Metabolism 2
Photosynthesis

Light energy is trapped in the form of high energy electrons. High energy electrons are used to synthesize ATP and reduce CO₂ to form carbohydrates. Oxygen is produced as a waste product.

A history of the unraveling of the process of photosynthesis:
1600 - van Helmont - discovered plants grow with little or no consumption of soil. Concluded: plant growth occurs through accumulation of water
1771 - Priestly - showed that plants could restore combusted air to a form that was suitable for breathing
1796 - Ingenhousz - proposed that the green parts of plants carry out photosynthesis using sunlight to split CO₂ into C and O₂ and then combined C with H₂O to produce carbohydrate
\[
\text{CO}_2 + \text{H}_2\text{O} + \text{light energy} \rightarrow \text{CH}_2\text{O} + \text{O}_2
\]
(a correct equation but an incorrect mechanism)
1930s - Van Niel - working with photosynthetic purple sulfur bacteria found that they do the following
\[
\text{CO}_2 + 2\text{H}_2\text{S} + \text{light energy} \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} + 2\text{S}
\]
They use light energy to strip H from H₂S and use H to reduce CO₂ to CH₂O, leaving H₂O and S as byproducts.
CO$_2$ + 2 H$_2$S + light energy $\rightarrow$ CH$_2$O + H$_2$O + 2S  
In this system the oxygen from carbon can't be confused with the oxygen from water.

Van Neil proposed the same mechanism for photosynthesis

CO$_2$ + 2 H$_2$O + light energy $\rightarrow$ CH$_2$O + H$_2$O + O$_2$

1950s - radioactive isotopes became available to researchers

C$^{16}$O$_2$ + 2 H$_2$$^{18}$O + light energy $\rightarrow$ CH$_2$$^{16}$O + H$_2$$^{16}$O + $^{18}$O$_2$

the results of experiments confirmed Van Niel’s hypothesis

Most of the carbohydrate plants produce is glucose. The complete equation for photosynthesis is

6 CO$_2$ + 12 H$_2$O + light energy $\rightarrow$ C$_6$H$_{12}$O$_6$ + 6 H$_2$O + 6 O$_2$

Photosynthesis consists of 2 separate processes

1. **Light dependent reactions** - light energy is trapped by chlorophyll in excited (high energy) electrons. Excited electrons are used to produce ATP by chemiosmosis and high energy electrons are used to reduce NADP to NADPH.

2. **Light independent reactions** - AKA dark reactions - ATP is used to combine CO$_2$ with an organic molecule and high energy electrons from NADPH are used to reduce the CO$_2$ to form carbohydrate.

In most plants both sets of reactions occur in the chloroplasts of the same cell.
Light

Light consists of tiny packets of energy called **photons**. Photons can be absorbed by some molecules. Photons are absorbed by electrons of those molecules and the electrons are raised to a higher energy state - they become “excited” high energy electrons.

Visible light consists of photons that have different amounts of energy (or different wavelengths) - shorter wavelength photons have more energy.
Not all wavelengths are absorbed by all molecules - The visible color of a substance is an indication of the colors that are not absorbed - they are reflected. The pattern of light absorption of a substance is called its **absorption spectrum**.

The pigments in the green parts of plants that absorb light for photosynthesis are **Chlorophyll a**, **Chlorophyll b**, and a set of accessory pigments called **carotenoids**.

The relative efficiency of different wavelengths of light to power photosynthesis is called the **action spectrum**.

In plants, the action spectrum and the total absorption spectrum are very similar.
How does light power photosynthesis?

Purple sulfur bacteria have a simple system - cyclic photophosphorylation.

Light energy is absorbed at the photosystem - an electron is excited. The excited electron is passed through an electron transport chain - protons are pumped. The proton gradient is used to drive ATP formation. The low energy electrons are returned to the photosystem.

T.W. Englemann revealed the action spectrum of photosynthesis in the filamentous alga Spirogyra in 1882. Englemann used the rate of oxygen production to measure the rate of photosynthesis. As his oxygen indicator, he chose bacteria that are attracted by oxygen. In place of the mirror and diaphragm usually used to illuminate objects under view in his microscope, he substituted a “microspectral apparatus,” which, as its name implies, produced a tiny spectrum of colors that it projected upon the slide under the microscope. Then he arranged a filament of algal cells parallel to the spread of the spectrum. The oxygen-seeking bacteria congregated mostly in the areas where the violet and red wavelengths fell upon the algal filament.
Green plants have a more complex system, involving 2 photosystems - **noncyclic photophosphorylation** (the Z-scheme)

In PS II, electrons are excited and passed through an electron transport chain - protons are pumped and ATP is made.

Electrons from PS II do not return, they are passed to PS I and excited again. The excited electrons are passed to Ferridoxin and then used to reduce NADP to NADPH.
Because the electrons do not return to PS II, they must be replenished by removing electrons from some other compound. Green plants remove electrons from H₂O. This leaves O₂ as a byproduct.

The electrons shared between H and O in the water molecule are of higher energy than the electrons of oxidized chlorophyll. Water can donate electrons to oxidized chlorophyll. The electrons can then be excited and donated to another electron acceptor. Electrons from another water molecule can then replace the donated electrons.
Where do the light reactions occur?

The light reactions are imbedded in the thylakoid membranes.
ATP is synthesized by chemiosmosis. Protons are pumped from the stroma into the thylakoid space. Protons flow outward through ATP synthase and drive ATP synthesis.

Many plants can use both noncyclic and cyclic photophosphorylation. To do cyclic photophosphorylation, they short-circuit the path of electron flow at photosystem I by returning the electron to the electron transport chain. They can use this system to generate large amounts of ATP.
The light reactions provide the energy and reducing power for the light independent reactions (dark reactions). ATP and NADPH power the fixation of carbon dioxide and the reduction of CO₂.

The light independent reactions are collectively called the Calvin cycle.

The first step of the Calvin cycle is carbon fixation - CO₂ and H₂O are combined with Ribulose 1,5 biphosphate to create 2 molecules of phosphoglycerate. This is catalyzed by Ribulose biphosphate carboxylase (RuBisCo).
For every 3 CO₂ molecules that enter the Calvin cycle 1 molecule of Glyceraldehyde 3-phosphate can be produced. Glyceraldehyde 3-phosphate can be used to make glucose and other carbohydrates.

To make 1 G3P it costs 9 ATP and 6 NADPH.

Thus, to make 1 glucose it costs 18 ATP and 12 NADPH.

The Calvin cycle has 2 phosphorylation steps and 1 reduction step.

The Calvin cycle occurs in the stroma of chloroplasts.

The Calvin cycle is also called the C₃ pathway for carbon fixation because carbon is first trapped in the form of a 3 carbon molecule, PGA.
An energy comparison of glycolysis & respiration with photosynthesis:

In the breakdown of glucose to CO₂ and H₂O, 36 ATP are produced.

To build one glucose from CO₂ and H₂O it costs 18 ATP and additional energy from 12 NADPH. If NADPH is worth 2.5 ATP (like NADH) then the additional energy from NADPH is equivalent to an extra 30 ATP, for a total energy equivalent of 48 ATP to construct 1 glucose molecule.

Chloroplasts and mitochondria carry out complimentary processes. Plants have both organelles and can use respiration for energy harvest from stored carbohydrate when sunlight is insufficient to meet needs.

The reactions of photosynthesis make glycolysis & respiration possible.
There is one important biochemical problem with photosynthesis as it is carried out by most plants. The enzyme RuBisCo, normally fixes CO₂ by combining it with Ribulose biphosphate, but RuBisCo can also degrade Ribulose biphosphate and release CO₂, essentially undermining the goal of photosynthesis. This loss of CO₂ is called **photorespiration**.

Rubisco has 2 enzymatic activities:
- **Carboxylation** - Addition of CO₂ to RuBP
- **Photorespiration** - Oxidation of RuBP by the addition of O₂

Photorespiration becomes a severe problem when temperatures exceed 28°C (82°F). Photorespiration is an important problem for agriculture in the tropics.

Photorespiration can only occur when oxygen is present, which it usually is, and when CO₂ levels are low, which they usually are.

Two different groups of plants have biochemical strategies that allow them to avoid photorespiration and this allows them to live in warmer environments than other plants.
One group of plants gets around photorespiration by separating the light reactions (which generate oxygen) from the Calvin cycle (where RuBisCo is) into different cells within the leaves of the plant. These plants are called C₄ plants because they use an alternative pathway for fixing CO₂, the C₄ pathway.

CO₂ is trapped in **mesophyll cells** of the leaf in the form of oxaloacetate (a 4 carbon compound). Oxaloacetate is then converted into malate.

It costs the equivalent of 2 ATP molecules to trap one CO₂ molecule as oxaloacetate. This is also called **Slack-Hatch pathway**.

Malate diffuses from the mesophyll cells into the **bundle-sheath cells**. Bundle-sheath cells are impermeable to O₂ and CO₂. Photorespiration doesn’t take place in the absence of O₂.

CO₂ is produced within the bundle-sheath cells by degradation of malate. CO₂ can then be fixed again by RubisCo without photorespiration.

Because it costs an additional 2 ATP per CO₂ fixed, it costs an equivalent of 60 ATP (48 + 12) to produce one glucose molecule via the C₄ pathway. However this allows C₄ plants to avoid photorespiration and to exist in tropical and other climates where high temperatures are sometimes a problem for C₃ plants.

C₄ plants that use the Slack-Hatch Pathway are the grasses and their relatives.
Another group of plants avoids photorespiration using another C₄ system called **Crassulacean Acid Metabolism (CAM)**. CAM plants are the cacti, pineapples, and relatives. The CAM system allows these plants to avoid photorespiration and severe dehydration that can occur in the very arid climates where they are found.

All higher plants have stomates (pores) in their leaves that can be opened to allow CO₂ in, but this also allows water to escape.

CAM plants only open stomates at night when dehydration is less of a problem and capture CO₂ as oxaloacetate (C₄).

During the day, when the air is dry, they close their stomates and degrade the oxaloacetate to produce abundant CO₂. The use it in the Calvin cycle and because CO₂ is abundant they avoid photorespiration.