Introduction to Photosystem II And Molecular Principles of Redox-Coupled Protonation Dynamics in Photosystem II

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KEYWORDS: Photosystem II; Redox-Coupled Protonation Dynamics; Chloroplast.

ABSTRACT: Photosynthesis system is a very important transformation system between inorganic and organic substances in nature. Photosystem II is related to the dark reaction in photosynthesis system. This paper briefly introduces photosystem II and its molecular principles of Redox-Coupled Protonation Dynamics .

1. Introduction

Chloroplast is a unique energy conversion organelle of plant cells. Its main function is photosynthesis. Photosynthesis is the most important chemical reaction in nature. It is the basis for the survival and reproduction of organisms including human beings. It is also an important direction of energy utilization and development. Global green plants and other organisms can convert solar energy into 220 billion tons of bioenergy through photosynthesis every year, which is equivalent to 10 times of global annual energy consumption. If the large-scale bionic use of solar energy is really possible, there will be a new solution to the food and energy problems that perplex mankind.

1.1 Morphological structure of chloroplasts

The shape, size and quantity of chloroplasts vary greatly with plant species. At the same time, chloroplast is an unstable organelle, which can produce different adaptive changes with different environmental conditions, such as light conditions. The chloroplasts of higher plants are mostly convex lenticular or banana shaped, with a width of 2~4 μm. Length 5~10 μm. Most mesophyll cells contain dozens to hundreds of chloroplasts, accounting for 40%~90% of the cytoplasmic volume. Algae usually have only one giant chloroplast, which has banded, spiral and stellate shapes, depending on the cell morphology.

Under the electron microscope, chloroplast is composed of three parts: chloroplast membrane, thylakoid and the space between them is called matrix. (Fig.1)

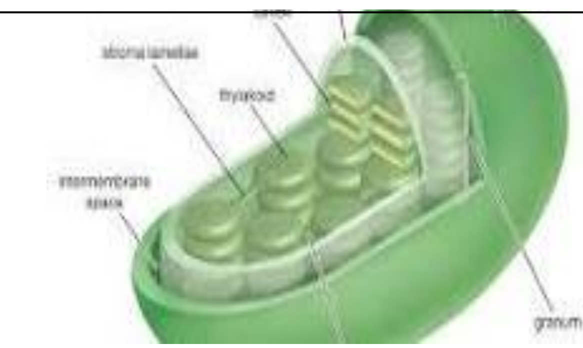

Fig. 1 Morphological structure of chloroplasts.

Chloroplast membrane is composed of outer membrane and inner membrane. The thickness of each layer is 6~8nm, and the gap between the inner and outer films is 10~20nm wide. Like the outer membrane of mitochondria, the outer membrane of chloroplasts has high permeability and contains porins, allowing molecules with a relative molecular weight of up to 104 to pass through. The permeability of chloroplast inner membrane is relatively poor, which is the functional barrier between cytoplasm and chloroplast matrix. Only O_2, CO_2 and H_2O molecules can pass freely. There are many transporters on the inner membrane of chloroplast, which can selectively transport molecules in and out of chloroplast, and their transport is driven by concentration gradient. An important transport mechanism of these transporters is exchange transport. For example, phosphate exchange carriers can transport inorganic phosphorus in the cytoplasm to the chloroplast matrix, and release glyceraldehyde phosphate produced in the chloroplast matrix to the cytoplasm.

The closed flat membrane sac developed from the inner membrane of chloroplast is called thylakoid. The space inside the thylakoid capsule is called the cystoid cavity. In some parts of chloroplasts, many round cake shaped thylakoids are stacked orderly in stacks, which are called grana. A chloroplast contains 40~60 or more grana, and a grana consists of 5~30 thylakoids, up to hundreds. The number of grana thylakoids varies greatly according to different plants or cells in different parts of the same plant. Thylakoids stack into grana, which is a unique membrane structure of higher plant cells[1]. This structure greatly increases the total area of the membrane layer, and can more effectively capture light energy and accelerate light reaction. The thylakoid cavities are connected with each other, so all thylakoids in a chloroplast are actually a complete and continuous closed membrane capsule, separating the membrane capsule of the membrane system from the matrix, which plays an important role in the establishment of electrochemical gradient and the synthesis of ATP. The chemical composition of thylakoid membrane is different from other membrane components of cells. It contains very little phospholipids and rich glycolipids with galactose. The fatty acids in these lipids are mainly unsaturated linolenic acid, accounting for about 87%. Therefore, the lipid bilayer of thylakoid membrane has very large fluidity. The fluidity of lipid bilayer promotes the lateral movement of photosystem II, cytochrome b6/f complex, photosystem I and ATP synthase complex on thylakoid membrane during photosynthesis, which is conducive to photosynthesis. In addition, the protein / lipid ratio of thylakoid membrane is very high, which is also related to chloroplast photosynthesis.

The compartment between chloroplast inner membrane and thylakoid is chloroplast matrix. The main components of the matrix are soluble proteins and other metabolic active substances. Ribulose-1,5-bisphosphate carboxylase / oxygenase is an important enzyme system in photosynthesis. It is abundant in the matrix and is also the most abundant protein in nature. The substrate is a place for photosynthesis to fix CO2. It also contains circular DNA, ribosomes, lipid droplets, plant ferritin and starch granules.

1.3 Photosynthesis

Photosynthesis is a process in which green plants use solar energy to convert water and carbon dioxide into organic compounds and release oxygen to convert light energy into chemical energy. Its essence is the reverse process of respiration. Respiration in mitochondria reduces oxygen to water, while photosynthesis in chloroplasts oxidizes water to produce oxygen. The former process releases energy, while the latter process requires energy. Photosynthesis of higher plants involves two processes: light dependent light reaction and dark reaction with or without light. Light reaction only occurs under light, and dark reaction (also known as carbon reaction) is driven by the products of light reaction. Photoreaction includes two steps: water photolysis, electron transfer and photophosphorylation[2]. It is to absorb and transfer light energy through photosynthetic pigment molecules such as chlorophyll on thylakoid membrane, convert light energy into electrical energy, and then convert it into active chemical energy to form ATP and NADPH, and also produce O2. Dark reaction is an enzymatic chemical reaction in the chloroplast matrix. ATP and NADPH produced by light reaction are used to reduce CO_2 into sugar, that is, active chemical energy is converted into stable chemical energy, and finally stored in organic matter.

1.4 Photoreaction

In addition to its volatility, light also has particle properties, which means that light behaves like tiny energy "particles", which are called photons[3]. Different wavelengths of light have different photon energies. The energy in the photons of each wavelength of light is fixed. The shorter the wavelength, the more energy in the photon. For example, photons of violet light carry about twice as much energy as photons of red light. The essence of pigment absorbing light is that an electron in pigment molecule gets the energy in photon. At this time, the electron enters the excited state from the ground state and becomes an excited electron or high-energy electron. So the moment chlorophyll molecule absorbs photons, the energy of photons has become the energy of electrons, that is, it has become chemical energy. The excited state of the pigment molecule is extremely unstable and almost immediately changes back to the ground state after formation. The excited state of chlorophyll molecule only lasts for 10-8s. When chlorophyll molecules return to the ground state from the excited state, the light energy absorbed by them will radiate or change into fluorescence in the form of heat.

The results showed that not all chlorophyll molecules in chloroplasts directly participated in the light reaction to convert light energy into chemical energy. About 300 chlorophyll molecules form a functional unit to absorb photons. This functional unit is called the photosystem, which is the smallest structural unit for photosynthesis. In the light system, there is only a pair of special chlorophyll a molecules, called reaction center pigment molecules, which have the special function of converting light energy into chemical energy, while the other photosynthetic pigments are called antenna pigment molecules. They absorb light energy and transfer it quickly and effectively to the pigment in the reaction center. The transfer of energy follows the principle from antenna pigment molecules with higher energy requirements to antenna pigment molecules with lower energy requirements. In other words, the direction of energy transfer is from absorbing short wavelength light waves to antenna pigment molecules absorbing long wavelength light waves. Chlorophyll molecules in the reaction center are pigments with the longest wavelength of light waves, which makes the light energy absorbed by all antenna pigment molecules inevitably and irreversibly transmitted to the pigments in the reaction center. The most important characteristic of the reaction center pigment is that it generates charge separation and energy conversion after being excited by directly absorbing light energy or receiving light energy transmitted from antenna pigment molecules[4].

1.5 Dark reaction and photosystem II

There are three pathways of carbon assimilation in higher plants: Calvin cycle, C4 pathway and Rhodiola acid metabolism pathway. Calvin cycle is the most basic way.The initial product of Calvin cycle for CO_2 fixation is glyceric acid-3-phosphate (three carbon compound), so it is also called C3 pathway. This was discovered in the famous experimental research conducted by Calvin et al. Using CO_2 tracing method in the 1950s. Calvin won the 1961 Nobel Prize in Chemistry for his great contribution to the photosynthetic carbon assimilation pathway. C3 pathway is a basic pathway shared by all plants for photosynthetic carbon assimilation. It includes a series of complex reactions, but can be simplified into three stages, namely carboxylation (CO_2 fixation), reduction and RuBP regeneration.

Light harvesting complex Ⅱ (LHC Ⅱ) is also called light harvesting chlorophyll protein complex, or antenna complex. It contains 40-60% of the total chlorophyll of thylakoid membrane. The function of this complex is to absorb light energy and transmit light energy to the action center. LHC Ⅱ isolated from pea plant is a three body complex, which contains three membrane integrated peptides. Each peptide has at least 12 chlorophyll molecules (7 chlorophyll a and 5 chlorophyll b) and two carotenoids attached by non covalent bonds5.

PS Ⅱ consists of peripheral light trapping (antenna) pigment protein complex (LHC Ⅱ), inner light trapping (antenna) pigment protein complex (CP43 and CP47, etc.), reaction center pigment protein complex (PS Ⅱ -rc) and manganese cluster, as well as peripheral proteins 33kDa and 17kDa. In general, the residual PS Ⅱ after LHC Ⅱ removal is called PS Ⅱ core complex, while the isolated and purified PS Ⅱ -rc is only composed of D1 protein, D2 protein and cytochrome b559 (Cyt b559) α Subunit sum β Subunits and five proteins of PSB Ⅰ gene products and their bound chlorophyll a (Chl-a), PHEO (PHEO) and β - Carotenoid (car) composition. In a PS Ⅱ -rc, only two Chl-a have photosensitization properties. They form a special "molecular pair" and play the role of primary electron donor in the photocatalytic primary photochemical reaction, and their primary electron acceptor is PHEO. Because this special "Chl-a molecular pair" has an obvious peak at 680nm of its redox absorption difference spectrum, it is called P680. The composition and structure of the oxygen evolution Center complex are not clear. It is generally recognized that it is composed of PS Ⅱ reaction center, PS Ⅱ inner peripheral antennas CP43 and CP47, and 33kDa peripheral protein, with a molecular weight of 250~300kda [5]The function of PS Ⅱ is to use the energy absorbed from light to split water and transfer the electrons released to plastoquinone. At the same time, h+ proton gradient is established on both sides of thylakoid membrane through water oxidation and pqb2- reduction.

The premise for PS Ⅱ to function is to absorb light energy. PS Ⅱ transmits the light energy absorbed by LCH Ⅱ to the PS Ⅱ reaction center, so that the central pigment produces a high-energy electron and transmits it to the primary electron receptor. This process produces a positively charged donor (p680+) and a negatively charged primary electron acceptor (pheo-), which are very important for the formation of oppositely charged substances and can trigger further reactions. Because p680+ can be used as an oxidant to accept electrons and cause the photolysis of water, resulting in the transfer of electrons released from water oxidation to PS Ⅱ; Pheo- can be used as a reductant to lose an electron and cause electron transfer to plastid quinone.

It is generally believed that the two photosystems come from a common ancestor because they have similar structural proteins and cofactors. So why do cyanobacteria have both photosystems I and II, while other prokaryotic photosynthetic organisms have only one photosystem? There are two hypotheses. According to the fusion hypothesis, the two types of photosystems developed independently in non oxygenic photosynthetic bacteria, and then combined through the fusion of two individuals, and then developed the ability to oxidize water; The selective loss hypothesis holds that the two light systems originated from one ancestor, and the loss of one or the other in the light system resulted in these organisms having only one of them, and the ability to oxidize water was added later

2. Molecular Principles of Redox-Coupled Protonation Dynamics in Photosystem II

The PSII system captures the energy of visible-light photons; powering water oxidization catalysis at the Mn4O5Ca cluster (see Fig2) and reduction of plastoquinone at the QB site;[6]

Photoexcitation of chlorophyll induces a charge separation (ChlD1•+/PheoD1•–) followed by electron transfer from PD1 to ChlD1•+, from PheoD1•– to QA, the first quinone acceptor, and then from QA•– to QB, the exchangeable quinone

A full enzyme cycle is completed, each photochemical charge separation results on average in the release of one proton into the lumen from water oxidation (2H2O → O2 + 4e– + 4H+lumen)

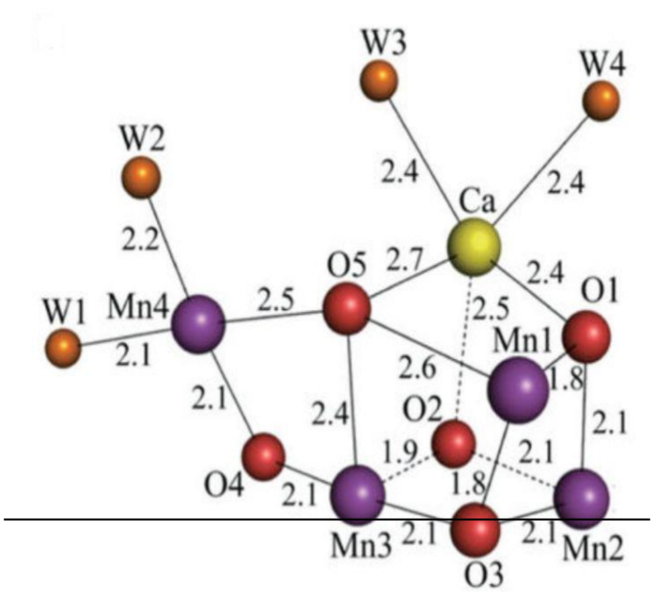

Fig 2: Mn4O5Ca cluster: The center binds four water ligands (W1–W4) ;five oxo/ hydroxo bridges that connect the metal O5 between Mn1 and Mn4 is considered to be a likely candidate for one of the substrate water molecules (Er）

The full principle (Fig 3.) can be divided into five steps:

1.Each light-flash leads to the formation of Tyrz• and a cationic His190 (HisH+)

2. Opens up the Asp61/Lys317 ion-pair (solid black arrow), inducing an electric field toward Asp61

3. The electric field drives the proton transfer reaction from W3 and O5 via the Asp61/Lys317 gate.

4. O2 formation between the Mn1-bound W3 and O5 leads to formation of a new O5 ligand from the Ca2+-bound W5 upon reorganization of the water structure.

5. Deprotonation of the new O5 oxo-bridges initiates the next photocycle[7].

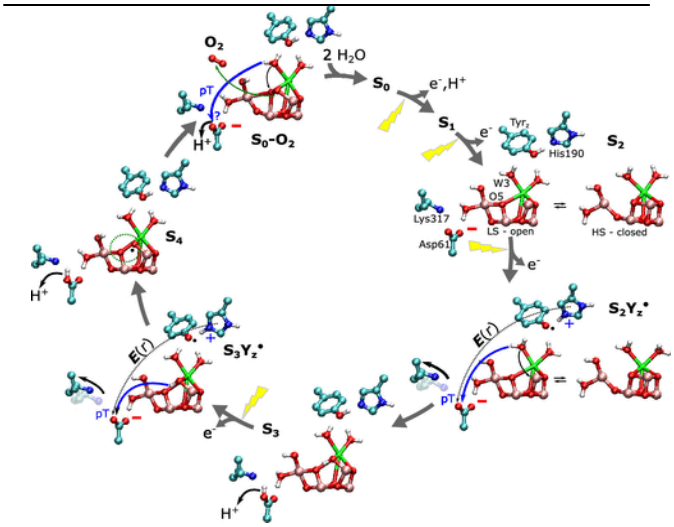

Fig 3. The full cycle of the molecular principle.

3. Summary and Discussion

Photosystem II (PSII) catalyzes light-driven water oxidization, releasing O2 into the atmosphere and transferring the electrons for the synthesis of biomass.

Much very detailed information is now available concerning the mechanism of excitation energy transfer and electron transfer in plant photosystems, many details about how these supercomplexes attain their outstandingly maximal photochemical efficiencies, which always exceed 80%, are still unknown.

A high-resolution structure of plant PSII is not available yet，photosynthesis is probably one of the most multidisciplinary fields of research.

ASSOCIATED CONTENT

Supporting Information

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Notes
The author declare no competing financial interests.

ACKNOWLEDGMENT
Thanks for the Help from Prof.Chong

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