Bioelectricity
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Lecture – 33

Welcome back to the NPTEL lecture series on bioelectricity. So, let us resume the story of photosynthesis. So, we have already discussed about some of the initial plan of nature or how nature has evolved its complete light to chemical energy transformation system.

So, one thing which is very remarkable to observe the most remarkable feet of nature is the way this whole chlorophyll the assembly of the chlorophyll, and the whole chloroplast structure this whole evolution itself, because since during the last century when the microscopic techniques developed, and we are trying to understand the intricate details, and the molecular self assembly of this whole process the more, and more we are learning about it more, and more we are looking at it with amazement, and all that I mean what a wonderful photovoltaic system nature has developed over a period of billions of years of evolution.

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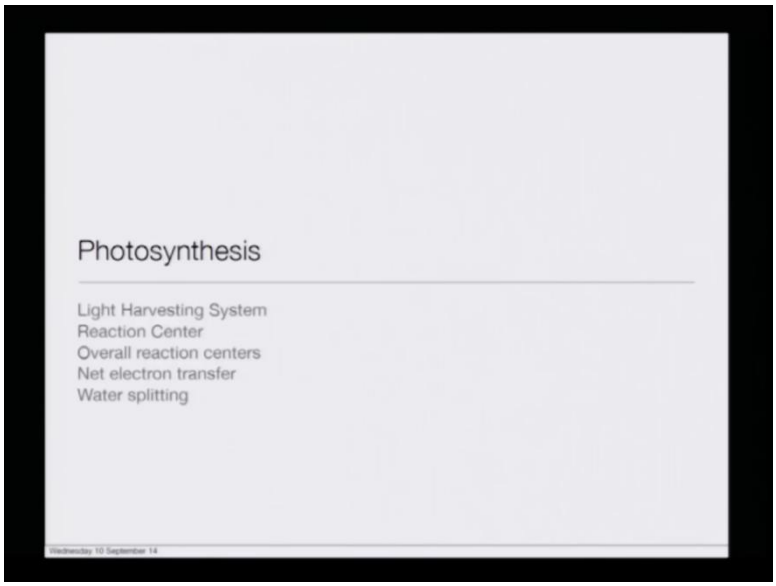

So, today what we will do we will talk about in this lecture this is the thirty third lecture. So, we will be talking about some of the intricate details at the level of chloroplast membrane, and at the level of stromal membrane, and how the electron transfer takes

place, how the light energy gets converted, and how this leads to a proton gradient which eventually leads to the synthesis of energy stood by the process eventually leads to the synthesis of energy rich molecules. So, let us move step by step.

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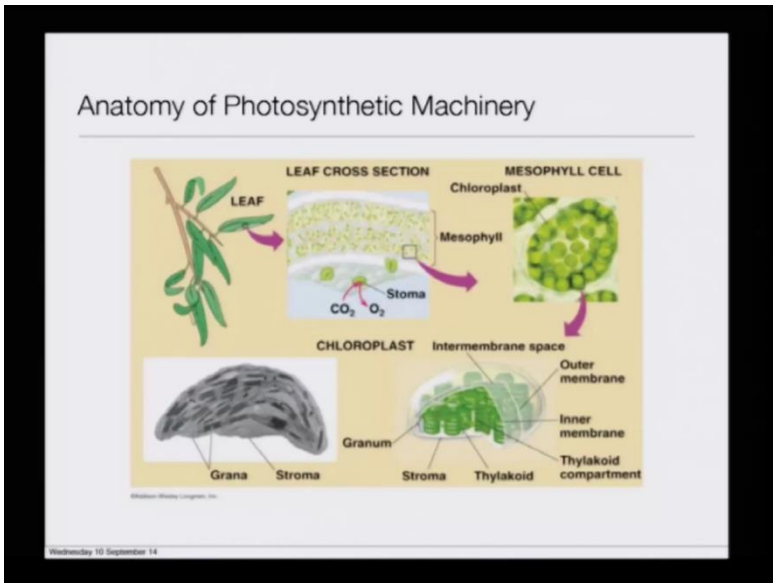

So, coming to the first slide just a bit of a recap, if you want to you know kind of get a global feel of the whole phenomena. So, here is a leaf, and if you take a cross section of the leaf this is how it looks like a cross section of the leaf, and within that there are something called mesophyll cells, and these mesophyll cells are rich in chloroplast if you follow this slide, you will see they are rich in chloroplast, and if you could take a cross section of the chloroplast in the microscope this is how you will see the stroma, and the granum, and the thylakoid membrane, and the thylakoid compartments, and these different thylakoid membranes are connected by the connecting tubes, and this is a double layer structure in which this thylakoid membrane is being housed.

So, if you even just by looking at this self assembly, you will be able to appreciate that how wonderfully this self assembly has been made out there, and it is on those thylakoid membrane the actual molecular assembly or the molecular machinery of photosynthesis is housed which is playing a critical role in the energy transfer process. So, and there is one more picture here in black, and white which essentially shows actual microphotograph of the chloroplast.

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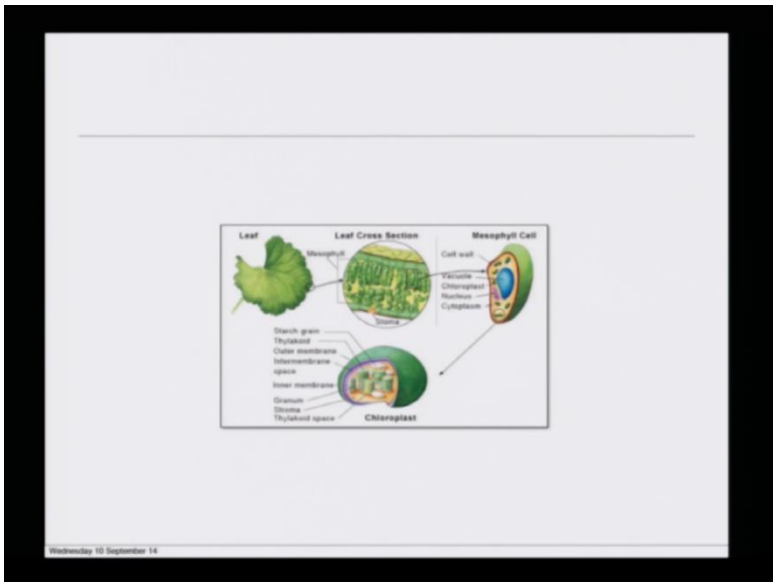

So, if you go in a further little bit of a detail just to get a more bit view of the mesophyll cell you can go through this slide, where you will see the cross section in multiple way, and see the cell wall the vacuole, and the chloroplast and you see the nucleus, and you could observe one very interesting feature that along that small organ, which it is believed that is it has been parasitized this. So, at the level of self assembly the level of kind of you know what I should say level the dimension at which all these very precise assembly of these structures have taken place this is exceptionally important, and one really needs to appreciate that if some day we really can like even if you try to mimic this kind of a structures using nanotechnology tools really have to learn much better ways how we can manipulate molecules have such a wonderful self assembly the guiding principle first self assembly. Now coming to the light show you have to realize that this structure. So, this structure what you see here is equipped with three interesting features.

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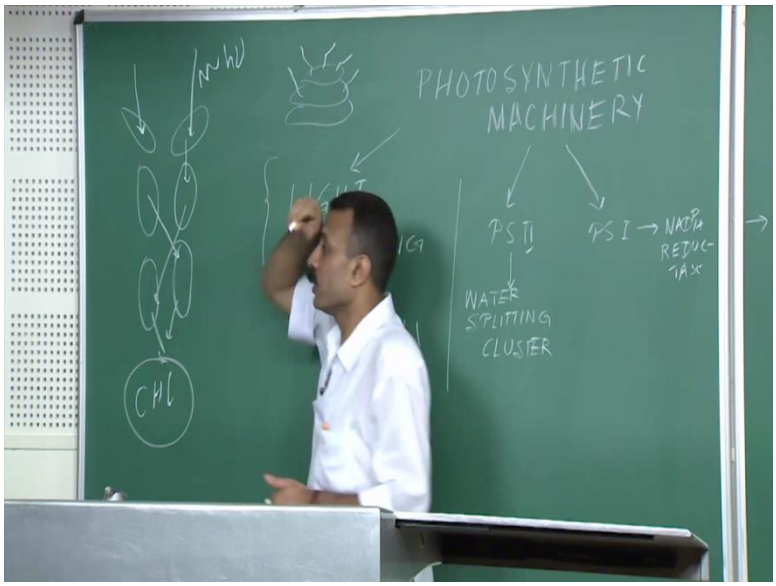

So,. So, photosynthetic machinery the three important features what is equipped with is the light harvesting component that is what we are going to discuss ion the next class light, and then you have photo system two followed by photo system one, and then underneath photo system you have water splitting cluster, and from photo system one of course, the m a d p h sorry n a d p h reductive what we are not dealing with in this, and synthesis of energy molecules . So, this is the overall component of these naturally evolved system.

So, the first level is the light harvesting. So, this light harvesting phenomena. So, you always exclusively talks about the you have the chlorophylls which are present there. So, I just putting c h l followed chlorophyll. So, it is not the chlorophyll which is exclusively doing the task chlorophyll is being supported by several other molecules which helps to funnel the light to chlorophyll something there are series of proteins which are sitting like this, and when the light energy falls on them they kept on funneling this thing all the way, and it finally, reaches the chlorophyll molecule, and what you see out here in the slide is some of those key.

So, these are like on the surface of the these are acting as antennae molecules, that is what you see that which is written like the antenna pigments or antennae molecules which are present there a photo system, and its light harvesting antenna.

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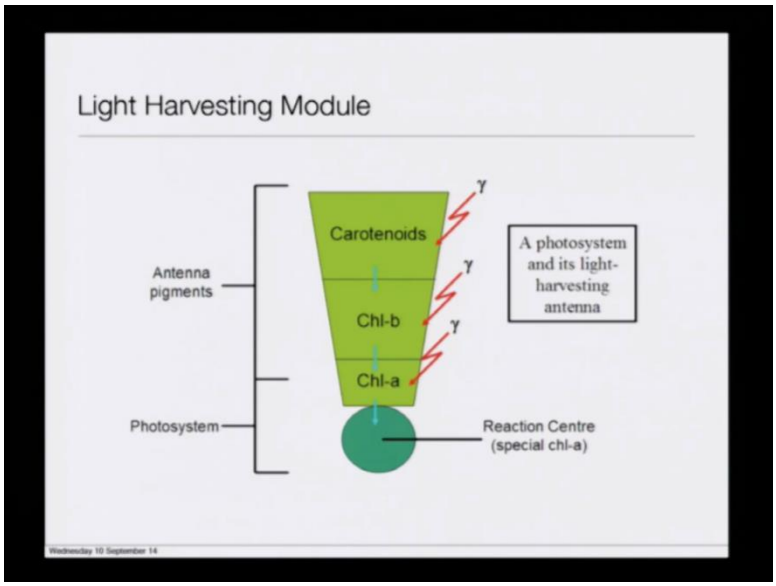

So, it is just like on the top of a building you have this antenna to you know catch the or any kind of electronic gaggers like TV or you know radio whatever you have these antenna which is catching the radio signals. So, same way there are the molecule at the molecular level there are molecules which has the ability to capture the sunlight, and not only they could capture they are arranged in a three-dimensional geometry in such a way they transmit it to the final candidate which is chlorophyll. Of course, there is some degree of loss, but this what ensures that there is a maximum capture of sunlight as possible.

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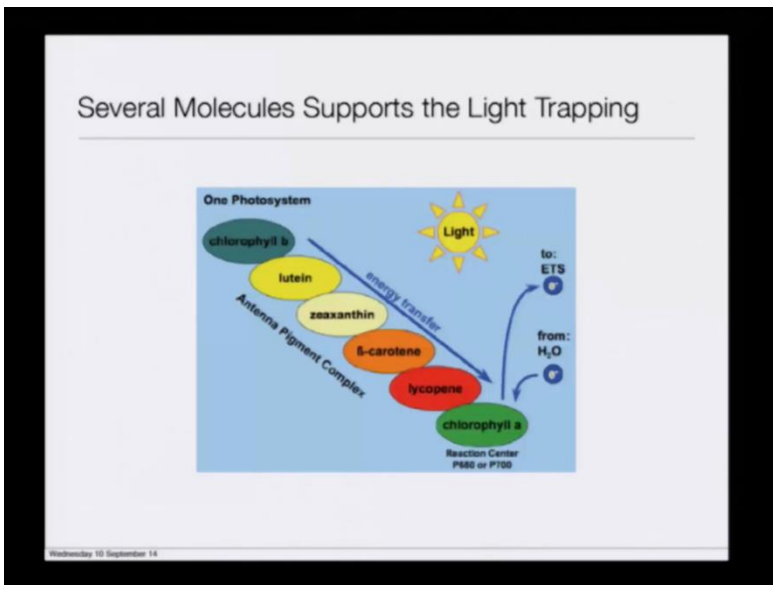

And if you look at the center like this there are several molecules that support the light trapping, of course you always talk about chlorophyll, and chlorophyll a chlorophyll b, but there are you have lutein you have zeaxanthin you have beta carotene you have lycopene there are series of antenna pigment complex which helps in funneling the electron to their specific site now coming to the specific site what you meant by specific site.

So, the antenna molecule has funneled it here, but is it this chlorophyll immediately ejects an electron, and gets activated actually does not work like that it is very interesting to know at this level also there are some very interesting flosses which taking place this what I am circling are all chlorophyll molecule. Now what happens is this energy transmitted to this, this is transmitted to this, this is transmitted to this, this is transmitted to this. So, there is a kind of hopping motion if you see the slide you will see there is a hopping motion of the ejected electron, because of the action of a photon at the reaction center. So, it is never it is never remember one molecule of light say one molecule of or one molecule or one photon.

Say for example, leading to one electron it is never like that it is multiple photon leading to finally, one activated chlorophyll molecule you might wonder why nature has designed a system which is from a simple perspective will sounds very one second will sounds very inefficient possibly one of the possible thing which I can upfront tell if there is a continuous ejection of electron from this chlorophyll molecule, because the as soon as the chlorophyll molecule ejects an electron it behaves like a free radical.

So, if there are too many at a place, then the funneling or it may cause a self damage. So, possibly this is all speculation possibly in order to avoid such self damage nature has designed it in such a way that not all chlorophylls are reaction centers there are specific reaction centers where the electron is ejected out and that electron is accepted by several series of carriers, and the one which is say for example, if this one the one which I am shading is a reaction center in an around this there is series of other proteins which are there, but again what we do not know say for example, in a pool of chlorophyll is the reaction center unique does it remain unique throughout the life of that particular cell or does it change, you know we do not have an answer to that. What we indeed know if there are ten thousand or 20000 or one million chlorophyll molecule present here it is not each one of them are reaction centers there are specific moieties which are reaction

center, and nobody knows really what decides which one will become a reaction center this is something still mind boggling thing.

So, the take home message at this stage is we indeed have reaction centers if you this slide there are. So, many in the dark green sphere you see lot of chlorophyll molecules, but the reaction center is the in this picture is shown only one semi likewise you can know imagine there are there is only one specific there are multiple such reaction centers.

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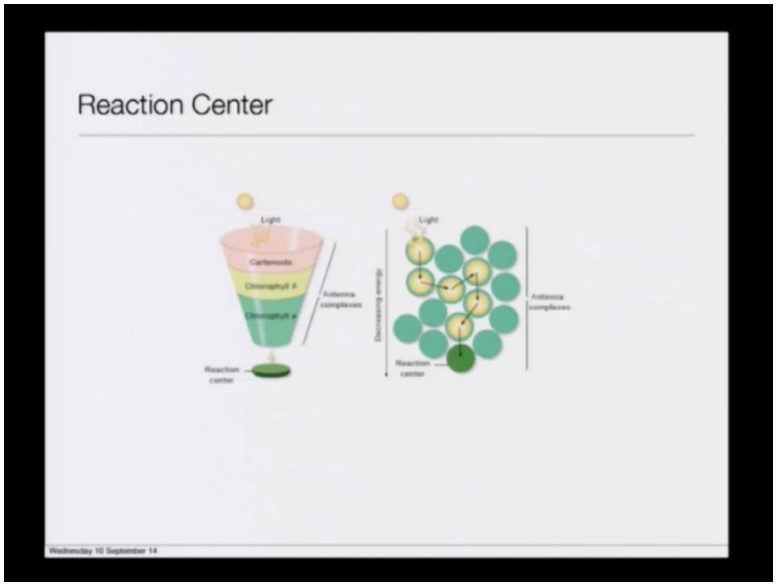

So, this is the first take home message that we indeed have reaction centers which are which has unique properties, and they have the ability to you know initiate the whole cascade of reactions which eventually leads to the formation of the sugar molecules, and everything now just I put a picture on the slide side by side.

So, light is there characinoid chlorophyll b chlorophyll a, and the light reaches the reaction center at the reaction center now what is happening, then the molecular level as I have already told you there is a motion of these in the antenna complex. So, at the reaction center the reaction is getting initiated from here. So, you can now get a better view of exactly what is happening, and exactly what it is happening. So, you have to realize that this structure what you see on the slide now which is a single chloroplast.

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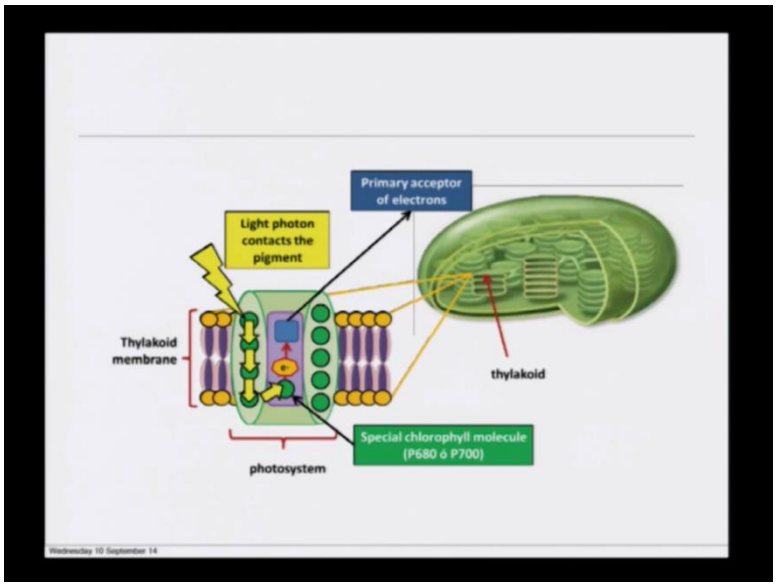

These chloroplast at every site you have these accessory molecules in the form of lupine characinoid likewise, which acting as a antennae they are funneling the electron to the chloroplast a pool within the within sorry within the chlorophyll pool, sorry within the chlorophyll pool with in the chlorophyll there is a hopping taking place, and then what you see out here is something like this there is a specific reaction center where the reaction gets initiated. So, where the reaction is getting initiated what does that mean. So, now, you talked about light has reached. So, there are specific reaction centers. So, at the reaction center what is happening this is very interesting to understand.

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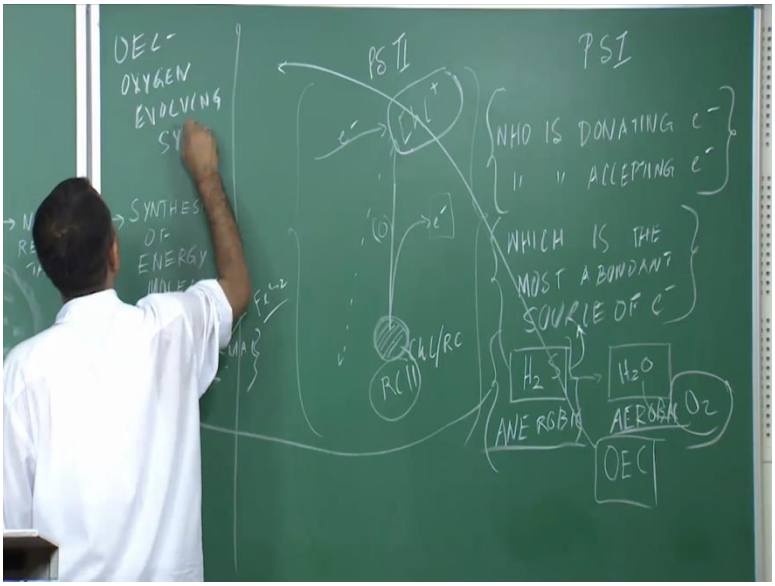

So, here there is a chlorophyll molecule, and it has I am just putting as r c there are two reaction centers in this whole process one is called photo system two which is also is short called p s two, and there is another one which is called p s one, and there is specially separated from each other. So, if you see a pool like this of chlorophyll this is a pool of chlorophyll. So, there is specific p s one, and there is specific p s two, and they are specially different, and they have a different name one is called p six eighty, and other one is called p 700 will get into all those things six eighty seven hundred likewise do not get worried about the numbers what is important here is you understand there are two specific reaction centers which are distinct from each other, and they have different kind of surrounding complexes around it. So, now, this is a reaction center.

Say for example, I call this as reaction center one or two what is ever we are going to call that. So, what is the exact chemical event what is taking place here. So, this chlorophyll molecule gives out an electron, and become positive. So, now, where it is divide of this chlorophyll molecule is one second while this chlorophyll molecule is divide of an electron this essentially got oxidized. Now this one has already donated an electron in order to bring, it back to its ground state this has to be supplied with an electron once it gets an electron, it will come back to its ground state as long as you understand this basic phenomena of accepting an electron or getting oxidized, and getting reduced the whole photo system one or two is all about who is.

So, remember this who is donating electrons, and who is accepting electrons as a matter fact or whole story about evolution is about who is donating electron, and who is accepting electron, and which is the third question here is which is the most abundant source of electron the section, where I will be dealing with iron disulfide molecule, and ancient molecular highlight that fact that very early in the evolution, if you are aware about iron sulfur theory of evolution you will see very early in the evolution nature was using hydrogen sulfide h two s as the major source of electron as earth cool down. And that is a time when we were living anaerobic environment as earth cool down the next source of electron which is also currently existing is water, and the byproduct of these water is nothing but oxygen, and this is how we have evolved from an anaerobic world or without oxygen world to an aerobic world which is rich in oxygen, and I will also highlight at still there are zones on the floor of earth where this kind of situation exist specially these kind of situation you will observe in the deep down inside the ocean in

the hydrothermal vents, and will talk more about this while will be talking about iron disulfide as a energy molecule in one of our I think probably that will be your thirty eighth lecture where will be talking about Fes2.

So having seen this there is something called this kind of complexes are called o e c complex oxygen evolving complex just let me oxygen, and I will put all of them in perspective sorry, sorry this is not system its complex so. So, now, the question is who is donating electron here chlorophyll is donating electron there must be an acceptor who are the acceptors will talk about them. Now who is donating this chlorophyll, because you have to realize in this pool, you cannot keep on you know damaging your cell, because if you damage this, if good enough of free radical which could damage rest of system. So, it has to be immediately brought back.

So, who is donating electron to this. So, that it comes back to its ground state will talk about that. So, this is where which whole scheme of things have developed, and always remember in this whole process there are only three things we have to understand very like clearly who is donating electron who is accepting electron, and who is the most abundant source of electron, and we are going to answer these three fundamental question through the photosynthesis, and this is this whole process, and if you see this this is what mankind are the whole humankind is trying to emulate which will be our next lecture essentially will be talking about how we are trying to emulate this electron transport phenomena, because it is the electron which is the key to all the power what we use across the world apart from the fuels, and everything.

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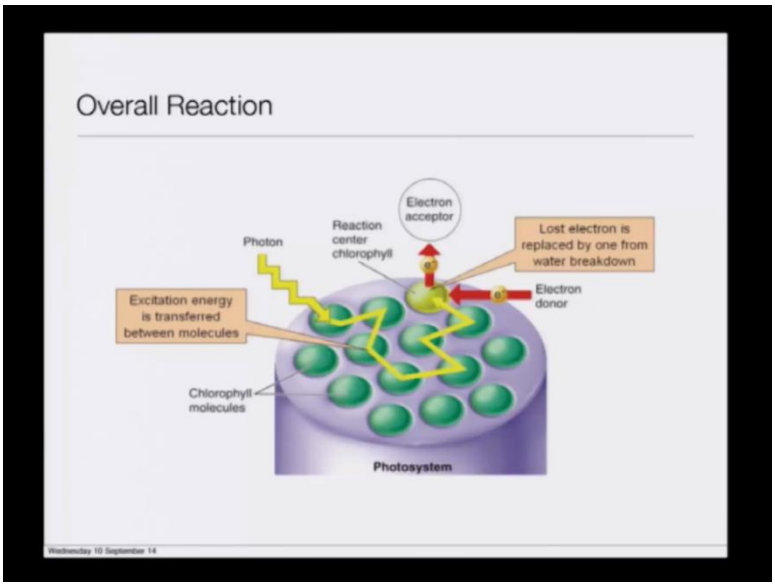

So, this is the overall situation of the photo system how far we have gone. So, there is an electron donor there is an electron acceptor lost electron is replaced by one from the will come to that water breakdown, and that is what is you see water breakdown is about this situations what I highlighted which is the donor of electron excitation energy is transferred between molecules.

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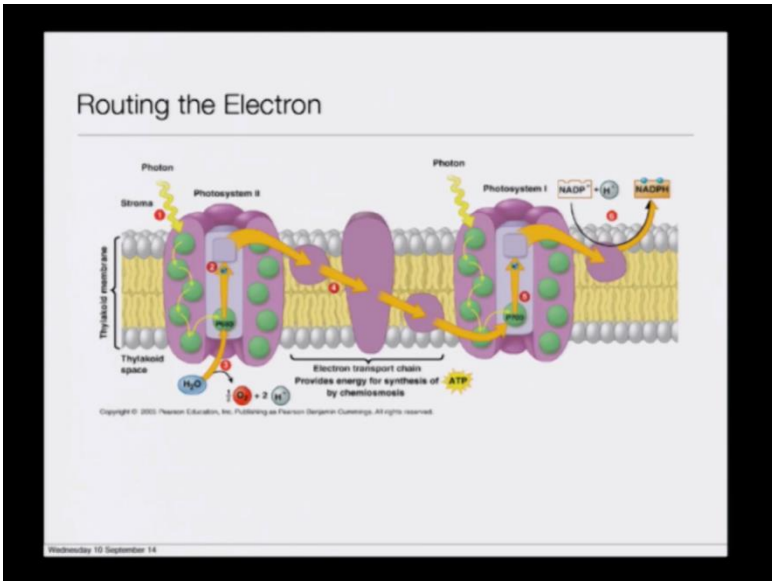

So, with this overall geometry let see the overall map where these different reaction centers are there. So, there are two basic reaction center, if you look at it one is called

photo system two on your left hand side you could see on the slide the another called photo system one photo system two is a complex assembly.

So, as I was trying to tell you each one of these are complex assemblies of several proteins, and we will come in depth about those what are those complex assemblies are protein . So, now, what is happening there is a light you see on the left hand side keep on following from the left hand side there is something written in red circle one that is where the photon is falling on. So, photon is cascading if you go through the slide very carefully you will see photon is photon has ejected an electron that electron is cascading through the chlorophyll molecule eventually it reach to something called p six eighty if you remember what I was trying to tell you p six eighty which is the reaction center at photo system two at p six eighty, and electron is being ejected.

So, now what is happening is one second p six eighty is the chlorophyll molecule uni-chlorophyll molecular the reaction center. So, this has donated an electron and. So, electron has been donated, and now p six eighty is a free radical which has excess positive charges. So, essentially this is an oxidation reaction which is taking place. So, now p sixty sixty is the first donor of electron now see the slide you will see p six eighty, then you see there are three different complexes where you see the number four is being shown, and that arrow is showing how the electron is getting transferred. So, now, follow what I was trying to tell you who is donating electron who is accepting electron.

So, what you see now all those three complexes with the yellow arrow on the slide are who are the acceptors of electron, and then this electron eventually reaches. So, in the mean time there is another simultaneously another event has taken place in another reaction center which is called photo system one that photo system one parallelly which I was trying to tell you that p seven hundred. So, which is p s one which is p seven hundred simultaneously another chlorophyll molecule out here, because of the light got oxidized. So, there are two electrons which have been given out by the two different photo systems at p six eighty there is an electron which has been ejected simultaneously at p seven hundred there is another electron which has been ejected.

Now, you have two free radical dangling out there one is p six eighty astrix, and the other one is p seven hundred astrix. Now what happens not sure before that I will show all the whole process from p s two which is p six eighty the electron eventually brings

this p seven hundred free radical back to its reduces state, and this p six eighty astrix which is in a excess positive state is supply with an electron from water which brings it back to its ground state now coming back to the slide if you look at it. So, here now follow me at p six p at p six eighty which is photo system two, because of the light there is an electron which is ejected that electron travels through three different complexes which is called the electron transport chain provides the energy for the synthesis of by chemiosmosis of a t p will come to that how it is being done. And then this electron brings back the p seventy with simultaneously at number five if you look at it with simultaneously got into the excited state by you know getting oxidized, and the electron [whi/which] which is ejected by photo system one is, then use by another enzyme call n a d p h reductase to make a energy rich molecule called n a d p h, and if you see that there are two dots. So, basically it has got two electrons out there to make the n a d p h molecule now what will do in the mean time. If you look underneath p six eighty there is water which is getting split, and this is the seat for water splitting cluster now what will do I will give you the exact it is not the exact what is ever we know about the photo system two.

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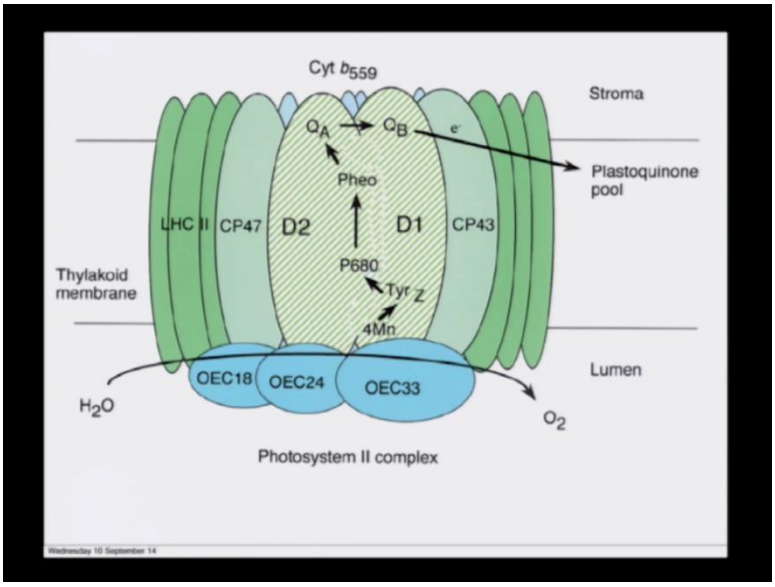

So, here the how the photo system two looks like p six eighty is the reaction center there is a tyrosine residue very closed under to it, and underneath you see there is something written o six eighty twenty four o e c thirty three this is oxygen evolving complex this oxygen evolving complex is nothing but externally beautiful manganese cluster

embedded in a protein surrounding, and with calcium close by, and this is the cluster which does the magic of nature by splitting water into hydrogen oxygen, and electron the most perennial source of electron. So, as I was telling you in the hydro thermal world it was h two s and.

In the modern world is water now look at this these are the o e c is stands for your oxygen evolving complex which is sitting just underneath it, and just follow that there is an stroma, and there is lumen which is telling that is semi symmetric membrane, then you see few p h u that is phiofitine that is another complex protein out there, then you see plastoquinone which are q a, and q b, and then what you see cytochrome b five fifty nine I will come to that in the mean time if this this complex not appreciated you have to go to this. So, here now all the names are there. Now I was telling you that how this a t p is being synthesized out.

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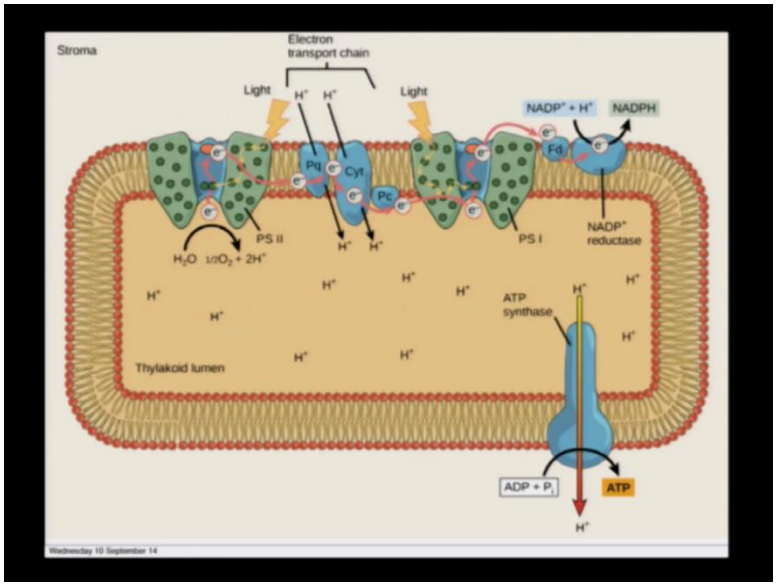

Now, follow me this is. So, you have the stromal site, and you have the lumen site lumen is the inside the thylakoid membrane which is kind of enclosed site. Now your photo system p six eighty is sitting on your left where you see the water is getting split up on the left hand side, and see the left hand side complex on the slide carefully. So, when the light falls here. So, then it is an ejecting an electron that electron through the cascade of all those different proteins what you see phiofintine to plastoquinone likewise. So, you see the plastoquinone p q, it goes to a complex called cytochrome b f six complex what

you see c y t there is cytochrome, and the electron is traveling all along this membrane. So,, then it moves to a p c complex called plastocynine complex from the plastocynine complex this electron moves to photo system one which is written out there p s one you follow me very carefully at p s one what is happening p s one the p seven hundred .

The chlorophyll molecule which got oxidized is brought back to its ground state, and the electron which was ejected out there is further used in initially the electron which before of the oxidation of the p six eighty. So, you have to realize that there is an electron which is donated by p six eighty this electron is now being utilized in order to reduce the n a d p h. So, it is the n a d p h redutase there you see that in enzyme which is sitting there on the right hand corner n a d p reductase n a d p h reductase basically convert n a d p plus proton to make n a d p h, whereas on the other hand what you see is very interesting inside this thylakoid lumen while the water is getting split up it is evolving oxygen. So, this is what I was trying to tell you that evolution of oxygen is nothing, but a byproduct of water splitting process.

So, this is that oxygen is sitting apart from oxygen what it is being generating is a series of protons out there if you see the reaction carefully on the slide you will see h two o plus half o two plus two h . So, now, your thylakoid lumen is rich in a proton rich very rich in proton. So, essentially if this is your luminal part of it. So, this has very very high concentration of the protons which are present there. So, now, there is a proton gradient across. So, you see a proton gradient across the thylakoid membrane, and it is this proton gradient which eventually leads to the synthesis of a t p by a t p synthase which present on the thylakoid membrane. So, you see that a t p synthetise on the right hand bottom corner just underneath n a d p h reductase.

So, this is how this whole transport electron transport, and leading to you know the production of energy rich molecule, and likewise so and so forth. So, what you can appreciate in this whole process is water here is playing a critical role as the currently as the abundant source of free electrons, but in order to do. So, nature has to have a very amazing critalic machinery by which you can you know split water or you can rip water, and get the electrons out of it, and nature has done it the most elegant way even one can ever think of…

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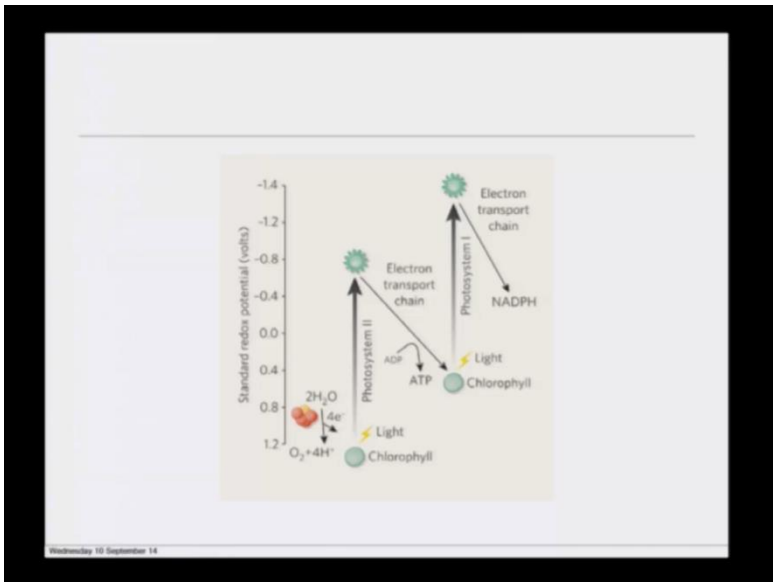

So, coming back. So, these are the standard redox potential of change I will come to that manganese cluster, and the how that o e c complexes there. So, just before we get into that. So, see how these electron transport is it is going against the gradient mind it you look at it standard redox potentials are going towards negative, then again falling back, and then against going up one might wonder that how why this process is like this there is no absolutely answer to this question if you look at this slide carefully that as if, but one thing you can appreciate from the slide at possibly in this whole process the system is bind time by doing it in a slightly convoluted way, and thereby ensuring these complexes are not getting damage, because of the free radical existence, because they are exposed to nature. So, they are they are purposefully you know increasing the time of doing this reaction with a slight delay, and you know kind of changing the redox potential up down up down likewise.

So, possibly again if this is the most correct explanation I would not claim that, but this is something which you know comes in my mind that possibly nature has done something like this in order to you know minimize the damage or you know in order for the whole machinery to function in much better way, but at the cost of efficiency. So, the efficiency of the system goes down, but may be within the theoretical I mean within the practical real amount or within the practical constraints of working in such small area of may be one or two micron I much less than that may be this is a best nature is evolved till date.

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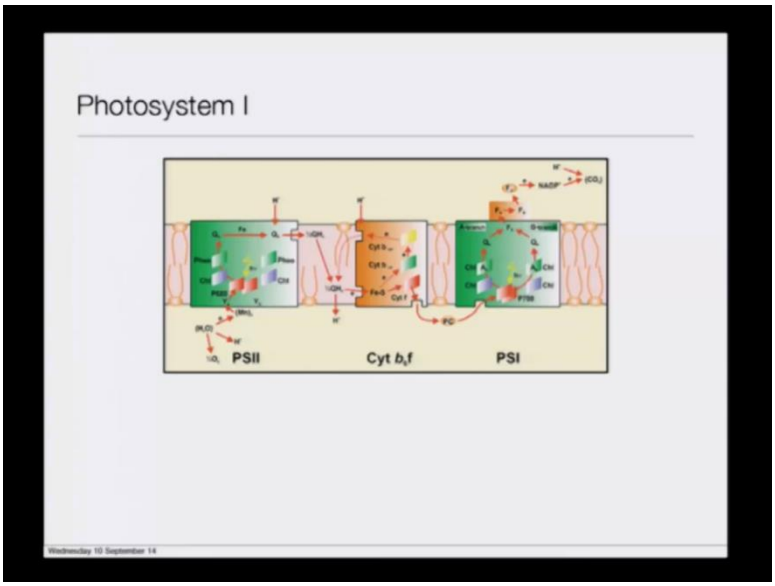

So, from here I will just put the photo system one in place what is happening to that electron from p seven hundred p seven hundred is going through again series of proteins, and it is transferred to f x q x, and you could see all those proteins, and eventually goes to the n a d p h reductase. So, if you see this this is how the whole assembly of this photo system two cytochrome b six f complex, and p s one is arranged on the membrane of on the thylakoid membrane separating this stroma, and the thylakoid lumen now the overall layout of the system is something like this. So, you see the membrane where you have the photo system two you have the photo system one you have the electron transport complex.

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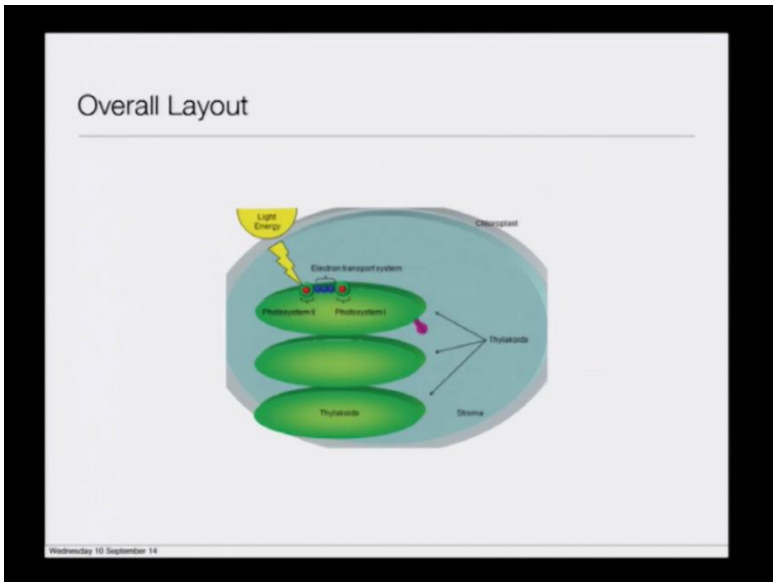

Now, from here I will move on to something called the manganese cluster.

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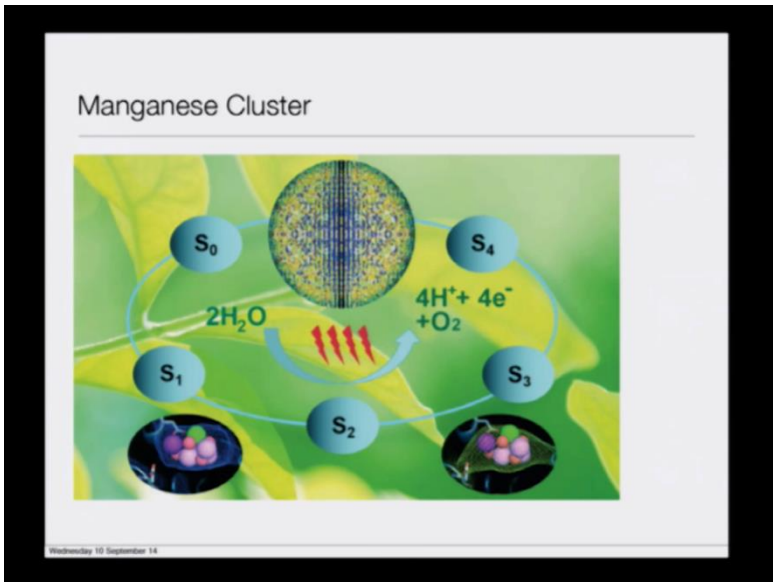

So, the critical part of the game where the water is getting split. So, this is the inspiration to make photoelectrochemical cells the modern day, but how this exactly takes place there are several theories what I will try to simplify it in in a which is understandable way, and of course I will give you the references there are series of references you can go through, and you can appreciate it much better, but possibly happens is that

manganese remain in multiple oxidation states it remains from two to six it is multiple oxidation state where it is staying.

So, in the in this complex nature has managed, and most of the time you will see the manganese in the highest oxidation state, because we are in oxygenated environment. So, you will see the manganese state of six. So, nature is manage to whole manganese these manganese molecules out there at lower oxidation state like two three four five likewise, and the manganese in that oxidation state could only change to one state change it could you know become three by you know throwing an electron it can come back may graving an electron it has only that much privilege.

So, each one of them if there are sitting at say manganese one manganese say state two say state three manganese sitting at state four manganese sitting at state five and each one of them say for example, can shift one degree on both sides you know they can either get reduce oxidized that is all they cannot fully become six or likewise the the one which is standing at two two will become three or likewise, and in that whole process they could you know make this movement. So, whenever the grab a water molecule they shifts.

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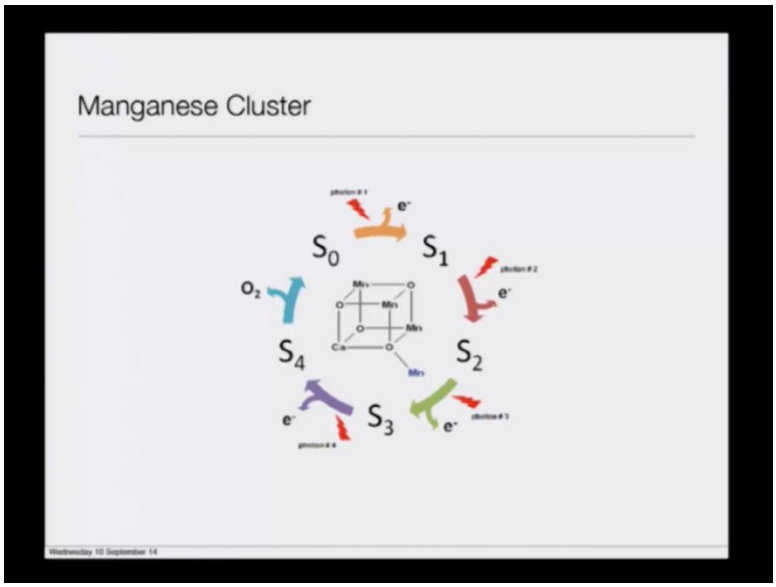

There something like this happens just one second something like this happens a water molecule gets trapped, and they could you know really split the water molecule by oxidizing it, and still the mechanism is yet to be worked out in depth like a universal

mechanism which we all can really appreciate, but I will recommend you go through a book of strior biochemistry of strior, you will get a much more better feel about it, and there is a role of calcium in this whole process.

So, since this is out of the periphery of this course I am not really getting in depth with the manganese cluster how it is splitting, but overall this is something like it, it remain same multiple state, and thereby it kind of you know, but one of the challenge of mi mimicking such cluster is that how you could really hold manganese at a lower oxidation state I mean it is very tough, because we are leaving in a oxygen rich environment. So, this is problem.

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These are different states or different manganese clusters, and it is it is been observed that this graph is very important, this called how the coke cycle there is something called a coke cycle which evolved it says after every this is oxygenation evolving is that for every flash there will be one oxygen, it does not work like that it is actually after every poor flash there is one oxygen.

So, you see the flash number, and you see the oxygen yield oxygen in maximizes after every fourth flash. So, that is basically wanted to say there are four stages in which the water is getting split into you know oxygen, and the protons, and donating the electron that is why it is shown in the fourth cycle, and if you follow this graph you will see at four at eight at twelve at sixteen at twenty likewise at every fourth interval, there is

maximum evolution maximum emission of oxygen. So, this is the overall how the manganese cluster looks like. So, one of the challenge what I now moving on to the or moving on to the next ah topic on this which will be the next lecture on which will be the thirty fourth lecture where we will be talking about how people are trying to you know utilize this whole idea of generating hydrogen.

So, this is a source where you can really generate hydrogen, and which could be used as a fuel. So, manganese cluster remain you can say remain dream thing for those who are interested in energy to emulate this kind of structure whereby you can split water you will have ready source of electrons ready source of hydrogen, and you really can store the energy according to your convenience how you could have hydrogen energy you could have the electrons you could you know flow them on a circuit likewise several efforts have been made, and will be talk we will be talking little bit in that context about this in dye sensitized solar cells, and likewise.

So, I will closing here just to summarize what all we have you know covered today we have talked about let us again go through all the slides real quick. So, we talked about the anatomy of the photosynthetic machinery where we talked about the stroma, and the thylakoid in the granum, and we talked about meso the real geometry of mesophyll cells we talked about the light harvesting module where several different molecules are involved lutein zeaxanthin beta-carotene, and lycopene, and then we talked about the reaction center how the reaction centers are talked about why possibly nature has made reaction centers, and this is side by side view of the whole thing.

And then we talked about the two different photo systems which are involved in it photo system two, and photo system one, and the electron cascade from photo system two to photo system one the n a d p h reductase adjacent to photo system one, and the water splitting cluster which is in the form of in the photo system two. So, which is the oxygen evolving clusters? So, this is the overall what we have talked, and what we need it to know. So, the inspiration what are being drawn is out here it could be emulate this chlorophyll structure as of photovoltaic material. So, that will be our next lecture where we will be talking about all these things.

Thank you.