

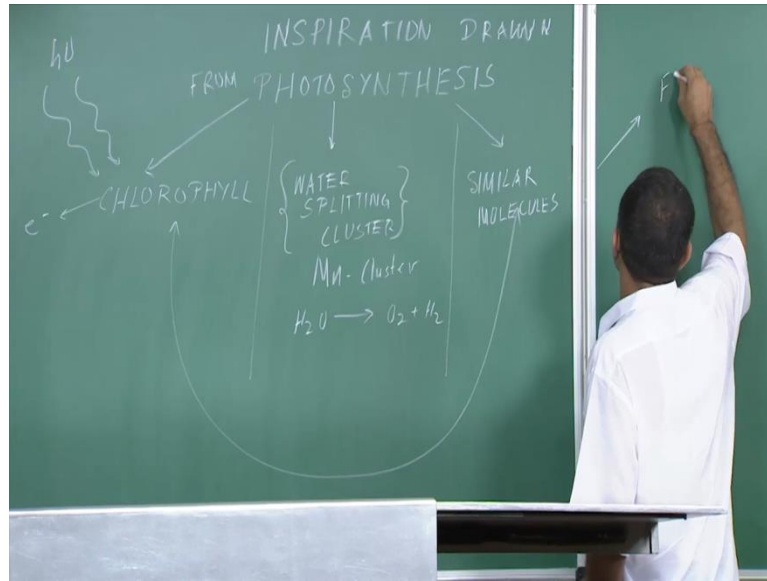
**Bioelectricity**  
**Prof. Mainak Das**  
**Department of Biological Sciences and Bioengineering**  
**Indian Institute of Technology, Kanpur**

**Lecture - 35**

Welcome back to the lecture series on Bioelectricity. So, today we will be starting our thirty fifth lecture. So, as of now while dealing with the plant bioelectricity we have dealt with the process of photosynthesis, the photo system 1, photo system 2, and the electron transfer followed by the breaking of the water molecule in the manganese cluster and the overall implication of this whole process. So, one common theme which kind of emerged out of the plant bioelectricity or from the photosynthesis is that the harvesting of the solar energy is the key to all the evolving processes of life across the earth or across this echo system.

So, whether it is chlorophyll or in one of the lectures after this we will be talking some of the very ancient inorganic molecules or if we talk about the synthetic world of energy harvesting talk about silicon. So, it is all these different light absorbing molecules which has the ability to absorb light and eject out an electron and in that process leads to a current generation. These kind of molecules remain a key in the whole evolving process. So, while we finish the basic photosynthesis, we highlighted the different areas where all you know the technologically intervention could take place. So, you could have a technological intervention.

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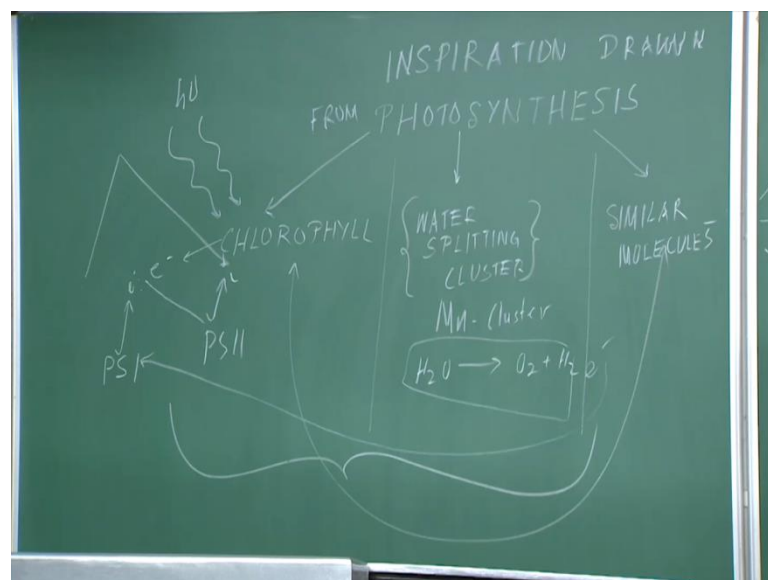
So, if we just enumerate again, where all the technological interventions could take place and what are the inspiration we are drawing from photosynthesis. So, one of the molecule in the most inspiring molecule is of course chlorophyll itself which has the ability to absorb light and eject an electron and then of course, leading to the whole electron transport and synthesizing energy rich molecules. Then the next inspiration is within the photosynthesis system water splitting cluster or manganese cluster where your water molecule is split up into oxygen and hydrogen, this is a second inspiration where people are working. We have already discussed this part in previous lecture.

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Now there is another inspiration, which is if we could use there are several other dyes several other molecules, which has the ability to eject out electron upon absorbing light. So, similar molecules, which could be utilized, say for example, the inspiration can be drawn from the flower dyes like anthocyanin and several other dyes which are involved in it. Or you could synthesize synthetic dyes where inorganic dyes and all of them have one common feature, they could utilize the solar energy in order to generate electron. Having said this if we see the whole photosynthesis process out here, and if we recall what is happening in photosynthesis, where there are two-photo system standing there. If you just for you recall, let me do it out here.

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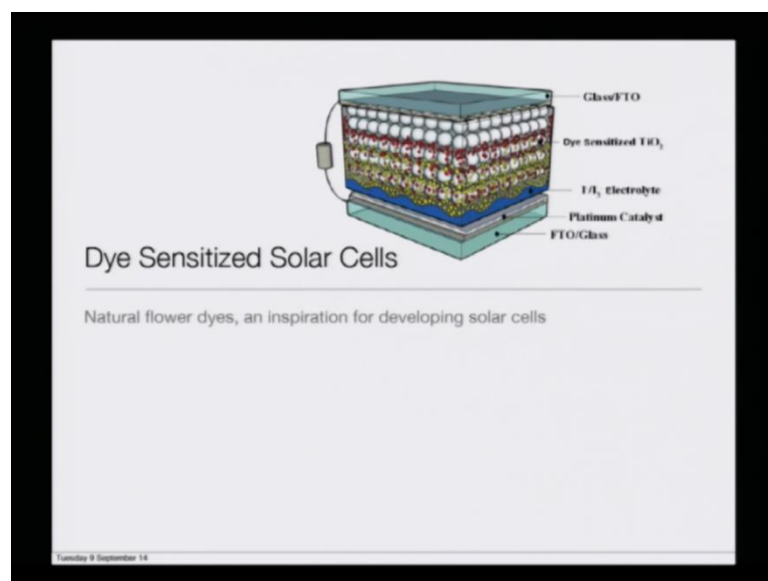


So, photo system one, photo system two sitting and both a photo system are ejecting an electron; and the one of the electron, which is ejected by one of the photo system comes back and brings back the chlorophyll molecule. So, if you just recollect what is happening in the actual thylakoid membrane. When the light falls, electron is ejected out from one of the photo system. So, as soon as the electron is ejected out from so what is essentially happening is the chlorophyll molecule is losing an electron. As soon as it is losing an electron, this electron jumps out, but then this particular molecule - the chlorophyll molecule almost behave like a free radical after losing that electron. So, this chlorophyll molecule has to be brought back to its ground state, while this electron start to take part into the cascade of reaction.

In order to bring this photo system or this chlorophyll molecule back to its ground state, another electron is needed that electron is supplied by the second photo system. Remember that how the electron is kind of coming. So, this second electron we see which is ejected by another chlorophyll molecules sitting in another photo system is bringing this chlorophyll molecule divide of electron back to its ground state. But if when it does so, the second chlorophyll molecule loses an electron. So, it has to be brought back to its ground state; and it is being brought back to its ground state by this process while the electrons are ejected, this electron brings back the other one into its ground state.

So, now having said this just with this brief recap one has to realize for these molecules which has the ability to eject an electron. So, if molecule eject an electron it has to come back to its ground state. If it fails to come back to its ground state then this all these different molecules will behave like a free radical, and there is something called a whole electron you know pairing and coupling and all those things. So, there is a very complex process which goes on. So, in order to derive energy from these kind of material, it is imperative that we need some source of free electron, nature is already devised in its armoria workstation called water from where it is deriving by splitting the water. It is deriving sufficient amount of electron to take care of the chlorophyll molecule which is divide of one electron, but here we have to do that synthetically.

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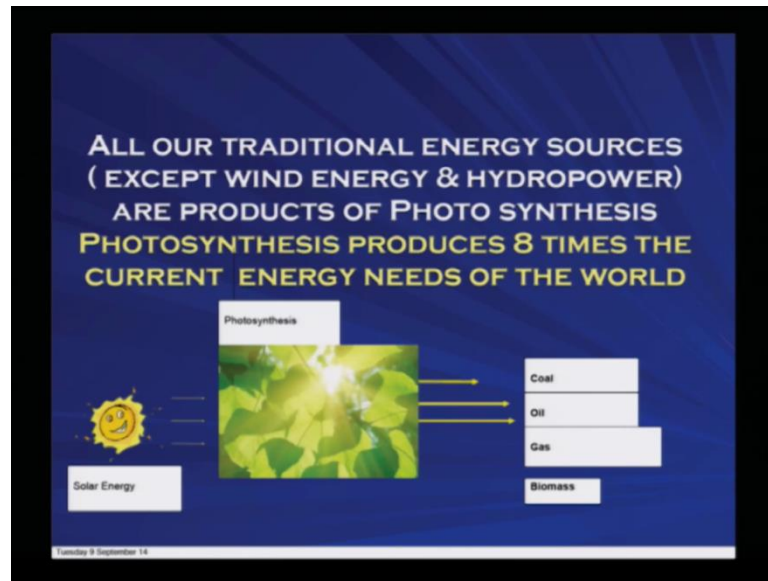
And today now let us start formally what will be talking about is a third generation of solar cells which is called dye sensitized solar cells, and you can draw the inspiration from the natural flower dyes, and there is a small kind of cartoon shown here, but we will be talking about this cartoon later. But you have to understand the basic principle of dye sensitized solar cell.

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Before I go into that just have a fairly, clear notion that what is the current energy status on the floor of earth about 1.8 billion of people are without electricity. So, if we really dreaming of a sustainable society, we have to ensure that all the people across on the planet earth receives sufficient amount of electrical energy in order to sustain their livelihood.

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So, if you look at all the traditional energy sources, you will realize all our traditional energy sources except wind and hydrothermal are product of photosynthesis. If you see coal, it is basically the trees and the plants which over a period of time in the deep core inside the earth get transformed; oil the same way; gas the same way; the biomass the same way. It is a photosynthesis produces eight times the current energy needs of the world. So, we have always dependent photosynthesis in order to you know sustain our day to day livelihood.

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The slide is titled "PHOTOSYNTHESIS" and describes it as "AN ELECTROCHEMICAL PROCESS: A REDOX REACTION OF EXCITED CHLOROPHYLL MOLECULES". It explains that chlorophyll absorbs light photons to produce excited electrons, and carbon dioxide acts as an electron acceptor while oxygen is produced as an oxidation product. A central image shows green leaves with sunlight. To the right, the word and symbol equations for photosynthesis are provided.

**PHOTOSYNTHESIS**  
AN ELECTROCHEMICAL PROCESS: A REDOX REACTION  
OF EXCITED CHLOROPHYLL MOLECULES  
Chlorophyll, an organic dye, absorbs the light photons to produce  
excited electrons. Carbon dioxide acts as electron acceptor while  
Oxygen is produced as oxidation product

Photosynthesis

Word equation

Carbon dioxide + Water  $\xrightarrow[\text{Chlorophyll}]{\text{Light}}$  Glucose + Oxygen

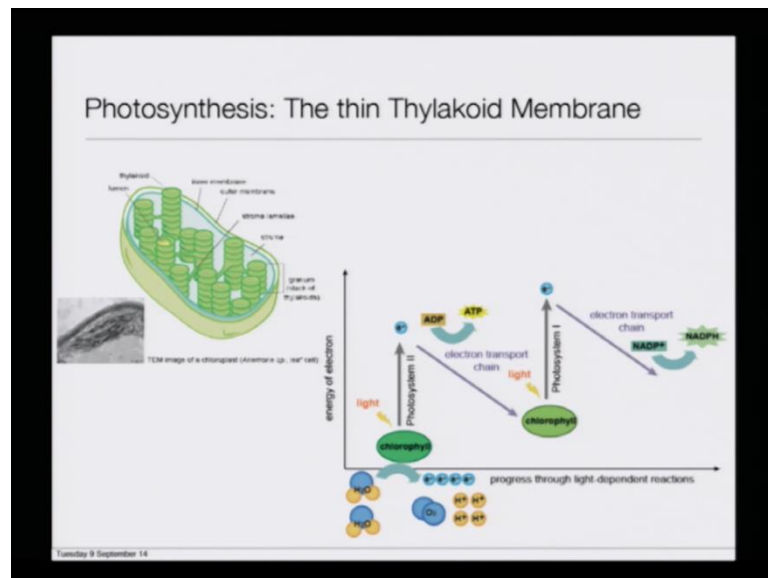
Symbol equation

$6\text{CO}_2 + 6\text{H}_2\text{O} \xrightarrow[\text{Chlorophyll}]{\text{Light}} \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$

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And if you look at the overall reaction of the photosynthesis wait just a kind of a recap for you people the carbon dioxide plus water living to glucose and oxygen and symbolically we show it. But in that whole process, it is basically you can termed it as an electrochemical process, a redox reaction of excited chlorophyll molecules, chlorophyll and organic dye. So, exactly that is what I was trying to tell you at this is an organic dye which upon absorbing light ejects out the electrons, and organic dye absorb the light photons to produce excited electrons; carbon dioxide acts as a electron acceptor, while the oxygen is produced as oxidation product. But remember carbon dioxide is an electron acceptor, but that excited chlorophyll has to be brought back to its ground state, and that is what I was trying to explain. In order to do that there should be a infinite supply of electrons and those electrons are supplied by the water molecules by the splitting of the water molecule in the manganese cluster cage what we have just discussed in the previous lecture.

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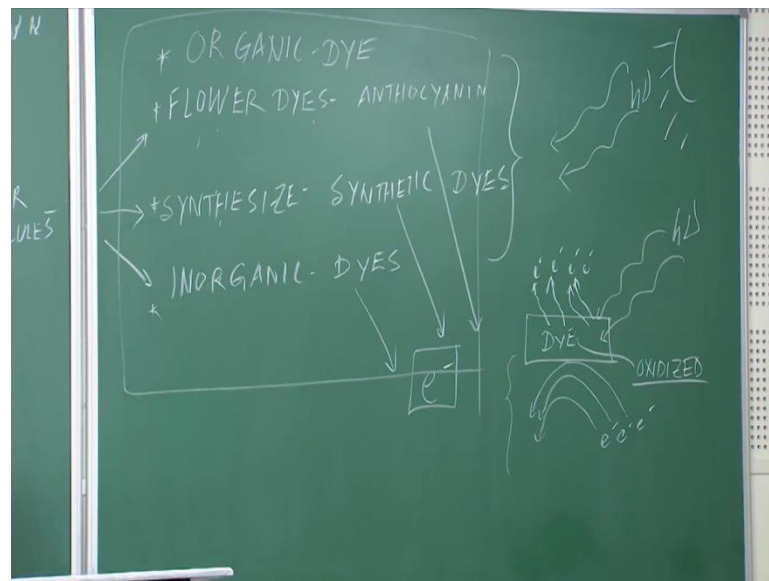


Now if you look at the thin membrane, this is the thylakoid membrane and this is what I was trying to explain. So, you have this photo system 1, photo system 2. So, photo system one is ejecting out electron where as just drawing it, it should have done like this, this is the two. So, photo system one, if you now follow the slide, so this whole process is taking place in the thylakoid membrane which is shown in the slide now. It is a very thin membrane having embedded with photo system 1 and photo system 2. Photo system

1, chlorophylls are receiving light energy, ejecting an electron that electron is being absorbed in order to reduce the carbon dioxide.

Whereas this chlorophyll molecule has to be brought back to its ground state that is done by the electron ejected out from the photo system 2. And photo system two(s) electron comes back and brings the chlorophyll back to its ground state, whereas photo system two(s) chlorophyll is being brought back to its own ground state by the splitting of water and that was what I was showing out here. Where you are the water splitting is taken place and this is how this whole process continues. So, now, what is the very basis of the dye sensitized solar cells, now if you replace chlorophyll out here, say for example, instead of chlorophyll you want to use any of these as a organic dye or a inorganic dye or whatsoever.

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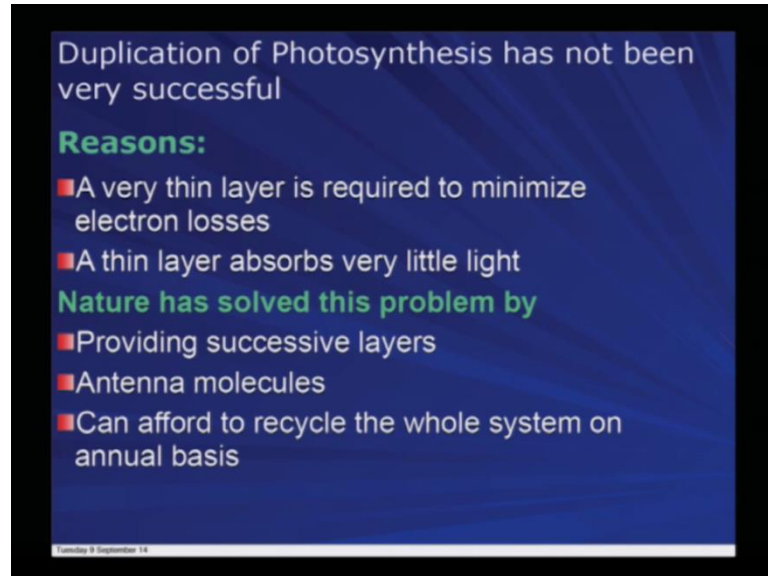


So, you have to ensure. So, you have a dye layer here, say for example, just like the chlorophyll, you have this dye out here and the light is falling on it  $h\nu$ . So, when the light is falling, these dye molecules are ejecting electrons. And if they ejecting electrons, so it means these dyes are getting oxidized, they are losing electrons. So, they have to be brought back to its ground state. In order to bring them back to their ground state, you need continuous supply of electron from some other source which is not this source; otherwise, they will recombine, this is not really going to work. So, the other source in



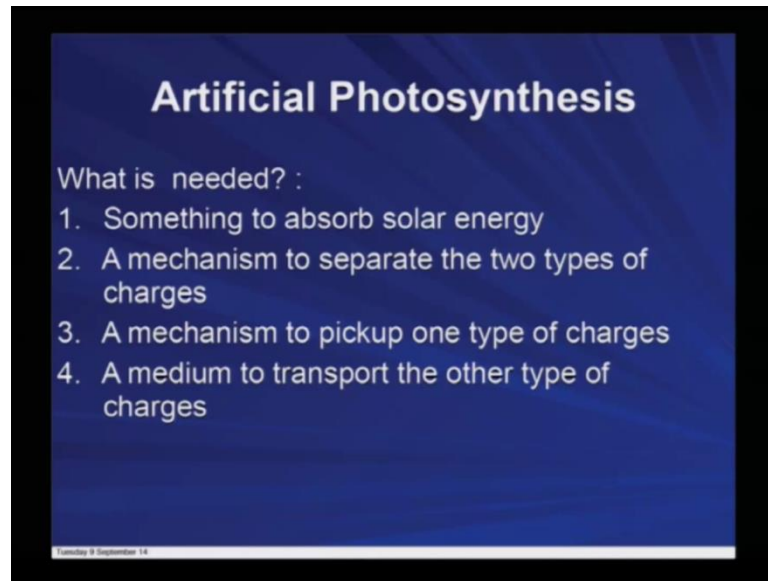
case of photosynthesis is manganese cluster. So, you need something else here or you mimic the manganese cluster.

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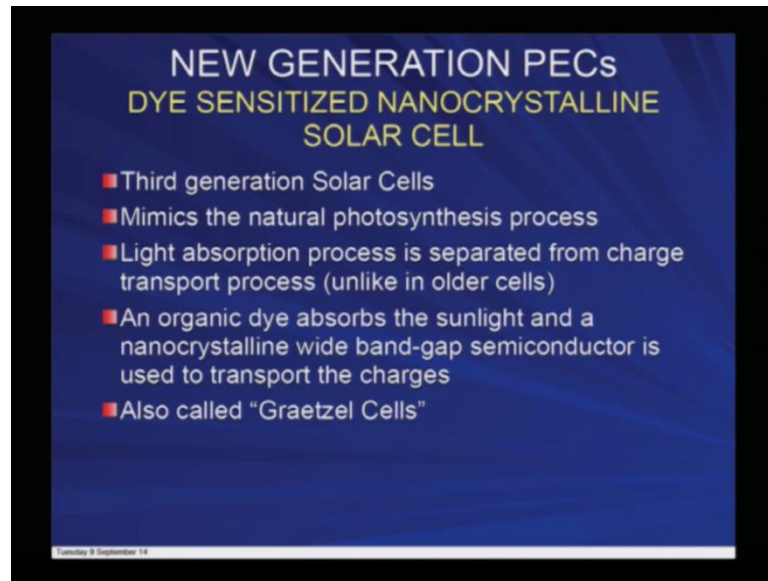
So, coming back what is that what is being replaced here. So, if you see, why the duplication of photosynthesis has not been really successful as of now. A very thin layer is required to minimize the electron loss as I was trying to tell you and you will see dye here this layer really really has to be as much thin as you can think off, thinner the better. They would not be any further loss of electrons. A thin layer absorbs very little light and nature has solved this problem of course, in the form of photosynthesis, but if you look at this picture by stacking the thylakoid membranes. If you look at the thylakoid membrane, there is stack like this; microscopic stacking which are taking place on nanoscopic stacking which is taken place. So, nature has its own way to solve that problem providing successive layers, and the antenna molecule and can afford to recycle the whole system on annual basis.

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So, in order to have an artificial photosynthesis for energy harvesting, what all we need. Something to absorb the solar energy there is could be an organic dye, could be a flower dye, could be a synthetic dyes, could be an inorganic dye anything which could you know absorb like in the whole spectrum. A mechanism to separate two types of charges. So, there will be always electron and a hole which is divide of electron. So, we should be able to you know separate out the charges, which very efficiently has been done in photosynthesis by the membrane by the thylakoid membrane. A mechanism to pickup one type of charge. So, when these electrons are ejected, you need a mechanism by which you can siphon out the charge. If you cannot siphon out, you cannot put it in a circuit, you really cannot put it to the load to glow a light or you know or run a machine. And a medium for transport of other type of charges. So, the other kind, if there is hole and the electron, so there should be way that you should be able to you know transfer those charges. So, these are the four fundamental requirement in order to mimic the photosynthesis what you are seeing here.

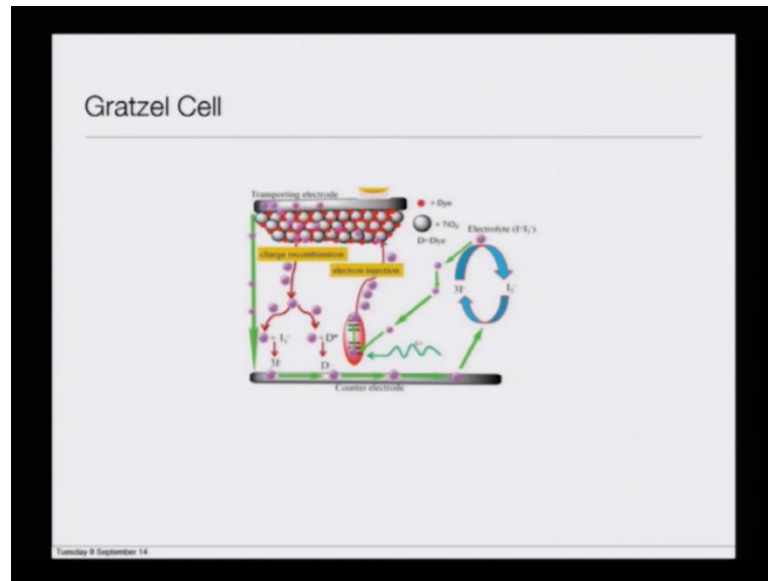
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So, there is a new generation of solar cells, which is called dye sensitized nano crystalline solar cells, which is also called after the name of its innovative Prof. Gratzel, it is also called a Graetzel cells. And I request you people to go through the work of Gratzel in detail, where the websites it is really beautiful pieces of work which has been done by Gratzel. So, which are called the third generation of the solar cells. It mimics the natural photosynthesis processes. There is a light absorption process is separated from the charge transfer process; unlike in the older cell. An organic dye absorbs the sunlight and a nano crystalline wide band-gap semiconductor is used to transport the charges.

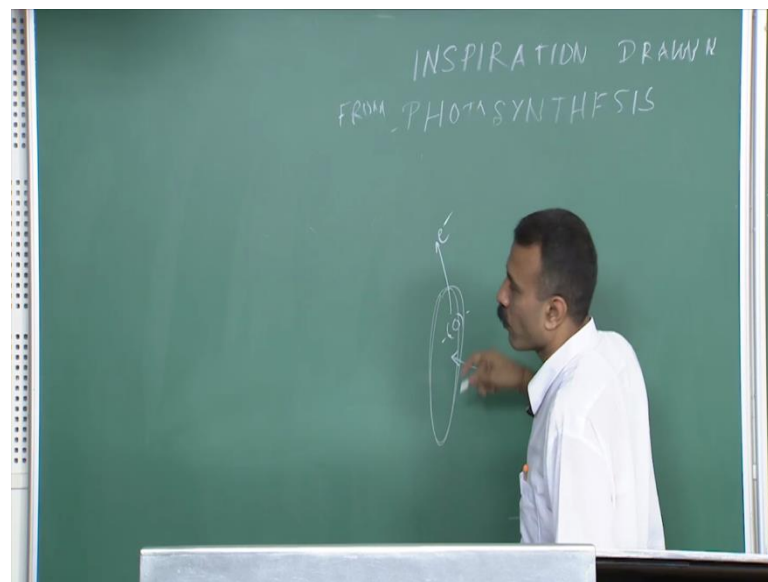
So, what essentially is being done you are playing with a band-gap of different known or existing semiconductor material, and you are coupling it. What you are doing here you have this organic dyes as one of the component could be any of these or plus semiconductor material. And there should be significant difference in the band-gap, and this is also called the Graetzel cells.

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Now coming back, how really the Graetzel cells work. So, this is a very kind of basic slide, but will go through this slide very carefully. So, what you see in the center out here. So, what you see is, let me just draw it, you see this molecule out here.

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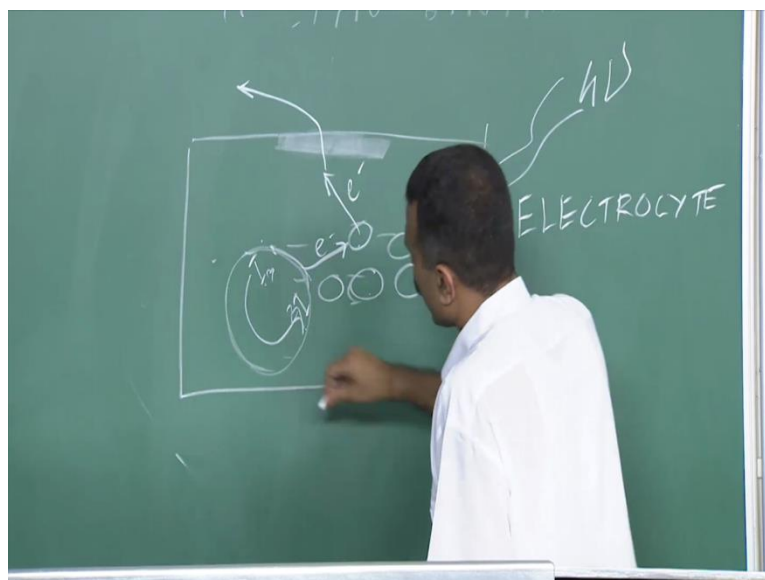


So, imagine this is the dye molecule. So, the light is falling on the dye molecule, and it is ejecting an electron. So, now, this dye is in a oxidized state, which is divide of electron. So, now let us follow the slide you will see. So, the dye is absorbing the electron  $h\nu$  and it is ejecting the electrons. Now the first thing which has to be done is that these

electron which are ejected out has to be separate it. So, if you go back to previous slide, what you all you need is that you basically need a mechanism to separate the two charges and mechanism to pickup one type of charges. So, here what you are doing is these ejected electrons has to be picked up and which is being picked up out here on the top you see that titanium dioxide. So, this is the titanium dioxide which is picking up those electrons.

So, now these electrons are being transported along with the electrode across that electrode to the other end, from the anode to the cathodes. You could see the electrons are moving on there. Now in that whole process what is happened? The dye-molecule has got oxidized. So, it has to be brought back. So, it is being brought back by the presence of a electrolyte which is present there in the form of iodine, if you see this reaction out here iodine to iodide reaction. So, this is one of the common mode by which that electron is being supplied by the iodine-iodide transformation and that electron comes back. So, whatever this electron which is generated out here is helps to so let us clean this up and let us let us do it in a right way.

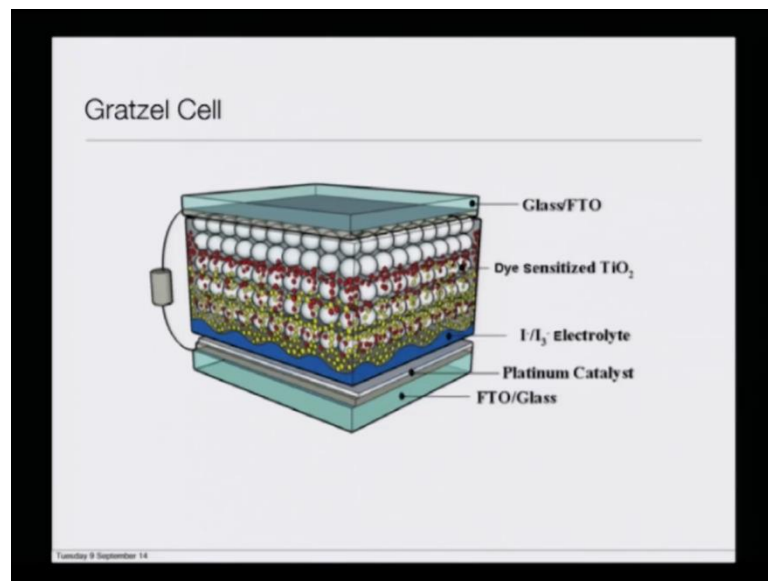
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So, here you have the cell. So, you have the electrolyte, here you have the dyes present. Light is falling on them, electrons are ejected, these electrons are picked up by specific electrode and transported out for running any kind of device. And in the mean time, there is iodine to iodized transformation, the electrons which is ejected out helps it to come

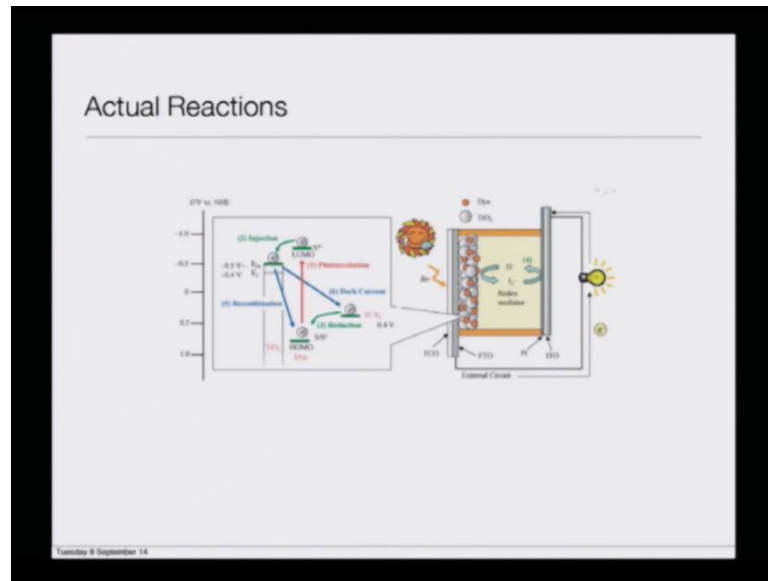
back to its ground state. Whereas there is depletion, which is taking place here is being taken care by the other electrode, which supplies the necessary electron in order to bring it back. So, in this whole process is good enough to power several devices. Of course, not very high-end devices as of now and but this is how so you can use any of these different kind of dyes you can use organic dye, you can use a floral dye, you can use synthetic dye, you can use inorganic dyes like in and so on and so forth. You can use several kind of dyes by which you can start mimicking the photosynthetic machinery.

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So, now this was the first cartoon what I was trying to show you. So, if you look at this. So, you will see, there is a glass sheet on the top, it is basically transparent. So, you both side is transparent, in order to get maximum amount of sun light. You have the dye sensitized titanium oxide, which is present there. Then you have iodine-iodide electrolyte and you have a platinum catalyst which is present there. So, this is how and there is a load on the other side. So, this is the whole overall compact assembly of this kind of dye of this kind of cells.

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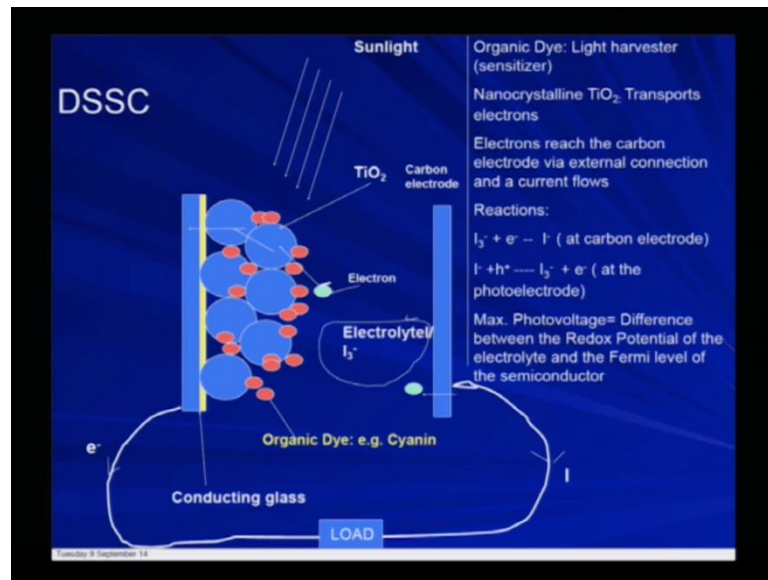


If you tried to figure out what is the reaction which is taking place. So, this is how it is going. So, titanium oxide, these molecules of titanium oxides are like this. The lot of surface area where these dyes are bounds like this. So, the picture what you are seeing is  $TiO_2$  bound with the dye. So, then there is a platinum on top of the ITO sheet, if you see on the slide. So, here you have the ITO sheet and the reaction what is taking place now if you look at it carefully. So, first of all the dye loses an electron, you see the red arrow going up, there is a photo excitation process; from the homo state it goes to the LUMO state, and where the dye is not divide of one of the electrons. So, it is kind of almost like a free radical there.

Now this dye has to be brought back it has to be reduced. So, you see the green color there number three which says the reduction, so that is where the dye is getting reduced. So, bring the dye back into its ground state, there is that other electron which is present there, it is injected into the circuit. So, there are at least four or five processes taking place. So, the first step is the photo excitation what you could see there. So, this first step photo excitation process. The second process if you look at followed by your injection of the current. So, this is where this electron is being injected out, this is the second process. And there is a third process which is involved where this photo excited molecule is being brought back, you see the reduction step which is basically bringing in back. Then there is the fifth and the sixth, where basically there is the recombination and there is a dark current which is involved. So, we are not getting in depth on those ones, but at this point

what I expect you people to understand the basic circuit and the external circuit, the electron comes back and activates a load and moves on. So, this is how dye sensitized solar cell works.

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And if you want to get a much more schematic picture exactly where the electron is, you can use an carbon electrode, you can use organic dye like cyanides, you have conducting glass. So, this is what is happening here all these dyes which are you know embedded on the titanium dioxide, and light is falling, the electron is being ejected out, and the electrolyte which is present there. So, if you follow the whole sequence on the right hand side organic dye which is essentially the light harvester or sensitizer. So, then you have the nano-crystalline titanium oxide which is helpful in transporting the electrons because these electrons have to be transported electrons reach the carbon electrodes by external connection external connection and a current flows. So, this is what you are seeing there is an external connection.

And if you follow this picture, there is an electron flow you could see on the left hand side of the slide and of course, the current goes in the reverse direction as per the assumption. So, electron reach the carbon electrode via external connection and a current flows. What are the reactions add the carbon electrode which is on your right hand side in this slide there is  $I_3^- + e^- \rightarrow I^-$ . So, it is ejecting an electron whereas at the photoelectrode that same  $I^-$  gets an proton and it forms  $I_3^-$




which is comes back to its original state plus an electron. So, you see there are two reversible reactions which are taking place, but one is at the cathode one is at the anode.

So, at the carbon electrode there is one set of reaction taking place where this I 3 minus is you know picking up an electron and getting reduced. Whereas, in the second situation, it is you know ejecting out an electron and getting oxidized, and maximum photo voltage is equal to the difference between the redox potential of the electrolyte and the Fermi level of the semiconductor. Those of you are interested, there are several other very good concise mechanisms which are involved in order to you know kind of understand this whole thing, which is this is beyond the scope of this course. So, I am not really getting into the what are the different Fermi level electrons and how they are kind of Fermi levels, how they are kind of involved in this whole process, but for your reference you can go through the work of Gratzel Arthur Ratori. I will forward you some of these work and you can go through them, and you will see that the nicely people have you know model this whole system.

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Efficiency achieved ~ 10.5 %  
Commercial Solar Cell efficiency ~ 15-17%  
Tropical Forest Ecosystem efficiency ~ 1%  
Theoretical limit for natural Photosynthesis ~ 13%

Commercial Production : Sustainable Technologies International (Australia)- Under license from EPFL



STI DSSC Façade Panel  
DSSC Façade Panel

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So, coming to the next slide let us look at the efficiency of these kind of processes, it is around 10.5 percent efficient. There are commercial solar cells efficiency is 15 to 17 percent. But that you know very 17 percent efficiency is in a very very I should say ideal condition. So, it is slightly less, it is almost five percent less than solar cell efficiency, but this is a technology which is newer as compared to the solar cell, and it could really

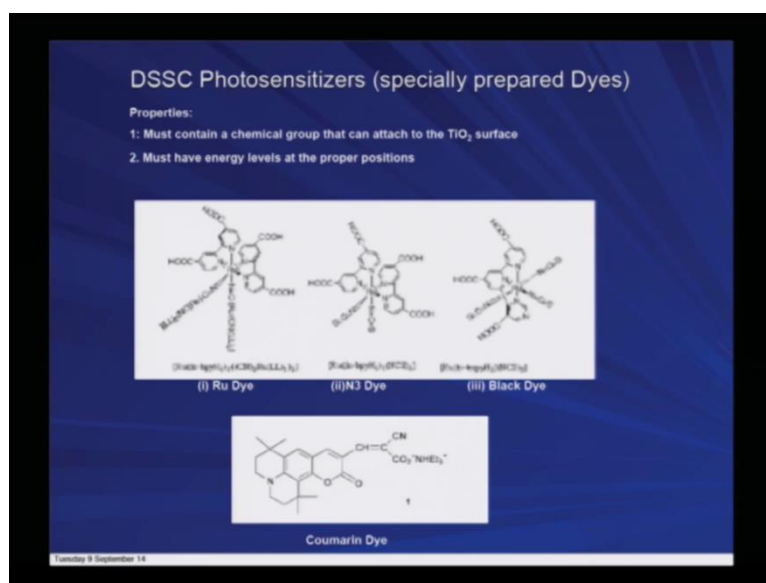
go further up. Tropical forest ecosystem efficiency is around one percent; theoretical limit for natural photosynthesis is thirteen percent. So, if you now compare these numbers this is very interesting number to compare; 13 percent is the theoretical limit for natural photosynthesis, solar cell efficiency is 15 percent - 15 to 17 percent with the best great devices using crystalline silicon. Your efficiency achieved for the dye sensitized solar cell is around ten and the tropical forest ecosystem and efficiency is around one percent that is of course, tropical forest ecosystem has the lesser efficiency for different reason.

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So, if you look at where all these have been used, various colors of dyes, several corporations which are involved in it, and they are coming a big way to you know promote this.

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So, now let us look at some of the special dyes which have been prepared. So, if you look at it you will see, you can please I mean and print this pictures are not really coming neat. So, you can really refer to the work of Gratzel and other which I will be putting on on the reference. You can go through them and you can exactly get pictures of these dyes how they look like, but what it is important for you to understand is, what are the properties which are essential, they must contain a chemical group that can attached to titanium oxide surface, so this is where thing is that. So, this molecule whatsoever this molecule is these dye molecule, this dye molecule should have a hint by which chemical hint by which it can bind into  $\text{TiO}_2$ . So, that is what it meant by we should be able to bind it to  $\text{TiO}_2$  because that will minimize the loss of electron transfer.

Must have a energy level at the proper position. So, it has to be oriented in such a way that you get the best out of it. The dyes which are currently in use they you could look at there are ruthenium dyes n three dye there are black dyes, coumarone dyes these are the organic. So, several different kinds of dyes, which are currently available in the market.

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**Experimenting with natural dyes**

**Anthocyanin dye**

The dye is obtained from the berries (Rubiaceae family)

Step1:  
A nanocrystalline (porous) film of  $\text{TiO}_2$  was coated on a conducting glass slide.

Step2:  
Sensitizer dye was derived from the berries.

Step3:  
 $\text{TiO}_2$  film was coated with the dye

Step4:  
A cell was constructed by putting a second conducting glass slide on top of the coated one with few drops of electrolyte between them

Step4:  
Cell characterization:  $V_{oc}$ ,  $I_{sc}$ , FF, Efficiency

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Now, hit me on that there are people who are working this is from Arthur Ratore is work in Fiji Island, you will see there are experimentations which are being done using natural dye. These some of these slides what I have collected from his own presentation. So, there are dyes which have been utilized the anthocyanin dye, and I will give you some of the things where you can really develop these kind of dye sensitized solar cell in your lab. These are very I mean highly doable, these are not something like you know out of the world, there are very straight forward thing and I will send you I will out as some of the reading materials or you know practical material.

So, experimenting with the natural dyes Ratore is working you see they have used anthocyanin dye, they have used several floral dyes available at the flowers available in Fiji Island. So, the way it works is the nano crystalline porous film of titanium oxide was coated on a conducting glass like which is an I tube - Indian tin oxide. Sensitized dyes was derived from the berries or you know anthocyanin or whatsoever flower you want to use. Titanium oxide was coated with the dye the cell was constructed by putting the second conducting glass on top of the coated one with few drops of electrolyte between them. So, I will characterization was done, the  $v_{oc}$ , the open circuit voltage and efficiency and everything is being measured.

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**DSSC commercialization**

2nd INTERNATIONAL CONFERENCE  
on the INDUSTRIALISATION of DSC  
**DSC-IC 2007**  
St Gallen, Switzerland, 11-12 September 2007

**DYES**  **L**

**G24 Innovations**

**DSSC Market**  
2007- 3.5 billion Yen  
2010- 58.1 billion Yen  
Manufacturing costs : 1/2 to 1/10 of  
crystalline  
cells

**RWTE**

**SOLARONIX**  
"In sun we trust"

Thursday 9 September 14

So, if you look at the nature what is the most important is now coming to what are the different commercialization market if you look at it currently. This is again I have derived it from Prof. Arthur Rathore's slides I was kind going through. So, this is very you know neatly given. So, this is the kind of numbers what we are looking forward to in the years to come like this technology is will definitely grow in a big way, where you know several different things which could be developed out of it.

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**CONCLUSION**

DSSCs have great potential for providing low-cost Photovoltaic power to billions of people around the world , living in remote areas without any access to electricity. These cells can be produced easily without the expensive set-ups needed for conventional solid-state solar cells.

This is an example of BIOMIMICRY proving that Nature is our greatest teacher.

Thursday 9 September 14

And this is the classic example what is believed as you know as a case of Biomimicry dye sensitized solar cell have the great potential providing low cost photovoltaic power to billions of people around the world living in remote areas without any access to electricity. These cells can be produced easily without expensive set-ups need for conventional solid-state solar cells.

So, now coming back what I wanted to highlight is if you look at nature carefully nature has given us abundant resource of say different kind of energy trapping molecules, energy transforming molecules. It is as we have to look or we have to kind of thing very sustainable manner in order to you know explore, harvest and make the best out of these different available opportunities, which are scattered all over the nature. So, if you look at dye sensitized solar cells, what we discussed today, you can draw inspiration from anything. I mean like and remote places like Fiji, remote places of the world like where you do not have extraordinary facility to develop a current crystalline silicon systems. You can develop this kind of a wonderful energy harvesting devices.

Of course, at this stage their efficiency is only ten percent, but you know within ten research who know some day they may out smart existing solar cell technology, this is the matter of time how much investment we do. So, overall what we see, bioelectricity we started with the bioelectrical phenomena and different bioelectrical things in plants and everything. What is very essential to appreciate that we have to think very globally, very holistically that we can derive inspiration from multiple things across nature and you can you know biomimic them and you can you know develop some extraordinary thing for the futuristic sustainable societies.

So, with this lecture, I am pretty much closing on the photosynthesis and other inspirational devices which could be or the technological intervention which could help you know to appreciate photosynthesis as well as mimic it. So, post this will be talking about some of the plant movements, but let us closing here, and I will leave it to you people to you know dream and think in a very sustainable way how these developments can be taken place. Again with a request that please go through the work of I will be providing all the relevant literatures of Gratzel cells as well as Rathori's and several other people, please go through them, you will be able to appreciate it lot better.

Thank you.