Solar Photovoltaics:
Fundamental Technology and Application
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Lecture-18
Novel Dyes/Sensitizers for DSSC

Welcome everyone to our solar photovoltaics course, to recapitulate whatever you have learnt so far we started with first generation solar cell that is single crystal silicon solar cell, then we have talked about second generation solar cell are thin film solar cells and from last 2 lectures we have started talking about third generation solar cell. Now we mention that in third generation solar cell there are different varieties of solar cell like dye sensitized solar cell, organic photovoltaics and then perovskite solar cells etc.

Out of that dye sensitized solar cell was for quite a long time and in last 2 classes we have learned what is the working principle or working mechanism behind a dye sensitized solar cell devices. We also learnt how to fabricate the dye sensitized solar cell, we found that it is quite easy to make a dye sensitized solar cell. In today's lecture we will learn about some other components of this DSSC file.

For example sensitizers and also the redox couple, some advantage like which makes is DSSC technology very very popular.

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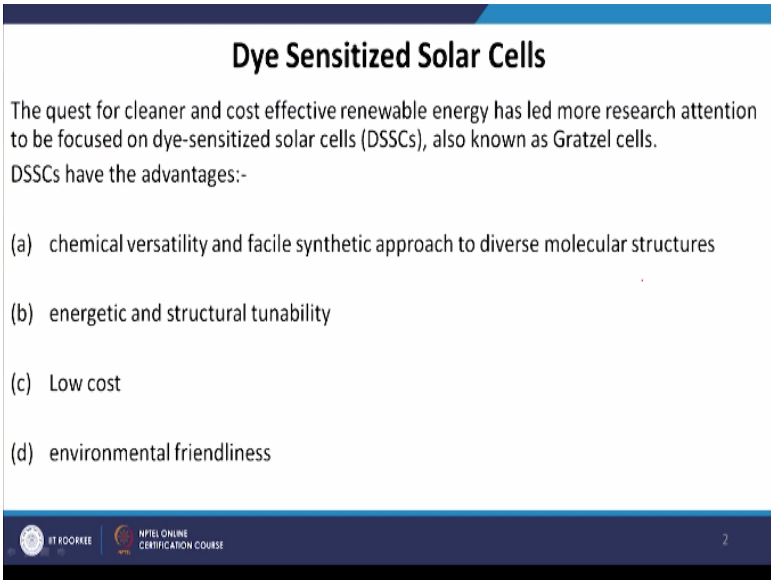

Like chemical versatility and facile synthetic approach to diverse molecular structure, so we can take different kind of synthesizer, a different kind of dye molecule to fabricate this DSSC device. Similarly the fabrication method is very facile and you can make it in a simple solution base method and from the last class demonstration we have seen that even undergraduate student with minimum facility can make a DSSC device in the lab.

Then the second point is that the energetic and structural tunability, so depending upon in which region of the electromagnetic spectrum we like our dye to observe the sunlight we can make their band gap accordingly and we can choose the material accordingly. So we have a freedom on the choice of the material according to their band gap and according to their structural properties.

The third important point is the low cost, yeah so obviously this DSSC device has a cost which is much lower than the first generation and second generation technology and the last but not the least point is that the environmental friendliness, so since we are using organic materials to fabricate this kind of devices. For example you have seen that we are using titanium dioxide are TiO2 to make this dye-sensitized solar cell.

But where we use this TiO2 we use in our everyday life in making the toothpaste also we used TiO2, in the paint in our house that is also made from TiO2, it is also to use a good antibacterial agent. So this products are biocompatible and they are environmental friendly. So this kind of you can call it as a green approach of fabricating solar cells.

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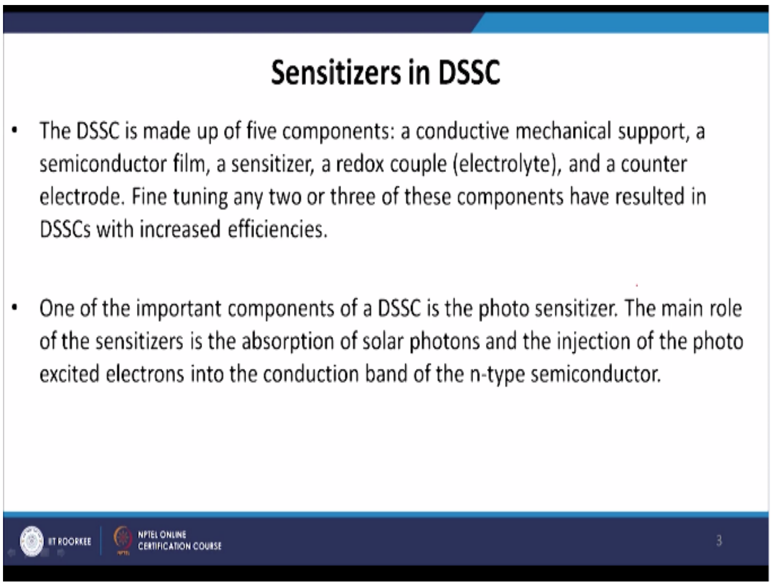

Next what are the components of the solar cells, so we learn that there are 5 different components in a DSSC device, the conductor mechanical support, a semiconductor film, a sensitizer, a redox couple electrolyte and counter electrode. So there are 5 different components there in this devices, first was the conductive mechanical support, if you remember what we have used in the last class indium tin oxide coated glass substrate or ITO glass substrate.

The second a semiconductor film, what we use a semiconductor conductor film titanium dioxide, so we put a layer of titanium dioxide on top of the ITO substrate that is a semiconductor film, third is the sensitizer, sensitizers are dye molecule, the role of the dye molecule is to absorb the sunlight and we did the photoanode the titanium dioxide anode in a sensitizer solution in the last class we have dipped in the propylene solution and we use propylene as a sensitizer.

And we also mention that we can choose even some laser die or any other sensitizer molecule to make this device. So this sensitizer molecule or die molecule go inside the pores of the semiconductors and they get absorb at the conductor surface. Now they are ready to absorb the sunlight. So they will observe the sunlight and what will happen to them. So the electron will be excited from the valence band to the conduction band of the dye or it will go from the ground state to the excited state of the dye.

Now electron cannot stay in the excited state for a long, so they will inject back, where they will inject to the conduction band of the titanium dioxide. So that is why it is very important the energy level matching of the dye and the conductivity titanium dioxide. So that means that layer to excited state should be higher than the conduction band of the TIO2. The dye excited state should be higher than the conduction band of the TIO2.

Then only the dye molecule in an excited state can inject electron to the conduction band of titanium dioxide. Now the fourth compound is a redox couple. A redox couple is nothing but an electrolyte, in our particular case we have used iodine trihydrate as an electrolyte and if you remember what you have talked about the role of electrolyte to regenerate the whole process. So that the dye comes back to the ground state and ready to observe the light for the next cycle.

And the whole process cycles, and finally to complete the device structure we need a counter electrode. So finally we put the electrolyte and then on top there is a counter electrode. Now we mention that as a counter electrode we use the platinum counter electrode platinum also helps to catalyze this electron oxidation reduction process and also it acts like the middle counter electrode.

Now in many cases we replace this counter electrode by several other materials. For example even we can take graphite like some pencil and we can put a layer on the glass substrate to make it a counter electrode and there is sever other examples like graphene, CNT like carbon nanotubes and some conducting polymer they have also used as this counter electrode. So these are type main components in the DSSC device.

Fine-tuning any 2 or 3 of these components have resulted in DSSC with increase efficiency. Now it is worthwhile to mention that the efficiency in any device not only in DSSC but for any kind of solar cell including silicon solar cell the efficiency is a multiplicative factors or the efficiency is not an additive function, it is a multiplicative function, what do you mean by that.

There are so many parameters on which efficiency depends on, so if the one of the parameters goes wrong then the efficiency of the whole device goes back. So that is why when we fabricate these devices we have to optimise each and every parameters. So that we get a maximum efficiency. Now since I have DSSC device has 5 different components. So we would be optimise all the 5 components simultaneously to get a good efficiency.

So optimization of the 5 different components means that optimisations of the ITO substrate and optimisation of the (()) (07:46) now this substrate this photoanode and photocathode they are already optimized. So the next thing which we can optimise is a semiconductor oxide and the dye and the electrolyte. Now people have used different choice of the material. For example for semiconducting oxide people have used titanium dioxide, they have used zinc oxide or any other metal oxide also.

Not only the metal oxide in the bulk mesoporous form may have this different nano structures also for this metal oxides, like titanium dioxide, nanorods, titanium dioxide, nanocube for example like that. And for sensitizers or dye molecules similarly we can choose different kind of materials. Now we have to keep some points in mind while choosing the sensitizers molecule.

One important choice or one important parameters to pick up a sensitizer is its absorption property, where does it observes and how much it absorbs and of course it should get absorb on the clear to surface or the zinc oxide mesoporous surface. So that is why the solubility is also an important parameter. Similarly for an electrolyte is energetic should match in such a way that it will be able to reduce back that dye in its ground state.

So today will discuss in details about all this properties of the sensitizers and electrolyte. So that we can pick up the right sensitization and the right electrolyte by fabricating the device. One of the important components of the DSSC is the photo sensitizers. The main role of the sensitizer is the absorption of solar photon and the injection of the photo excited electrons into the conduction band of N type semiconductor.

So we have seen that if you consider this is the ground state of the dye which we write like S0 and this is the excited state is stands by the excited state of the dye which we write as S* and if the electron jumps from the ground state to the excited state by the photon absorption. So after some time what will happens this electrons has to comes back to some lower energy state and titanium dioxide has an energy level such that this is conduction band.

And this is valence band and we know that the band gap is somewhat around 3.2 electron volt. Now energetically the positions of the conduction band is matching with the excited state of the dimolecule. So the electron can inject to the conduction band of the TIO2. So the role of this dimolecule is to hold fast to observe the sunlight and second to inject the electron to the conduction band of the TIo2 or the semiconducting oxide.

Now electrons starting from the CV it goes to the O2 substrate and comes back to the external circuit which participate in the electric conductance. So dye is like crucial part in the DSSC device.

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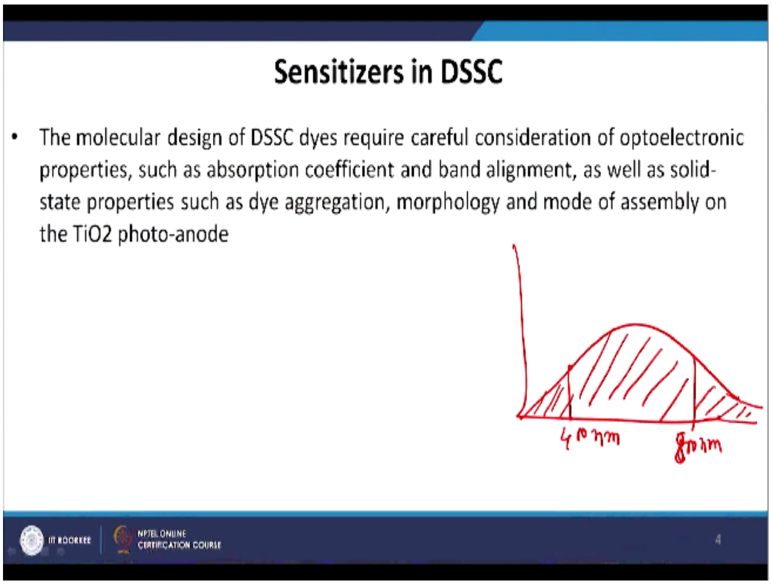

The molecular design of DSSC dyes required careful consideration of optoelectronic properties such as absorption coefficient and band alignment as well as solid state properties such as dye aggregation, morphology and mode of assembly on the TiO2 photoanode. So what does it means, so as you just mention first important parameter to consider a dye is absorptions, so where does it absorbs.

Does it absorbs in the hill region, does it absorbs the visible region or in the near region, so if you plot the electromagnetic spectrum so you see that a dye which has an absorption spectrum which bands from the UV range let us say this is 400 nanometre and this is my 800 nanometre. So this dye molecule has an absorption in the UV range, it has absorption in the visible range as well as which has some absorption in the near IR range. So this dye molecule is ideal for our study.

Because it is an absorption which spends all one of the electromagnetic spectrum. Now we know that the sunlight that resembles like a blackbody spectrum which has maximum intensity in the near IR range. So will prefer a dye molecule which will have a good amount of absorption in the near IR or IR range. Now most of the dye molecule which we used commercially like M3 or Z-7 dye they are good amount of absorption in the visible range with some absorption in the near IR range.

So absorption is an important parameters while choosing a dye molecule or sensitizer molecule. Second point is that the absorption coefficient and band alignment so the dye molecule has to be chosen in such a way it will be able to inject the electron to the conduction band of the n-type semiconductor. So the energetics of the semiconductor and sensitizers also has to be kept in mind. Third point is that some of the other properties like dye aggregation.

So some of the dye molecule has to show the aggregation, so what will happen they will accumulate in a particular area, so if they accumulate in the particular area only those regions will ready to absorbs the light. So the rest of the TiO2 area will not be able to absorb the sunlight. So that is not a good scenario. So we do not what the dye molecule to aggregate in a particular place.

The next things is the morphology, how does the dye molecule distributed over the surface and also the assembly on the TiO2 photoanode, we know that titanium dioxide photoanode is usually centred at 450 degree Celsius to make it mesoporous structure. So the objective behind making is mesoporous which can absorb as much as dye molecule as possible. So the dye molecule in principle should go beyond the certain distance from the surface.

If the dye molecule is only absorb, only on the surface, so it is a monolayer absorption, then the amount that photo generated or the amount of charge carrier generated by the photon absorption is not as high because that dye absorption is only limited to the surface of the semiconductor. In ideal case it should also go inside the bulk of the material. So how the dye molecule is distributed among the n-type semiconductor that also plays an important role.

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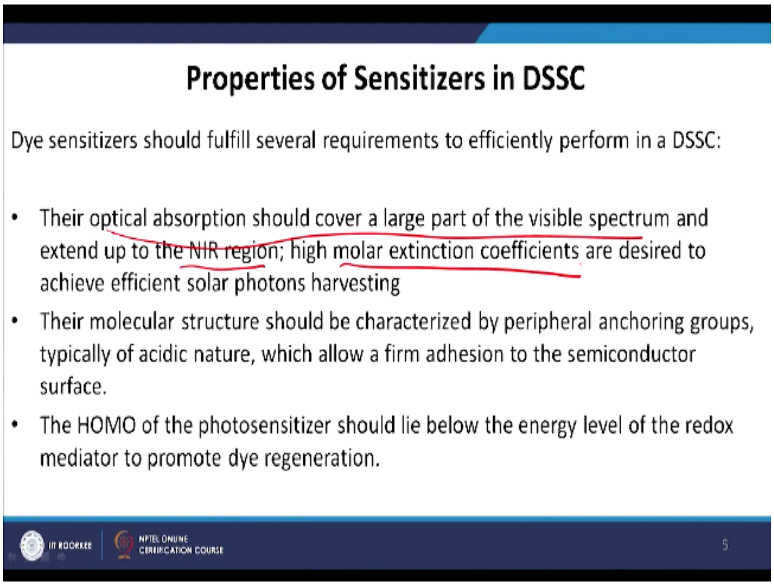

So dye-sensitize will fulfil the several recruitment for the efficiency evolution for higher efficiency in DSSC devices. Their optical absorption should cover a large part of the visible spectrum and extended up to the NIR regions. So it should have a large part in the visible spectrum and it should also extending the NIR region, they are high molar extinction coefficient. So the amount of light absorption per unit length per unit mole of these dyes should also be very high.

So let us 2 different example, let us say I have 2 different materials A and B, both of this material has the same kind of semiconductor TiO2 but different kind of that, let us say A1 and B1, now A1 has a higher molecular absorption coefficient than B1. So obviously I need a thinner layer of A1 for the similar kind of light absorption like a B1 and it will be material wise it is more inexpensive to have a material which absorbs more amount of light in a thin layer.

And that is only possible in the absorption coefficient is high, so in our particular example will choose A1 because absorption coefficient is high and probably if we make a layer of 100 nanometre it will do the same job as like 200 nanometre or 300 nanometre of dye beyond dye **zoo** zone. Their molecular structure should be characterized by peripheral and anchoring groups, typically of acidic nature which allow a firm adhesion to the semiconductor surface.

So this dye molecule should also be able to adhere to that layer to surface. Now most of their dye which we choose that we will encore to the n type semiconductor oxide, (()) (15:34) of the highest occupied molecular orbital of the photo sensitizer should lie below the energy level of the rest mediator to promote dye regeneration, so we have to also make sure this dye get user native.

And that is why the highest orbital molecular orbital or highest occupied molecular weight of the photo sensitizer should be below the energy level of the redox mediator iodine tri hydrate electrolytes to promote the diet regeneration.

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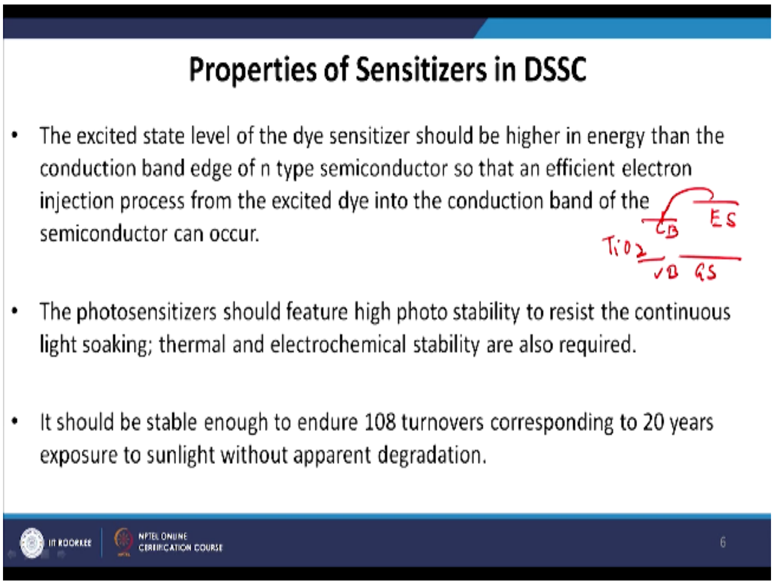

The excited state level of the dye sensitized should we higher in energy than the conduction band edge of the n type semiconductor. So that an efficient electron injection process from the excited dye into the conduction band of the semiconductor can occur. This point we already expand. So what do you mean that, if this is the ground state of the dye and this is excited state of the dye.

So let us say this is the ground state and this is the excited state GS stands for the ground state and ES stands for the excited state. Now the excited state of the dye should always be higher than the conduction band of the titanium dioxide. So that the electron can inject from the excited state to the conduction band. This point is that the photo sensitizer should feature high photo stability to reduce the continuous light soaking, thermal and electrochemical stability are also required well.

What is the job of the photo sensitizer to absorb the sunlight and to maintain the job very well it is to observe the light for a long amount of time. So we have to make sure that the material does not degrade or does not change its structural and optical properties of an exposure to the light for a long time. So that is why photo stability and as well as thermal and electrical stability is also very important while choosing the sensitizer molecule.

Next point is that it should be stable enough to endure 108 turn off corresponding to 20 years exposure to sunlight without apparent degradation. Of course if you wanted to make a solar cell module then it has to be there for quite a long terms, so usually in industry we **we** inspect it for the time period of 20 years. Now this DSSC device suitable to keep its efficiency or is turnover period for a time period of 20 years without the dimolecule showing any degradation.

Because if the dye degrades then the light absorption property will be happen, if the light of the vision property gets suffered then the efficiency will also decrease. So we do not want that situations to happen.

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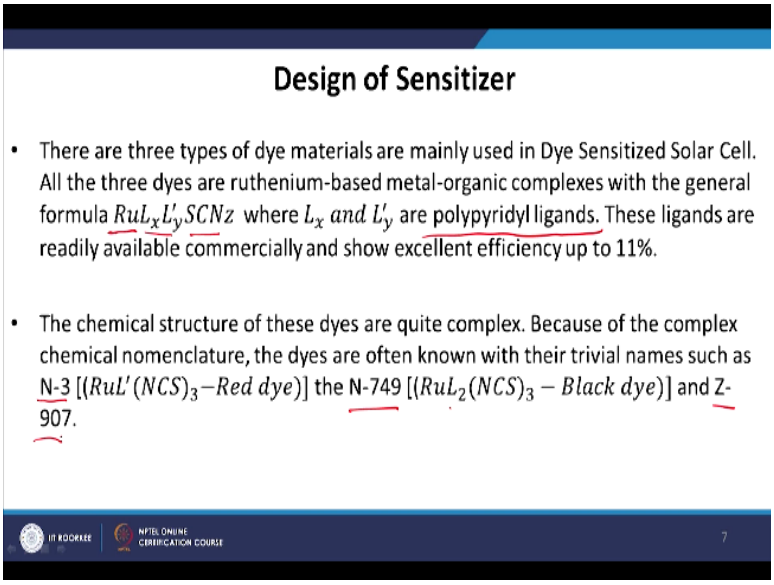

Now while designing a sensitizer there are 3 types of dye materials are mainly used in this kind of solar cell, all the 3 dyes are ruthenium based metal organic complex with the general formula of Ru Ru stand for ruthenium Lx Ly prime SCNz where this Lx and Ly prime are porphyrin based compounds polypyridyl ligands. So ruthenium Ru and Lx and Ly stands for the some porphyrin based ligands.

This ligands are really available commercially and so excellent efficiency up to 11%, the chemical structure of these dyes are quite complex than the material dyes, so ruthenium is at the centre and the remaining components is surrounded the ruthenium, because of the complex chemical structure the dyes are often known with the trivial names such as N-3 which full name is RuL prime NCS 3 Red dye, the N-749 RuL2 NCS 3, black dye and Z-907.

So N-3 N-749 and Z-907, this 3 dyes are commonly used for fabricating the DSSC devices. They fulfil all the design criterion for an optimum sensitizer.

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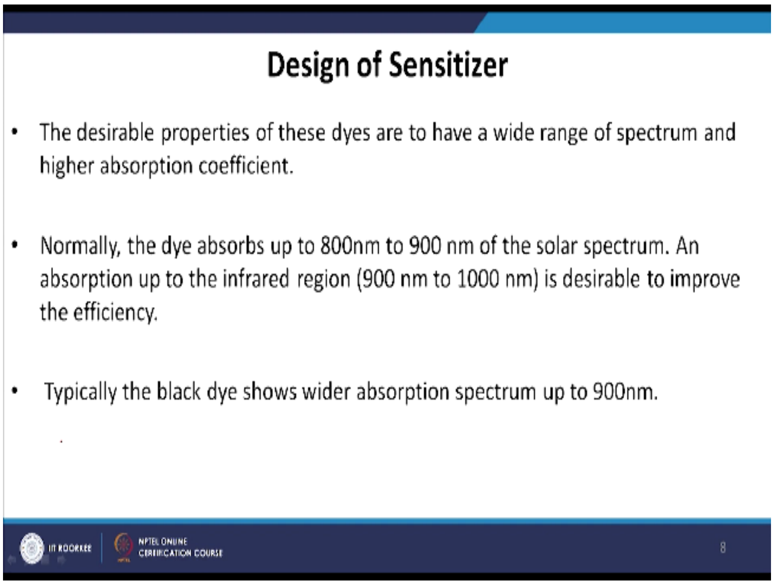

The desirable properties of these dyes are to have wide range of spectrum and higher absorption coefficient. Normally the dye absorbs up to 800 nanometre to 900 nanometre of the solar spectrum and absorption up to the infra region 900 nanometre to 1000 nanometre us desirable to improve the efficiency. So if you want to improve the efficiency we wanted to have the adjacent in the near IR range.

Typically the black dye shows wide absorption spectrum up to 900 nanometre. So that is why nowadays the most of the emphasis is going on to synthesise this kind of black dyes for using the DSSC devices.

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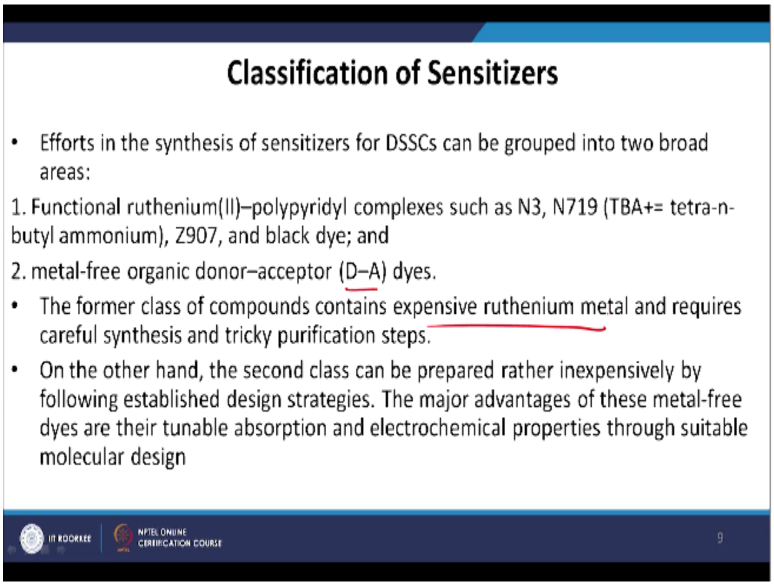

Efforts in the synthesis of sensitizers for DSSCs can be grouped into 2 broad areas, the first is the functional ruthenium **per** porphyry, polypyridyl complex such as N3, N719 which is also used in the presence of the TBA like tetra butyl ammonium Z907 and black dye and the second approach is metal-free organic inorganic dye which we write as D-A do not accepted kind of dyes. The former class of compound of the ruthenium base compound they contains extensive ruthenium metal.

And require careful synthesis and very tricky purification process, now ruthenium is very very expensive, which makes this dyes very very costly, also at the same time fabrication of this dyes are very very cumbersome and it inhales lot of cost and purification tips, on the other hand the second class the metal-3 organic donor acceptor best dyes they are prepared in rather inexpensively by following established design strategies.

The major advantage of this metal 3 dyes are their tunable absorption and electrochemical properties **su** suitable molecular design.

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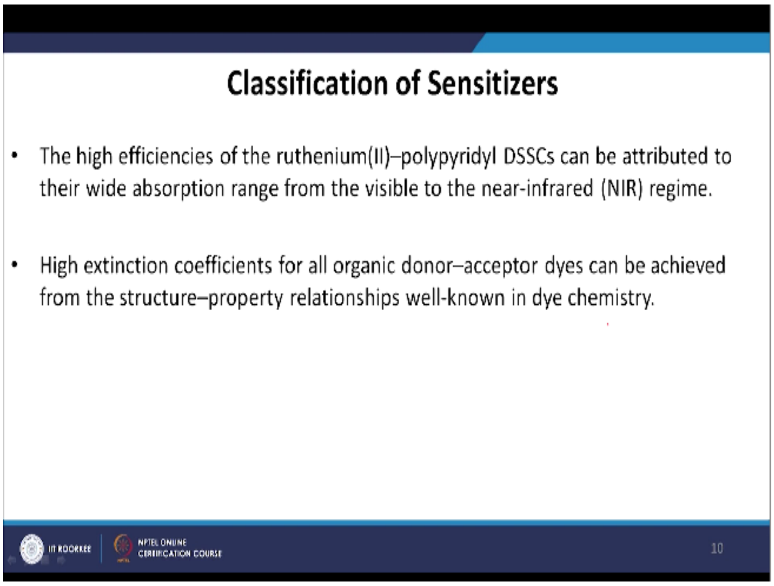

The high efficiencies of the ruthenium polypyridyl DSSCs can be attributed to their wide absorption range from the visible to near IR region, high extinction coefficients for all organic donor accepted dyes can be achieved from the structure property relationship well known in dye chemistry. Now obviously while we design a new dye we know its structure, but the same time we need to know its optical properties.

Like its absorption properties, now in chemistry it is very very well known how to design an optimum structure property relationship, that means like you know any kind of structure which synthesizes at the same time we have to keep in mind it shows a good optical properties, good absorption properties and its extinction more extinction coefficient also should be very high.

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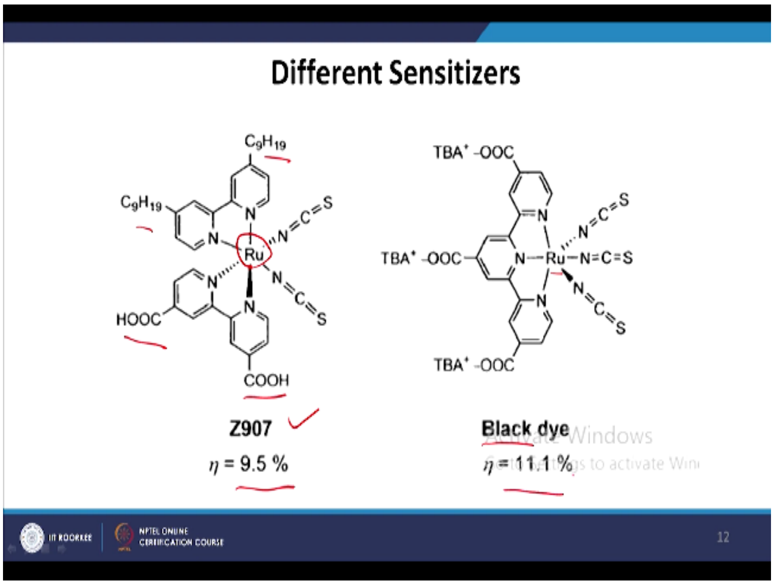

Here we are showing the structure of the different dye as you can see here the ruthenium is at the centre and the different other group there anchor of their coordinated surrounding the ruthenium molecule and you can see that there are COOH molecules at the end of this dye molecule. Now this COOH molecule helps to anchor with the TiO2 surface. The second example is N719.

In this case also we have ruthenium at the centre and there are some other complex or other materials which is surrounded here and then finally we have COOH and which tertiary butyl aminopyridine which replace the H proton from the CH and make it a cationic dye and this COOH can also anchored on the TiO2 surface. The efficiency for an N3 dye is 11.3% and for N719 11.18%.

But this efficiency number can be further improved by optimising from the parameters, another common example used in the DSSC device is Z907. So here again we have ruthenium at the centre and we have COOH group at the end and some alkyl chain CNH19 on the 2 other end. So these dyes show the moderate efficiency of 9.5%. On the other hand t. black dye which is again we use the ruthenium.

But we have changed the structural properties so that they can absorb in the near IR range and their efficiency increase to 11.1%.

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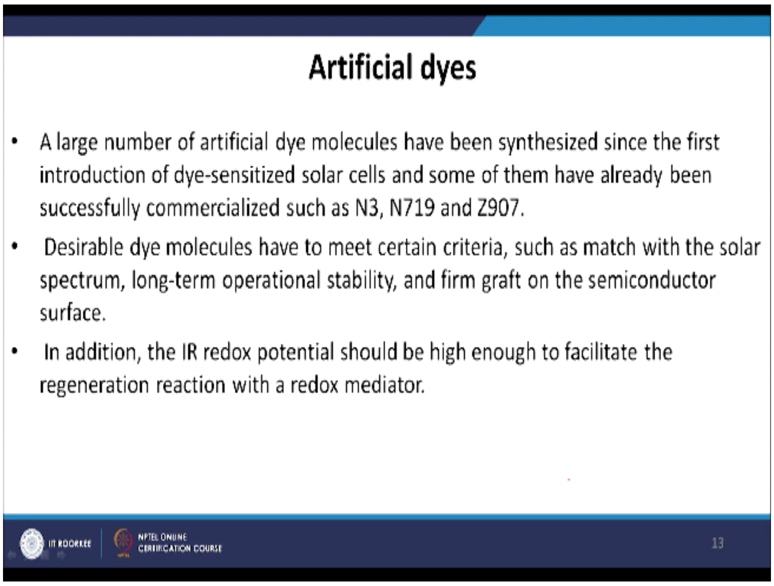

The large number of artificial dye molecules have been synthesized since the first introduction of the dye sensitized solar cells and some of them has already successfully commercialized. For example N3 N719 and Z907, this 3 dyes has already been commercialized and some people have already making solar panels using this 3 dyes. Desirable dye molecules have to meet certain criteria such as match with the solar spectrum.

So there should have a good absorption properties, long term operational stability, so that means if I exposed them to the sunlight for quite a long time they will not degrade over the time and form draft on the semiconductor surface and those dimolecule will be able to anchored or adsorbed on the n type semiconductor surface. In addiction the IR redox potential should be high enough to facilitate the regeneration reaction with redox mediator.

And let the same time whatever the dye molecule we choose we have to choose the redox mediator accordingly because this will be an electron oxidation reduction reaction and finally the dye has to be regenerated to its ground state. So that this cycle can regenerate again and again just like this synthetic dye we have also several natural dyes.

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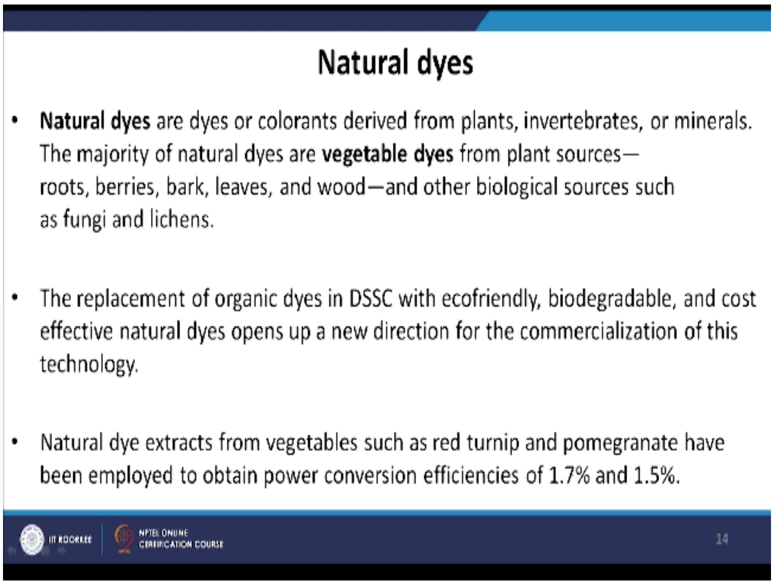

Natural dyes are dyes are colorants derived from the plants, invertebrates or minerals. The majority of natural dyes are vegetable dyes and they are get from the plant sources. For example roots, berries, bark, leaves and wood and also some biological sources like fungi and lichens. The replacement of organic dyes in DSSC with ecofriendly biodegradable and cost effective natural dyes opens up a new direction to the commercialization of this technology.

If we replace this dye sensitized solar cell technology with an organic dyes since is a bio compatible and also less in expensive is also a less expensive then it will be also good for the industry purpose. Natural extracts from the vegetables such as red turnip and pomegranate have been employed to obtain a power conversion efficiency of 1.7% and 1.5%. Now the efficiency obtained from this natural dyes is not as high as a synthetic dye.

And their reason behind it also ,so in most of the time this natural product comes with an isomer of several other products, so let us say I have a good natural dye pomegranate but at the same time there is so many different isometric form of one particular material along with the useful material. Now in plant chemistry or in natural chemistry it is very very difficult to extract one particular kind of useful isomer from the other.

So that is why the material is not very pure and due to this impurity sometimes the efficiency is not as high as a synthetic material, but it bring some method if you can extract only the particular kind of material then we can boost out this number.

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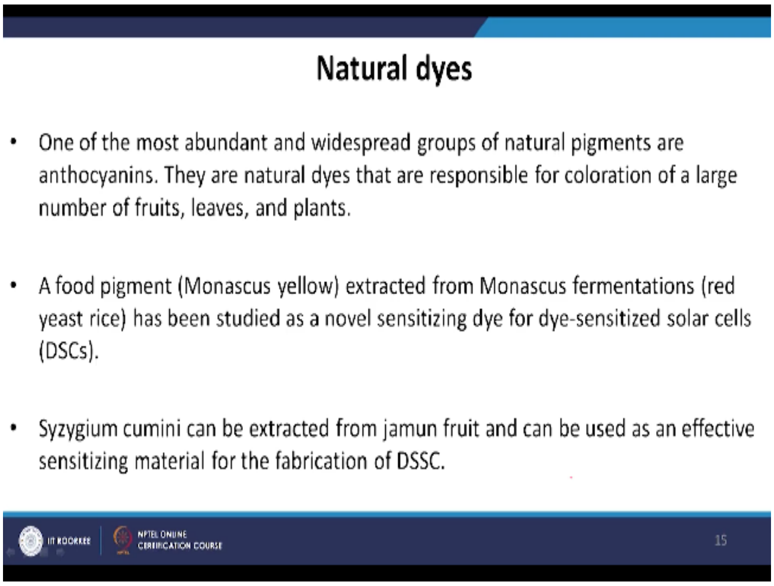

One of the most abundant and widespread group of natural pigments are anthocyanins. They are natural dyes that are responsible for coloration of a large number of fruits, leaves and plants. Recently in a work we have so that the anthocyanin present in the Indian jamun fruit can also be used to fabricate solar cell and this kind of solar cells are popularly known as the jamun solar cell.

So that jamun which is the dark fruit which is also used for the anti cancer and different kind of antique tumour activities. So that is full of this pigment call anthocyanin. Now anthocyanin also has a good light absorption properties, we have explain this light absorption properties of the anthocyanin to fabricate the dye sensitized solar cells. So basically what we did we have did that TiO2 photo anode inside this anthocyanin solution which was extracted chemically from the jamun fruit.

And overnight and then complete the DSSC device by putting some electrolyte solution and platinum counter electrode and we got a reasonable efficiency and current from these devices right, further optimizations we can increase the efficiency of the solar cells and it will be a good alternative to the conventional method. A food pigment for example Monascus yellow extracted from the Monascus fermentations red yeast rice has been studied as the novel sensitizing dye for dye sensitized solar cells.

Syzygium cumini can be extracted from the jamun fruit and can be used as an effective sensitizing material for the fabrication of DSSC.

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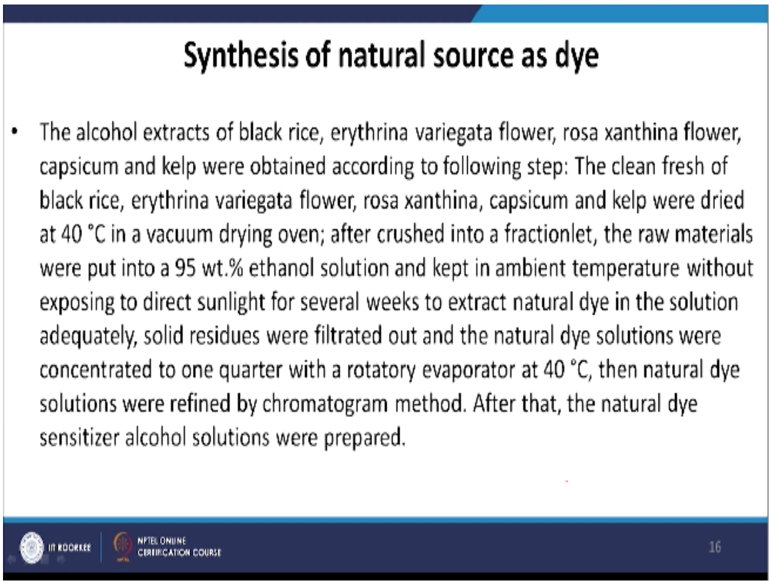

The alcohol extracts of the black rice, erythrine variegeta flower, rosa xanthina flower and capsicum and kelp were obtained according to the following steps. The clean fresh of back rice, erythrine variegeta flower, rosa xanthina and capsicum and kelp were dried at 40 degree centigrade in a vacuum drying oven after crushed into a fractionlet. The raw materials were put into a 95 wt% ethanol solution and kept in ambient temperature without exposing to direct sunlight for several weeks to extract the natural dye in the solution adequately.

Solid residues were filtered out and natural dye solutions are concentrated to one quarter with rotatory evaporator at 40 degree centigrade. Then finally the natural dye solutions were refined by chromatography method, after that this natural dye sensitized alcohol solutions were prepared. So then that photo sensitizer or the photoanode was dipped in this natural dye sensitized alcohol solution overnight.

And then they put the electrolyte solutions and counter electrode platinum counter electrode to complete the device architectures. So the second important components in the dye-sensitized solar cells devices is the electrolytes.

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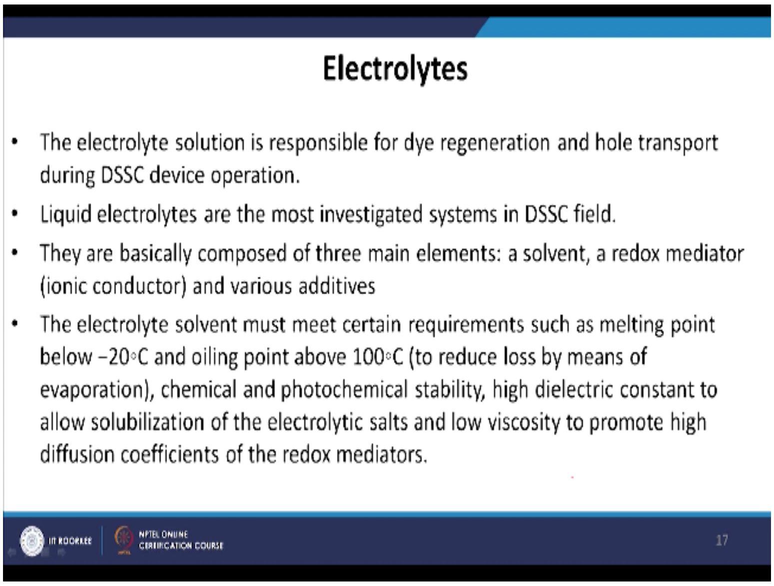

The electrolyte solutions is responsible for the dye regeneration and hole transport during their DSSC device operation. Liquid electrolytes are the most investigated systems in DSSC field. So as we mention in the last demonstration that we use iodine tri hydride as a liquid electrolyte for this regeneration as in process. They are basically composed of 3 main elements a solvent.

In the case of iodine tri hydride we use acetonitrile as a solvent. A redox mediator ionic conductor and various additives, the additives are used to increase the conductivity for example one can use popularly tertiary butyl pyridine and additive which is used to increase the conductivity. The electrolytes solvent must need certain requirements such as melting point below -20 degree Celsius and boiling point above 100 degree Celsius.

The reduce loss by means of evaporation, chemical and photochemical stability high dielectric constant to allows solubilisation of the electrolytes salts and low viscosity to promote high diffusion coefficient of the redox mediator. So we need a high dielectric constant value for the redox mediator because high dye electric constant implies the solubility the polarizability is high.

If the polarizability is high then the solubility of this material will also be high. At the same time the viscosity of this material should be low. So that we can make a ideal solution and the diffusion coefficient should be optimum.

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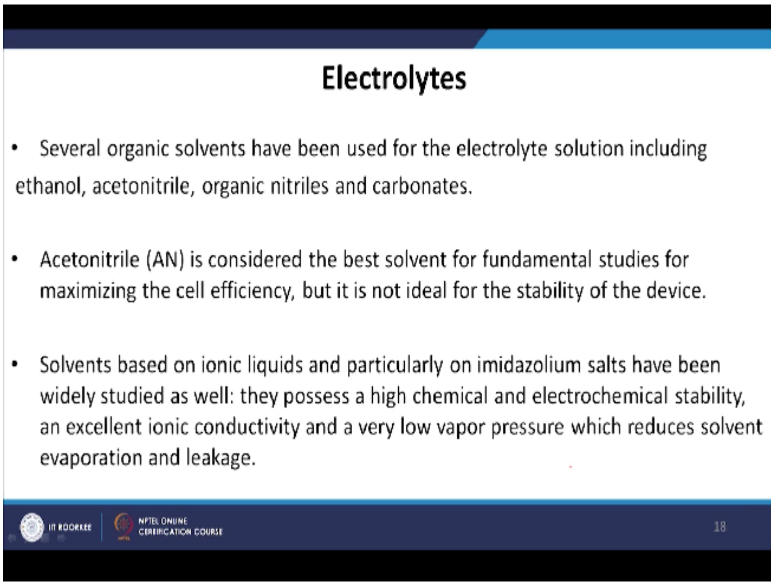

Several organic solvents have been used for the electrolyte solution including ethanol, acetonitrile, organic nitriles and carbonates. Acetonitrile is considered the best solvent for fundamental studies for maximizing the cell efficiency but it is not ideal for the stability of the devices. Solvent based on ionic liquids and particularly on imidazolium salts have been widely studies as well.

The process the high chemical and electrochemical stability, an excellent ionic conductivity and every low vapor pressure which reduces solvent evaporation and leakage. So this iodine tri hydrate electrolytes that are volatile and corrosives. So we do not want the volatile and corrosive systems that why people have tried imidazole salts, so not only imidazole salts people have tried different other kind of ionic mediums.

And ionic liquids even to make this kind of electrolyte solutions. In today's lectures we have learnt so far about how to choose a good sensitizers of the dimolecule and will give a just a overview of the basic introduction to the electrolyte solutions, in the next lecture we will study in details about what are the different varieties of the electrolysed, how to fabricate electrolytes and how an electrolytes used in a DSSC device, thank you very much.