Chapter 1

What Is Photosynthesis? — A Broader and Inclusive View

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Abstract

In general, the word, *photosynthesis*, is considered synonymous with *oxygenic photosynthesis*, a process by which cyanobacteria, algae, aquatic, and terrestrial plants produce oxygen and carbohydrates, using light (photons), water and carbon dioxide. Further, we have *anoxygenic bacterial photosynthesis* where oxygen is not evolved, but a substrate, other than water, is oxidized, and *rhodopsin- type systems*, where ATP is produced. In principle, one could expand the concept of the term *photosynthesis*, provided appropriate caveats are added, to include light-driven assimilation of molecular nitrogen, photoproduction of molecular hydrogen, and even synthesis of vitamin D in skin. We conclude with a glimpse of the rapidly developing field of artificial photosynthesis.

Keywords: oxygenic photosynthesis, anoxygenic photosynthesis, energy conversion, photochemistry, artificial photosynthesis

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Abbreviations

ADP	Adenosine diphosphate
ATP	Adenosine triphosphate
BChl	Bacteriochlorophyll
Chl	chlorophyll
Cyt b_6f	Cytochrome b_6f complex
Fd	Ferredoxin
FNR	Ferredoxin-NADP- reductase
Mn_4CaO_5	Manganese-calcium-oxygen complex
$NADP^+$/ NADPH	Nicotinamide adenine dinucleotide phosphate (oxidized/reduced forms)
PC	Plastocyanin
Pheo	Pheophytin
pmf	Proton motive force
PQ/PQH_2	Mobile plastoquinone molecules (oxidized/reduced forms)
PSI	Photosystem I
PSII	Photosystem II
P680	Primary electron donor of PSII that includes Chl *a* molecules
P700	Primary electron donor of PSI that includes Chl a molecules
Q_A/Q_B	Primary/secondary plastoquinone electron acceptors of PS II
RC	Reaction center
RuBisCO	Ribulose-1,5-bisphosphate carboxylase-oxygenase
Y_D/Y_Z	Redox-active tyrosine D/Z

1. Introduction

Most life on our planet, directly or indirectly, depends on oxygenic photosynthesis, in which water is oxidized to oxygen and carbon dioxide is reduced to carbohydrate. In this chapter, we have included other types of photosynthesis. In anoxygenic photosynthetic bacteria, water is not used as an electron donor, and thus oxygen is not evolved, but, instead, sulfur may be released, in case hydrogen sulfide (H_2S) is used as an electron donor. In a broader context, photosynthesis (*photo* is light and *synthesis* is the formation of a new chemical compound from simpler ones) may not be always connected with the assimilation of carbon dioxide (CO_2); in some cases, it is connected with the assimilation of molecular nitrogen. In all cases, various forms of this process are extremely important for life on our planet.

The processes, thus far, included, in most cases, use chlorophyll (Chl) or bacteriochlorophyll (BChl), both for absorbing energy from sunlight, and for receiving it from other auxiliary pigments and converting it to chemical energy. For a basic understanding of this process, see Rabinowitch and Govindjee (1969); Björn et al. (2009); Shevela et al. (2019); and Blankenship (2021). But, taking a broader view of the word 'photosynthesis', we include, here, other types of photosynthesis, *e.g.*, even those somewhat related to vision, where rhodopsin is a light absorber; this is done, *e.g.*, by *Halobacterium salinarum* (which despite its name is not a bacterium, but an archaeon, where light energy is used to create a proton gradient which is then used to synthesize ATP (Racker and Stoeckenius 1974; Henderson 1977; R. Govindjee et al. 1980; R. Govindjee et al. 1990; Grote 2013).

But, to cite the American Constitution, "we the people," also carry out a sort of 'photosynthesis', namely of vitamin D by ultraviolet (UV) light. It may sound strange, but we include it here for completeness. This vitamin is a substance which is essential for many processes in our body. Vitamin D, called the 'sunshine vitamin', is produced either by a type of 'photosynthesis' in our own bodies, or by a photochemical reaction in other organisms. It is an important process because almost 50% of humans in our World suffer from its deficiency (Nair and Maseeh 2012).

In fact, were it not for other types of synthesis of organic compounds, using light, there would not have been any life at all on our Earth. We begin our discussion with 'Oxygenic Photosynthesis' that gives us oxygen and food.

2. Oxygenic Photosynthesis

The reaction that distinguishes oxygenic photosynthesis from all other types of photosynthesis, and from all other metabolic processes, is the oxidation of water using the energy from light.

Algae as well as higher plants have chloroplasts, which contain pigments (chlorophylls and carotenoids) located in protein complexes in their thylakoid membranes. Although cyanobacteria (earlier called blue-green algae) do not have chloroplasts, they are themselves what corresponds to chloroplasts. During evolution, the ancestors of algae acquired chloroplasts by incorporating cyanobacteria, or, in some cases, other algae, into their cells (Sabater 2018; Larkum et al. 2020). The light used in oxygenic photosynthesis is roughly the same as what is visible light for us, with photon energy ranging from ~1.63 electron volt (eV) for red light to 3.26 eV for violet light. This corresponds to, per mol of photons, 157 kilojoules (kJ) for red light, and 315 kJ for violet light. To oxidize two molecules of water to one molecule of oxygen, at least 4 photons of light are needed; however, as is well-established, two light reactions are needed for water oxidation when CO_2 is reduced, and, thus, at least 8 photons are needed for the evolution of one O_2 molecule (Nickelsen and Govindjee 2011).

The process of water oxidation is catalyzed by a charge-accumulating catalyst, a Mn_4CaO_5 cluster, localized in a pigment-protein complex called Photosystem II (PSII) (Figure 1). This complex is incorporated in the thylakoid membranes in chloroplasts and in cyanobacteria (Dau and Zaharieva 2009; Vinyard et al. 2013; Junge 2019; Shevela et al. 2021); it is also known as *water: plastoquinone oxidoreductase* since it oxidizes water and reduces plastoquinone. The process of water oxidation by PSII can be, and has been, described by an elegant model developed by Bessel Kok and co-authors more than 50 years ago (Kok et al. 1970). This model, also known as the Kok cycle, is shown in Figure 1.

We know that PSII is not the only photosystem involved in photosynthesis by cyanobacteria, algae, and plants. As one would guess from the name, it has a counterpart, the Photosystem I (PSI) (Grotjohann and Fromme 2005; Suga et al. 2016; Caspy and Nelson 2018; Hippler and Nelson 2021). Most of the components involved in light-induced redox chemistry of oxygenic photosynthesis are sort of 'floating' in the lipids in the thylakoid membranes in the chloroplasts or cyanobacteria (Figure 2A). Apart from the PSI and PSII protein complexes, there are two other large complexes, the cytochrome (Cyt) b_6f (Baniulis et al. 2008), and the ATP synthase (ATPase) (Junge and Nelson 2015); there are also molecules of plastoquinone 'floating' in the thylakoid membrane lipids.

In addition, in the aqueous phase on the inner (lumen) side (also known as the *p* side; where "*p"* signifies "positive," *i.e.*, plus (+) charge) of the thylakoid membrane, there is a small copper-containing protein, plastocyanin (PC) that transfers electrons from the Cyt b_6f to PSI (see Figure 2A). In some cases, PC is substituted by the iron-containing protein Cyt c_6 (also known as Cyt c_{533}) (Zhang et al. 1992). In the aqueous phase on the outer side of the membrane (the stroma side), there are molecules of iron-containing protein ferredoxin (Fd), and NADP (nicotinamide adenine nucleotide phosphate). All these components are redox-active, *i.e.*, they function to transfer electrons from one component to another (Figure 2A). In addition, NADP reduction includes protons as well; it exists both as $NADP^+$ and NADPH, the latter is formed after a proton and two electrons are added to the former.

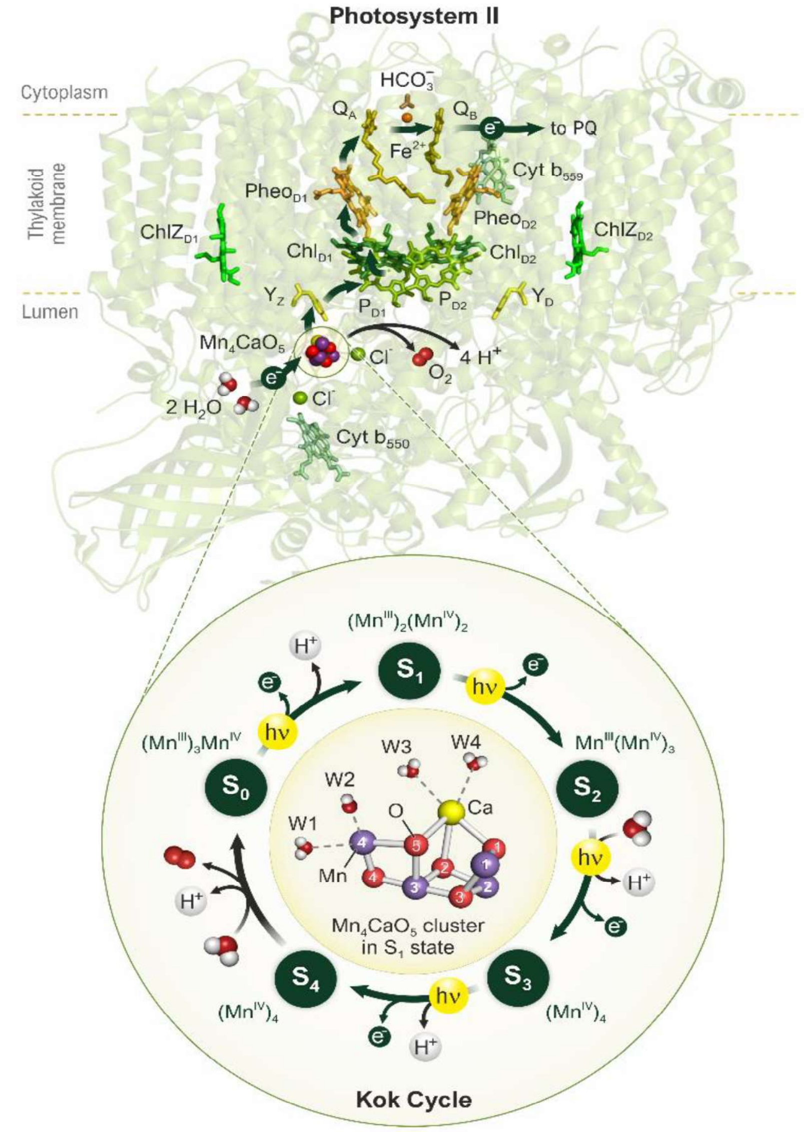

Figure 1. A central enzyme of oxygenic photosynthesis, Photosystem II (PSII), with its electron-transfer cofactors (in the thylakoid membrane) and the *Kok Cycle* – a model of photosynthetic water oxidation and evolution of molecular oxygen by the Mn_4CaO_5 cluster.

Figure 1. (Continued). The protein scaffold of PSII monomer is shown as a light background. All redox cofactors are located in two branches of the D1 and D2 proteins. However, the electron transfer (direction is depicted by dark green arrows) occurs mainly through the cofactors located on the D1 protein of the PSII reaction center (the *active branch*) and includes the following redox-active cofactors: inorganic Mn_4CaO_5 cluster, redox-active tyrosine Z (Y_Z), two chlorophyll (Chl) *a* molecules (P_{D1} and P_{D2}) and two accessory Chls *a* (Chl_{D1} and Chl_{D2}), the electron acceptor pheophytin ($Pheo_{D1}$), the primary quinone (Q_A) on the D2 protein and the secondary quinone (Q_B) on the D1 protein. Note that an ensemble of P_{D1}, P_{D2}, Chl_{D1}, and Chl_{D2} is traditionally and collectively known as the primary electron donor P680. The electron transfer from the reduced Q_A to Q_B involves the non-heme iron (Fe^{2+}). Here, bicarbonate ion (HCO_3^-) bound to Fe^{2+} plays a unique regulatory role (Shevela et al. 2012; Brinkert et al. 2016). The Kok cycle consists of five S-states (S_0, S_1, ..., S_4), where the subscript signifies the number of oxidizing equivalents stored within the Mn_4CaO_5 cluster. The light-induced S state transitions of the cluster are indicated by arrows with yellow "hν." Thus, four light-induced transfer of electrons to the Y_Z leads to the release of four protons and one O_2 molecule from two water molecules per each turn of the S-state cycle. After long dark adaptation of the photosynthetic system, the Mn_4CaO_5 cluster exists mostly in the S_1 state. The structure of the Mn_4CaO_5 cluster in the S_1 state, surrounded by four substrate water molecules (W1–W4), is shown within the Kok cycle. It consists of four atoms (1, 2, 3 and 4) of manganese (purple), five atoms (1, 2, 3, 4 and 5) of oxygen (red), and one atom of calcium (yellow), surrounded by four water molecules (W1, W2, W3 and W4), acting as substrate. The structure of the Mn_4CaO_5 cluster was generated by using the coordinates of the PDB with ID 6w1o (Ibrahim et al. 2020). The PSII structure with redox cofactors and protein scaffold was generated by using the coordinates deposited at PDB with ID 3arc (Umena et al. 2011). Note that the phytyl tails of both Chls and Pheos, and the isoprenyl chains of the quinones, have been left out here for clarity. For Chl structure, see Figure 3. Modified from Shevela et al. (2019).

The two photosystems (PSII and PSI), working together, energize the linear electron transfer pathway from H_2O to $NADP^+$. The redox-active cofactors that make this transfer possible can be arranged according to their redox potentials as shown in Figure 2B. Such an arrangement, known as *the Z-scheme*, was proposed by Robert (Robin) Hill and Fay Bendall more than 60 years ago (Hill and Bendall 1960). For the historical development of the Z-Scheme, see Govindjee et al. (2017). We note that the yellow circles, labelled as "*hv*" in Figure 2, are for photons (light quanta) that are absorbed by hundreds of light-harvesting antenna pigments (not shown), and from which the excitation energy is transferred to a few special reaction center Chl *a* molecules, designated as P680 (for PSII) and P700 (for PSI).

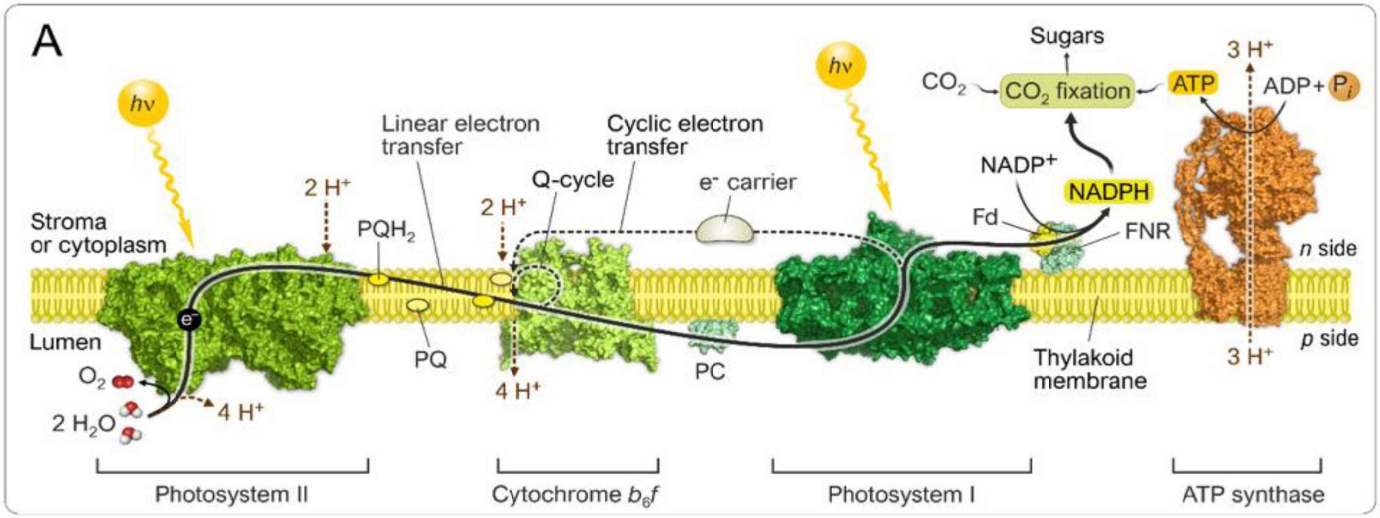

Figure 2. (Continued).

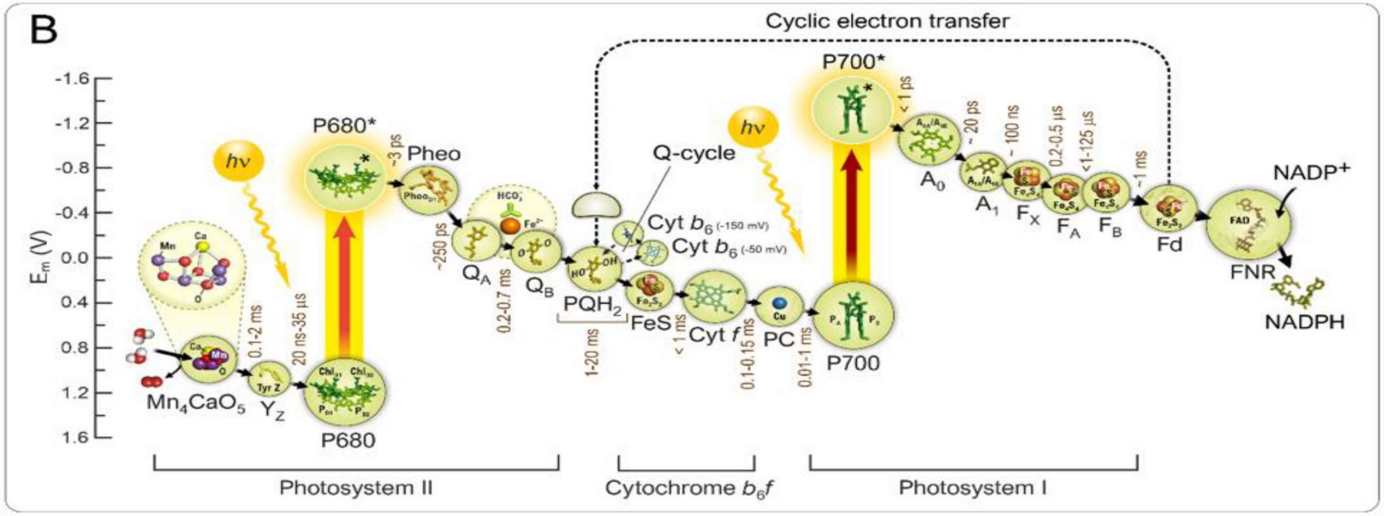

Figure 2. Photosynthetic protein complexes, light-induced electron and proton transfer reactions, and the Z-scheme of oxygenic photosynthesis. (A) A simplified schematic representation of photosynthetic protein complexes (embedded in the thylakoid membrane), involved in *linear light-induced electron transfer* (the long black bold arrow) from H_2O to $NADP^+$, and proton transfer reactions (dashed arrows, highlighted in yellow). The end products of these reactions are NADPH and ATP. These two molecules drive the "dark reactions" of CO_2 fixation in the stroma of the chloroplast *via* a cyclic metabolic pathway, known as the Calvin-Benson-Bassham cycle (see Figure 4). Under certain conditions, electrons from Photosystem (PS) I cycle back towards Cytochrome (Cyt) b_6f complex and then again back towards PSI, thus performing a *cyclic electron transfer* (dashed black arrow). Together with the Q-cycle that takes place in the Cyt b_6f, the cyclic electron transfer increases the number of protons moved from *n* (the negative)- to *p* (the positive)-side of the thylakoid membrane. Functional connections between PSII and Cyt b_6f and between Cyt b_6f and PSI complexes are accomplished through diffusible plastoquinone (PQ) and mobile copper-containing plastocyanin (PC) molecules.

Figure 2. (Continued). (B) The *zig-zag* or the *Z scheme*, representing the linear electron transfer from H_2O to $NADP^+$, is plotted on a redox midpoint potential (E_m, at pH 7) scale. This diagram also shows approximate half-times for electron transfer reactions between most redox-active components. The two large vertical arrows symbolize the transition of the reaction center chlorophyll (Chl) *a* molecules (P680 in PSII and P700 in PSI) from their ground to their (singlet) excited states (P680* and P700*, respectively) attained largely after excitation energy transfer from their respective antenna systems and to a lesser extent by a direct absorption of photons (hv). *Abbreviations:* Mn_4CaO_5, manganese-calcium-oxygen cluster; Y_Z, tyrosine (Tyr Z); P680, primary electron donor of PSII that includes Chl *a* molecules P_{D1}, P_{D2}, Chl_{D1}, and Chl_{D2}; Pheo, pheophytin ($Pheo_{D1}$), the primary electron acceptor of PSII; Q_A and Q_B, primary and secondary plastoquinone electron acceptors; FeS, Rieske iron-sulfur protein; Cyt *f*, cytochrome *f*; P700, primary electron donor of PSI that includes Chl *a* molecules P_A and P_B; A_0, primary electron acceptor of PSI (a special pair of Chl *a* molecules); A_1, pair of phylloquinone (vitamin K) molecules; F_X, F_A, and F_B, iron-sulfur clusters of PSI; Fd, ferredoxin, and FNR, ferredoxin-NADP+ reductase. Protein complexes in panel A and the redox-active cofactors in panel B were generated using coordinates deposited at PDB with the following IDs: 1ag6, 1vf5, 1sm4, 2mh7, 2gim, 3arc, 3w5u, 3wu2, 4y28, 5l8r, 6b8h, 6w1o. Phytol tails of Chl and Pheo molecules as well as the isoprenyl chains of the Q_A and Q_B were omitted for the sake of simplicity. Modified from authors' earlier publications (Govindjee et al. 2017; Shevela et al. 2021).

In plants and green algae, these antenna pigments are Chl *a*, Chl *b*, and various carotenoids (Björn et al. 2009; Chen 2014; Hashimoto et al. 2016). In other phototrophic organisms, *e.g.*, in the red algae and cyanobacteria, they are open chain tetrapyrroles, phycobilins, covalently bound to light-harvesting phycobilin-proteins: phycocyanins, allophycocyanins, phycoerythrins, and phycoerythro-cyanin (Brown et al. 1990).

Molecular structure and a model of Chl *a* is shown in Figure 3. Other forms, such as Chl *b,* are present in the chloroplasts of plants and green algae; the difference in the chemical structure of Chl *a* and Chl *b* is shown in Figure 3; further, Chl *c* (in diatoms and brown algae), Chl *d* (in cyanobacterium *Acaryochloris marina*), and Chl *f* (*e.g.*, in cyanobacterium *Halomicronema hongdechloris*) are very similar in structure (Grimm et al. 2006; Scheer 2006; also see Chen 2014). Note that in *Acaryochloris marina,* Chl *d* also takes the place of Chl *a* in the reaction centers (RCs) of PSI and PSII (Itoh et al. 2007).

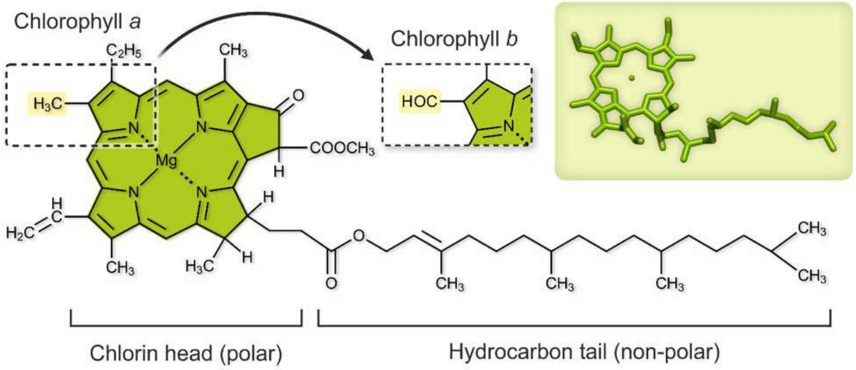

Figure 3. Molecular structures of chlorophylls *a* and *b*.

The numbers 680 and 700 in P680 and P700, mentioned above, refer to the absorption maxima in nanometers, in the red region of the spectrum, for these two special RC ensembles of photoactive Chl *a* molecules. When P680 absorbs a photon (or has received a quantum of energy from an antenna pigment), it changes to an energy-rich form P680* (Figure 2B) and soon (within picoseconds) transfers an electron to a pheophytin (Pheo) *a* molecule, which is similar to Chl *a*, but has its magnesium ion replaced by two protons. Thus, P680* becomes the cation radical $P680^{\bullet+}$ and Pheo becomes the anion radical $Pheo^{\bullet-}$, *i.e.*, the process known as *'primary charge separation'* occurs. The $P680^{\bullet+}$ is known to be the strongest oxidant that can be generated in biological reactions (Ishikita et al. 2005; Rappaport and Diner 2008). Its high midpoint redox potential (~ +1.25 V!) allows P680$^{\bullet+}$ to oxidize a tyrosine residue, Y_Z, of the D1 protein, which in turn oxidizes the Mn_4CaO_5 cluster (see Figures 1B and 2B).

We emphasize here the important role of bicarbonate ions (HCO_3^-; hydrogen carbonate, as recommended by IUPAC nomenclature) in light-induced reactions of PSII, and thus, in oxygenic photosynthesis. Extensive studies over the last decades have shown that HCO_3^-, bound as a bidentate ligand to the non-heme iron between Q_A and Q_B in RCs of PSII (see Figures 1 and 2B), regulates their light-induced electron and proton transfer reactions (Van Rensen et al. 1999; Shevela et al. 2012; Brinkert et al. 2016; Shevela et al. 2020; Fantuzzi et al. 2022). Anoxygenic photosynthetic bacteria do not have bicarbonate in the structure of their evolutionary related RCs (Michel and Deisenhofer 1988; Shopes et al. 1989), indicating that bicarbonate is important only in oxygenic photosynthesis. However, the story with bicarbonate in PSII is more complex, since on the electron-donor side of PSII, mobile HCO_3^- ions enhance and thus, most likely, regulate water oxidation, by acting as proton acceptors, after which they dissociate into CO_2 and H_2O (Koroidov et al. 2014; Banerjee et al. 2019; Shevela et al. 2020).

As mentioned above, when P680 is oxidized, an electron is transferred to Pheo, which passes the electron on to other compounds of the "electron transfer" chain, located between the two photosystems. On the other hand, P700 has, at the same time as P680, been oxidized after having absorbed another photon, or having received excitation energy from the antenna pigments in PSI; P700$^+$ is then reduced by the electron arriving through the mobile "electron carrier" PC. The electron transferred by P700* to the various electron acceptors A_0 (a Chl *a* molecule), A_1 (phylloquinone molecules), F_X, F_A, and F_B (bound iron-sulfur clusters) to the outer side of the membrane, is picked up by the membrane-associated enzyme ferredoxin-NADP$^+$ reductase (FNR), transferred to ferredoxin (Fd), and then (in two steps) on to NADP$^+$, present in the external aqueous phase, which at the same time picks up a proton from the water to become NADPH (Aliverti et al. 2008; Medina 2009). The NADPH is subsequently used for the reduction of carbon dioxide to sugars in a complicated chemical process, known as the Calvin-Benson-Bassham cycle (see the section below), which, in addition, requires additional *chemical* energy available in the molecules of ATP.

The needed ATP is formed by ATP synthase, located in the thylakoid membrane, by using energy provided by *proton motive force* (*pmf*), which includes both membrane potential and proton gradient, developed during the electron transfer by PSII and PSI. ATP is made by adding a phosphate group to adenosine diphosphate (ADP), but this requires energy. Where does the energy come from? Looking back at Figure 2, we can see that for each "turn" of the Kok cycle, four protons are released on the *p*-side of the thylakoid membrane (Figure 2A). On the other hand, on the electron-acceptor side of PSII, protons are consumed by plastoquinone (PQ) at the Q_B-site on the *n*-side (*n* for "negative") of the thylakoid membrane (Figure 2A). This reaction, in a simplified way, is: $PQ + 2\ e^{-} + 2\ H^{+} \rightarrow PQH_2$.

The whole process is equivalent to a transfer of protons from the outer *n*-side to the inner *p*-side of the thylakoid membrane. Thus, by releasing four protons into the lumen associated with the water oxidation reaction, and by the uptake of protons from the stromal/ cytoplasmic side of the membrane, associated with the reduction of PQ, and their subsequent release to lumen upon oxidation of PQH_2 by the Cyt b_6f complex (Cramer et al. 2008), PSII contributes greatly to the generation of the 'transmembrane proton electrochemical potential gradient' (*pmf*). The *pmf* is made up of both a pH gradient (ΔpH) and an electrical potential gradient (ΔΨ) (Mitchell 2011). This is a way of energy storage. Moreover, when the *cyclic electron transfer* around PSI and the so-called *Q-cycle* around the Cyt b_6f complex are involved (Cramer et al. 2011), much more protons are available for energy storage by the ATP synthase (Crofts 2004) (Figure 2A). We do not have to worry about the consumption of protons in the conversion of $NADP^{+}$ to NADPH mentioned above, since these protons are released again in the further reactions of the conversion of carbon dioxide to carbohydrate (Figure 4).

3. Assimilation of Carbon Dioxide

In cyanobacteria, and most algae and plants, carbon dioxide, that is photosynthetically assimilated, is processed by an enzyme ribulose-1,5-bisphosphate carboxylase-oxygenase (RuBisCO); the name 'oxygenase' is there since it can use oxygen in addition to carbon dioxide in a process called photorespiration. It is one of many enzymes acting as catalysts in the Calvin-Benson-Bassham cycle (Figure 4), named after Melvin Calvin, Andrew Benson, and James Alan Bassham of the University of California, Berkeley, who discovered it more than 70 years ago (Martin et al. 2000; Berkowitz et al. 2007). We focus here on the assimilation of carbon dioxide as well as what the presence of oxygen does to it.

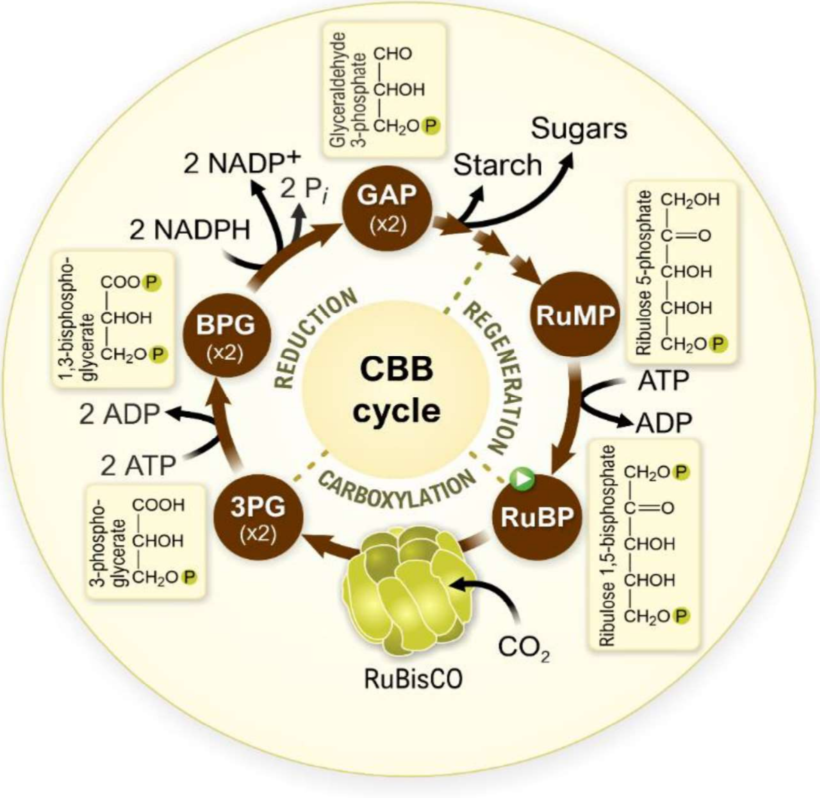

Figure 4. A simplified representation of the Calvin-Benson-Bassham (CBB) cycle (also known as the C3 cycle). The cycle begins with RuBP (ribulose 1,5-bisphosphate) producing 3-phosphoglycerate (3PG), which is phosphorylated by ATP to 1,3-biphosphoglycerate (BPG), and then reduced to glyceraldehyde 3-phosphate (GAP) by NADPH with the release of inorganic phosphate (P_i). This is followed by a fraction of GAP molecules leaving the cycle and forming starch or sugars. Finally, regeneration of RuBP takes place *via* ribulose 5-phosphate (RuMP). The diagram is a courtesy of SciGrafik (Sweden) & Agrisera (Sweden).

Inorganic carbon assimilation has its problems. The affinity for carbon dioxide is not high; thus, the carbon fixation cycle cannot function efficiently when the concentration of available carbon dioxide is too low. This situation is exacerbated since oxygen competes with carbon dioxide for the binding site on RuBisCO. Binding of oxygen, instead of carbon dioxide, results in photorespiration (Ogren 1984), which consumes organic carbon instead of producing it. This was, obviously, not a problem when the Calvin-Benson-Bassham cycle had evolved, since at that time, the CO_2 in the air and the water was high, and the oxygen was very low. When the ratio of CO_2 to O_2 decreased, some plants and algae started to remedy this in various ways, and the most important one was the evolution of the so-called Hatch-Slack pathway, the C-4 pathway (see below). For other ways of increasing the concentration of carbon dioxide at the RuBisCO, see *e.g.*, Espie and Colman (2005) and Raven et al. (2012).

Looking at Figure 4, we may assume that, if we feed a plant radioactive CO_2, the first labeled organic compound would be 3-phosphoglycerate (3PG), and this is what Melvin Calvin and coworkers had found, using *Chlorella* as experimental material (Benson 2002; Bassham 2003). However, Hugo Kortschak and co-workers, while essentially repeating the above experiment using sugarcane, found the early label to heavily concentrate in malic and aspartic acids (Kortschak et al. 1965). Soon after, Hal Hatch and Roger Slack began to chart what has become known as the Hatch-Slack pathway (Hatch and Slack 1966). This is a way of increasing the concentration of carbon dioxide at the RuBisCO, and, thus, it increases the efficiency of carbon dioxide assimilation and counteracts the interference by oxygen. Many of the enzymes for this pathway are also present in other organisms that do not use this pathway, which has facilitated the evolution of this pathway multiple times, but for somewhat different reasons.

In land plants, in addition to the decreasing levels of carbon dioxide, the difficulty in obtaining sufficient water has also contributed to problems in the supply of carbon dioxide. It has made it necessary to keep stomata partly closed, which has led to lower internal concentration of carbon dioxide. However, the Hatch & Slack pathway has evolved also in some aquatic plants, or even algae (Haimovich-Dayan et al. 2013; Liu et al. 2020a; Zhang et al. 2021b).

4. Anoxygenic Photosynthesis in Bacteria

As the name implies, anoxygenic photosynthetic bacteria do not release molecular oxygen. Each of them employs only one kind of photosystem, similar either to PSI or to PSII, but without the ability to oxidize water and evolve molecular oxygen (cf. Blankenship et al. 1995).

The classification of anoxygenic photosynthetic bacteria was originally based on pigmentation and metabolism: purple sulfur bacteria, purple non-sulfur bacteria, green sulfur bacteria, and green non-sulfur bacteria. However, the classification is now based on their DNA sequence, which has radically, but not in all cases, changed the relationships between them (Imhoff 2017; George et al. 2020).

These simpler (anoxygenic) forms of photosynthesis (*i.e.*, similar to PSI or PSII) are spread all over among the various groups of bacteria. Although most cyanobacteria carry out oxygenic photosynthesis, some do not. Apart from the fact that in their special cells, the heterocysts, many cyanobacteria are equipped with enzymes to assimilate molecular nitrogen, by using only PSI, some cyanobacteria do not evolve oxygen from any of their cells! This may, however, be due to the inhibition of the electron donor side of PSII by sulfide (Castenholz 1976, 1977; Klatt et al. 2015; Hamilton et al. 2018), or because of the (genetically) missing key components. Such genetic changes may have evolved naturally when there was too much sulfide in the environment (Grim and Dick 2016); in addition, in some cases, inactivation of PSII may have occurred when they were growing under strong light (Lewis et al. 2022).

Note that anoxygenic photosynthetic bacteria were introduced above as being simpler than cyanobacteria and other organisms with oxygenic photosynthesis; this may imply that they may have been evolutionary precursors to cyanobacteria. However, oxygenic photosynthesis may have originated in proto-cyanobacteria which then gave rise to cyanobacteria, and on the way, they are the ones that gave rise to the anoxygenic photosynthetic bacteria (Cardona et al. 2019). Future research is needed to get the final picture. In fact, several non-photosynthetic organisms, discovered recently, may be the precursors of cyanobacteria and could just be the organisms in which photosynthetic reactions evolved on the primitive Earth (Soo et al. 2017; Soo et al. 2019). In addition, several non-photosynthetic organisms have also been found in Melainabacteria, which are related to cyanobacteria (Hofer 2013).

PSI-like systems, in photosynthetic bacteria, are distributed among Firmicutes, Acidobacteria, and Chlorobi, whereas, PSII-like systems are found among Proteobacteria, Chloroflexi, and Gemmatimonadetes, as well as in the recently discovered *Candidatus,* a Eremiobacterota (Figure 5; "*Candidatus*" means that the name is preliminary, not yet officially recognized). This implies that there is almost no correlation between the relatedness of the bacterial groups and the distribution of the two photosystems (Ward et al. 2019). For further details, see chapters by Adessi et al. (2017), Imhoff (2017), and Miao et al. (2017) in a book edited by Hallenbeck (2017).

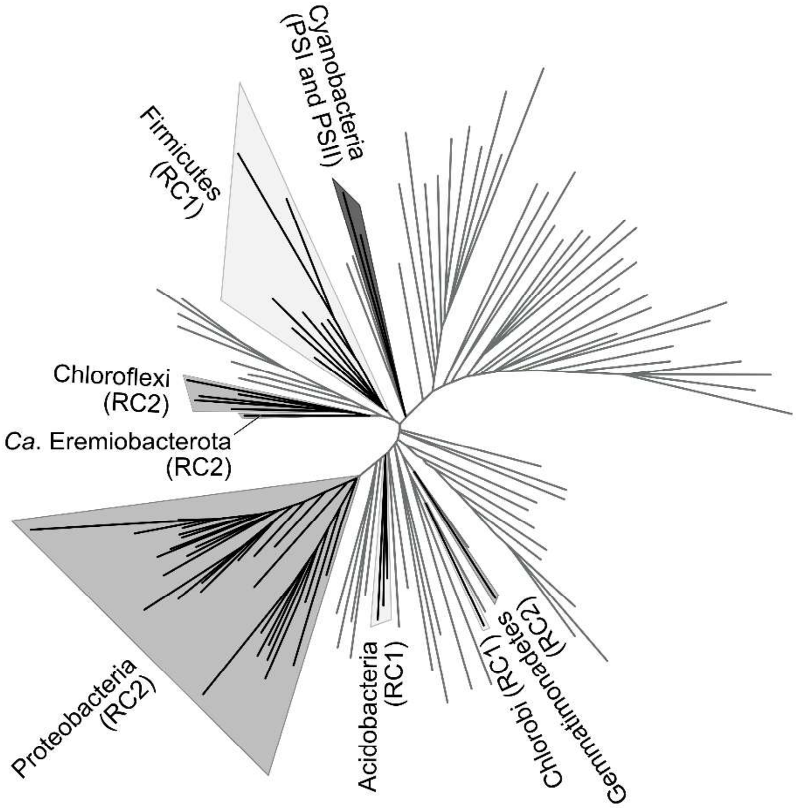

Figure 5. Phylogenetic relations between different photosynthetic bacteria according to Ward et al. (2019). Also shown is the distribution of a type of Photosystem I (PSI) and of Photosystem II (PSII), as well as their reaction centers (RC1 and RC2). *Ca.* Erimiobacterota is *Candidatus* phylum of Eremiobacterota, uncultured bacteria, which have been found to contain RC2.

5. Bioproduction of Compounds by Photosynthetic Organisms

In this chapter we do not deal with agricultural products of plants. However, we point out that cyanobacteria, algae and anoxygenic photosynthetic bacteria have the potential to produce many value-added carbon-based products in the future. At present, non-photosynthetic microorganisms are being used to produce many biochemicals and pharmaceutical products in chemostats and fermenters; in these systems, energy is provided by carbohydrates (most often from sugars by fermentation or respiration); we expect that, in the future, light will be used to provide the needed energy. This would be especially true for algae which can be grown in algal ponds or in sea-farms. The rich variety of algae which have evolved over the last 2 billion years provide a vast opportunity to produce value-added products in the future (Larkum 2010).

6. Photoassimilation of Molecular Nitrogen

Many anaerobic photosynthetic bacteria, capable of CO_2 assimilation, are also able to assimilate molecular nitrogen (N_2), using the energy of light. This nitrogen assimilation ability is present in Alphaproteobacteria (e.g., *Rhodobacter*, *Rhodomicrobium*, *Rhodospirillum*, and *Rhodopseudomons*), in Gammaproteobacteria (e.g., *Amoebobacter*, *Chromatium*, *Thiocapsa*, *Thiocystis*, and *Ectothiorhodospira*), in Chlorobi (e.g., *Chlorobium, Pelodictyon*, and *Prosthecochloris*), and in Firmicutis (e.g., *Heliobacterium*) (Gallon 2001). The nitrogenase, the enzyme, needed for nitrogen assimilation, is, indeed, present in a wide variety of eubacteria and Archaea. Furthermore, in some cases, the energy needed is obtained through a light-driven membrane-bound proton pump, which includes a rhodopsin. Gleason et al. (2019) have shown that even fungi are able to utilize this reaction for nitrogen fixation.

On the other hand, cyanobacteria have different ways of dealing with both oxygen evolution and nitrogen assimilation. Many of the filamentous forms have developed a special cell-type as a complement to the oxygen producing cells. These special cells, the so-called heterocysts, mentioned above, do not contain any oxygen-evolving PSII, but only PSI; further, they are protected from the atmospheric oxygen by a very thick cell wall (Figure 6). Using PSI, heterocysts produce a large amount of ATP needed for nitrogen assimilation. And, from the neighboring cells, they obtain all the carbon compounds needed to produce amino acids and more. Ten to 20% of the cells in heterocyst-forming cyanobacterial filaments differentiate into heterocysts (Figure 6). These heterocysts never form together, *i.e.*, in cells next to each other; there are always many other cells in between them. Interestingly, a great potential of using immobilized heterocysts, for instance, in alginate films, has been shown, when isolated from cyanobacteria under anaerobic conditions; this system has sustainable nitrogen fixation, concomitant with the production of potential biofuels, such as H_2 and “green” ethylene (C_2H_4) (Kosourov et al. 2014; Volgusheva et al. 2019; Vajravel et al. 2020).

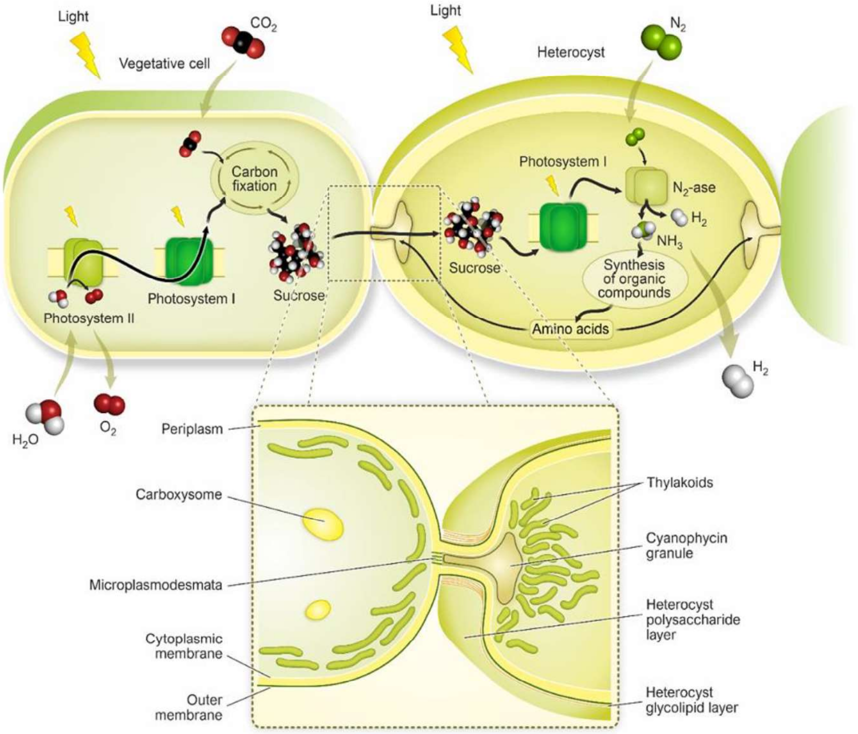

Figure 6. Many cyanobacteria have cells of two kinds (vegetative cells and heterocysts), carrying out different processes. Most of the cells are vegetative cells (top left). Using PSI and PSII they carry out oxygenic photosynthesis with the assimilation of CO_2, and the evolution of O_2. However, about 10–20% of the cells are heterocysts (top right), spaced widely apart. They not only carry out the conversion of molecular nitrogen to organic nitrogen with the help of nitrogenase, but produce hydrogen (H_2). Note that in the zoomed region (see the bottom diagram) the layers surrounding both cell types have a cytoplasmic membrane, outer membrane, and a periplasm. In addition to these layers, the heterocyst has glycolipid and polysaccharide layers. Modified and redrawn from earlier publications (Flores and Herrero 2010; Volgusheva et al. 2019).

Cyanobacteria that do not form heterocysts do other interesting things. For example, *Lyngbya*, *Oscillatoria*, *Gloeothece*, *Cyanothece*, and *Synechocystis* evolve O_2 during the daytime, but fix nitrogen at night (Lundgren et al. 2003). On the other hand, *Trichodesmium* assimilates N_2 during the day, and, at the same time it evolves O_2. It seems that, in this organism, net O_2 evolution is restricted to short periods in the mornings and in the evenings. Further, the net O_2 uptake, in respiration, takes place during the light period, while nitrogen fixation is taking place; we note that nitrogenase is protected since oxygen is being consumed by respiration at the same time (Eichner et al. 2019; Inomura et al. 2019).

Furthermore, in cyanobacteria, molecular hydrogen is also evolved, using nitrogenase, during nitrogen assimilation, as shown below:

$$N_2 + 8\ H^+ + 8\ e^- + 16\ ATP \rightarrow 2\ NH_3 + H_2 + 16\ ADP + 16\ P_i \qquad (1)$$

where, P_i stands for inorganic orthophosphate; and the electrons (e^-) are from organic substances (mainly sucrose), imported from the vegetative cells and oxidized in the oxidative pentose phosphate cycle (Kruger and von Schaewen 2003); further, a large amount of ATP is consumed in the above reaction. In case a suitable source of bound nitrogen (organic nitrogen, ammonia, or nitrate) is available, nitrogen fixation is stopped, and the cyanobacterium then uses bound nitrogen instead. For further discussion, see the next section on the "Photoproduction of Molecular Hydrogen."

Going beyond nitrogen fixation, we note that cyanobacteria are also equipped with a type of hydrogenase that can recycle the hydrogen into its metabolism, avoiding the loss of reducing power. Most hydrogenases can work both ways, *i.e.*, they produce hydrogen, or use it (Tamagnini et al. 2007; Lubitz et al. 2014; Ogata et al. 2016; Morra 2022).

In summary, vegetative cells of cyanobacteria have both PSI and PSII, as well as the Calvin-Benson-Bassham cycle for the normal assimilation of carbon dioxide (Figure 6). They export organic carbon, mostly sucrose, to the heterocysts, which use the carbon and reducing equivalents in the sucrose for the conversion of molecular nitrogen to organic nitrogen compounds, which are then exported back to the vegetative cells; these cells then use the synthesized compounds for growth and multiplication. An interesting fact is that when these vegetative cells reach to be around ten cells in a row, the cell in the center turns into a heterocyst; we still do not know the details of its how and why!

7. Photoproduction of Molecular Hydrogen

Hans Gaffron and Jack Rubin (1942) were the first to observe photochemical production of hydrogen from algae; for further information, see Kaltwasser et al. (1969) and Eroglu and Melis (2011). Within a few years, Gest and Kamen (1949) reported photochemical production of molecular hydrogen by an anoxygenic photosynthetic bacterium, *Rhodospirillum rubrum*. Since then, many experiments have been conducted on the photogeneration of hydrogen, mostly using several anoxygenic photosynthetic bacteria, but also cyanobacteria and algae (Yagi et al. 2016; Masukawa et al. 2017; Kosourov et al. 2018; Kosourov et al. 2021; Li et al. 2021). In algae, hydrogen is generated by using hydrogenase, an enzyme which is sensitive to molecular oxygen, a problem that requires special attention (Jokel et al. 2020). However, in this chapter, we focus on the non-oxygenic (i.e., anoxygenic) photosynthetic bacteria for hydrogen production.

Unfortunately, at this time, hydrogen production by photosynthetic bacteria is not economically viable, except when it is combined with sewage treatment. However, this may change when methods improve and costs of other fuels increase due to shortage of the material, or due to environmental considerations. One species, being seriously considered for future exploitation, is the photosynthetic purple non-sulfur bacterium *Rhodobacter sphaeroides*. Like many other photosynthetic bacteria, it is equipped with two hydrogen-producing enzymes, hydrogenase and nitrogenase. Among many procedures with various *Rhodobacter* (R.) species listed by Akroum-Amrouche et al. (2019), the highest production rate, of 169 mL L^{-1} h^{-1}, was obtained by using *R. sphaeroides* with an illumination of 8000 lux, when the cells were grown in a culture medium containing racemic malate (Li et al. 2009). Here, the hydrogen gas was obtained at the expense of an organic substance. However, hydrogen production, using photosynthetic bacteria, in this way, seems to be uneconomical.

In green algae, hydrogen production requires several minutes to a few hours of anaerobic incubation in darkness (Ghirardi et al. 2000; Ghirardi et al. 2009). This pretreatment seems to induce the synthesis or activation of a reversible hydrogenase and probably some other enzymes that enable the alga to photoproduce molecular hydrogen. For the genomic aspects of hydrogen photoproduction by green algae, see Melis et al. (2004).

On the other hand, Li et al. (2021) have attempted to improve the overall situation by using microbial electrosynthesis systems. Using light and an applied potential of –0.9 V *vs.* Ag/AgCl to the cathode, *R. sphaeroides* was shown to produce a high amount of hydrogen gas with CO_2 as the sole carbon source; a hydrogen production rate of 328 mL L^{-1} day^{-1} was achieved, which lasted for seven days of operation (Li et al. 2021). Currently, several similar systems, using *R. sphaeroides* and *R. capsulatus*, are also being investigated (Grattieri 2020). In addition, a relatively efficient photobioreactor for *R. capsulatus* has been described in detail (Turon et al. 2021).

Craven et al. (2019) have produced a gas mixture with a H_2/CO_2 ratio of 33, compared to 2 that would have been the result if all the hydrogen had been obtained only from acetate. This experiment was done with *Rhodopseudomonas palustris* (also a non-sulfur purple bacterium) in combination with plasmonic optically resonant gold–silica core–shell nanoparticles and a medium containing acetate as the only organic component. We note that this reaction could be driven by near infrared radiation, with a maximum at 850 nm, absorbed by BChl, or even with broad band irradiation in the same region.

We now ask: what is the biological advantage for an anoxygenic photosynthetic bacterium to produce molecular hydrogen? Using *Rhodopseudomonas palustris*, Muzziotti et al. (2016) have concluded that it is a way for the bacteria to avoid damage by strong light. Further, they showed that when, instead of molecular nitrogen, other nitrogen nutrients are used, the production of H_2 indeed increases.

Returning to cyanobacteria, we note that molecular hydrogen can be produced also by nitrogenase (Stal 2015). There are two kinds of cyanobacterial nitrogenases, operating with different stoichiometries (Harwood 2020). The most common is molybdenum (Mo)-nitrogenase, which operates together with a Mo/Fe protein, releasing as many moles of H_2 as it consumes of N_2 (Harris et al. 2019):

$$N_2 + 16\ ATP + 8\ e^- + 8\ H^+ \rightarrow 2\ NH_3 + H_2 + 16\ ADP + 16\ P_i \qquad (2)$$

On the other hand, the vanadium-nitrogenase catalyzes the following reaction which produces three times as many moles of H_2 as it consumes N_2 (Harris et al. 2019):

$$N_2 + 24\ ATP + 12\ e^- + 12\ H^+ \rightarrow 2\ NH_3 + 3\ H_2 + 24\ ADP + 24\ P_i \qquad (3)$$

However, in some bacteria, there exists an Fe-only nitrogenase, which catalyzes the release of an even greater proportion of H_2, but using much more ATP per mole of N_2 assimilated than the systems, mentioned above (Harris et al. 2019):

$$N_2 + 40\ ATP + 20\ e^- + 20\ H^+ \rightarrow 2\ NH_3 + 7\ H_2 + 40\ ADP + 40\ P_i \qquad (4)$$

It is interesting to note that some organisms, such as the photosynthetic bacterium *Rhodopseudomonas palustris*, contain all the three types of nitrogenase, described above (Larimer et al. 2004).

Detailed overviews of biological hydrogen photoproduction and novel ways of using light for the generation of molecular hydrogen are available in a large number of publications (Weaver et al. 1980; Ghirardi et al. 2007; Tsygankov and Kosourov 2014; Batyrova et al. 2015; Khanna and Lindblad 2015; Kosourov et al. 2017; Kosourov et al. 2018; Jokel et al. 2020; Dutta 2021; Goswami et al. 2021; Kosourov et al. 2021; Zhang et al. 2021c; King et al. 2022; Redding et al. 2022).

8. Photo-Induced Synthesis of ATP in Archaea

Thus far, we have dealt mainly with types of photosynthesis in Bacteria and in Eukarya. Now, we ask: What about Archaea? After their recognition as a very special group of prokaryotes (Woese and Fox 1977), they were later renamed as Archaea, the third domain of living organisms, the other two being Bacteria and Eukarya, just mentioned (Woese et al. 1990). Some archaea, the so-called halobacteria, are capable of photophosphorylation, which is the synthesis of ATP, using the energy of light. The name halobacteria existed before it was discovered that they are archaea, not bacteria. The best-known species is *Halobacterium salinarum* (formerly called *Halobacterium halobium*), and another one is *Haloferax volcanii*; the first one (*H. salinarum*) can grow in darkness in the presence of oxygen, but in the absence of oxygen, it requires light (Figure 7). Unlike the usual photosynthesizers, it cannot assimilate carbon dioxide, but it gets its carbon from a mixture of amino acids (Hartmann et al. 1980).

Halobacteria possess several types of rhodopsin (light-sensitive pigment-containing protein). Two of them are sensory rhodopsins that are used for light sensing, just as the rhodopsin is in our eyes, whereas halorhodopsin is used to pump chloride ions, and the bacteriorhodopsin extrudes hydrogen ions from the cytoplasm to the outer side of the plasma membrane. When the hydrogen ions (protons) flow back through the ATP synthase located in the plasma membrane, ATP is formed from ADP and inorganic orthophosphate (Danon and Stoeckenius 1974; Mukohata et al. 1992; Bickel-Sandkötter et al. 1996). The energy stored in the new phosphate bond is then used for various synthetic or transport purposes. The effect of light on growth of *H. salinarum* is shown in Figure 7. Similar rhodopsins are found not only in Archaea but are also broadly distributed in many bacteria (Béjà et al. 2000; Pushkarev et al. 2018).

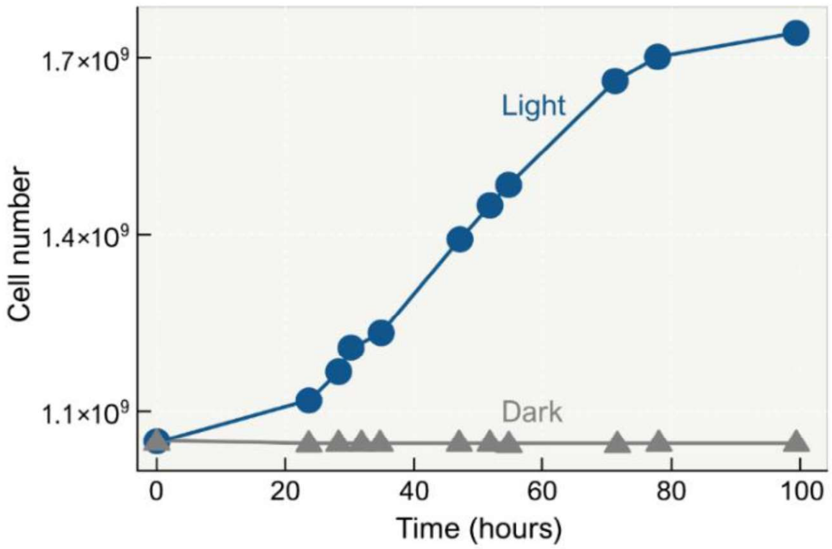

Figure 7. Growth of *Halobacterium salinarum* (previously known as *Halobacterium halobium*) under anoxic conditions in light and darkness. Redrawn from Hartmann et al. (1980).

9. Photochemistry and Photobiology of Vitamin D

We humans are also capable of doing a form of "photosynthesis," which is the synthesis of vitamin D from provitamin D *via* previtamin D (Figure 8). Although most biologists would disagree to call it photosynthesis (and some may even laugh at the idea), but there is synthesis and light is used; thus, in a broad sense, we prefer to include it for completeness, realizing its difference; further, in contrast to the usual photosynthesis, it is driven by UV radiation absorbed by provitamin D. Its action spectrum follows the absorption spectrum of provitamin D, modified by the absorption of pigments in the skin. Thus, it differs between various parts of the human body, and from person to person, depending on the pigmentation (van Dijk et al. 2016), as it would be for the authors of this chapter.

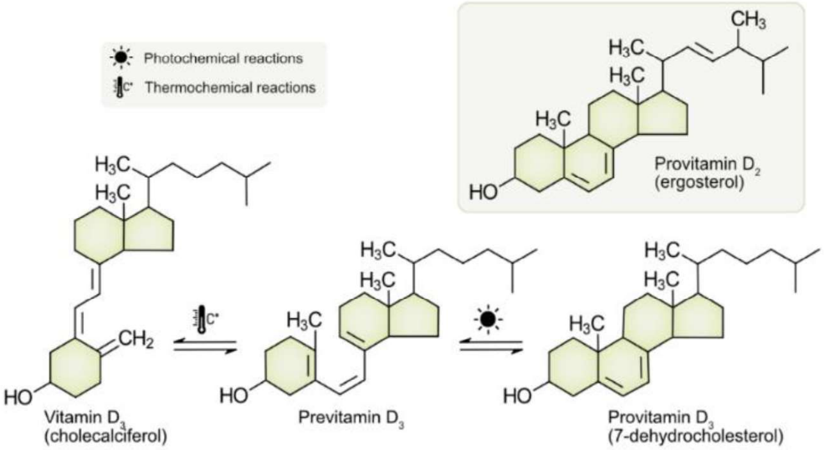

Figure 8. The structural formula of provitamin D_2, and the synthesis, in light, of previtamin D_3 from provitamin D_3, and its further transformation to vitamin D_3.

Under certain circumstances, UV radiation of previtamin D can lead to a number of other radiation products, not only provitamin D (Figure 9).

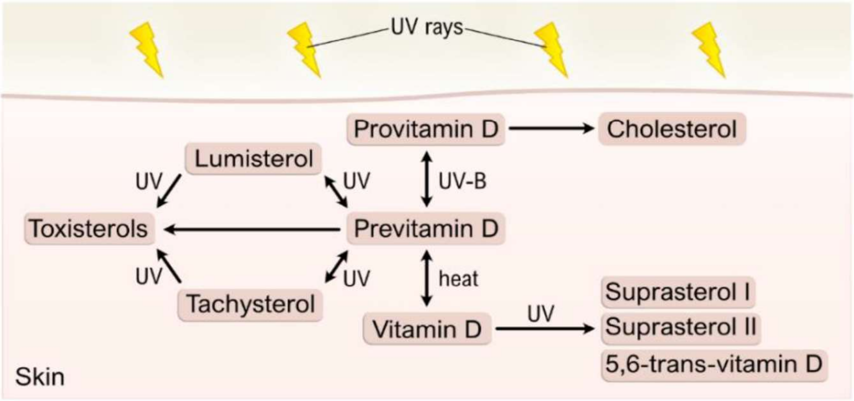

Figure 9. Photo-transformation of compounds related to vitamin D. UV-B is a subtype of UV radiation with a wavelength range from 280 to 315 nm. Modified from van Dijk et al. (2016).

Vitamin D has been studied in many animals, both in invertebrates, *e.g.*, spiders (Zachariah and Mitchell 2009), and in various groups of vertebrates (Uva et al. 1983; Michaels et al. 2015; Oonincx et al. 2020; Chen et al. 2021).

How much a vertebrate depends on vitamin D in the food and how much it depends on sunlight for vitamin D production varies among species, but probably all the vertebrates need vitamin D. Thus, not only cyanobacteria, algae and plants use the sun's life-giving rays, but we and other vertebrates, do it in a direct or indirect way (Watson et al. 2019; Neville et al. 2021). Some of us need light to make vitamin D in our own skins, others get what they need by ingesting what some others have synthesized!

For the role of photochemical and photobiological reactions on living organisms and on the origin of life, see Björn et al. (2015) and references therein. We also note that even synthesis and transformation of elements can take place in reactions driven by photons with extremely high energy, in this case by gamma (γ) radiation (Descouvemont 2020; Nunes et al. 2020; Vodin et al. 2021).

10. Artificial Photosynthesis

In view of concerns for future climate change due to increasing greenhouse-gas emissions, and over the risks (though minimal) of the possible use of nuclear energy, and because of the slow progress in safe fusion energy research, there has recently been an enormous interest in finding novel ways of using solar energy. One major approach towards the above goal is to use completely artificial systems, although much has been done, and is being done, to modify organisms so that they can produce fuels or other commodities. Although this field is relatively young and has limitations, there is an enormous literature. Thus, we mention here some of the papers, published in 2022, for the readers to explore this area (Dai et al. 2022; Droghetti et al. 2022; Hann et al. 2022; Kim et al. 2022a; Kumar et al. 2022; Li et al. 2022; Morawski et al. 2022; Nguyen et al. 2022; Rehman et al. 2022; Soo 2022; Tada 2022; Tao et al. 2022; Wang et al. 2022; and, Yamazaki et al. 2022). For an early attempt in this field, see Hou et al. (2014) and Najafpour et al. (2012, 2013).

For producing fuel with the help of sunlight, one might first think of the possibility of using electricity-producing photocells for the electrolysis of water. Such a process, however, is very inefficient, because there is a considerable wasteful "overvoltage" at the electrode-electrolyte interface. Further, many of the devices described, thus far, contain chemical elements that constitute an environmental hazard, but there has also been research on the so-called "green" methods of harnessing solar energy for chemical synthesis.

About 50 years ago, Fujishima and Honda (1972) pointed out that oxygen can be evolved from water in a system, when a platinum electrode, forming a circuit with a TiO_2-electrode, is irradiated with light of wavelengths shorter than 415 nm, corresponding to ~3.0 eV. A voltage of up to 0.5 V was developed between the electrodes in this system. Although the quantum efficiency was estimated to be only about 0.1, the process could be made more efficient, in the future, by replacing the platinum electrode with a *p*-type semiconductor electrode, *i.e.*, one that uses (positive) electron holes for conducting electrical current (Fujishima and Honda 1972). However, TiO_2 has been suggested, by many, to be a good photocatalyst with many advantages over other metal oxide semiconductors. Concerning this idea, Rehman et al. (2022) stated:

> It is not expensive, while production on a large scale is cost effective. It has excellent ability to resist corrosion as well as having good photostability. Many physical and chemical techniques have been well developed already to synthesize the porous film and nanoparticulate powder of TiO_2. It has exhibited excellent photocatalytic efficiency. It can be activated in visible sunlight and can start a chemical reaction.

On the other hand, production of molecular oxygen by artificial photosynthesis is hardly meaningful, although it has been considered for submarines and space travel. More important goals, however, are the production of fuels and various other useful products, as discussed below.

Interestingly, many of the current artificial devices are inspired by the Z-scheme used for describing oxygenic photosynthesis by cyanobacteria, algae, and plants (Govindjee et al. 2017). The earlier literature on artificial Z-schemes has been reviewed by Li et al. (2022). In addition, we urge the readers to consult recent papers on artificial photosynthesis related to the Z-scheme (Miyoshi et al. 2018; Raizada et al. 2021; Zhang et al. 2021a; Dai et al. 2022; Kim et al. 2022b; Kumar et al. 2022; Rehman et al. 2022). We note that not all the schemes designated as Z-schemes use two different photosystems connected in series as the biological photosynthesizers do. The so-called S-system (short for Step-scheme) is the term often used by those who work with artificial photosynthesis for what can be regarded as a technological Z-scheme construct (Ye et al. 2021; Nguyen et al. 2022).

Artificial photosynthesis is still in its infancy; in view of our current energy problems and the dangers of the increase of greenhouse gases and global warming, it is a research field that must be given high priority[1].

11. Artificial Photoproduction of H_2

Molecular hydrogen has the advantage over other fuels since its combustion does not necessarily result in the production of greenhouse gases. Under certain conditions, however, nitrogen oxides, some of which are powerful greenhouse gases, may be formed. Gai-Li Ke and coworkers have recently reviewed the use of transition metal oxides as photoelectrode material for photo-electrochemical water splitting (Ke et al. 2022). However, in many artificial systems, the components that have been used are either very rare and expensive, or are of great environmental hazard, such as cadmium (Tian et al. 2022). Further, Antoni W. Morawsky and coworkers have stated that the use of environmentally friendly chemicals is impractical since UV radiation is needed as source of energy (Morawski et al. 2022). In addition, molecular hydrogen itself has the disadvantage of being difficult to store safely in large quantities; thus, preferably, it is to be produced on demand only!

12. Photoproduction of CO and CH_4 and Other Compounds from CO_2

Recently, Zhu and Qiao (2022) have provided data on the photoreduction of CO_2 to CO and a smaller amount of CH_4, using variants of $SrTiO_3$@-NiFe layered double hydroxide composites (Zhu and Qiao 2022). The most efficient type had 1.3 as a molar ratio of $SrTiO_3$ to NiFe-layered double hydroxide; further, visible light was used for the reaction just mentioned. The authors showed that for CO production, its rate was practically linear for the six hours of the experiment, while the production of CH_4 gradually levelled off, so that after six hours it was about 12% of the CO production (Zhu and Qiao 2022). We recommend that future scientists follow this promising lead.

Another novel direction is the use of *quantum dots*. A quantum dot is a small (in relation to the wavelength of light) semiconductor particle, having

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[1] See also: https://bigthink.com/the-future/artificial-photosynthesis-improve/.

optical and electronic properties that differ from those of larger particles of the same material. The use of quantum dots has been recently reviewed (Domingo-Tafalla et al. 2022). Here, we learn the use of what is called *carbon dots*, in aqueous solutions, for photocatalytic and electrocatalytic reduction of CO_2 to obtain a variety of products such as CO (carbon monoxide), CH_4 (methane), CH_3OH (methanol), HCOOH (formic acid), and CH_3COOH (acetic acid).

Carbon dots consist mainly of carbon (graphite), but with other functional atoms or groups attached to it. Compared to the traditional quantum dots containing cadmium/lead, rare-earth nanomaterials, and organic dyes, carbon dots have the advantage of better light stability, higher quantum yield, lower toxicity, abundant low-cost sources, and excellent biocompatibility (Liu et al. 2020b). Quantum dots are artificial, but, as we will see in the next section, they can be combined with living cells.

13. Inorganic Crystal-Microorganism Interactive Photoreactions

Several organisms that are not photoactive, in themselves, carry out light-induced reactions together with light-absorbing semiconducting minerals. We agree with Lu et al. (2012) who state that "minerals may be important in delivering solar energy to non-phototrophic organisms." Common natural, light-absorbing semiconducting minerals are rutile (TiO_2), sphalerite (ZnS) and goethite (FeOOH). The deep-sea bacterium *Idiomarina sp*. OT37-5b, by itself, does not carry out any type of 'photosynthesis', but when supplied with cadmium chloride and cysteine, it precipitates cadmium sulfide (CdS) nanoparticles on the surface. In contrast to bacteria without CdS nanoparticles, cells with CdS nanoparticles grow faster in light than in darkness (Ma et al. 2021). Liu et al. (2021) have obtained similar results with *Thiobacillus thioparus* that normally assimilates carbon dioxide chemotrophically, using the Calvin-Benson-Bassham cycle. With CdS nanoparticles on its surface, it can photoassimilate carbon dioxide.

The systems described above, with photoactive material on the external surface of cells, are often slowed down by the time taken for the diffusion of substrates across the cell membrane. Luo et al. (2021) devised a method for the uptake of artificial $CuInS_2$/ZnS quantum dots in the so-called periplasmic space of the gram-negative bacterium *Shewanella oneidensis*, which contains the enzyme hydrogenase that catalyzes the reversible reduction of protons to molecular hydrogen. In this way, Luo et al. (2021) have obtained a system for efficient photoreduction of protons to hydrogen gas (Figure 10), a remarkable achievement.

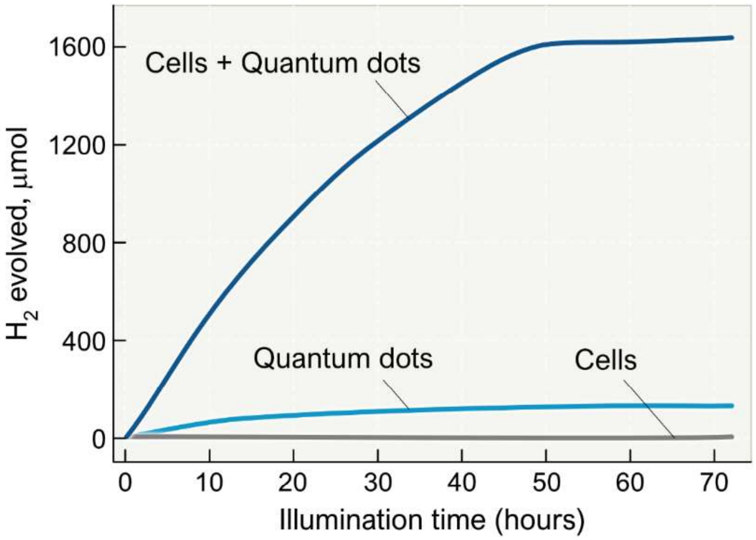

Figure 10. Hydrogen (H_2) evolution with cells of *Shewanella oneidensis* charged with $CuInS_2/ZnS$ quantum dots (dark blue line). Controls are quantum dots only (light blue line) and cells only (grey line). Redrawn from Luo et al. (2021).

Sakimoto et al. (2016a) have constructed an artificial "Z-scheme" in which "PSII," consisting of TiO_2, generates molecular oxygen from water, and "PSI," consisting of CdS, transfers electrons to the cells of *Moorella thermoacetica*. The electrons are used by the bacterium used for the reduction of carbon dioxide to acetic acid *via* the Wood-Ljungdahl pathway (Sakimoto et al. 2016b). This field of research is moving rapidly, combining knowledge from biology with that from chemistry, physics, and engineering.

Conclusion

The term, *photosynthesis*, has been usually used for the process that provides food and oxygen to those organisms, including all of us, that are incapable of carrying out photosynthesis themselves. In this chapter, we first provided the basics of oxygenic photosynthesis which included, in order of presentation, figures describing first the basic steps of "oxygenic photosynthesis" itself:

- PSII (water-plastoquinone oxidoreductase), the very system that enriched Earth's atmosphere with molecular oxygen, with a brief description of the period 4 "oxygen clock" (*the Kok* cycle; on the electron donor side), and the unique presence and function of "bicarbonate" (on the electron acceptor side);
- The Z-scheme of photosynthesis – their components, their arrangements on the thylakoid membrane, their redox levels and their function(s): including those in the non-cyclic and cyclic reactions;
- The molecular structure of the key pigment molecule, chlorophyll *a*; and,
- The basic steps of the carbon fixation cycle – where the reducing power and ATP, made by Photosystems I and II, and by ATP synthase, are used to produce carbohydrates.

This was followed by a brief discussion of other types of *"Photosynthesis,"* such as:

- Anoxygenic bacterial photosynthesis, of different types, as related to their RCs;
- Photoassimilation of molecular nitrogen, especially in cyanobacteria (with two types of cells: vegetative and heterocysts);
- Photoproduction of molecular hydrogen;
- Photoinduced synthesis of ATP using different types of 'rhodopsin'-containing Archaea.
- Then, for 'inclusiveness', we have even mentioned a phenomenon far away from oxygenic photosynthesis: How vitamin D is synthesized in our own skin. Indeed, there is synthesis, which requires UV light.
- Finally, we discussed the most futuristic photosynthesis, which is *artificial photosynthesis*, including production of many compounds including hydrogen, carbon monoxide, methane, and more where natural photosynthetic systems are 'married to' to chemical systems

> to give us the needed compounds and energy in a 'clean' and 'efficient' way.

This is the future where *photosyntheses* are being changed and improved for our own benefit. Indeed, because of different types of photosyntheses, the future seems brighter than before. In parallel, efforts are being made on a totally different and equally important front: that of making plants and algae do more efficient photosynthesis and produce more and better products for our use (see *e.g.*, Zhu et al. 2010).

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