the plane (Fig. 4). The central Mg atom is coordinated to four nitrogen atoms. The antenna pigments are in most cases associated with proteins to form a set of light-harvesting (LH) pigment-protein complexes that either are integrated into the membrane or attach to the membrane surface (see Chap. 22 for details on the case of purple bacteria). Since the Chls are highly conjugated molecules, they strongly absorb

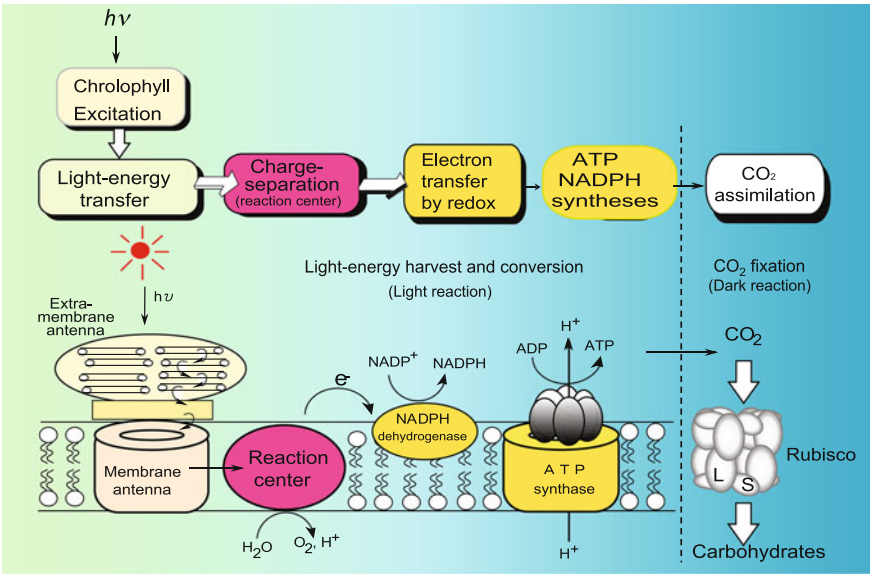
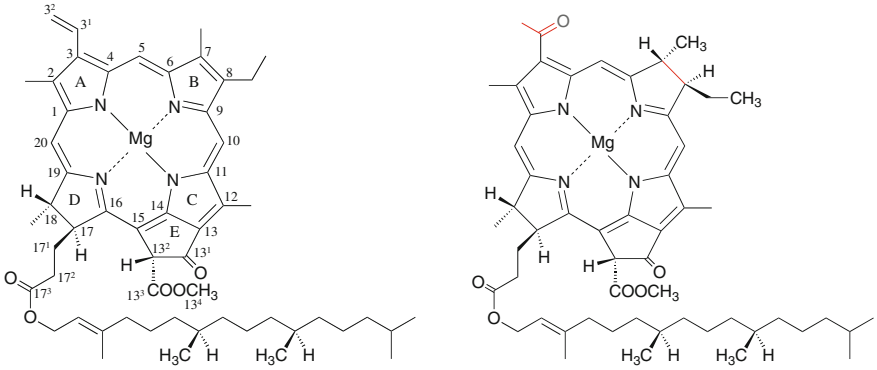


Fig. 3 A flow chart illustrating the whole process of photosynthesis. *ADP* adenosine diphosphate; *Rubisco* ribulose 1,5-bisphosphate carboxylase/oxygenase. Other symbols are the same as in Fig. 2



Chlorophyll *a* Bacteriochlorophyll *a*

Fig. 4 Chemical structures of chlorophyll *a* and bacteriochlorophyll *a* based on the numbering scheme of IUPAC nomenclature. Five rings are lettered *A* through *E*. The chemical differences between structures of Chl *a* and BChl *a* are marked by *red* color

visible light with the molecular extinction coefficients over 10^5 M^{-1} cm^{-1}, which are among the highest known for organic molecules [3].

When a Chl molecule is excited by a quantum of incident light (a photon), the absorbed energy is transferred directly to a neighboring unexcited Chl molecule by

a process called exciton transfer, also known as resonance energy transfer, if the two pigments are separated by more than several Ångstroms. As illustrated in Fig. 5, this process occurs through interactions between the molecular orbitals of the weakly coupled molecules, and is of particular importance in funneling light energy to photochemical reaction center [4]. There is an alternative view for the energy transfer, known as exciton coupling, when the pigment molecules are located closely to each other, typically less than 10 Å for Chls. In this case, an exciton is serially transferred between members of a group of molecules. If their electronic coupling is strong enough, the entire group may act as a supermolecule with delocalized electronic transitions, rather than a collection of individual molecules with localized transitions [4]. Experimentally, the exciton coupling can be observed by a split of the absorption band or a derivative-shaped signal in the circular dichroism spectra. This is the case for the pigments B850 in peripheral light-harvesting complex (LH2), the pigments B880 in core light-harvesting complex (LH1) and the special pair in reaction center of purple bacteria as shown in Fig. 5.

The process of energy conversion begins when the excitation energy reaches a pair of nearly parallel and closely spaced Chls (Mg–Mg distance: ~7 Å), the so-called "special pair" (sp in Fig. 5), in reaction center where an electron is excited and delocalized over the Chl dimer to form an excited state. The special pair serves as an irreversible trap for excitation energy since its excited state is unstable and the excited electron is immediately transferred stepwise from the special pair to nearby pigments, resulting in a charge-separated state [5]. For purple photosynthetic

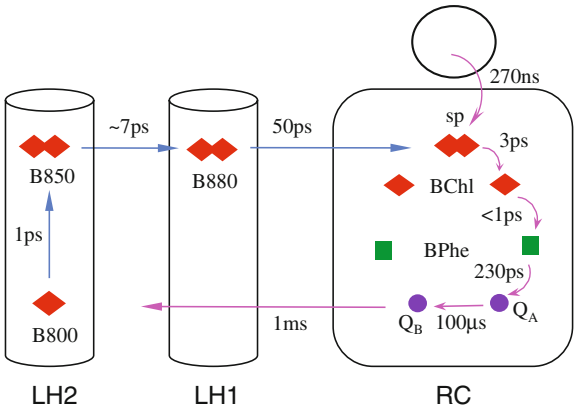


Fig. 5 Organization of a photosynthetic unit composed of light-harvesting complexes (*LH*) and reaction center (*RC*) in purple photosynthetic bacteria. The directions of excitation energy and electron transfers are indicated by *blue* and *purple arrows*, respectively. Typical time constants are shown for each step. *LH2* peripheral light-harvesting complex; *LH1* core light-harvesting complex; *B800* the monomeric pigments that absorb at 800 nm; *B850* the dimeric pigments that absorb at 850 nm; *B880* the dimeric pigments that absorb at 880 nm; *sp* special pair; Q_A quinone-binding site A; Q_B quinone-binding site B (Color figure online)

bacteria and evolutionarily related photosystem II in plants and cyanobacteria, the final electron acceptor in reaction center is an ubiquinone molecule (UQ). When the UQ receives two electrons induced by two photons to become anionic ubiquinol UQ^{2-}, it takes up two protons from solution to form UQH_2. Thus, UQ is a molecular transducer that converts two light-driven one-electron excitation to a two-electron chemical reduction [3]. The energy consumed in each photochemical reaction center is provided from several hundred Chl molecules, i.e. most Chls actually function as light-harvesting antennas. The energy conversion process in reaction center is finely tuned so that in most cases the quantum yield per photon absorbed is close to 100 % [4].

The consequence of UQH_2 formation and its transport to a membrane-bound quinone pool and other redox carriers is the formation of a proton gradient across the membrane. Synthesis of ATP, the cell's "energy currency", is driven by the dissipation of this pH gradient. However, ATP is not sufficient as the sole source of cellular free energy [4]. Reduction of CO_2 to form carbohydrates requires a second source, the reducing power that is the reduced form of NADPH (NADH in anoxygenic photosynthetic bacteria). Plants and cyanobacteria produce both ATP and NADPH directly by a two-step process called noncyclic photophosphorylation [5]. The two photosystems I and II in these organisms are used in a series to extract electrons from water and transfer it to NADPH. As the high-energy electrons pass through the coupled photosystems to generate NADPH, some of their energy is used for ATP synthesis. Since the UQH_2 is thermodynamically unable to directly reduce NAD^+ (+0.04 V vs. −0.32 V, Fig. 2), in purple photosynthetic bacteria a reverse electron flow takes place (Fig. 2, left scheme) [5, 6], in which reduced quinone is the electron donor and NAD^+ is the electron acceptor [4, 6]. The energy is supplied by a transmembrane chemiosmotic potential that is built up by the light-driven cyclic electron transport system [4, 7]. In green sulfur bacteria, the quinone molecule is a menaquinone instead of ubiquinone, the former has a much lower redox potential (−0.06 V, Fig. 2 right scheme). In this case, the reaction center can directly reduce ferredoxin and then NAD^+ without the need for energy-consuming reverse electron flow [4].

The final step of photosynthesis is the conversion of CO_2 to carbohydrates using the ATP and NADPH produced by photosynthetic electron transfer. The initial carbon-fixing reaction involves incorporation of one molecule of CO_2 from atmosphere into a five-carbon compound, ribulose 1,5-bisphosphate (RuBP), to yield two molecules of the three-carbon compound 3-phosphoglycerate (3PG) (Fig. 6). This carboxylation reaction is catalyzed by ribulose 1,5-bisphosphate carboxylase/oxygenase (Rubisco), the most abundant enzyme in the biosphere. Most Rubiscos are hexadecameric proteins, consisting of eight large catalytic subunits ($M_r \cong 53{,}000$) and eight small regulatory subunits ($M_r \cong 14{,}000$). In some purple photosynthetic bacteria, the Rubisco is comprised of only large subunits (either L_2, L_4, or L_8). Following the carboxylation reaction, the resulting 3PG is converted to 1,3-bisphosphoglycerate (BPG) using ATP and then to glyceraldehyde 3-phosphate (GAP) using NADPH. The GAP is an important intermediate for subsequent biosynthesis of various compounds, such as sugars, fatty acids and

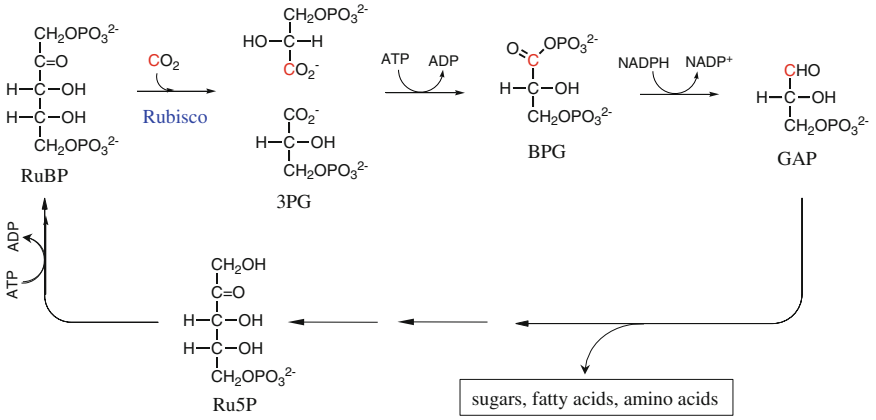


Fig. 6 The carbon-fixation cycle. A total of 3 molecules of ATP and 2 molecules of NADPH are consumed for each CO_2 molecule converted into carbohydrate

amino acids. A two-carbon keto unit is added to the GAP through reactions catalyzed by transketolase to form a five-carbon compound ribulose-5-phosphate (Ru5P) that is the precursor of RuBP.

4 Summary

All photosystems are composed of an antenna complex and a photochemical reaction center. Photosynthesis begins with absorption of sunlight energy by various pigment molecules. The absorbed energy is transferred to reaction center where the charge separation occurs. The electrons are utilized to generate reducing power (NADPH) and transmembrane electrochemical proton gradient that finally lead to generation of the high energy molecule ATP. These molecules serve as energy sources in carbon-fixation reaction. Photosynthetic bacteria contain only a single photosystem with a simple composition, whereas green plants, algae and cyanobacteria have two photosystems connected in series which are capable of extracting electrons from water molecules to generate molecular oxygen (O_2) as a by-product.

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