Natural Dyes
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Lecture No. # 38

Today, we will learn about dye-sensitized solar cells. This is yet another method where dyes have been used for a non-textile purpose. We saw how dyes could be use particularly natural dye and rose anthocyanin could be used as an acid base indicator or even to make pH paper, for change in finding out the change in pH.

Similarly, dyes can also have another non-textile use and that has in the recent years been very popularized for making solar cells. So, in this lecture, I want to introduce you to this new concept of dyes-sensitize solar cells, and let us try to take a look as to what is the role of dye in trapping the sunlight and how does it convert it into electricity. So, this is the whole concept, but the concept is seems to be just above one liner. But as we go along you will see that there is a lot to understand and lot to talk about.

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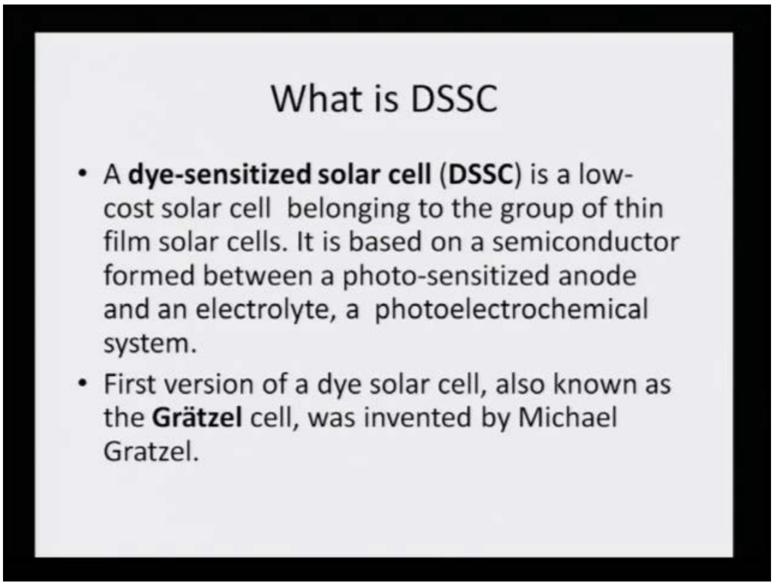

What is a dye-sensitized solar cell? A dye-sensitized solar cell is a low-cost solar cell belonging to the group of thin film solar cells. It is based on semiconductor formed between a photo-sensitized anode and an electrolyte, a photoelectrochemical system. So, it must have a thin film, which is of solar cells and it must be made up of a semiconductor material, which should have a photo-sensitized anode working as a photo sensitized anode, and there should be an electrolyte to carry out the photo electrochemical reaction.

First version of dye solar cell also known as Gratzel cell was invited by Michal Gratzel. So, it is more popularly known as Gratzel cell, because that was the first model of trapping solar energy and converting into electrical energy and then we will see where does the dye play a role.

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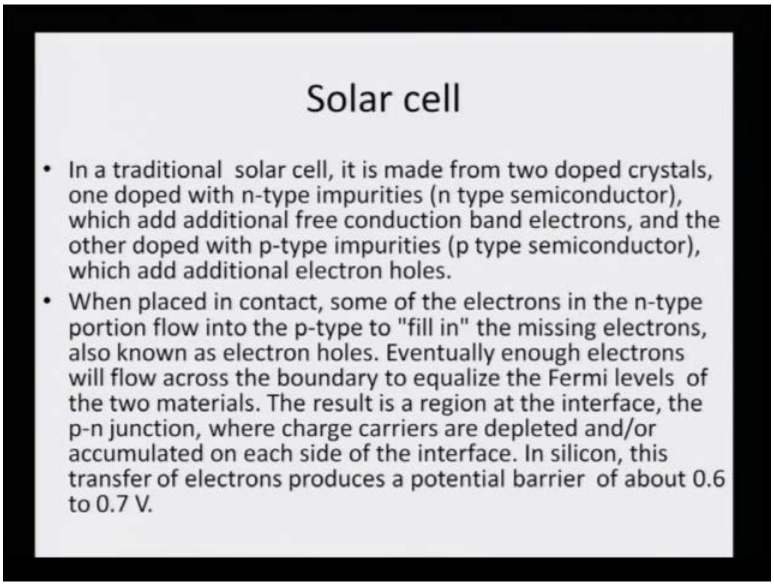

In a tradition solar cell, it is made from two doped crystal, one doped with n-type impurities - that is it is n-type semiconductor, which add additional free conduction band electrons, and the other doped with p-type impurities which is p-type semiconductor, which add additional electron holes. So, basically you are trying to conduct make more and more electrons conduct by using two different types of semiconductors, one is the n-type semiconductor and the other one is p-type semiconductor.

When placed in contact, some of the electrons in the n-type portion flow into the p-type to fill in the missing electrons also known as electron holes. Eventually enough electrons will flow across the boundary to equalize the Fermi levels of the two materials. The result is a region at a interface the p-n junction where charge carriers are depleted and or accumulated on each side of the interface in silicon the transfer of electron produces a potential barrier of about 0.6 to 0.7 volt.

So, you see all that happens at the interface of these two materials and because there are conducting electrons in one region and there are some holes of electrons. That means, these electrons have been ejected out. So, those holes have been filled by the conducting electrons. So, this is what the broad spectrum you know fundamental of solar cell, is how does it work. When placed in sun photons of the sunlight can excite electrons on the p-type side of semiconductor a process known as photo excitation. So, these electron holes were generated by the incidence of sunlight and this process in the p-type of semiconductor is called photo excitation.

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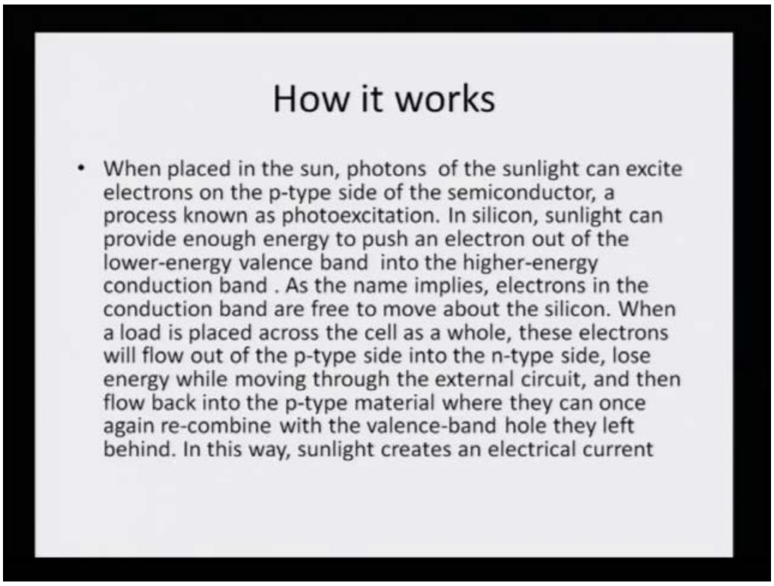

In silicon, sunlight can provide enough energy to push an electron out of lower-energy valence band into a higher energy conduction band. At as the name implies electrons in the conduction band are free to move about the silicon. When a load is placed across the cell as a whole these electron will flow out of the p-type side into the n-type side lose energy while moving through the external circuit and then flow back into the p-type material. Where they can once again recombine with the valence band hole they have left behind in this way sunlight creates an electrical current.

So, the whole process is that from the p-type it gets excited goes to the n-type and then in the conduction band joins the conduction band of the n-type, And then finally, through the outer circuit it moves out and because there are holes created in the p-type they are then the electrons will flow out of the p-type side into the n-type lose energy while moving through the external circuit, and then flow back to the p-type and there by generating electrical current.

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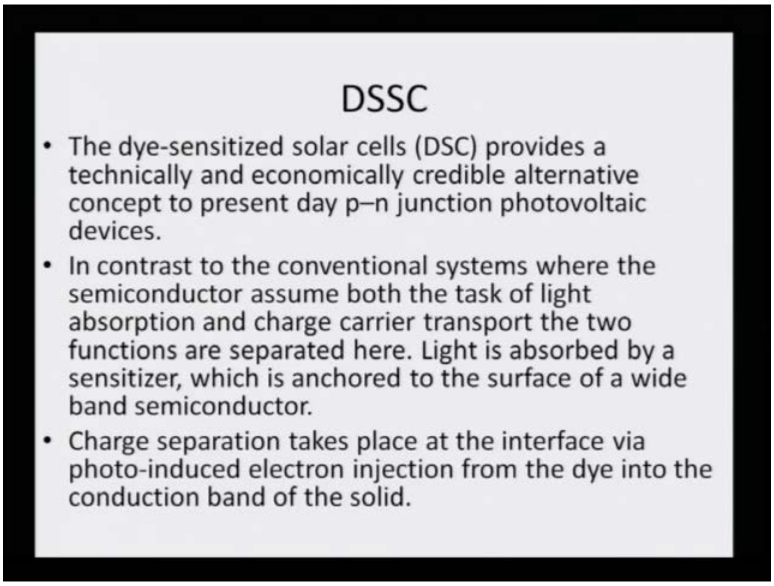

So, similarly when we use this is a normal solar cell, but if we use dye sensitize solar cell where what is the role of the dye, because the dye sensitize solar cell provides technically and economically incredible alternative concept to present day a p to n junction photovoltaic device. So, it is like from the p-type of semiconductor the electrons move to n-type and that is what is causing the photovoltaic device to form. In contrast to the conventional systems where the semiconductor assume both the task of light absorption and charge carrier transport the two functions are separated here. Light is absorbed by a sensitizer which is anchored to the surface of a wide band semiconductor.

Charge separation takes place at the interface via photo induced electron injection from the dye into the conduction band of the solid. So, it is slightly different as compare to taking two semiconductors of the p-type and the n-type. Here, they you know the light is absorbed by this dye which is a sensitizer, and then this sensitizer is actually anchored on to the wide surface of the semiconductor. So, there then excites the semiconductor charge separation takes place at the interface via photo induced electron injection from the dye.

So, from the dye it goes in to the semiconductor which is a joining it and then the whole process takes place so the rest of the part that the semiconductor pushing the electron to the conduction band remains the same. So, it is only the role of the dye is to trap sunlight and act like a sensitizers. So, the name dye-sensitized solar cell. Carriers are transported in the conduction band of the semiconductor to the charge collector the use of sensitizer having a broad absorption band in conjunction with oxides of nano crystalline morphology permit to harvest a large fraction of light.

So, now the importance of these carrier, that they are transporting electrons to the conduction band from one semiconductor to another is acting just like a charge collector, and these sensitizers can absorb a lot of sunlight and through the help of a micro crystalline you know film preferably titanium dioxide or thin oxide kind of nano crystalline material. It permits to absorb more and more light through the dye that is impregnated on to the titanium dioxide material or tin oxide material.

Nearly quantitative conversion of incident photon into electric current is achieve over a large spectral range, extending from the UV to the near IR region. So, the sunlight which is nothing, but a source of electromagnetic spectrum has various types of light ravs and these light rays are ranging which can be trap are ranging from UV to IR region. Overall standard you know solar cell such dye sensitize solar cell can handle current conversion efficiencies up to 10 percent that much has been achieves. So far, you see it is one has many such cells in alignment then one can generate substantial amount of current which can be used for lighting lamps and for all other domestic as well as industrial processes.

There are good prospects to produce these cells at low cost than conventional devices. Here we present the current state of the field, discuss new concepts of dye-sensitized nano crystalline solar cell including hetero junction variants and analyze the perspective for the future development of the technology. Already the technology is quite develop, but there is always a scope of finding different variables and different variants of material many new dyes and let me tell you that these dye-sensitized solar cells can be from dyes from the synthetic or from natural.

So, that is an advantage, that here is one field which can used both types of dyes, because the primary function of the dye is to take the sunlight particularly, the sunlight from the UV to IR region electromagnetic radiation. For this photo excitation work which is then transfer to the semiconductor and then the semiconductor then does the job of creating the electrons an through the excitation.

Photovoltaic devices are based on the concept of charge separation at an interface of two materials of different conduction mechanism if there are two materials which have different conducting band at the interface there is a kind of a potential that is generated. And because of that generation of a difference in the conduction capacity, they cell has a charge separation and that act is the fact that is made use of when one is designing photovoltaic device.

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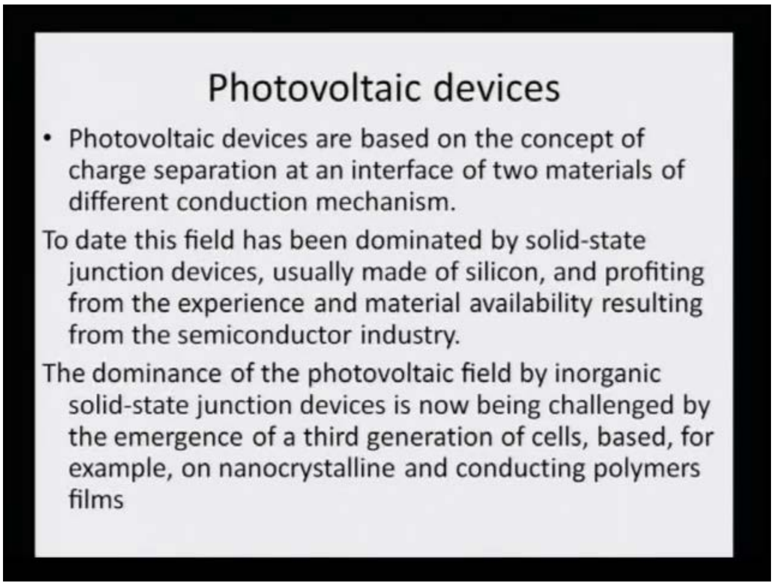

Today this field has been dominated by solid state junction devices specially made of silicon and profiting from the experience and material availability resulting from the semiconductor industry. So, it has been silicon and materials of silicones that have been develop which have been extensively use from making photovoltaic cells. Why because silicon has this very unique power of conduction and it has been found that it is an ideal material for these devices.

The dominance of photovoltaic field by inorganic solid state junction devices is now being challenged by the emergence of the third generation of cells based. For example, on nano crystalline and conducting polymer films, so many new advances have come, but the first cell that was made was with silicon.

Now, how can we introduce newer and newer material of the nano region or nano crystalline quality. So, that the basic conduction band can be increased, because it is this conduction band and this conduction band gets a reinforcement from the photons, that I have actually hitted the dye or the polymeric substance and that excitation then help goes on for photo excitation and this photo excitation, then creates electron holes and so, and so forth and then the rest of the story remains the same.

Now, in order to have a low cost because these materials are all very expensive so, is there a possibility to have low cost dye sensitize solar cell. Otherwise why should one go if one can make photo voltaic cell or solar cell by cheaper material. Then dye sensitize solar cells nobody would offer dye sensitize solar cells. So, in order for popularization of those dye sensitize solar cell which is our main subject of today lecture.

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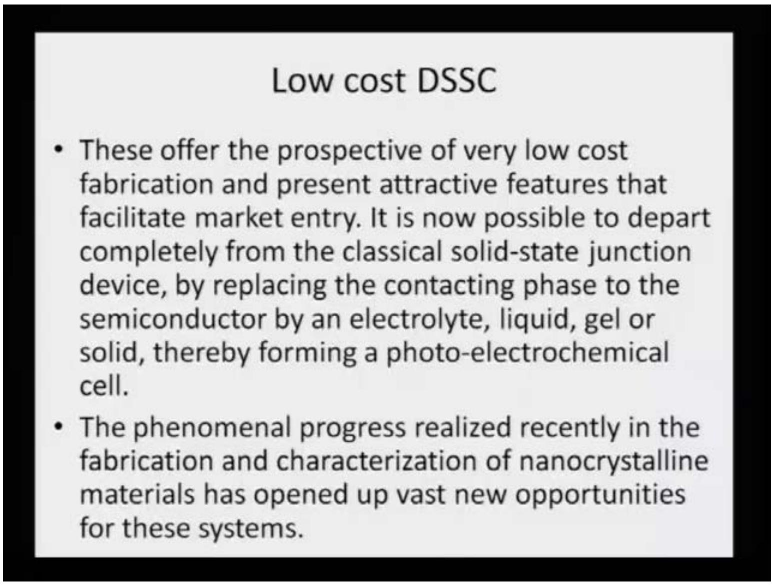

These offer the perspective of very low cost fabrication and present attractive features that facilitate market entry. It was nothing will be taken up commercially. If it is not cost effective, it is now possible to depart completely from the classical solid state junction device. By replacing the contacting phase to the semiconductor, by a electrolyte liquid gel or solid thereby forming a photo electrochemical cell. So, the only difference here is that one is design a material which is low cost material only then the cost will come down.

The phenomena progress realized recently in the fabrication and characterization of nano crystalline material, has opened up vast new opportunities for these systems and as you would understand, that nano materials are in the nano scale as the name suggest, and the UV light is also you know we said nano meters. So, they are kind of very compatible light is falling on to these dyes and these dyes are impregnated on a very fine nano crystalline material I told you titanium dioxide or tin oxide mostly these are oxides and these material can then its start doing the photo excitation process.

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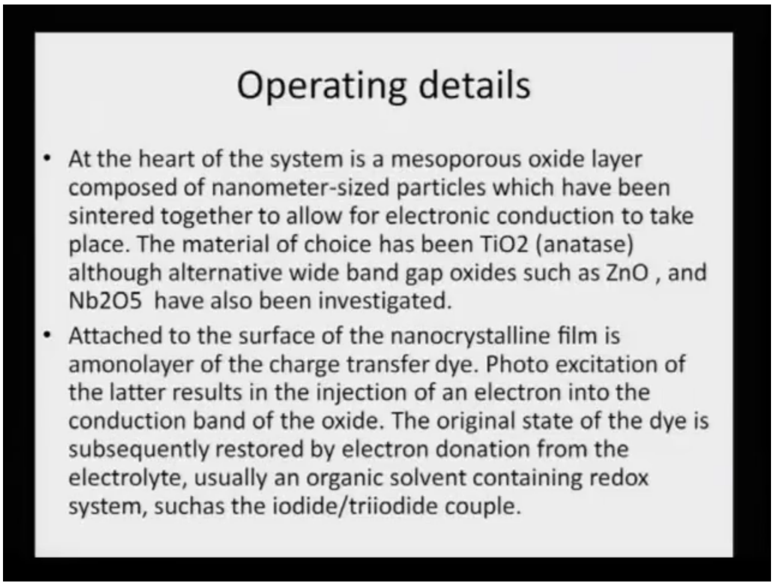

The operating details, at the heart of the system is a mesoporous oxide layer compose of nano meter sized particles which have been sintered together to allow for electronic conduction to take place. So, it is the sintered oxide the material of choice has been titanium dioxide although alternative wide band gap oxides, like zinc oxide and niobium oxide and tin oxides are also have been investigated. So, it is not hard and fast rule only use to titanium dioxide, but titanium oxide nano crystalline material have been popularize. But there are other alternatives like zinc oxide tin oxide niobium oxide and so on.

The two have been investigated attach to the surface of the nano crystalline film is a monolayer of charge transfer dye. So, now, this on the surface of the this titanium dioxide or zinc oxide or tin oxide material is the charge transfer dye just one layer of it you do not have to put a thick coating of it.

Photo excitation of the latter results in the injection of the electron into the conduction band of the oxide, the original state of the dye is subsequently restored by electron donation from the electrolyte. Usually an organic solvent containing redox system such as iodide tri iodide couple so you see the electron, that has gone into the conduction band from the dye to the titanium dioxide conduction band is replenish by the electro or the redox system of the electrolyte, which is taken as the you know as the part of the solar cell.

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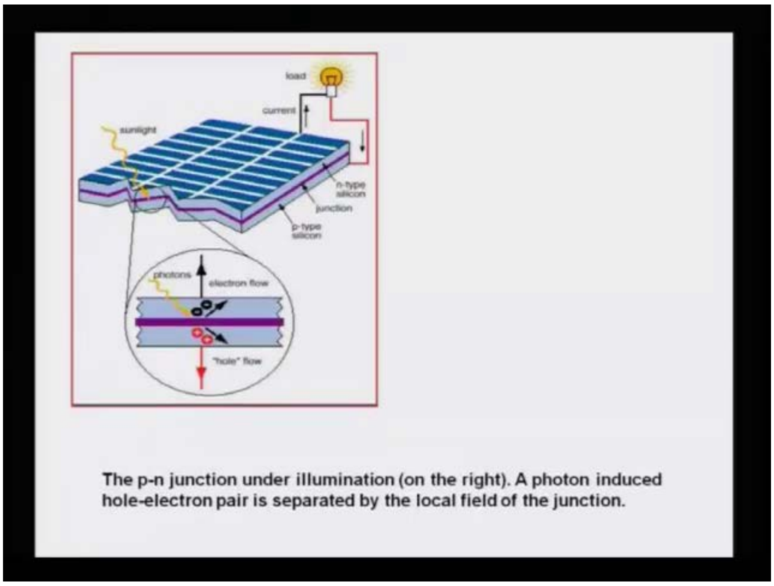

So, this is how the solar cell looks like where the photo excitation of from the sunlight onto this and you see that the photons create holes in the titanium in the dye sensitize cell, and then the electrons are push into the titanium dioxide. So, this is the kind of n and p junction. This is the typical example of the silicon and the n and p junction under elimination a photo induced hole electron pair is separated by local field of the junction. So, there is an interface and that is what is connected to the outer circuit and the bulb starts lighting.

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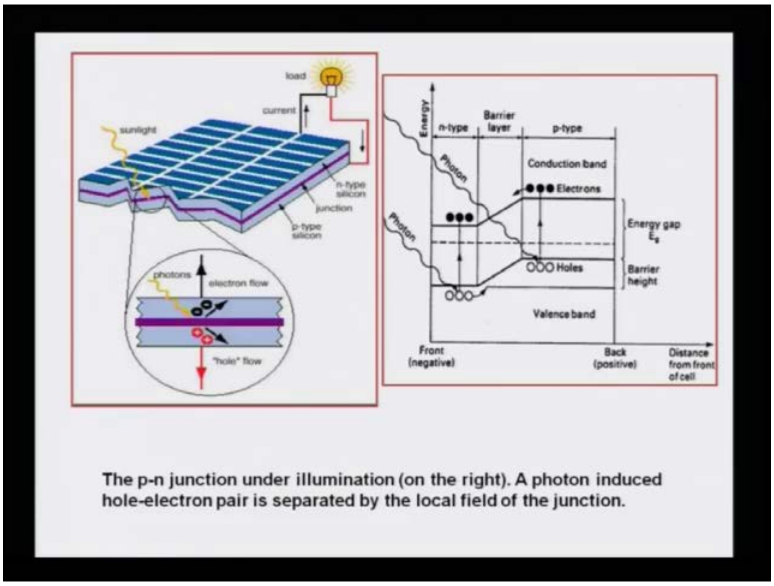

So, this is a typical example of a solar cell which is described here and you can see that the same thing happens in the desensitized cell also. Where the barrier between the n-type and the p-type can be covered up, and there is this conduction because what is important is that there should be enhancement of electron in the conduction band. So, whether it is done by the help of just trapping the solar cell. Between the two different types of semiconductors or by using a titanium dioxide, nano crystalline material coated with dye thin layer of dye both would do the similar function.

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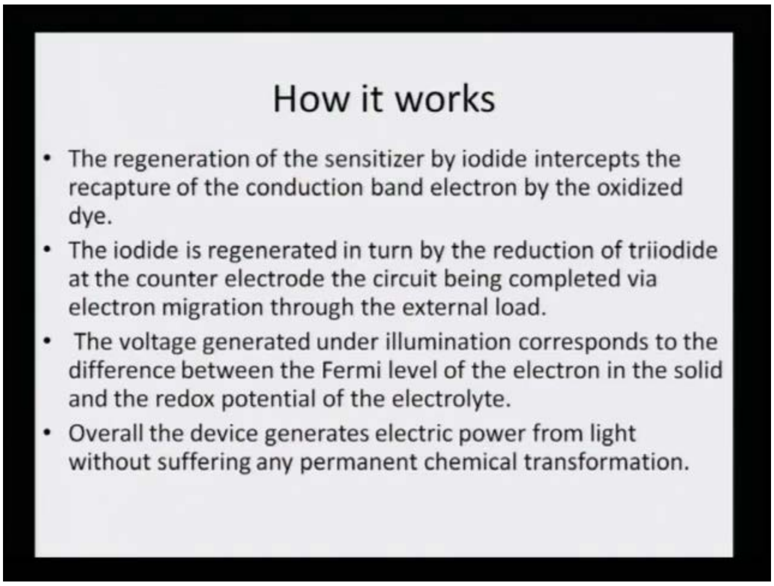

How it works? Let see the regeneration of the sensitizer by iodide intercepts the recapture of the conduction band electron by the oxidized dye. So, during the process of sunlight attacking the dye what happens there is an oxidation that occurs on the dye. We had learned about the oxidation of colors, if you recall we have spent a whole lecture that was primarily to make you understand that dyes undergo oxidation particularly. Such you know special dyes can undergo oxidation, and so the similar type of thing is happening here.

The regeneration of the sensitizer dye by iodide actually takes place and the conduction band is the electrons are enhanced from the dye, and the dye in turn is then oxidized, because loss of electron is also oxidation. So, the iodide is regenerated in term by the reduction of the tri iodide at the counter electrode, the circuit being completed via electron migration through the external load. So, this iodide is giving electron and that is regenerated from the tri iodide. So, that is why the electrolyte is taken as a iodide and tri iodide system.

The voltage generated under illumination corresponds to the difference between the Fermi level of the electron in the solid and the redox potential of the electrolyte. So, obviously there is a redox potential, because the tri iodide must replenish the electron deficiency of the iodides and subsequently the iodides are actually giving back the electron to the oxidize dye and so on. So, there is a kind of a chain cycle which is happening and the initiator or the sensitizer of this program is a dye.

So, you see that is why the name dye sensitize solar cell. Overall the device generates electric power from light without suffering any permanent chemical transformation. So, you see is only the electrons being transferred from one end to another. So, there is note complete loss of any kind the light is being trapped from the solar energy, and that triggers the entire reaction and it does not have any permanent chemical transformation. Nothing goes from one state to another in an unreversible manner.

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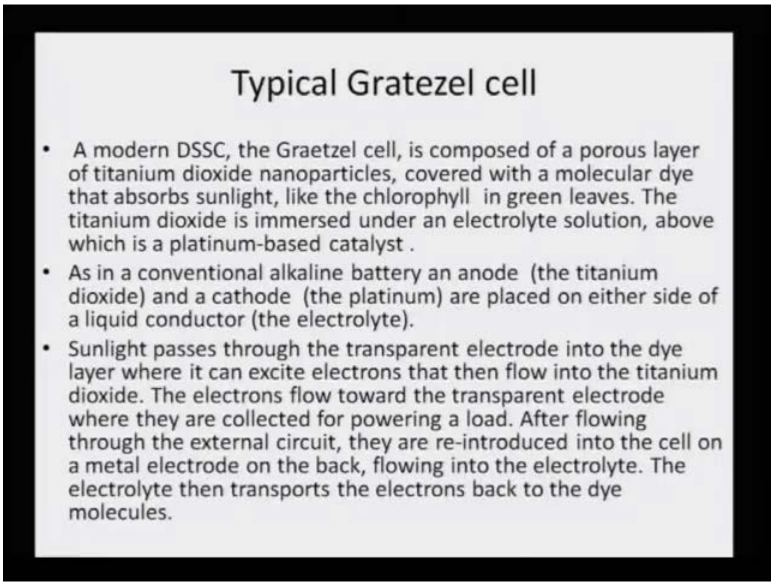

So, the material can go and working very efficiently typical Gratezel cell. We talk about Gratezel, Michel Gratezel was the first one to make desensitize cell. So, therefore we must always remember his name and know his substantial contribution the modern dye sensitize solar cell. The Gratezel cell is composed of a porous layer of titanium dioxide, nano particles covered with a molecular dye. That absorbs sunlight is a simple phenomenon like what chlorophyll you know takes the sunlight in green leaves and starts doing photosynthesis.

Similarly, here instead of chlorophyll there is a dye which absorbs sunlight the titanium dioxide, is immersed under an electrolyte solution above which is a platinum based catalyst as in the conventional alkaline. Battery, an anode the titanium dioxide and the cathode that is the platinum are placed on either side of the liquid conductor that is the electrolyte. So, that is what you know it is just a very conventional platinum acts as a cathode and titanium dioxide acts as a anode.

Sunlight passes through the transparent electrode into the dye layer where it can excite electrons that then flow into the titanium oxide conduction band the electrons flow towards the transparent electrode. Where, they are collected for a powering for powering a load after flowing through the external circuit. They are reintroduced into the cell on the metal electrode on the back flowing into the electrolyte. So, it is that is how the circuit is completed.

The electrolyte then transports the electron back to the dye molecules. So, the electron replenishing is done through the outer circuit back into the electrolyte, and from the electrolyte to the back to the dye. So, that is how the circuit is complete and it is you would see that nothing has got destroyed nothing is like nothing needs to be replaced as the whole cell is quite is not getting disturbed or not getting replenished or not getting used as what we will say like alkaline battery it gets used up.

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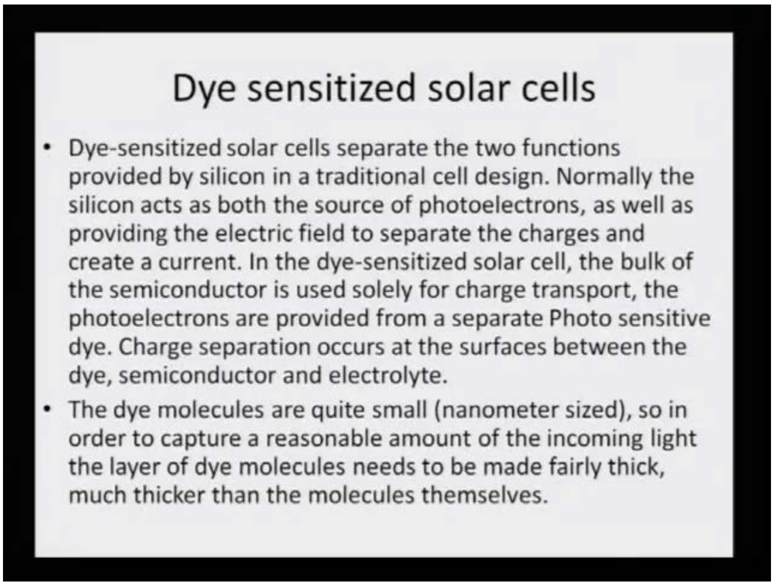

The Dye-sensitized solar cells: Dye-sensitized solar cells separate the two functions provided by silicon in a traditional cell design. Normally the silicon acts as both the source of photoelectrons, as well as providing the electrical field to separate the charges and create a current. In a dye sensitize solar cell the bulk of the semiconductor is used solely for the charge transport, the photoelectrons are provided from a separate photo sensitive dye.

So, here in the only difference between the silicon-type and the dye sensitize solar cell. You should know the difference between the two is that here the silicon is doing all the part dye electron generation electron transfer where as in this dye sensitize the electrons are being generated by the dye, but transported by the semiconductor to carry out the charge transport. The charge separations occurred at the surface between the dye and the semiconductor and the electrolyte. So, here we have another component which is an electrolyte which replenishing the loss of the electron all the why

The dye molecules are quite small nano meter size. So, in order to capture reasonable amount of the incoming light, the layer of the dye molecule needs to be made fairly thick much thicker than the molecule themselves. So, you see because the coating or the titanium dioxide is of the nano scale particle size, even the dye molecule is nano size.

So, there should be enough coating. So, that the trapping of the electron the generation of the electron is substantial, but it still it cannot be like you know a coating of this order it is still very fine coating dye. Sensitize solar cell based on titanium dioxide or promising low cost alternative to conventional solid states.

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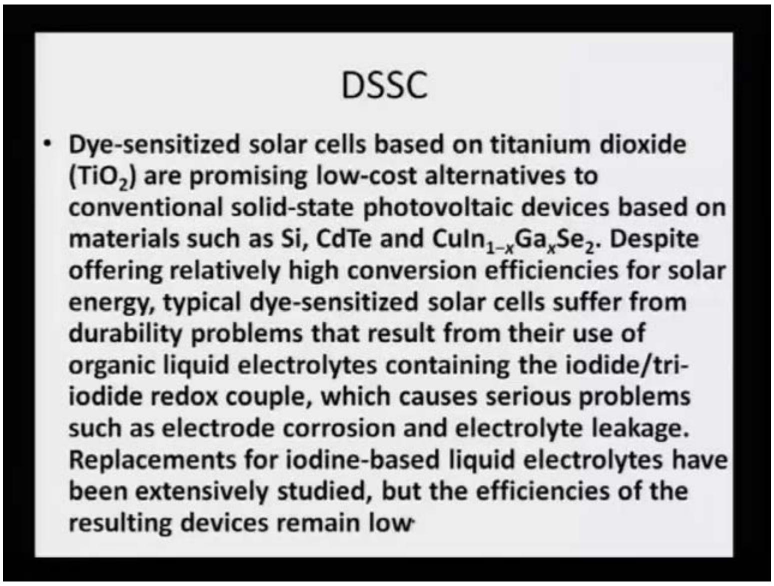

So, photovoltaic cell based on materials, such as silicon cadmium and so on. Despite offering relatively high conversion efficiencies for solar energy typical dye-sensitized solar cell suffer from durability problems. That result from their use of the organic liquid electrolytes containing the iodide and the tri iodide redox couple, which causes serious problems as the electrode corrosion and electrolyte leakage takes place. So, for every system you see there are advantages and there are disadvantages.

Also it is not that a this dye sensitize solar cells have no disadvantage, but one has to then try to find out how to come about, because the compositional situation the cost of dye and making this dye sensitize solar cell is fairly low cost. So, can we find and alternative to these problems replacements of iodine base liquid electrolytes have been extensively studied, but the efficiencies of the resulting devices remain low. So, it has been found that although iodide try iodide electrolytes system is the best, but it has its own problems and when other type of electrolytes were tried out the cell efficiency was not match with this. So, therefore, one has to rely on this particular.

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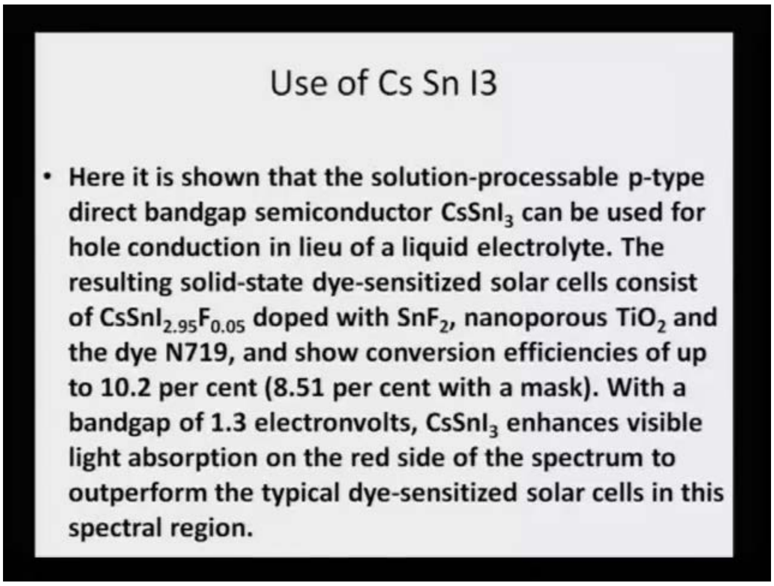

Electrolyte, but there was some suggestions that some other cesium material having tin can having tin iodide try iodide can also be used here. It is shown that the solution-processable p-type direct band gap semiconductor that is cesium tin bio conductor can be used for whole conduction in lieu of the liquid electrolyte. So, one replacement that was thought was C s S n I 3 the resulting solid state. You know, it is a solid state electrolytes not in a liquid situation. Dye-sensitize solar cells consisting of this doped with tin fluoride nano on the nano porous titanium dioxide and a dye which was of synthetic type N719 show convergent efficiency up to 10.2 percent, with the band gap of 1.3 electro volts. Now this definitely this compounds C s C n I 3 enhances visible light absorption on the red side of the spectrum to outperform. The typical dye sensitize solar cells in this spectral region, but then you see what is the main issue how to get an easy availability of this iodide compound.

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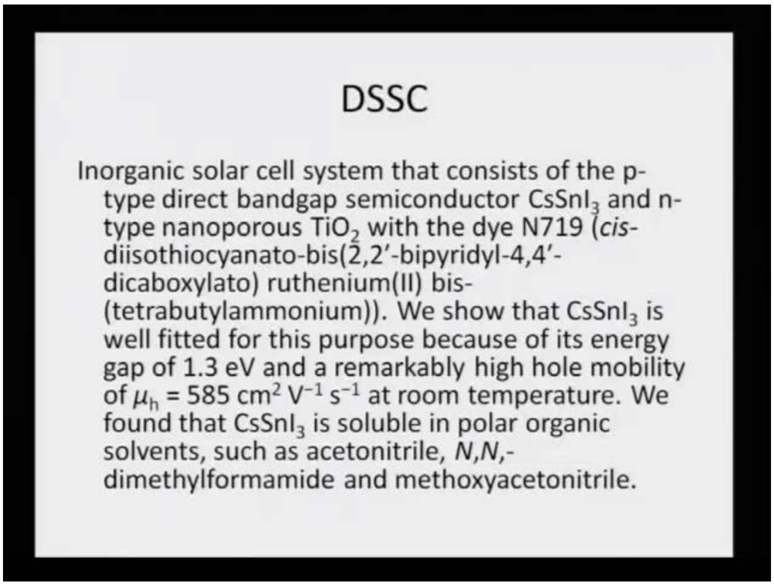

Inorganic solar cell system that consist of p-type direct band gap semiconductor,that is C s C n I 3, S n I 3 with nano porous titanium and using cis-isothiocyanato-bis, bipyridyl, dicarboxylato, ruthenium, tetrabutylammonium compounds, if this dye is N719 is actually a dye made out of inorganic substance ruthenium. We it shows that this particular material is very fitted for this purpose, because it creates 1.3 electro volt of energy and therefore, it was found that this is a good substance for carrying out the, this particular dye in order to have a replacement of a liquid electrolyte in place of a solid state electrolyte this was a good option.

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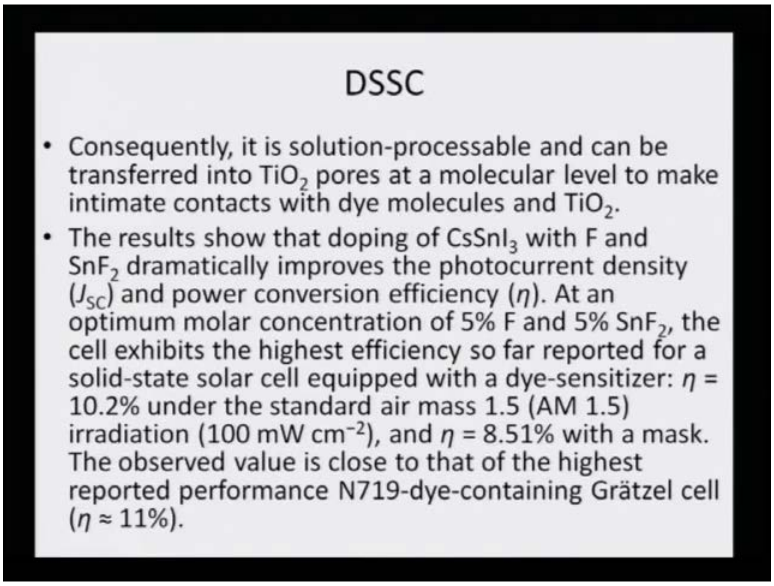

However consequently, in the solution-process able it can be transferred into titanium dioxide pores at a molecular level to make intimate contact with the dye molecule and it was also compatible with you know that impregnation or dye coating. So, than this material along with tin fluoride doping can act as a good material of a solid state to convert this energy and Gratezel cell containing this N719 dye was giving an efficiency of almost now from 10.2 it is started giving an efficiency of 9, 11 percent.

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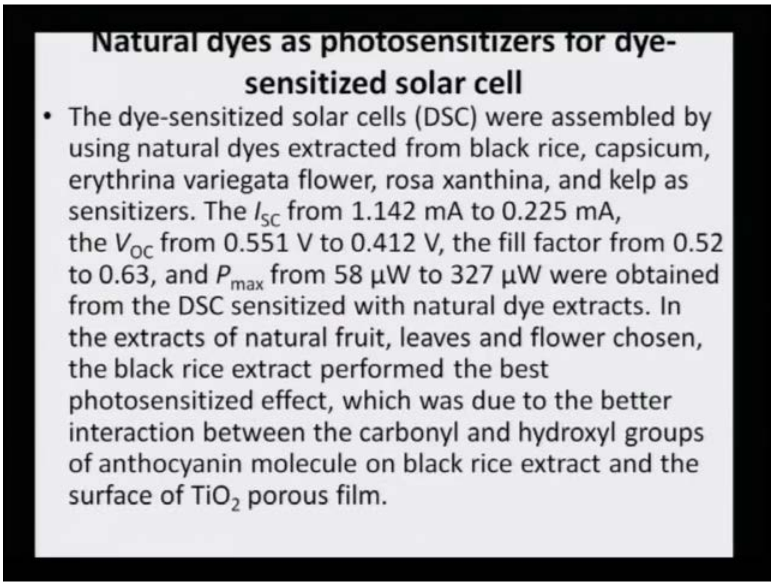

Similarly, natural dye as photosensitizers for dye-sensitized solar cells have also been explore the dye-sensitized solar cell. That is because in the beginning itself I had told you that there is a possibility that both synthetic dyes. Where we saw that ruthenium type of dye could be use or even natural dye can be use and it was found that dye-sensitized solar cells using natural dye, extracted from black rice capsicum erythrina variegate flower, rosa xanthine have been used as a sensitizer and as good as 0 point 55 to 0 point 4 volt has been achieve through this and it was found that these dye-sensitized with natural dye extract are fairly good as sensitizer dye in the extract the natural food leaves or flowers chosen the black rice extract perform the best; that means, the photosensitization effect from the darker dye was better which was due to the better interaction, between the carbonyl and the hydroxyl group of the anthocyanin molecule. On black rice extract and the surface of the titanium porous film. We were talking. So, now, you see anthocyanins can be a good source for even dye-sensitized solar cells they are good for making pH papers and for acid based titration and of course, time and again we have been talking about this anthocyanin which are.

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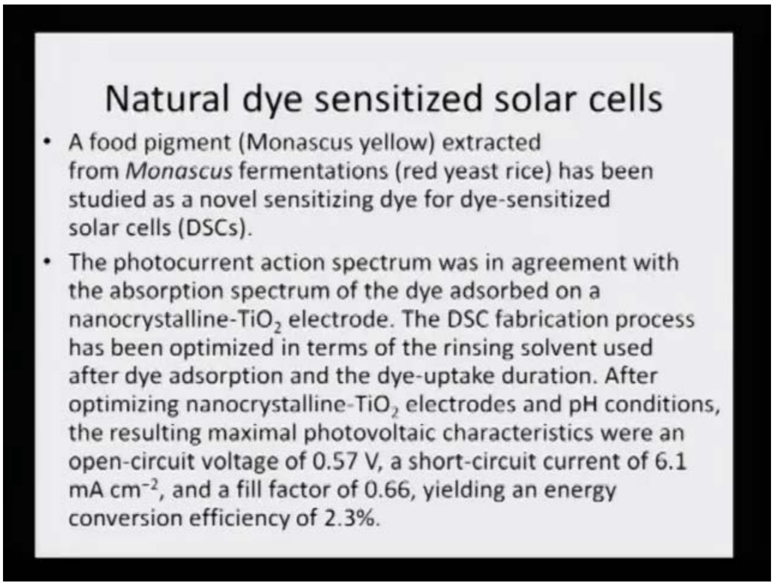

So, widely occurring in nature, that they can be used for dying purposes also, the yellow the food pigment from monascus yellow extracted from monascus fermentations. Which is a red yeast rice has been studied for the novel sensitizing dye as dye-sensitized solar cells. So, here also the efficiency was found to be 2.3 and the photocurrent actions spectrum was in agreement with the absorption spectrum of the dye absorbed on the nano crystalline titanium dioxide electrode.

The dye-sensitized solar cell fabrication process has been optimized in terms of rinsing solvent use after dye absorption and dye uptake duration after optimizing mono crystalline titanium dioxide electrode and pH condition the resulting maximum photovoltaic characteristic that could be obtained was 0.57 volt.

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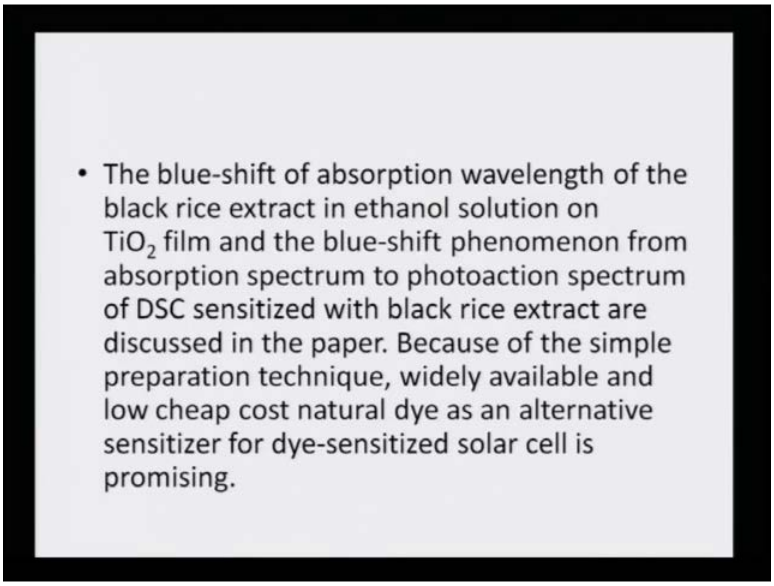

So, which is a very good situation because you know from a cheaply available dye, if these cells can be made, there can be nothing better than this the blue shift of the absorption wavelength of the black rice extract in ethanol solution on titanium dioxide film, and the blue shift phenomena from the absorption spectrum of the photo action spectrum of the dye. Sensitized with the black rice extract are have been you know discuss in this lecture and has been made clear to you, that they are so very important because they are from the anthocyanin, because of the simple preparation technique wide availability and low cheap cost of the natural dye the anthocyanin natural dye. It is a good alternative for making sensitizers for dye-sensitized solar cell and there is a lot of promising work that is going on in this technology area.