

**Solar Photovoltaics:  
Fundamental Technology and Applications  
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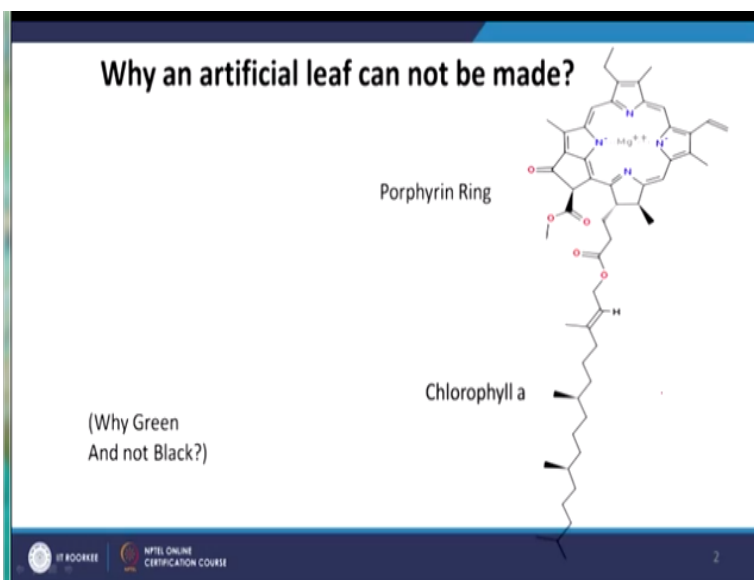
**Lecture-16  
Dye Sensitized Solar Cells – Structure and Properties**

Hello everyone welcome to our course solar photovoltaic fundamental technology and application. Today is our week 4 and module first, so far we have learned about first generation and second generation solar cell. In first generation solar cell we have talk about single crystal silicon solar cell and we have see how to process a single crystal silicon and how to make a solar cell from this single crystal silicon.

In next thing we have learnt about the second generation solar cell, there we have seen how to make a thin film base or amorphous silicon solar cell. In today's lecture we will start about third generation solar cell, now as we have also mention previously this third generation solar cell that includes lot of different varieties of materials. As the new and new materials where discovered new and new varieties of the solar cell also come into the picture.

For example dye sensitized solar cell, organic solar cell and perovskite solar cell. In today's lecture we will learn about dye sensitize solar cell.

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Now one of the biggest challenge or questions which came to our mind of our scientific community is that why an artificial leaf cannot be made. So we all know that the plants make their own food by a process called photosynthesis. So where they do that they take the water molecule from the ground and they absorb the carbon dioxide and using this carbon dioxide on water molecule by a process known as photosynthesis the plant make the food.

And in this process the chlorophyll pigments in the plant leaves helps to convert this water and carbon dioxide to generate glucose molecule and as a byproduct oxygen is also generated. And we take that oxygen and release that carbon dioxide and on the return plant take that the carbon dioxide. So the main power house or main cooking place of all this glucose food is happening in the plants leave and if we look closely this plant leaves contains the chlorophyll pigment.

Now what is this chlorophyll, chlorophyll is a biomolecule which is attached to a porphyrin ring just like here. Now the question is that the green color of the chlorophyll, the green color of the leaf better comes from we know from the chlorophyll pigment. So if we make this green color pigment or if we make a chlorophyll light molecule in the laboratory can you also mimic the photosynthesis process in the lab, so let us look at that.

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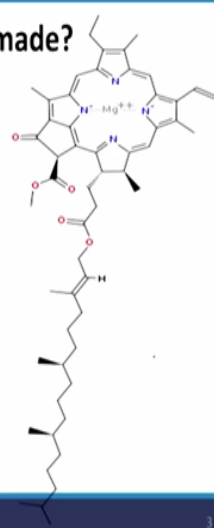
### Why an artificial leaf can not be made?

Incident light excites electrons in porphyrin ring.

Chlorophyll is in a protein complex that separates charge.

Charged chlorophyll is reduced by oxidation of water. 2 Water molecules are oxidized releasing  $O_2$  and protons,  $4H^+$ .

The released electrons power the transport of protons further interact with ATP for cell energy eventually reducing  $CO_2$  to sugars.



Porphyrin Ring

Chlorophyll a

Light

Chlorophyll a

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So the question is that when light falls on a material like in this case our plant leaves when light excites, so what happens it excites the porphyrin ring. And chlorophyll is a protein complex that separates the charge carriers, charge chlorophyll is reduced by oxidations of water, 2 water molecules are oxidized releasing oxygens and protons  $4H^+$ . And the released electrons power the transport of protons further interact with adenosine tri phosphate for cell energy eventually reducing carbon dioxide to sugar. This is like you know in a natural the process happens in a plant.

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### Why not make an artificial leaf?

- 1970 Helmut Tributsch and Melvin Calvin wanted to study the electrochemical properties of chlorophyll in an extra cellular environment (away from the protein).
- They found they could achieve charge separation using large band gap semiconductors ZnO or CdS in contact with an electrolyte.
- Chlorophyll injects electrons from excited levels into the conduction band giving an anodic photocurrent.
- Charge separation is irreversible.
- The electrolyte is oxidized at the chlorophyll molecule and is reduced at the cathode to complete the circuit.

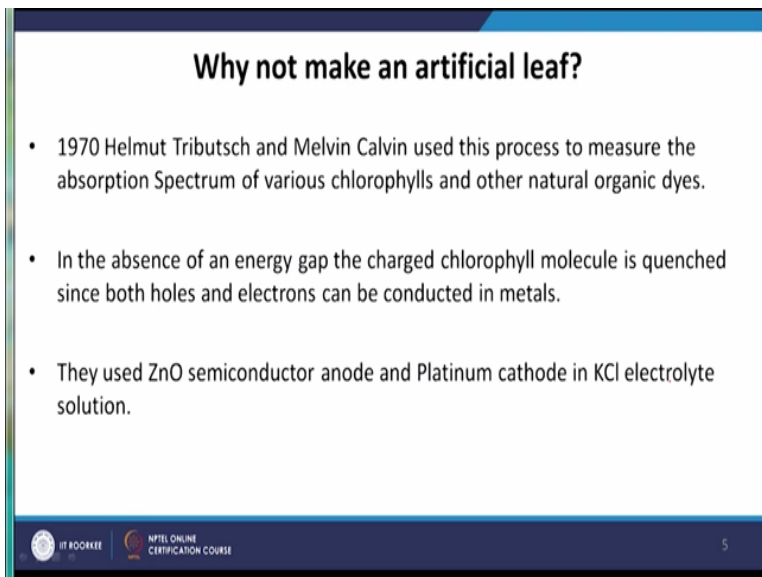
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Now in 1970 Helmut Tributsch and Melvin Calvin wanted to study the electrochemical properties of chlorophyll in an extracellular environment, extracellular environment means like

away from the plant resistant or it is away from like you know any in-vivo system. So whether you can mimic this things in our laboratory, they found that they could achieve charge separation using large band gap semiconductors, for example zinc oxide and cadmium sulfide in contact with an electrolyte.

Later on we have found that even a common semiconductor which is a large band gap is titanium dioxide. And this titanium dioxide is used very commonly to fabricate the dye sensitize solar cell. A chlorophyll injects electrons from excited levels into the conduction band giving an anodic photocurrent and charge separation is irreversible. The electrolyte is oxidized at the chlorophyll molecule and is reduced at the cathode to complete the circuit.

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**Why not make an artificial leaf?**

- 1970 Helmut Tributsch and Melvin Calvin used this process to measure the absorption Spectrum of various chlorophylls and other natural organic dyes.
- In the absence of an energy gap the charged chlorophyll molecule is quenched since both holes and electrons can be conducted in metals.
- They used ZnO semiconductor anode and Platinum cathode in KCl electrolyte solution.

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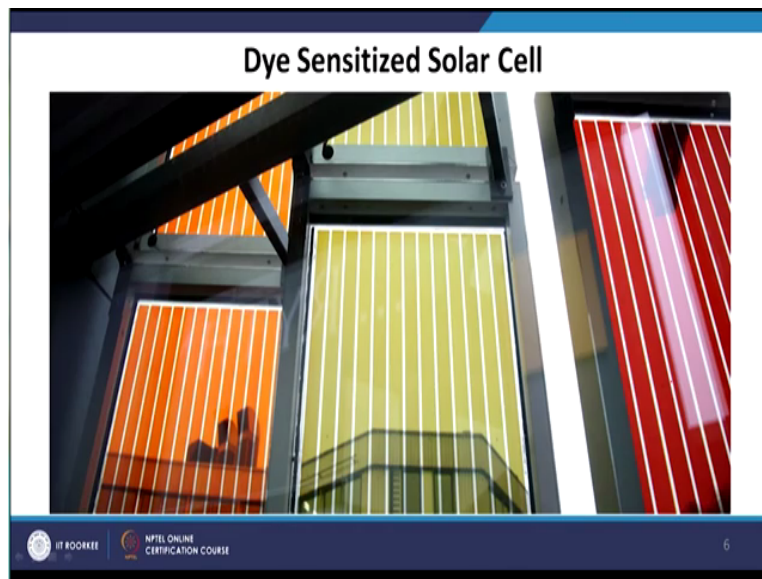
In 1970 this 2 guys Helmut Tributsch and Melvin Calvin, they use this process to measure the absorption spectrum of various chlorophylls and natural organic dyes. In the absence of an energy gap the charge chlorophyll molecule is quenched since both holes and electrons can be conducted in the metals. They use zinc oxide semiconductor anode and platinum cathode in KCl electrolyte solutions.

So long before the concept of dye sensitize solar cell came into the market already there was a the existing idea like we can use some kind of semiconductor and some kind of pigment where the pigment will play the role of absorbing light and a semiconductor will play the role of

conduction of the charge carrier all we need is to regenerate this process. And the regeneration of the process usually is done by the electrolytes.

And in the earlier days in the place of electrolyte people use to use some kind of casual electrolyte solutions in conjunction with the semiconductor layer. Now this concept later on further converted to that today's so called the dye sensitized solar cells or DSSC.

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Here in this picture we are showing there are some transparent window or even transparent door which was fabricated by this dye sensitized solar cells. Now one of the biggest advantages that we already mentioned previously is that this organic photovoltaic, including this dye sensitized solar cell, can be made flexible as well as transparent. So that means we can put it on any substrate on which we like to put it and at the same time light can also transmit through them.

So the benefit is that let us say I have a wall and I can replace that with some transparent dye sensitized solar cell, so that we get a complete amount of light in the daytime and also it can generate the energy. So the concept of a 0 energy building can only be realized by this kind of design and dye sensitized solar cells do that. Now this DSSC or dye sensitized solar cell is also commonly known as Grätzel cell.

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## Dye Sensitized Solar Cell

- The dye – sensitized solar cell(DSC) concept is presented in 1991 by Regan and Gratzel.
- The DSSC solar cells can be made flexible. It has a good potential for being a low cost solar cell technology. This is mainly possible because of the large availability and low cost of the ingredient material as well as due to low processing temperatures.
- The DSSC is photo-electro-chemical device as its operation involves a photon, an electron and a chemical reaction. The operation of DSSC is considered similar to that of a photosynthesis process.

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Because this was first discovered by a swish scientist Micheal Gratzel in 1991. So this DSSC concept was first pioneered by in 1991 by Regan and Gratzel at EPF laboratory of Switzerland. The DSSC solar cell can be made flexible that mean we can put it on any flexible substrate it has a good potential for being low cost solar cell technology. The materials which we use to make these kind of solar cell is abundant in the nature even we can use some natural pigments or natural dye molecule to fabricate this particular kind of solar cell.

That is makes them really inexpensive, this is mainly possible because of the large availability and the low cost of the ingredient material as well as due to the low processing temperature. Later on we will show that one of the major ingredient of this dye sensitize solar cell is titanium dioxide, a large band gap semiconductor. Now this  $TiO_2$  or titanium dioxide is very very commonly used in paints and in toothpaste and many other day to day applications.

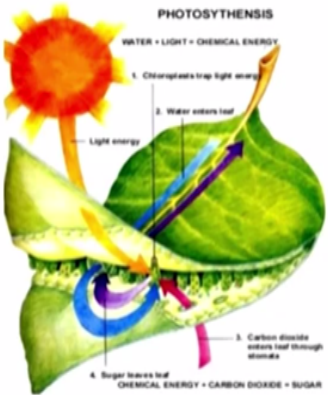
And it comes really very inexpensive way, we can use this titanium dioxide as a charge transport material in the dye sensitize solar cell. Now as a dye or sensitizer we usually use some metal complex dye like ruthenium dye but we have an option to go to some other sensitizer which can absorb or harvest the sunlight in a visible or near IR spectrum. The DSSC photo electrochemical device as it operation involves a photon and electron and a chemical reactions.

Sometimes this kind of reactions is also called electron ion interaction, the operation of DSSC is consider similar to that of a photosynthesis process. So this is somewhat you can think about an artificial photosynthesis in the lab.

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### Dye Sensitized Solar Cell

- Use of natural dye extracts provides natural, non toxic and low cost dye sources with high absorbance level of UV , Visible and near IR
- Examples of such dye sources are Bahraini Henna(*Lawsonia inermis* L) and Bahraini Raspberries(*Rubus* spp)



The diagram illustrates the process of photosynthesis in a leaf and compares it to a dye-sensitized solar cell (DSSC). On the left, a sun icon represents light energy. The leaf diagram shows four steps: 1. Chloroplasts trap light energy (indicated by a yellow arrow labeled 'Light energy'). 2. Water enters leaf (indicated by a blue arrow). 3. Carbon dioxide enters leaf through stomata (indicated by a pink arrow). 4. Sugar leaves leaf (indicated by a purple arrow). The overall equation for photosynthesis is shown as  $\text{WATER} + \text{LIGHT} = \text{CHEMICAL ENERGY}$ . Below the leaf diagram, the equation for a DSSC is shown as  $\text{CHEMICAL ENERGY} + \text{CARBON DIOXIDE} = \text{SUGAR}$ . The slide also features logos for 'IT KOOKEE' and 'NPTEL ONLINE CERTIFICATION COURSE' at the bottom.

Use of natural dye extract provide natural non toxic and low cost dye sensitize solar cell with high absorbance level of UV visible and near IR. Now one of the important parameter while designing the this sensitizer molecule for a solar cell is that it is absorption coefficient should be very high. Now the natural molecules, some of the natural molecule has a very high absorption coefficient and they are really suitable for fabricating dye sensitize solar cell.

Examples of some of the examples of this dyes are Bahraini Henna which is a the scientific name of *Lawsonia inermis* L and Bahraini Raspberries *Rubus* spp. Not only this there are several like you know kind of berries and several kind of the fruit ingredients or fruit extract also has been use to fabricate these dye sensitize solar cell.

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	SSC	DSSC
Transparency	Opaque	Transparent
Pro Environment	Normal	Great
Power Generation Cost	High	Low
Power Generation Efficiency	High	Normal
Color	Limited	Various

Now comparison to a solid state device and the dye sensitize solar cell we can see that DSSC has some major advantage over the conventional solid state device. So in the left column the SSC which stands for the solid state solar cell and the right hand column which is stands for the dye sensitize solar cell. We are showing some of the major difference in terms of some parameters, like the first parameters is the transparency.

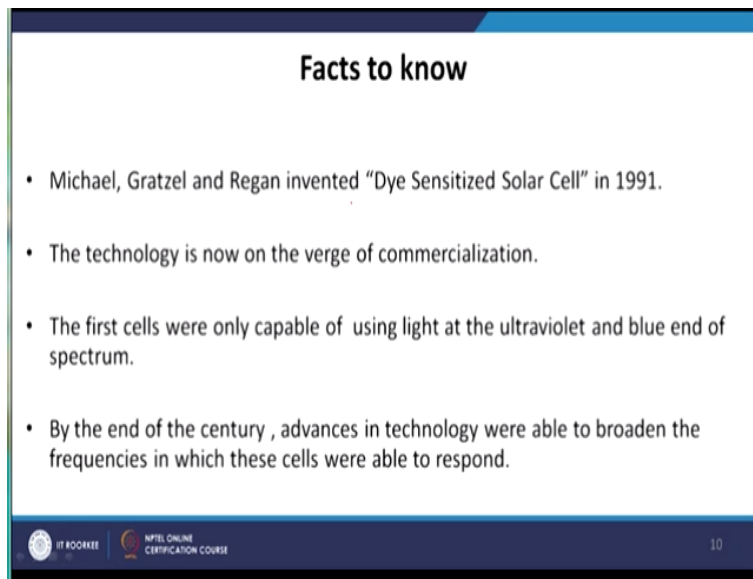
Now the solid state solar cell for example like you know thin film solar cell is a opaque, s the light cannot transmit completely through this kind of solar cell whereas this DSSC can be transparent. So one of the application or advantage for being so transparent is that we can make transparent window or transparent glass where the concept of the 0 energy building can be realized by implementing this kind of solar cell.

The second thing is that like you know these are environmental friendly although we claim that both thin film solar cells and DSSC both are environment friendly. But the kind of material we use to process the DSSC is more by degradable and more environmental and eco-friendly in comparison to the SSC devices. Power generation cost is relatively low in DSSC in comparison to the solid state devices because the ingredient material are inexpensive and the processing temperature is also very low.



The next thing is that power generation efficiency, power generation efficiency of course as we also mention earlier, the second generation solar cell is little bit higher in comparison to the DSSC or dye sensitize solar cells. In dye sensitize solar cell we can get 10 to 12% efficiency routinely. And this efficiency number almost remains constant during the last 20 years and the color of the solid state device is limited whether in the DSSC device depending on the pigments or the dyes one use the color of the device can be tuned.

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**Facts to know**

- Michael, Gratzel and Regan invented "Dye Sensitized Solar Cell" in 1991.
- The technology is now on the verge of commercialization.
- The first cells were only capable of using light at the ultraviolet and blue end of spectrum.
- By the end of the century, advances in technology were able to broaden the frequencies in which these cells were able to respond.

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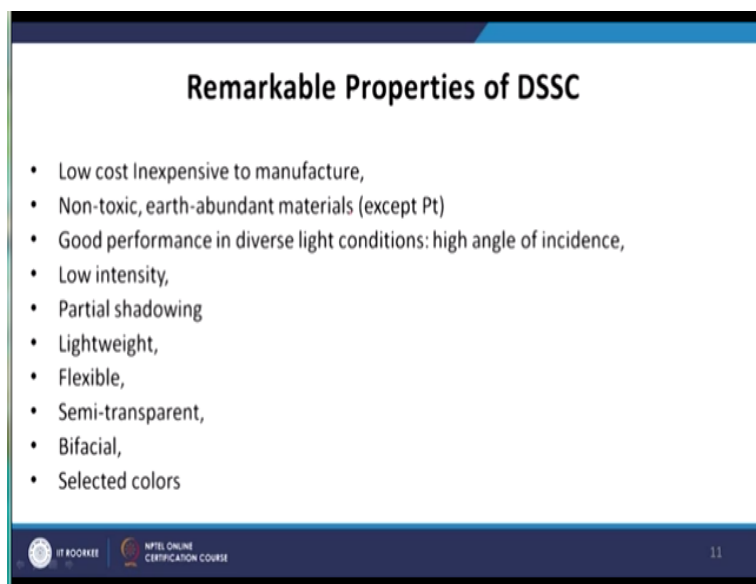
Now some of the important facts which is important to know in related to this dye sensitize solar cell technology is that the first you already mention Micheal Gratzel who invented this DSSC solar cell in 1991. And according to his name this solar cell is also called Gratzel solar cell, so in literature sometimes we will find that gratzel solar cell but gratzel solar cell is nothing but the dye sensitize solar cell.

This technology is now on the verge of commercialization, now this is a very important point like although there are last 20 years of research is going on DSSC technology. But still like lot of good roll to roll product has not came because of some of the disadvantages there. One of the disadvantage is that in this dye sensitize solar cell we use liquid electrolytes. So the device is not a complete and a solid devices.

And also the liquid electrolyte can be corrosive and at the same time they are volatile. So the lifetime or the stability of this device is not as per level as the solid state devices. But people have trying their base to overcome this shortcomings or disadvantage and there are some company mainly from the EPFA laboratory is right now making some roll to roll DSSC panel. The first cells where we capable of using light at the ultraviolet and blue end of the spectrum.

By the end of the century advance in technology where able to broaden the frequency in which these cells were able to respond.

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**Remarkable Properties of DSSC**

- Low cost Inexpensive to manufacture,
- Non-toxic, earth-abundant materials (except Pt)
- Good performance in diverse light conditions: high angle of incidence,
- Low intensity,
- Partial shadowing
- Lightweight,
- Flexible,
- Semi-transparent,
- Bifacial,
- Selected colors

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Now some of the remarkable properties of the DSSC first they are low cost they are inexpensive to manufacture. They are non toxic or we will better say they are low toxic earth-abundant materials like titanium dioxide they are used in making this solar cell, good performance in diverse light conditions, high angle of incidence. So as we know that during the day time sun moves on the earth surface and the aim are the intensity of the radiations over the earth surface that varies and it also varies geometrically.

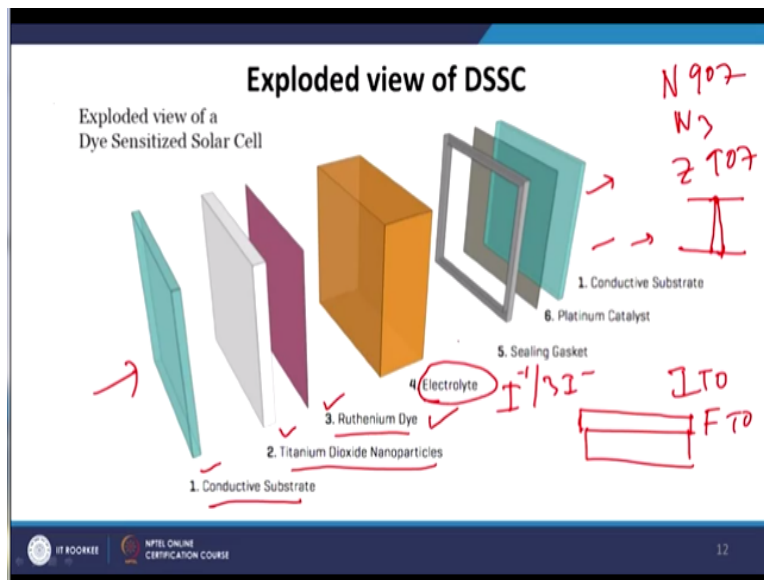
So DSSC has a good thing that it can take care for the variations of the intensity by modulating the absorption spectrum of the dye. So we can use a series of the dye which can take care for the different exposure level and different intensity exposure. It can also acts in a low intensity because like you know it has a high extension coefficient, partial shadowing, light weight. Any

organic device is always little bit compact and light weight in comparison to the inorganic devices.

They are flexible, that means one can make it on a flexible substrate, they are semi transparent or transparent. So light can transmit through them, bifacial, so either you can pass the light from the front electrode or you can pass the light from the back electrode. So that is why they are bifacial and also one have the freedom of choosing the color that means depending upon the pigments or depending upon the dyes where they absorb the light we can choose the color.

Now how a DSSC looks like if we explore the view of a DSSC or if you just do some cutting and looking at this thing how does it looking like that you will see that all kind of dye sensitize solar cell has 4 to 5 basic components, this is a sandwiched structure device.

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So in one end we have conductive substrate and the other end also we have a another conductive substrate. So this behaves like a anode and cathode, so this is a sandwiched type devices any kind of organic devices is basically says sandwich type of devices. In case of dye sensitize solar cell we put titanium dioxide and dye molecule between the sandwich layer. In organic photovoltaic devices we put polymers usually donor polymers and acceptor molecules in the sandwich region.

In perovskite solar cell we put perovskite materials in the sandwich region but they are all sandwiched kind of solar cells. Here like you know we have 2 different electrodes one is the conductive electrode which is usually made by putting some conductive layer on the glass substrate. As you know that you know this is a glass substrate, this is usually not conductive, how can we make a conductive by putting some kind of conductive layer.

So usually in the DSSC technology this is done by putting a doped indium oxide or doped fluorine oxide on top of a glass substrate. And then we call it as ITO which stands for indium doped tin oxide or FTO which stand for fluorine doped tin oxide. Now this doping makes them conductive and we can measure the conductivity by using some multimeter. The next thing is that on the other end we have another electrode which is also conductive and this conductive electrode usually we make by some platinum electrode by platinum catalyst.

One can have the choice of using any kind of conductive ink on glass substrate to make this kind of counter electrode or the back electrode. Now the front electrode which transparent usually light enters to this front electrode. In between these 2 layers like front electrode and the back electrode which you also can call as a photo anode and the cathode, we put our active layer, what are our active layer in the case of dye sensitize solar cell.

The active layer is mainly consists of 2 components, one is the titanium dioxide layer and another is the dye molecule layer. The titanium dioxide that is a semiconductor wide band gap semiconductor and the role of the titanium dioxide is 2 fold. First to absorb the dye molecule on the (( )) (15:30) of it and the second is whatever the electron whatever has been injected to the titanium dioxide molecule electron should be pass using the percolating network of the titanium dioxide.

So that is why once needs to make sure the titanium dioxide become as spongy as possible. We call it as a mesoporous structure in the literature, mesoporous means there are lot of large pores inside this material. So the dye molecule can go inside this pore and at the same time the electron can get a percolating network to travel through this force. The important ingredient is the

ruthenium dye, ruthenium is a metal and it has an absorptions which spans from the lower UV range to all the way to visible range to somewhat to near IR range.

And it is a very commonly use dye, so there are 2 different kinds of ruthenium base dye is used in the industry and they are known by the name of 2 scientist one is called N907 or N3 and another is Z907. So this N and Z they stands by the name of 2 scientist one is (( ) (16:35). So and this 3 and 7, 907 they actually stands for the number of experiments or number of the sample value which works for the best.

So they have tried, so Z907 means, so he has synthesized like you know 907 samples before that and 907th molecule shows a good property in comparison to the other and that is why that has been commercialized. And what is the role of the dye, the role of the dye is to absorb the light, so that the electron can goes from the ground state to the excited state or we can go say that electron can goes from the valance band to the conduction band.

Now once electron is in a conduction band what will happen, depending upon the energy level matching this electron will try to come to the next favorable energy level and titanium dioxide provide that matrix. So the whatever the electron that injects to the titanium dioxide matrix using the titanium dioxide mesoporous structure that electron percolates through and finally come to the photo anode whereas the hole whatever left behind that comes back to the ground state.

But this whole process needs to regenerate this is not a onetime process, so let us say I have an electron in the valance band and I put it in a conduction band. Now after this process has been completed again the dye molecule has to comes back to the ground state, so that it is ready for the next cycle of light absorptions. Now that role is played by the electrolyte, the number 4th component here, so in the electrolyte business we usually use iodine tri iodide as a complex electrolyte iodine- and  $3I^-$ .

So iodine tri iodide electrolyte actually what it does you know it participate in oxidation reduction reactions and it regenerates whatever the oxidized dyes in the ground state. So that this process can repeat and we can get regenerative electron flow inside the circuit. And finally we

put a sealing cascade to prevent it from the leakage and a platinum counter electrode on the back. So again like you know so basically this structure is very very simple, we have 2 electrode.

One is the conductive substrate ITO or FTO which is photo anode and in the back there is a counter electrode which is a platinum coated counter electrode in between we have active layer. Active layer consist of 2 components, 2 and 3 where we have a titanium dioxide nanoparticle and we have a ruthenium dye but we have a freedom to choose any dye depending upon it is absorption property.

And then to regenerate the whole process we use electrolyte and finally we sandwich the whole devices using some kind of banana clip or some kind of the encapsulation agent. So that is like you know I mean geometry of a solar cell, now if you look one by one components we learnt like you know how this different components play role or how does the device physically works.

Now as we said that since the name suggest dye sensitize solar cell, so the word dye actually plays a very important role in this devices, now there can be different source of the dyes.

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The slide is titled "Key Ingredients of DSSC" and is divided into three columns. The first column, "Sensitizing Dye", shows a pile of red powder and the chemical structure of N3 dye, which is a ruthenium complex with two bipyridine ligands and two terpyridine ligands. The second column, "Titania Nanoparticles", shows a white powder in a jar and a microscopic image of 20 nm titania nanoparticles. The third column, "Electrolyte", shows a bottle of orange liquid and the chemical structure of an ionic liquid redox couple, specifically I<sup>-</sup>/I<sub>3</sub><sup>-</sup>.

**Sensitizing Dye**

**Titania Nanoparticles**

**Electrolyte**

Chemical Structure of N3 Dye

20 nm Titania nanoparticles

Ionic liquid Iodide/tri-iodide redox couple

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Here we are showing certain kind of dyes like one of the very popular dye which is used in the DSSC device is N3 dye and it has a structure like this where the ruthenium molecule is in the center and it forms a very giant complex which is surrounded by some benzene ring and some

alkyl chain which helps into solubilize this thing and tune the absorption property. Now not only the ruthenium dye you can use any kind of dye.

In the next lecture we will talk about what are the different kinds of dyes we use in a dye sensitized solar cells. The second part of the device was the titanium nanoparticle or the titanium oxide base semiconductor device. Now this titanium plays a very important role it has to be very very mono-disperse and uniform. If the polydispersity in the titanium dioxide is very high then there is will be high chance of charge carrier recombination.

And that has been achieved by making a very sophisticated or controlled way of titanium dioxide usually something around 20 nanometer particle. And we put the nanoparticle on the top of the glass substrate which is conducting in this particular case and heat that substrate beyond a particular temperature to make the substrate more spongy or mesoporous. And finally everything this electrode is dipped inside the dye molecule and we put the electrolyte solutions which is an ionic liquid, iodide tri iodide complex which acts like a redox couple.

Now we as we said that there is a wide choice or wide varieties of the material we can choose for the DSSC which makes it inexpensive in the case of anode material we can take titanium dioxide which we know exist in 2 different forms (()) (20:55) we can take zinc oxide, we can take tin oxide or any different morphological forms of them.

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### Wide Choice of Materials for DSSC

- Anode Material: TiO<sub>2</sub>, ZnO, SnO<sub>2</sub> Morphological forms (Single crystal, Mesoporous film, Nano rods, nanowires, branched wires, Gyroid structures,...)
- Dyes  
Polypyridines, Porphyrins, Phthalocyanines, Organic dyes, inorganic semiconductors, 2nd generation dyes D-π-A, Quantum Dots/ ETA solar cells
- Redox Mediator  
I<sup>-</sup>/I<sub>3</sub><sup>-</sup>, S<sub>2</sub><sup>-</sup>/S<sub>2</sub><sup>2-</sup> (dithiolate), Co(LL)<sub>3</sub><sup>2+</sup>/Co(LL)<sub>3</sub><sup>3+</sup>, SpiroOMeTAD, ..
- Additives (TBP, GuNCS, ..) & Surface Treatment
- Cathode: Pt, C allotropes, PEDOT:PSS, ...

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Single crystal mesoporous film nano dots, nanowires, branched wires or gyroid structure, people have used different kind of structures. And this role of the structures is also manifold some of them actually help to confine the electric field, some of them actually helps to increase the internal electric field and to increase the output current in the devices. Now as a dye we have a choice of using different kind of polymers or different kind of small molecule.

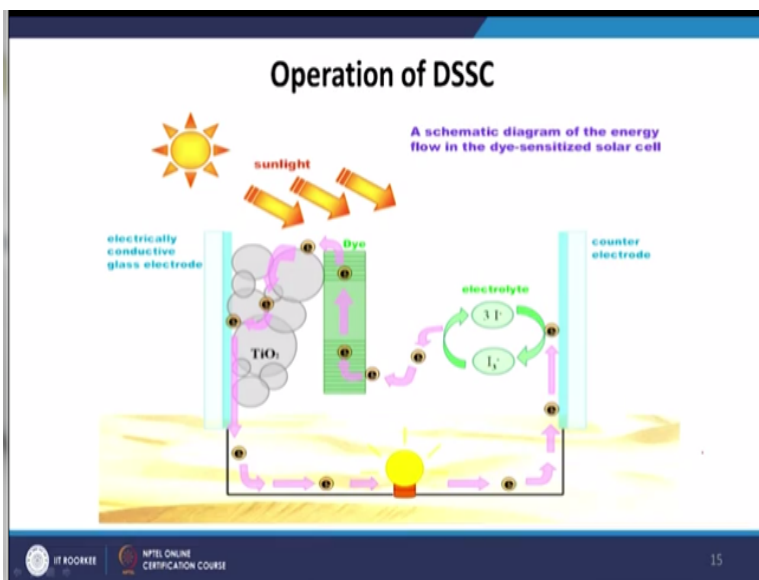
Organic dyes, inorganic semiconductors, second generation dyes which includes donor acceptor donor which is breached by a pi conjugation ring, quantum dot. And also like you know carbon dots and different kind of sensitizer molecule like laser dye one can also use. And as a redox mediator which usually use iodine tri iodide electrolyte we can also use like you know S<sub>2</sub>, S<sub>2</sub><sup>2-</sup>-dithiolate or like you know nowadays people are also using different kind of solid state electrolyte to prevent the possibility of leakage.

So that the device all become a solid state dye sensitize solar cells and other things like spiro omitted and every other things is also been used in DSSC solar cell. Now there are some engineering aspect of the DSSC technologies also by putting some kind of additive like tertiary butyl pyridine and the passivation of the surface treatment which reduce the defect states or the trap states one can also increase the open circuit voltage and the short circuit kind in the device which ultimately increase the efficiency of this device.



And as a cathode material we use platinum or carbon electrode or PEDOT.PSS even like highly conductive grapheme or CNTs is also used like in a for making this kind of counter electrode.

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Operation of the dye sensitize solar cell that you have explained first the light falls on the material, you see here this is a dye molecule it has a ground state and then the excited state. Now the electron goes from the ground state to the excited state then further it injects to the titanium dioxide and using the mesoporous structure of the titanium dioxide electron percolates and finally come through the photo anode.

And whereas now the dye is now in an excited state it has to be regenerated, who does this regeneration process electrolyte. Electrolytes gives up the electrons, so that the dyes can comes back to the ground state. Now once it is in ground state then it is ready to absorb the next cycle of the light and the iodine tri iodide electrolytes now this works as a redox couple. So they shuttles the electron chains between the dyes and the tri iodide molecules.

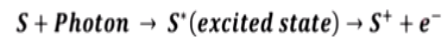
And finally we sealed everything between an counter electrode and a photo anode. So that you get a effective current in the outside circuit which is use to run a load and that is why the schematic of is dye sensitize solar cells.

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## Operation of DSSC

A DSSC absorb light, generate carriers, transport carriers to the external load at higher voltage and brings back the carrier in the cell at lower voltage. The operation of a DSSC can be explained using the following steps:-

**Step 1:-** In this step, the absorption of a photon by a molecule dye (S) takes place. After the photon absorption, the dye molecule goes into the excited state,  $S^*$ . Within a very short time, of the order of femtoseconds, the electron is given off to the semiconductor wide band. And the excited dye molecule gets oxidized (loss of electrons) to  $S^+$ . This can be put in the form of the following equation:-



Now the DSSC absorbs the light generate carriers, transport carriers to the external load at higher voltage and brings back the carrier in the cell at lower voltage. So as like all other solar cell there are 4 different operation takes place here, first the absorptions of the light and that is done by the dye molecule, second is the transport of the charge carrier that is done by the titanium dioxide, third thing is the regeneration of the charge carrier, that is done by that liquid electrolyte.

And fourth thing is the passage of the electron from the titanium dioxide to the electrode material. And that is done by the interfacing properly with  $\text{TiO}_2$  and the ITO substrate, that is why the  $\text{TiO}_2$  layer has to be also very optimum. Now the operation of the DSSC can be explained by this following step, the first step is that the absorptions of the light. Here the dye molecule absorbs a photon and what happens the dye molecule goes to the excited state.

If we call the ground state as S if we n number them by S and if we excited state we usually call it by putting a asterisk sign on the S. So  $S^*$  stands for the excited state and when S the dye molecule in the ground state absorbs the photon which is nothing but  $h\nu$  where h is the planks constant and  $\nu$  is the frequency of light, it goes to the excited state. And this excited state this dye molecule can then dissociate to a charged  $S^+$  and it gives of an electron.

And this electron percolates the  $\text{TiO}_2$  structure, so this kind of light absorptions happens in a very short span of line usually like you know in a femtosecond time scale. And this can also be

we can put it in terms of this equation  $S + \text{photon} = S^*$  which is an excited state. Finally, it disintegrates to  $S^+$  the positively charged dye ions + the electron and this electron actually participates in the charge carrier conduction.

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**Operation of DSSC**

- **Step 2:-** In this step, the excited electron is given off to the conduction band of semiconductor. A TCO layer is used to collect the electrons from the conduction band. Normally, fluorine-doped tin oxide ( $\text{SnO}_2:\text{F}$ ) is used for this purpose. The electrons then flow through the external load to the electrode counter, which is also made of the  $\text{SnO}_2:\text{F}$ .
- **Step 3:-** In this step, the oxidized dye molecule is reduced to the original form  $S$  by regaining electrons from the organic electrolyte solution. The electrolyte solution contains the iodide redox system in which the iodide ions are being oxidized to tri-iodide molecules back to their iodide state. This step requires catalytic presence of Pt at the electrode. This makes the dye molecules again available for the excitation/reduction cycle.

$$S^+ + \frac{3}{2} I^- + e^- \rightarrow S + \frac{1}{2} I_3^-$$

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Then the second step is that the excited electron is given to the conduction band of the semiconductor. So it is given off to the conduction band of the semiconductor, what is the semiconductor here  $\text{TiO}_2$ . Now a TCO layer or a transparent conductive oxide layer, so TCO stands for transparent conductive oxide. So for example ITO or FTO is a transparent conductive oxide, so light can pass through them that is why they are transparent.

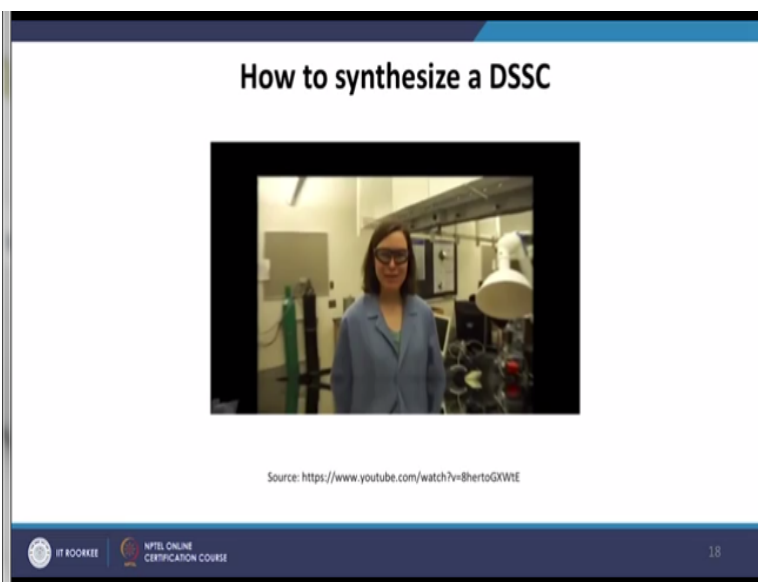
And they can conduct the electricity that is why they are conducting. So TCO layer is used to collect the electrons from the conduction band, normally fluorine doped tin oxide is used for this purpose, the electrons then flow through the external load to the electrode counter which is made of the fluorine doped tin oxide or FTO. In the step 3 the oxidized dye molecule is reduced to the original form by regaining electrons from the organic electrolyte solutions.

The electrolyte solution contains the iodide redox systems in which the iodide ions are being oxidized to tri-iodide molecules back to their iodide state. So this step requires catalytic presence of platinum at the electrode, this makes the dye molecule again available for the excitation or

reduction cycle. So basically the role of this electrolyte is nothing but to regenerate the dye molecule in its ground state and it is nothing but a oxidation reduction reactions.

So the  $S^+$  which was now oxidized by giving off an electron, so what it does it absorbs an electron and iodine does that job. So then it comes back to its neutral  $S$  state and we get iodine  $I_3^-$  and this process iodine to tri iodide process that that happens in the process of the platinum catalysis. And that is why the platinum catalysis not only plays the role of a counter electrode but it also catalytically helps this iodine to reduce back to the tri iodide and recycle this whole system again and again.

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Here we are trying to show a video of how to fabricate a dye sensitize solar cell and today we will demonstrate it you how to make a dye sensitize solar cells also.

**(Video Starts: 27:03)**

Hi I am Khanna I am a junior from (()) (27:05) college, I am a chemistry major and today I am going to be showing you a simple way to make a solar cells that convert light energy into electrical current. I am using very simple component such as blackberry juice. Hi I am (()) (27:19) I am also a chemistry major (()) (27:21) college, I am here to work with Khana to on the solar cells because solar cells are awesome to make them we are going to use blackberry juice, microscope slide, titanium dioxide and iodides solution.

The types of microscopes slide that will be using is coated on one side with a special conductive oxide, this will form one side of the solar cell. So the first thing we have to do is determined which side has the conductive oxide, to do this one thing we can do is use a UV lamp. One side will fluoros and one side will not, so you see that this side flourishing that mean to the glass side, so we do not want to use that side.

See this side does not fluoros so that is the conductive side, so we want to use the side that does not fluoros. We can also use a multimeter to see which of the sides has a voltage to cross it, your instructor can help you out with that version. Our next stage is (()) (28:16) this slide down to the table when you tape your slide down make sure that 3 of the sides are taped to up to 1 millimeter on the edge.

Now one of the sides is tape to that of 3 millimeters of tape covering the edge, also make sure the all of the sides which taped for sealed onto the table fixed on the slide. Our next step is to make the titanium dioxide plates that will form semiconductor for a solar cell. So here I weighed out 1 gram of  $\text{TiO}_2$  powder. Now I am going to take this and put it in a mortar and pestle, now I am going to add approximately 2 milliliters of ethanol.

In this step you can use ethanol, you can use propanol, you can use dilute nitric acid but for this and solar cell we are going to use ethanol. Now I am using a pipette to add it but all you really needed just some way at adding it slowly. So you can also use a graduated cylinder, so here I am adding 2 ml and now I am going to stir it with mortar and pestle, you can add more solvent if you need it to get it  $\text{N}_2\text{O}$  it should look like white paint or suns cream at the end.

Another way we have our paste, it is time to add our paste to the solar cell, your paste should have the consistency of watery shampoo, you can take a spatula and add 3 drops to the solar cell. Now you wanna smooth out these drops across the solar cell with the glass rod ok maybe little more that is what the (()) (32.07). Our next step will be to heat the  $\text{TiO}_2$  paste over an open flame, this will remove the solvent and allow the  $\text{TiO}_2$  to bind more strongly to the glass slide.

So in our step up we have a Bunsen burner underneath a ring stand with a wire mesh gauze on top and be very careful when using an open flame. And always have safety lab coat and safety goggles on. So now we will remove the tape from the glass slide, so that we can put it over the Bunsen burner, now (()) (32:50) we had the slide tapes down or a  $\text{TiO}_2$  now makes a nice neat square on top of the glass slide.

You should remove all the tape, now we are going to put this on top of the mesh and light the Bunsen burner, leave the slide dries off the solvent have we added to the  $\text{TiO}_2$  remember that this is a really hot system in that whole glass looks exactly like hot glass, so do not touch it we will get hurt. Also with your flame you wanna have the inner tip of the flame just about touching the microscope slide you have the hottest part of the flame.

A key component of the solar cell is a dye that can absorb light in turn into energy. For our dye we are going to the dye in blackberry, so you can crush up and put onto a solar cell. First you crush up the blackberries, once we mix the blackberries thoroughly we want to add 95% ethanol right here, you goanna add 4ml of 95% ethanol, we also goanna add (()) (34:24) of 15% acetic acid, now you goanna stir this up thoroughly too.

Once you stirred it up you take a coffee filter, place the coffee filter over a beaker and filter the dye. So now we have our final filtered blackberry dye, we are aiming to get about 10 ml that is plenty what we are going to do. Now I am going to pick up the  $\text{TiO}_2$  slide and simply submerge it in the blackberry juice it is goanna sit there for 10 minutes. So while our semiconductor slide is soaking in blackberry juice, we are going to prepare the second slide that makes up our solar cell.

So again I have determined that this the top side of the slide is the conductor side and now we are going to code a way or graphite on top of it to help the electron flow. Our source of graphite is going to be a pencil there, so I am just going to put this down and now I am just going to color basically a layer of graphite on top of the slide, do not be afraid just scrape hard on it oh drawn it again from another angle to make sure it is totally covered and that is our second slide.

Make sure that the entire square is coated thoroughly, so here you can see our graphite slide. So now with got our 2 final microscope slides, now we are going to assemble our solar cell. So here we have our slide that was removed from the blackberry juice was in and here we have our graphite slide. Now we are going to do is put a couple drops of this iodine redox couple which is going to serve as the filler for the dye.

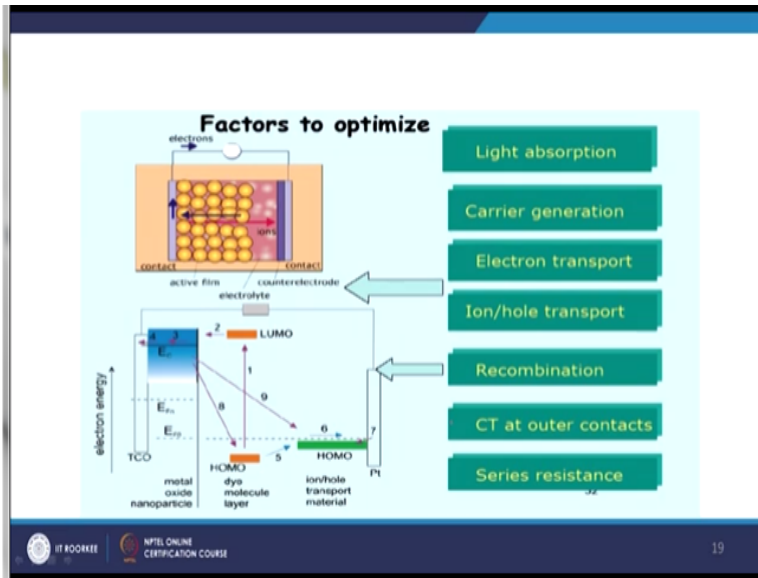
Once the dye molecule has lost an excited electron the redox couple refurnishes it, so that the circuit is completed. Now I am just going to take 2 drops of this and put them on the graphite slide and now I am going to laid one on top of the other making sure that on each side a little bit of the glass is hanging off, this will allow a slider to help test the slide. The final step is to seal the solar cell to do that we are going to use 2 binder clips.

Now I am going to clip the clips on the 2 sides are overhanging, so there is 1 clip and here is the other one and that is our solar cell. So this is our final and complete solar cell, so now the only thing left to do is to go outside and measure the voltage it produces. So now we are going to take our solar cell outside to test it here in sunny is on the California we have plenty of sunshine.

So we are going to do as we have a voltmeter, we are going to connect the 2 electrodes across the solar cell. And looks like we are getting about half over millivolt of electricity, so that is good, great. So this concludes our demonstration has making dye sensitized solar cell and good luck and building your own.

**(Video Ends: 39:06)**

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Let us talk about some of the factors which optimize the overall efficiency of a solar cell. First of all the light absorptions, so it as you say that it depends upon the dye molecule or the sensitizer's molecule as good as the sensitizer molecule the light absorptions will also be that good. So and also the sensitizer molecule should be good enough to absorb the IR part of the light, second thing is that carrier generation, carrier generation is also done by the dye molecule.

Third thing is the electron transport whatever the carrier has been generated that is been injected to the semiconductor oxide that has to be transport by the this semiconducting layer. So that is why semiconducting layer has to be very very uniform and optimum. Ion and hole transport that again depends upon the morphology of the devices, we have electron charge hole recombination, there are ways to prevent the recombination.

We do not want lot of recombination in the surface, band to band recombination is a very common process. And we can prevent that band to band recombination by doing some passivations of the semiconducting layer. And also there can be charge transferred outer context and then there are series resistance and sun resistance when you have learnt about the equivalence circuit we have seen that there are 2 different kind of resistance exist in a solar cell.

One is the series resistance another is the sun resistance, sun resistance is the parasitic resistance which comes from the leakage current and series resistance comes due to the metal



semiconductor contact or usually from the defect states. Now if we can minimize this defect states or the trap states during the fabrication process. If we can passivate the defect states then we can minimize this loss due to the defect state recombinations.

Now similarly if we can passivate the counter electrode and the TiO<sub>2</sub> interface then we can also reduce the amount of leakage current or we can reduce the amount of the sun resistance. So that is why like you know we can control the current or voltage here, in the language of the organic solar cell very often we replace this valance band and the conduction band by the word HOMO level and LUMO level.

So HOMO stands for the highest occupied molecular orbital and the over LUMO that stands for lowest unoccupied molecular orbital. You can think it as like a valance band and the conduction band in an inorganic semiconductor. So what happens the dye molecule absorbs the light and the electron goes from this HOMO layer to the LUMO layer, that means it goes from it is valance band to it is conduction band.

Then according to the energetics this electron will be injected to the conduction band of the titanium dioxide from there it goes to the TCO which is here ITO or FTO. Now the electrolytes is there this regenerates this process and what happens this ion and hole transport material. So the hole will transport in the opposite directions and electrons will come and that will shuttle and reduce back to dye to it is ground state.

And this electron which comes to the TCO using an external circuit it is comes back to the platinum counter electrodes and this whole circuit completes and we get a current in the external circuit. So that was the basic photo physics behind a dye sensitize solar cells, now some of the important application of the dye sensitize solar cells.

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We usually use for transparent door or transparent window in our building large area DSSC panel for outdoor and building integration especially for 0 energy building.

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DSSC panels have been used for example as EPFL conference center, some of the examples we are showing here.

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Like in another very popular example of the DSSC charging panel is in the e-vehicle. Now a days e-vehicle is becoming very very popular because of this lower pollution. So now the e-vehicle comes with a battery, now this battery is charged up with a solar cell. Many times in the western countries we use this solar cell as a dye sensitized solar panels. And also as a charging stoppage for the e-vehicle at the bus stops or at the intermediate stop.

We can use like a solar panel as example it is showing here in the left hand side or also like in a bus stops we can showing here at the right hand side. So the different color of solar panels has been installed here, so the bus comes stands here they plug and get charged up for some time and then again they can start. Now in some of the airports also people have use the dye sensitized solar cell panels.

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One such example is the Geneva airport at Switzerland where like you know DSSC panel has been used in the airport for indoor lighting purpose.

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### Problems with DSSC

- Lab efficiencies <12% and stagnating Low red and near-IR absorption
- Only I-/I<sup>3+</sup>-redox couple has slow recombination kinetics
- Liquid electrolyte is undesirable, but solid state hole conductors
- During the course of the lifetime of a fuel cell, the Pt cathode suffers from oxidation, migration, loss of active surface area, and corrosion of the carbon support. Impurities

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So there are some application, good application also do the DSSC but there are also some problems. As I said that the efficiency even after doing 20 years of research is still less than 20% whether in perovskite solar cell it has reach to 20 to 23 % efficiency or in single crystal or in amorphous even solar cell we can get routinely 12 to 15% efficiency. And this is due to the low absorptions in the near IR region.

Now we use liquid electrolyte in this device and the liquid electrolytes has a very slow recombination kinetics. At the same time since it is liquid whole the device is not a solid state package devices. So it is always a problem of the leakage and also moreover this liquid electrolyte is volatile. So what the time if we leave it for sometime this liquid electrolyte can evaporate, so that regeneration process stopped unless until we add again the liquid electrolyte, we cannot regenerate this process again and again.

So that is why this process not very (()) (44:10) or industry friendly. And second thing is that during the course of the lifetime of a fuel cell the platinum cathode suffers from oxidation, migration, loss of active surface area and corrosion of the carbon support and impurities. Now today we will stop here and now we will show you how to fabricate a dye sensitize solar cell in really in the lab.

We will start with a very simple dye sensitize solar cell and then we will demonstrate you about a popular kind of solar cell which is known as a jamun solar cell which is fabricated using a natural fruit called jamun which has a pigment called anthocyanin we extracted that anthocyanin from the jamun and we fabricate it a dye sensitize solar cell out of that. So but before going to the jamun solar cell first we will show you how to fabricate a standard solar cell or a standard dye sensitize solar cell, thank you.