7 Basic Principles of Photosynthesis

7.1 INTRODUCTION

In this chapter, the principles of photosynthesis will be examined in an elementary form since they are relevant for the understanding of photo-electrochemical cells. In its complete form Photosynthesis is a complex phenomenon involving various steps and only the basic principles of this process has a direct relevance to PEC and hence those aspects alone will be outlined in this chapter. In the simplest language, photosynthesis can be considered to be the reduction of carbon dioxide to carbohydrate (molecular state containing carbon and hydrogen with other atoms) species simultaneously making use of water and sunlight. A simple pictorial representation of the basis of photosynthesis is given in Figure 7.1.

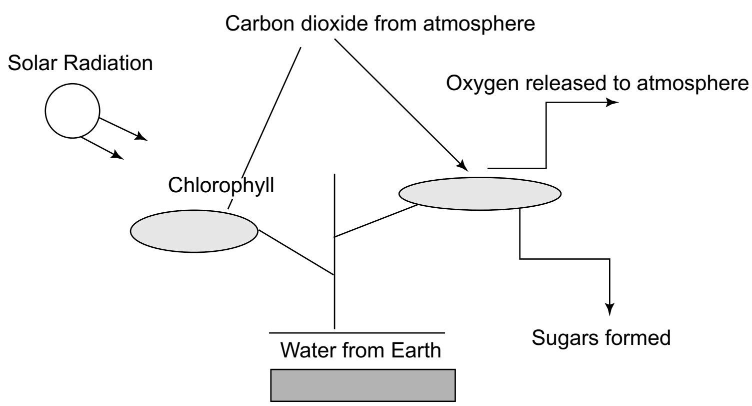

Figure 7.1 *A simple pictorial representation of the photosynthesis process*

It is known that the ecosystem of earth is directly connected with the solar radiation that the earth receives on daily basis. Essentially, in simple language photosynthesis involves the capture of photon energy and incorporating them in chemicals. This is what happens in green plants, algae, and some kinds of bacteria. Organisms can be put into two groups, namely autotrophs, which by themselves can carry out photosynthesis and thus manufacture their own food and also food for others and heterotrophs, which are incapable of carrying out photosynthesis themselves but must consume autotrophs or other organisms that ate autotrophs. In other words, photosynthetic organisms are at the base of the food chain, and with only a very few exceptions all organisms on earth depend upon photosynthesis as the source of their food and energy. Photosynthesis consists of two parts namely the light reactions wherein light energy is converted into high energy chemicals while in dark reaction carbon dioxide is converted into carbohydrates. This process requires hydrogen generated from the decomposition of water together with the evolution of molecular oxygen. In this sense, this process assumes importance for the photo-electro-chemical decomposition of water for the production of hydrogen which can be used as fuel. The evolved oxygen molecule can give rise to ozone in the upper atmosphere which can form a protective layer from ultraviolet radiation on earth. It is necessary to learn the light reactions from the point of green plants though other organisms may also follow a similar path. The first law of photo-chemistry states that for a photo-chemical reaction to take place, photons must be absorbed by the system. In plants the photon absorbing pigments are the chlorophylls and carotenoids. Chlorophylls consist of a light absorbing porphrin ring system with a central magnesium ion with suitable species that can attach to the membrane. Light reactions are generally considered as the energy conversion processes in all plants and since they absorb red and blue parts and hence appear green but other combination of absorbing colours and appearance colours are possible. Carotenoids are one such pigment which are always present but appear only when chlorophylls break down. The photosynthetic pigments are available in the membranes (choloroplats) and the porous system called stomata allow the passage of uncharged molecules like carbon dioxide and molecular oxygen. The pigment containing membranes are called thylakoids and their arrangement in stacks as pigment protein complexes and probably the arrangement of these species enables efficient harvesting of light energy. The non-membraneous portion of the chloroplast called stroma contains an aqueous solution of enzymes which is responsible for the reduction of carbon dioxide. There are some governing principles for the light reactions. They are:

(1) The pigment protein must be capable of absorbing the photon available and must go to the excited state
(2) The excess energy available in the protein from the photon must be capable being transferred to the adjacent molecule and this energy transfer path necessarily facilitates the ultimate energy transfer and reduction of normally difficult to reduce carbon dioxide.

(3) These molecules which receive the excitation energy are contained in a thylakoid membrane and thus probably create the necessary reaction centres in highly structured arrangement.

Two kinds of energy-containing molecules are formed in the light reactions of photosynthesis namely adenosine triphosphate (ATP) and reduced nicotinamide adenine dinucleotide phosphate (NADPH), which are the sources of reducing power. The Photosystems and other reaction centers are connected by a series of compounds that act as electron carriers. An excited electron in a Photo system II reaction center enters this chain of carriers and moves from one to the next until it reaches a Photosystem I reaction center. This transport of an electron between the two types of reaction centers results in the pumping of hydrogen ions (H^+) across the thylakoid membrane, thus forming a gradient with a high H^+ concentration inside the thylakoid compartments and a relatively low concentration on the stroma side. The potential energy associated with this gradient is then used to form ATP by a mechanism similar to that by which ATP is generated in mitochondria.

The next step in the process is that an excited electron in Photo system I is transferred to a molecule of NADP, along with an H^+, thereby reducing it to NADPH. Notice that the electrons leaving Photo system I are being replaced by ones that came through the electron carriers from Photo system II. Finally, in order for this process to continue, the electrons that were removed from Photo system II have to be replaced. This is achieved by the splitting of an H_2O molecule, which yields electrons, H^+, and oxygen. The oxygen from two water molecules forms O_2, which then passes through the stomata into the atmosphere. In summary, what has been achieved is the conversion of photon energy into chemical energy in the form of ATP and NADPH, with the concomitant formation of O_2.

7.1.1 Reduction of Atmospheric CO_2 to Carbohydrate

The second major phase of photosynthesis involves the conversion of CO_2 from the atmosphere into carbohydrates and other biological molecules. This set of reactions is sometimes referred to as the "dark reactions" of photosynthesis because light is not directly involved. However, this terminology is somewhat misleading because light is required for the formation of the ATP and NADPH needed for energy and reducing power. If a photosynthesizing plant was suddenly put in the dark, the so-called dark reactions would only continue until the supply of ATP and NADPH was depleted. The conversion of CO_2 into carbohydrate takes place in the chloroplast stroma and follows a complex metabolic pathway called the Calvin Cycle or the Reductive Pentose Phosphate Pathway, each step of which is catalyzed by a specific enzyme. Its overall form is shown in Figure 7.2.

Carbon dioxide first combines with a five carbon compound called ribulose-1,5 -bisphosphate (RUBP), which then immediately splits into two three carbon compounds. Using energy and reducing power from ATP and NADPH, these are converted into 3-phosphoglyceraldehyde (3PGAL), which can be used by the plant to manufacture carbohydrates and various other biological molecules and to regenerate RUBP.

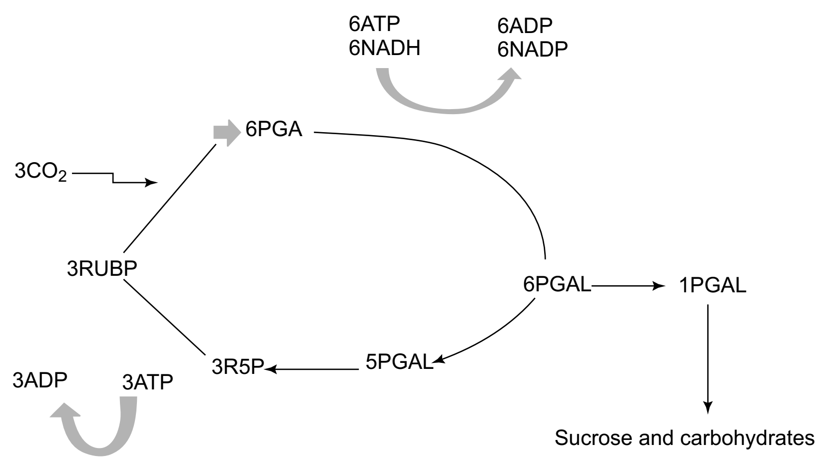

Figure 7.2 ***The Calvin Cycle. In this series of reactions, only a few of which are shown, carbon dioxide from the atmosphere is converted into carbohydrates. Understanding this cycle earned a Nobel Prize for Melvin Calvin in 1961.***

In order for the Calvin Cycle to continue, there must be a continuous supply of RUBP. Thus not all of the 3PGAL produced can go into the synthesis of carbohydrates - a significant portion (about 5 molecules out of 6) must be used to make fresh RUBP. This also requires ATP coming from the light reactions, and is what gives the pathway its cyclic nature. In summary, ATP and NADPH formed in the light reactions of photosynthesis are used to convert atmospheric CO_2 into carbohydrates, which represent a stable, long term form of energy storage. Overall, energy that originated as photons from the sun is now contained in carbohydrates and other molecules that serve as food for the plant or for an animal that eats the plants.

7.1.2 Environmental Aspects of Photosynthesis

Because of the fundamental biological significance of photosynthesis and its importance in agricultural productivity, a considerable amount of research has been directed towards understanding the effects that environmental factors such as light, temperature, rainfall, salinity, and disease have on the process. In recent years, the effects of elevated atmospheric CO_2 and of increased ultraviolet radiation exposure due to depletion of the Earth's ozone layer have received considerable attention. The potential for forests and other photosynthetic ecosystems to mitigate increasing atmospheric CO_2 is also an active area of research. Different species, and in some cases even different cultivaters of the same species, vary widely in their ability to tolerate the multitude of environmental stresses that a photosynthesizing plant may encounter. The natural geographic distribution of plant species can be understood in terms of their ability to photosynthesize efficiently under the range of conditions that they encounter in the Earth's various ecosystems. Likewise, environmental factors govern the range over which specific agricultural crops can be successfully introduced and cultivated. Both traditional plant breeding methods and the techniques of modern molecular biology are being used to produce plants that can maintain their vigor and sustain high rates of photosynthesis when subjected to environmental stress. These approaches have been very successful in the past and promise to further increase crop productivity and decrease the need for fertilizers, herbicides, and insecticides.

The overall reaction that takes place in plants in the photosynthesis can be represented by

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2 \tag{7.1}$$

(Carbon dioxide) + Water + light energy Sugar (carbohydrate) + Oxygen

The term Photosynthesis encompasses many dimensions. The simplest one is shown by the equation (7.1). However, it is necessary that we outline some essential aspects of photosynthesis in a simple language. These include:

1. If photosynthesis were to occur as has been shown by equation (7.1) with evolution of molecular oxygen with rearrangement of carbon dioxide and water to yield sugar then the process is termed as oxygenic photosynthesis.
2. Hence it must be possible that some bacteria can carry out the photosynthesis in an anoxygenic pathway without the release of oxygen.
3. Photosynthesis can also be understood in terms of carbon fixation wherein carbon dioxide undergoes reduction (probably stepwise) and hence involves reducing species and energy. This can be considered to be the opposite of cellular respiration wherein glucose and other sugars undergo oxidation to produce carbon dioxide, water and chemical energy.
4. Instead of water, it is possible to employ other reducing agents like arsenite which can act as electron donors and thus reduce carbon dioxide to carbon monoxide (which is subsequently reduced to sugars) and this type of harnessing can take place in some microbes.
5. It is possible one can write a variety of such possibilities for photosynthesis.

> However, essentially photosynthesis takes place in two steps wherein light dependent steps involves the storage of energy in molecules like ATP and NADPH. The light independent second reaction, namely, capture and chemical reduction of carbon dioxide takes place.

It may be necessary if one follows the whole act of photosynthesis in a sequence. The light is harvested by the proteins which are embedded in cell membranes. The membrane may be tightly folded into cylindrical sheets termed as thylakoids. This membrane architecture and its occupancy will be such that it provides large surface area to harness as much light as possible. There can be multiple layers of membranes and usually termed as phospholipid inner or outer membrane together with an aqueous fluid called stroma. This aqueous fluid contains the thylakoids where the act of photosynthesis is taking place. The thylakoid membrane contains membrane proteins together with some pigments that absorb light for the photosynthesis. Even though the primary pigment is chlorophyll, other pigments like carotenes, xanthophylls, phycocyanin (green algae), phycoerythrin (red algae) and flucoxanthin (brown algae) all these ppigments are embedded in special antenna-proteins. When these pigments are arranged in such a way that they work in conjunction, then these proteins are called light harvesting complex to denote that light harvesting effort is a joint effort and not by a single molecular species. This is one of the difficulties faced in artificial photosynthesis since light harvesting species though can be identified the sequence required has to be appropriately stitched and capturing antenna has to be provided for. This whole architecture has to be built mostly in leaves with a fine surface coating of the leaf with a hydrophobic waxy material so that water loss is restricted. Let us consider the light dependent reactions in a little more detailed form. The light dependent reaction has two components conventionally called cyclic and non-cyclic forms. The sequence of reactions is termed as Z scheme. In a simple language, the cyclic form in the Z Scheme generates ATP while in non-cyclic form NADPH is created. At the Photosystem II, light is harvested through light harvesting antenna complexes and other pigments and the electron is transferred to the electron acceptor molecule namely pheophytin. At the same time oxygen evolving complex dissociates water and produce molecular oxygen and protons. The electron from the phenophytin travels along a transport chain and passes through photosystem I to reduce the co-enzyme NADP to NADPH which has a role in the light independent reactions. The cyclic reaction also takes a similar route but is involved in chemiosmotic synthesis of ATP utilizing the energy provided by the electron transport chain of the Z scheme. The generation of the reducing agent NADPH at the terminal step of Z scheme means that the chlorophyll in photosystem II will be in the oxidized form (termed as P680) and its return to its original state is made possible by the oxygen evolving complex (consisting of four manganese ions and one calcium ion)which binds two molecules of water and thus is capable of storing four oxidizing equivalents. The hydrogen ions thus generated provides the chemiosmotic potential for proton migration and ATP synthesis. In the description given above we have not utilized carbon dioxide which is the source for the carbon fixation. This fixation and its conversion is carried out in photosynthesis in the so called dark reaction. Carbon dioxide from the atmosphere is captured by the enzyme called RuBisCO and the formed NADPH is utilized to generate three carbon sugars which is then converted to the final carbohydrate molecules. These are the starting material for the subsequent generation of cellulose, amino-acids and also the so called fuel for cellular respiration. There are other variations for carbon fixation. The important ones are: (i) The carbon dioxide can be directly fixed to three carbon molecule phophoenolpyruvate (PEP) promoted by an enzyme PEP carboxylase. The oxaloaceitc acid or malate synthesized is then decarboxylated to three carbon sugar3-phosphoglyceric acids. The plants that do not use PEP-carboxylase for carbon fixation are called C3 plants.

(ii) The CAM (crassulacean acid metabolism) plants fix carbon dioxide at night in the form of malic acid though carboxylation of phosphoenolpyruvate to oxaloacetate which is subsequently reduced to malate. The malate is then decraboxylated in day time releasing carbon dioxide thus facilitating the carbon fixation as 3- phophoglycerate by the conventional enzyme RuBisCO. The energy harnessing in photosynthesis takes place in four steps and the respective time scales are given in Table 7.1.

Table 7.1 ***Time scales of each of the steps of the energy harvesting in photosynthesis***

Details of processes	*Time scale*
1. Energy transfer in antenna chloriphyll	Femto second (10-15s) to pico second
2. Transfer of electrons in photo chemical reactions	Pico to nano second scale Micro to Milli second
3. Electron transport chain and ATP synthesis	Millisecond to second scale
4. Fixation of carbon and export of the stable product	

In this short presentation we have shown how the Photosynthesis is taking place and the redox processes are taking place in a step wise manner with appropriate species in relation to the redox potential values. Similar situation exists in Photo-electro-chemical decomposition of water but the only difference being the redox potential of water is fixed for hydrogen and oxygen evolution and hence the system (in this case the semiconductor) which absorbs radiation has to have its band positions at the appropriate values of water decomposition reaction. In the case of photosynthesis, these species are multiple in nature and also in sequence and hence appears to be a facile process.

REFERENCES

1. Blankenship, R. E. 2002. Molecular Mechanisms of Photosynthesis. Blackwell Science Publishers, Oxford, UK, Malden, MA, USA.
2. Jansson, J. 1994. The Light-Harvesting Chlorophyll a/b-Binding Proteins. Biochimica Biophysica Acta, 1184: 1919.
3. Long, S. P., E. A. Ainsworth, A. Rogers, and D. R. Ort. 2004. Rising Atmospheric Carbon Dioxide: Plants FACE the Future. Annual Review of Plant Biology, 55: 591-628.
4. Nelson, N. and C. F. Yocum. 2006. Structure and Function of Photosystems I and II. Annual Review of Plant Biology, 57: 521-565.
5. Raghavendra, A. S., ed. 1998. Photosynthesis: A Comprehensive Treatise. Cambridge University Press, Cambridge, UK, New York, USA.
6. Raven, P. H., G. B. Johnson, J. Losos, and S. Singer. 2005. Biology, 7th. ed. McGraw-Hill, New York.
7. Szalai, V. A. and G. W. Brudvig. 1998. How Plants Produce Dioxygen. American Scientist, 86: 542-551.
8. Taiz, L. and E. Zeiger. 2006. Plant Physiology, 4th. ed. Sinauer Associates, Sunderland, MA.
9. Wild, A. and R. Ball. 1997. Photosynthetic Unit and Photosystems: History of Research and Current View. Backhuys Publishers, Leiden.