Lecture – 34
Fabrication of Nanoparticles Based Solar Cells

Welcome everyone to our solar photovoltaics course today, we are having a seventh week and our fourth module, we are discussing about the organic nanoparticle solar cell. In the last lecture, we have seen that we have discussed about what are the advantage of using organic nanoparticles over the conventional bulk polymeric system and we have also seen that while the fabrication process that will depends upon what is our end objective or what is our ultimate objective.

So, now in today's lecture, we will discuss about the different fabrication method or the different synthesis method of this organic nanoparticles. Now, these methods for fabrications of the nanoparticles they can be broadly classified into 2 different categories; one is bottom up and other is the top down.

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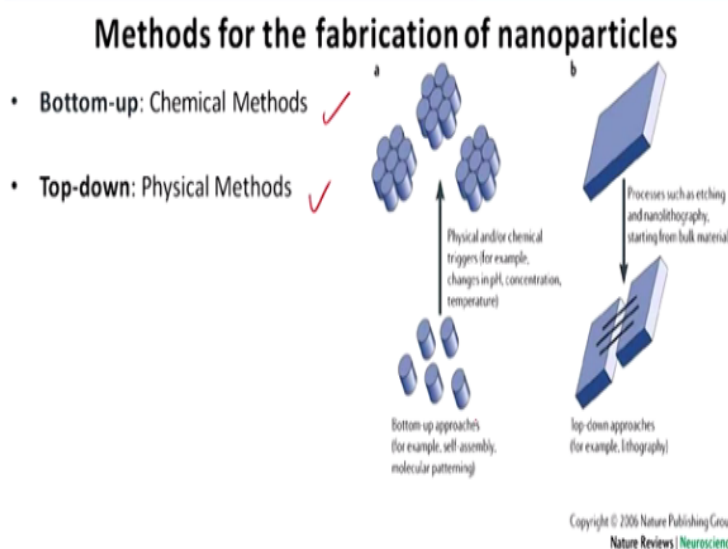
Now, the bottom up methods that is also called chemical methods and the top down method that is called the physical methods now, you see that for the bottom up methods as the names suggest again, the self-assembly is an example of a bottom up method so, for example you see that there are lot of these cylindrical structures are there, right in this picture there are 5 cylindrical structures are there.

Now, what you can do; you can assemble them together to make different, different kind of geometry, this is a self-assembly okay, so you start from a minimum number of the structure or unit structure and you make a larger structure, this is a bottom up technique. For example, self-assembly molecular patterning okay and to make this kind of from one of the unit structure to make this kind of structure or pattern, you need some physical or chemical triggers.

For example, changes in pH, concentration, temperature and then the top down approach for example, the lithography, where you start with like a big structure and then like by etching and by; or by nano lithography, you make like a small, small structure so, one from the smaller structural unit you make a bigger structure like but still it will be in a nano domain and in another case, starting from a macro molecular structure you come on the other direction and get a nanoparticle system.

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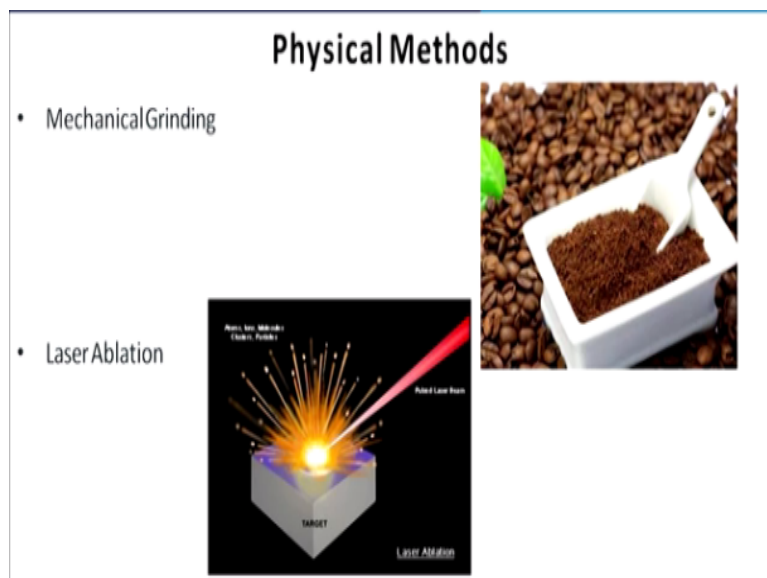
Now, this physical method they can be like you know either by mechanical grinding or by laser ablation now, the mechanical grinding is very, very like you know simple to understand, many of you has seen the grinding of the coffee powder, so once from the coffee bean, so they have been put in some kind of ball machine or grinder and then they have been grinded according to their like you know size to a very small powder.

Now, if you take up this; one of the spoon of this small powder and if you look under the microscope, you will see some kind of nanoparticle systems, in addition to that there are lot

of big particles are also there right, so the grinding method is same thing like that so, instead of this coffee bean let us say I take a carbon material, any kind of carbonaceous material and then I started grinding them in some kind of grinder.

So, what will happen finally like you know depending upon the force of the grinding and the duration of the grinding, we can control the size of the particle size of this finally whatever you obtain from that engineered carbon nano materials. The second method is the laser ablation; so, in the laser ablation what happens like on the target substrate, a pulse laser beam falls on this.

So, now pulse laser beam, the average intensity of the pulse laser beam is quite high somewhere around like giga watt per centimetre square now, if this intense laser beam falls on this substrate, so what will happen; whatever the atoms molecules or ions that stays on the top surface, so they will like in a pull up from the top surface or from the target and they will deposit on your material or you can get inside the chamber some small, small particles which have been ablated by the laser from the target substrate.

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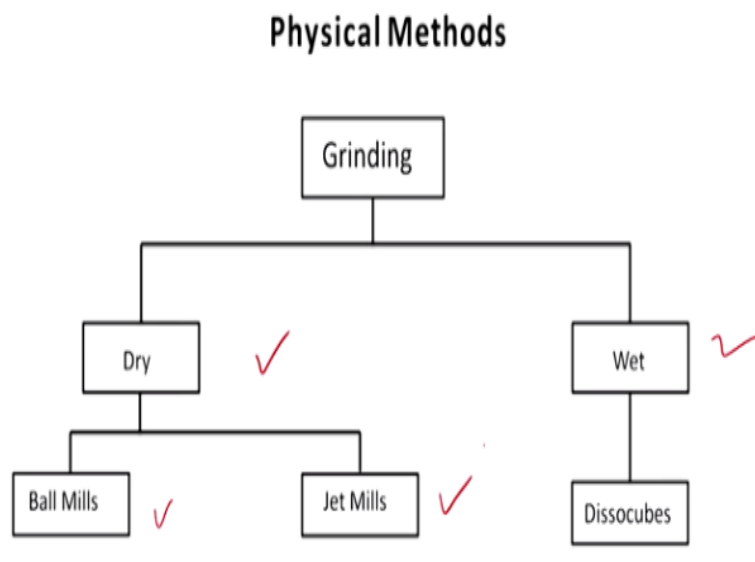
Now, this grinding they can be classified as a dry grinding or wet grinding okay, so dry grinding a very commonly used techniques is ball mills, so all these like in a metallurgical engineering or in material science, people use this ball mill grinding for making the smaller particle size and then there are jet mills are there and the wet grinding, they have dissocubes.

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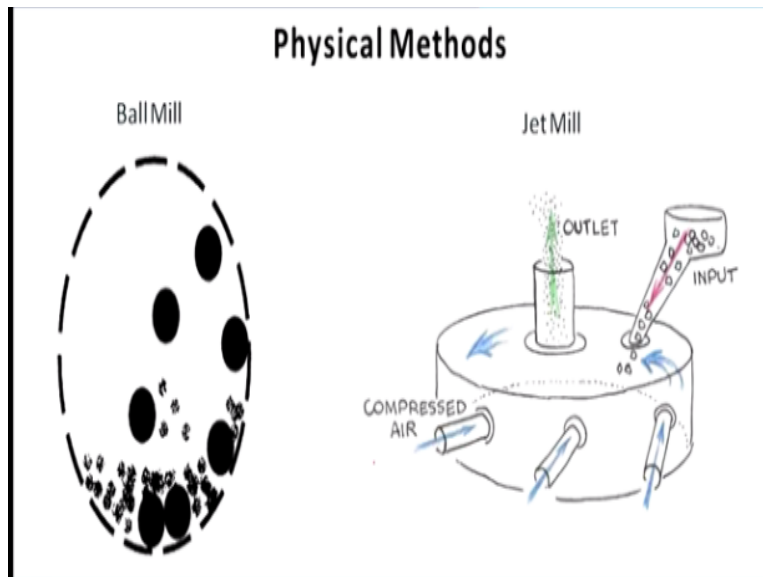
Now, ball mill is very, very like you know simple geometry, you have this kind of like you know spherical crucible and you put first your large particles and then by the mechanical force so, the milling happens and then by that successive collisions and by the force of the grinding, so it becomes smaller and smaller particle and a jet mill like you know, we use a compressed air.

And in the input, we use the larger particle and by pressing the compressed air and by the rotation of the jet mill, the smaller particle comes to the outlet.

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Now, what are the drawbacks of the mechanical synthesis; first of all like you know, I mean whether it is a ball mill or a jet mill, there can be impurities from the mill and then the destruction of the thermally unstable, so once you do these things, some of the particle

becomes like you know, some of the particles may be thermally unstable. The presence of a relatively large number of particles, yes so, the poly dispersity is quite high in this system.

And limited possibility of a control over the size so, in the ball milling process, we cannot control the size to a very, very finite or very, very fine tuning, we cannot do that and their wide size distribution and also their irregular shape, since this kind of like a rough mechanical process so, in addition to the poly dispersity also here we cannot get a very fine tuning over the particle size and you get a larger particle size and their wide distributions.

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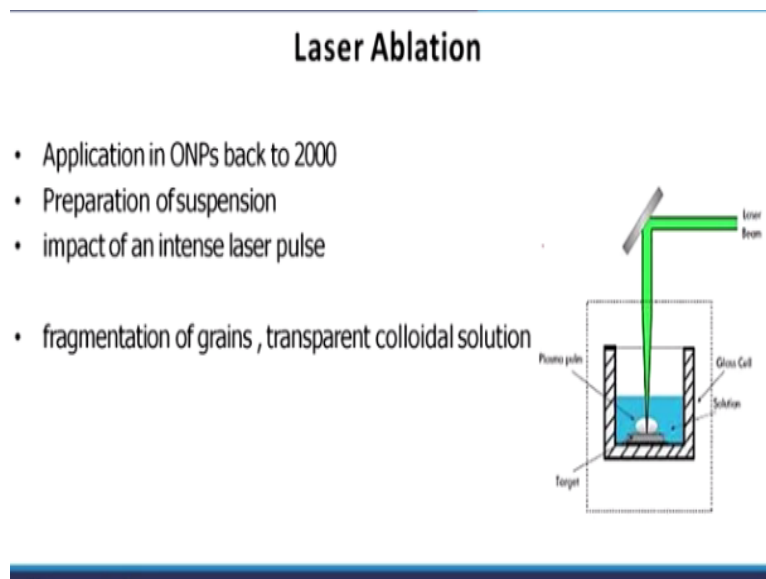
So, these are some of the disadvantages associated with the mechanical grinding now, in laser ablation that the organic nanoparticles fabrication by laser applications that dates back to 2000, so it was quite old method and we use it by preparation in the suspension and impact up an intense laser beam as you can see here like you know, this is the chamber and here is the solution and we have put a glass coil, right.

And then the laser beam is reflected by the mirror which is a pulse laser beam on the solution, okay and the fragmentation of the grains and the transparent colloidal solution we finally obtained in the solution method.

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Laser Ablation

- preparation of stable colloidal solutions in the absence of stabilizers.
- control the size : wavelength, the laser pulse width, and fluence
- increase in the laser-radiation fluence results in a decrease in the nanoparticle size
- **Nanosecond region:** photo thermal
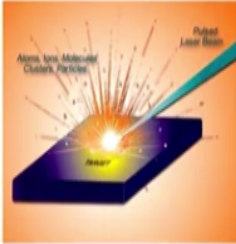- **Femtosecond region:** photo mechanical
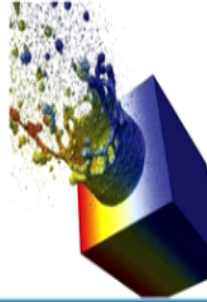
Preparation of the stable colloidal solutions in the absence of the stabilizers, control the size wavelength, the laser pulse width and fluence, increase in the laser radiation fluence results in a decrease in the nanoparticle size and in a nanosecond region, it is a photo thermal process, in a femtosecond region is a photo mechanical process so, the ablation; so since this depends or since it is done by using a pulse laser beam now, you know that like this pulse laser beam can be a nanosecond Nd YAG laser beam or can be a Ti-sapphire femtosecond laser beam.

Now, if you use a nanosecond Nd YAG laser beam, then basically the ablation process is the photo thermal process, so not only the light but the thermal heating that is providing the energy for fabricating this nanoparticle but in femtosecond region, where we are using a femtosecond 800 nanometre laser beam, then in addition there are some thermal effect will always be there but the mechanical; photo mechanical effect that plays the dominant role for fabricating this nanoparticle system.

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Drawbacks of the laser ablation method
- only a small amount of dispersion is formed
- may cause photochemical decomposition

Now, what are the drawbacks of the laser ablation method? First of all only a small amount of dispersion is formed, so since like you know we focused the laser beam on the solution okay, so and that beam diameter depending upon the expansion of the beam or the beam diameter how many particles will be formed that will be dependent right, so we cannot make a lot; large amount of particles by this method.

And may cause photochemical decompositions; what will also happen some of the materials they are like you know, susceptible to the chemical degradation now, once you exposed to the light so what will happen like you know because of the light; light induced degradation can also be prevalent so, this methods is also limited to certain materials, so you cannot use any materials.

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Chemical Methods
- Solvent Replacement ✓
- Anti solvents for Precipitation ✓
- Chemical Reduction in Solution ✓
- Ion Association ✓
- Synthesis of Nanoparticles in Water–Oil Emulsion ✓
- Photochemical Method ✓
- The use of Supercritical Fluids ✓
- Cryochemical Synthesis and Modification of Nanoparticles ✓

We have to make sure that this material is also photo stable okay, the another types of method is the chemical method now, there are several kind of chemical methods are there for example, solvent replacement so, basically you dissolve the your material in one kind of solvent where it dissolves well, then I can put an anti-solvent which has a huge polarity difference with their the parent solvent and the anti-solvent will gradually replace the parent solvent.

Anti-solvent for precipitation; again, like let us say, I take an arbitrary material A and I dissolve it in some kind of organic solvent let us say dimethyl formaldehyde DNF and then I take another solvent which does not mix with DMF okay, for example I can take a like you know chloro benzene or toluene, I know that you know DMF and chloro benzene or toluene has a difference or diethyl ether.

They have a huge difference in the dielectric constant almost around, if you take DMF and diethyl ether, their dielectric constant difference is almost 32, so they have a huge difference in their polarity, so what will happen like you know they will not try to mix with each other so, an one solvent is called the anti-solvent of the other. So, what will happen like you know once you put the anti-solvent, so the material will try to precipitate?

So, one can make another particle by that approach also, chemical reduction in solution that is like in a common technique, some kind of chemical reaction or the reduction can happen, ion association can happen, synthesis of nanoparticle in the water oil immersion. So, now we know that oil and water they do not mix with each other, if you put an oil drop in the water, so what will happen like you know this oil drop will try to minimize their surface energy, right.

So, they will make a micellar structures so, this kind of micellar structures like has also been used for fabricating or getting nanoparticles, there are several methods for making this kind of nanoparticle assembly, we will discuss that in later and then photochemical method; I mean one can also induce the chemical reaction by signing the light that is called photochemical method.

And the use of supercritical fluids so, if someone like you know I mean condense or evaporate or allow the fluids to condense beyond its super critical temperature, so one can

also get a supercritical fluids and then cryochemical synthesis and modification of nanoparticles and also another advantage of the nanoparticle is that you can surface engineer its side groups.

So that means you can put whatever the optical group, whatever the electrical group you want at the surface of the group and that actually, increase the diversity of the application of the nanoparticle, okay.

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Solvent Replacement

- Carotene and PVP were dissolved in chloroform, and then chloroform was evaporated in vacuum to form a solid mixture of β- carotene and PVP. Upon the addition of water to the solid mixture, an aqueous colloidal solution formed, which was called " hydrosol."
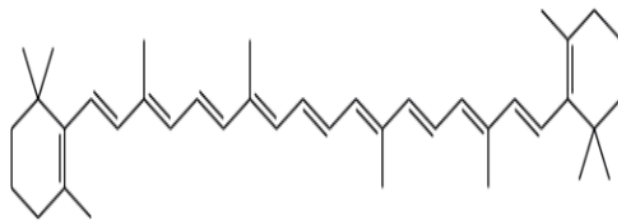
So, first is the solvent replacement; carotene and PVP were dissolved in chloroform and then chloroform was evaporated in vacuum to form a solvent mixture of beta carotene and PVP. So, basically we have taken carotene, okay and PVP, this is a solvent, this 2 has been like you know dissolved in chloroform and chloroform was allowed to dissolve, so the chloroform has a boiling point of 65 degree centigrade.

So, if you leave the chloroform in the ambient atmosphere so, it will slowly like you know evaporate and it will leave the system, so what will happen like you know I mean it will form a solid mixture of beta carotene and PVP, upon the addition of the water to the solid mixture, an aqueous colloidal suspension form which is called the hydrosol okay so, this is a very easy method like you know replacing a solvent and then make a colloidal dispersion of a nanoparticle.

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Benefits	Drawbacks
• mild conditions ✓	• Low production performance ✓
• for thermally unstable compounds ✓	• cannot be used for substances poorly soluble in organic solvents ✓
• relatively simple and accessible ✓	• Very dilute solutions are obtained ✓

Some benefits of there I mean, this process is very easy, I mean it is a very mild condition you use but thermally unstable compound, this method is good and relatively simple and accessible but solve the drawbacks is that low products and performance cannot be used for substance poorly soluble in organic solvent let us say beta carotene is soluble in chloroform but if it does not soluble in chloroform, then you cannot use that to make a dispersant or make a colloidal dispersant using that chloroform and very dilute solutions are obtained.

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Fabrication of Nanoparticles:

• **Mini emulsion**

It is an idealized concept in heterophase polymerization to generate small, homogeneous, and stable droplets of monomer or polymer precursors, which are then transferred by polymer reactions to the final polymer latexes, keeping their particular identity without serious exchange kinetics being involved.

• **Reprecipitaion**

Now, one of the very important technique which have been used for fabricating like you know organic solar cell devices is the mini emulsion technique, so it is an idealised; mini emulsion technique, it is an idealized concept in hetero phase polymerization to generate small homogeneous and stable droplets of monomer or polymer precursors which are then

transferred by the polymer reactions to the final polymer latexed, keeping their particular identity without serious exchange kinetics being involved.

So, this is the same concept like an oil in a water emulsion so, I gave an example like if I put an oil drop in a water what will happen; they will form a micelle, so similarly let us say I take a polymer which is soluble in some kind of organic solvent let us say chloroform, okay and then if I put this chloroform which contains the polymer in the water, so what will happen?

The chloroform and the water will not dissolve with each other, they will not try to mix with each other, so they will try to form; they will try to minimize the surface energy, how they can get a surface energy; by getting minimum surface energy by getting a spherical geometry right, so inside the spherical geometry, the polymer chain they will coiled up so basically, I will have a spherical geometry where the polymer chains has been coiled up inside the spherical geometry.

But the system is not very stable so, it is a dynamic system right, so now in the water if I put some kind of surfactant which is an ambipolar compound that means it has an hydrophobic group and it is an hydrophilic group, so then the surfactant molecule can decorate the polymer chains out siding or like you know decorating from the outside, so that the polymer chains or the chloroform phase stays inside and its hydrophilic gains of the surfactant stays outside in the major solvent.

So, this kind of system is a dynamic micellar like where you can get a nanoparticle of the polymer which have been embedded in a minor phase which have been decorated by a major phase of the water and the second method is that the re-precipitation technique so, the re-precipitation technique here we do not use the like you know I mean surfactant, here we use one solvent which is poorly miscible to the another solvent and we add an excess amount to make a nanoparticle.

Now, today we will discuss about the mini emulsion technique, it is a very, very simple technique even like you know you can do it in your undergraduate lab without requiring for a very sophisticated instrument. Now, this cartoon which I am going to show you now that will explain how simply one can make an organic nanoparticle in a dispersion.

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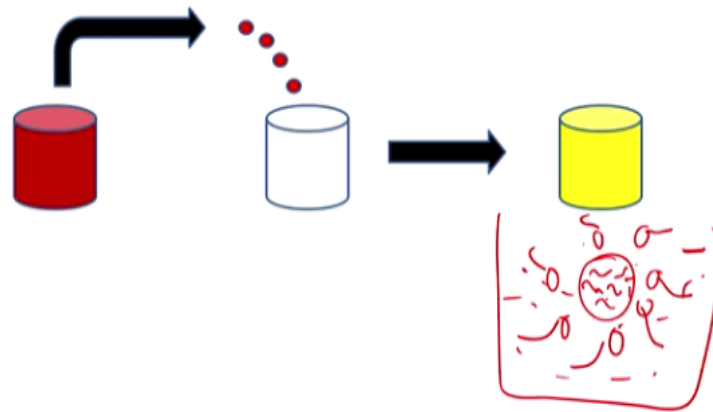
You first take any kind of organic material let us say, you take a polymer okay, P3HT and you dissolve it in some kind of organic solvent so, the red colour is showing a P3HT polymer which is dissolved in an organic solvent then, what you do; you gradually add this polymer solution droplet which is in chloroform to a water solutions and this water content surfactant, so what will happen now?

So, I have a chloroform phase and I have a water phase so, I have a basically an oil phase, I have a water phase, oil and water they will not mix with each other so, this oil phase they contains the polymer chain, once you put this oil phase in this water phase so basically, they will make a colloidal dispersant and how to get like you know how to get rid of this the size effect here, so once you put this chloroform inside this aqueous system so, they will try to minimize their surface area by getting a spherical volume.

Now, if I put an external mechanical force by some form of stirring either it by a bath sonication or by probe sonication, so I can make different size distribution of the particle and that is done here so basically, what we do here; we stir this dispersion by some kind of mechanical force and that mechanical force is provided by sonication either you can use a bath sonication or you can use a probe sonication.

So, what will happen like you know this chloroform in the water they will form a chloroform dispersion and this dispersant contains the polymer chain now, if I heat this dispersion beyond the boiling temperature of the chloroform, so whatever will happen the trap chloroform will detract from the solution so basically, like you know you have this let us

consider the spherical things where the polymer chains have been embedded now in this chloroform phase.

And now, I have this surfactant which is decorated from the outside which stays in a water systems right, this is your water system; is your water system and these surfactant provides the stability, so this is the chloroform phase and this is the water phase, you can call it this as a major phase, this is a minor phase, okay and this polymer chain has been decorated by this surfactant molecule.

Now, if I heat this chloroform or if I heat this dispersion beyond the boiling temperature of the chloroform but less than the boiling temperature of the water, so what will happen; the chloroform will slowly leave the system, leaving the polymer chain in the aqueous water systems, which have been decorated in a micellar structure by the surfactant. So, I have a very constant at volume of geometry which contains this nanoparticle of the polymer chain which has been decoded by the surfactant and all things remain stays in the water.
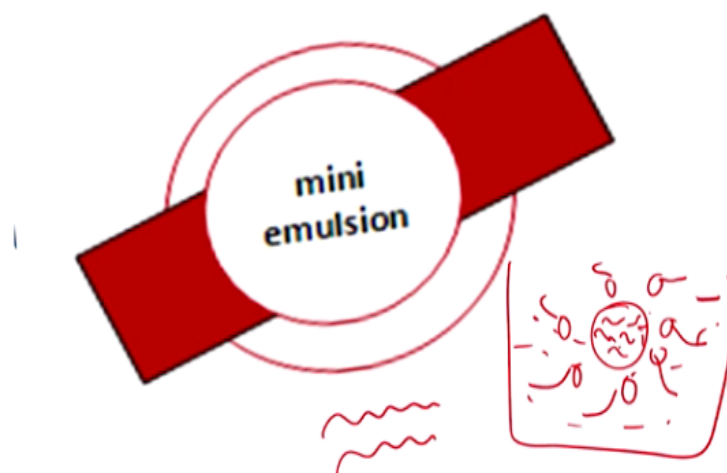
Or I basically, get an aqueous dispersion of the organic polymeric nanoparticles, once you heat this solvent beyond the boiling temperature of the chloroform, you can clearly see a colour change.

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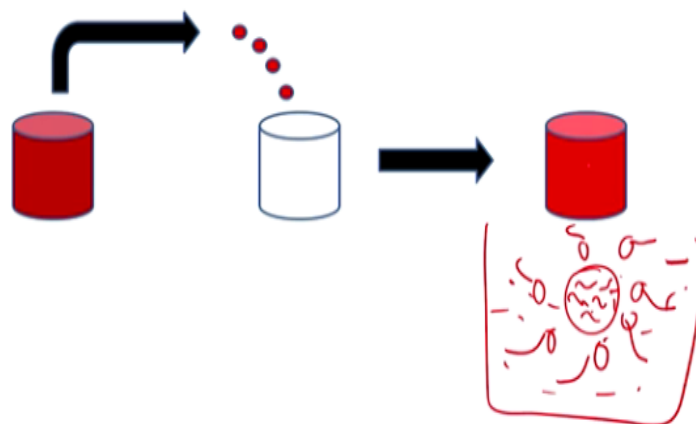
So, the colour of the polymer will change to a deep brown colour like you know nanoparticle dispersion.

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And this method is called the mini emulsion technique, so this is a very, very popularly used techniques which have been used for making solar cell light emitting diode and especially for the drug delivery. Now, I mean since I said that this method is very, very versatile that means one can take any polymer and make nanoparticle out of it so, basically even we can take a biocompatible polymer and we can take a drug molecule.

And we can encapsulate the drug inside this core and at the same time, we can encapsulate some kind of imaging probe inside the core along with the polymer and decorate with the surfactant molecule so, then this nanoparticle assembly they will contain the drug molecule as well as the fluorescent probe, so this had been used as a nano medicine so, in the case of that nano medicine or the drug delivery system this method had also been used very, very extensively.

Now, once we use this method like you can imagine that previously, I have a big, big polymer chain like that now, this polymer chain has been constant in a small volume so before that it was like this and now they have been confined in a small volume, so what is the consequence? Since they are now very close to each other, since they are now very close to each other, the electronic interaction or the electronic talking between each of them has been now increased.

Because now, they are very close to each other so, there is a possibility of the overlap of the electron cloud, so that we called the enhanced electronic interaction and because of that you will see a change in their optical properties so, if we measure the absorbance and the photo

luminescence of this nanoparticle and if we compare the polymeric system, we see a distinct change.

And you can imagine that so, if we do the absorption spectrum or the fluorescence spectrum of this nanoparticle system, we will see a red shifting in the absorption and the emission spectrum because this system now acts like an aggregated system or this system acts like a thin film analogue of a same polymeric bulk system.

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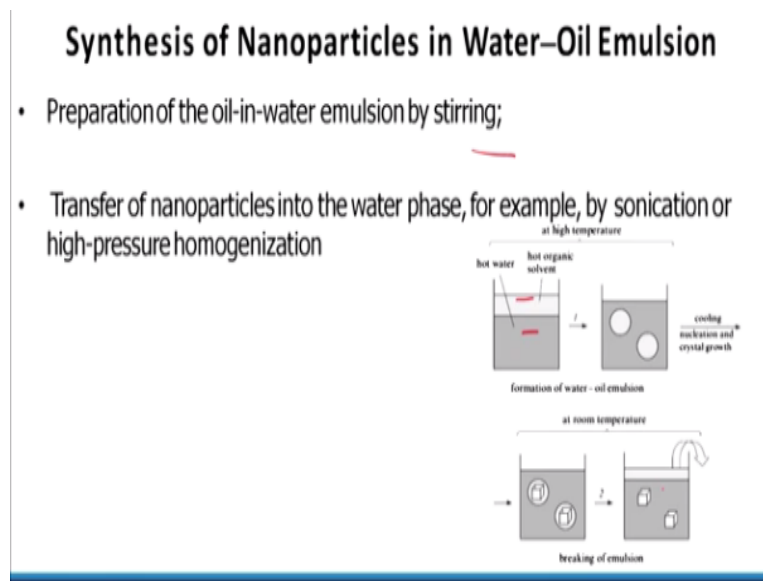
So, the synthesis of the nanoparticle in the water oil emulsion or the mini emulsion technique, it is a very, very commonly used in technique where the preparation of the oil in water emulsion has been used by stirring and that stirring is either can be a bath sonication or by probe sonication. Transfer of nanoparticles into the water phase for example, by sonication or high pressure homogenisations, you look at this figure here the same thing; formation of the water oil emulsion, we have a hot water here.

And then the hot organic solvent so, they are made at 2 distinct phase; oil phase and the water phase now, if you cool this thing what will happen; so there will be a nucleation, so oil phase and water phase they now stays with each other now, if you cool this thing, there will be a nucleation and if we can control the cooling, then you can also control the crystal growth and at room temperature so basically, what will happen if I apply some kind of pressure or if I apply some kind of mechanical pressure, so then you can get a smaller and smaller size of this nanoparticle.

And finally, if we heat it beyond the boiling temperature of this organic solvent, so the surrounding organic solvent thing that will go out and whole these things will come or whole these thing will come in the water, okay that is the emulsion polymerizations or mini emulsion polymerizations.

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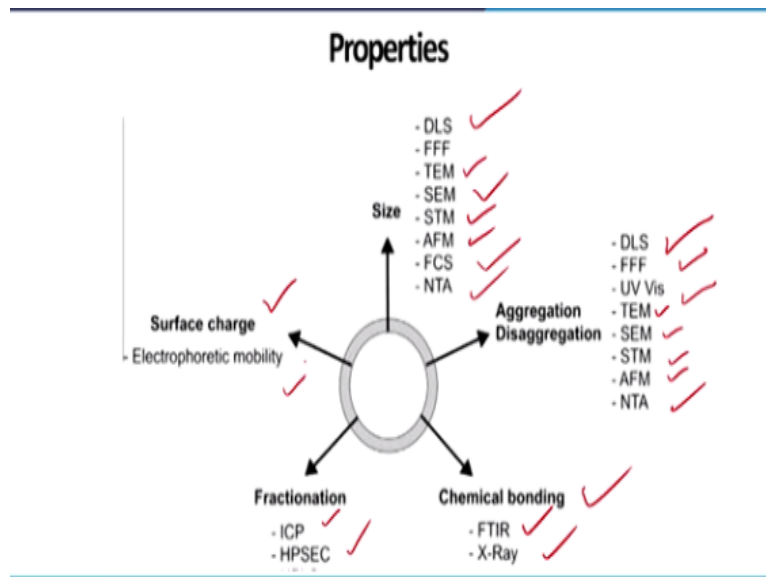
So, what are the properties of these things? So, first of all like you know you see the size, so how you can characterize the properties so, first thing when you make a nanoparticle, first question which comes in our mind what is the size of this nanoparticle. There are several techniques to characterize the nanoparticle size; one commonly used technique is called dynamic light scattering or DLS.

In a DLS technique basically it used Einstein scattering equation, so you know this Brownian motion, so if I put a pollen grain in some suspended water, so what will happen; pollen grains will do random Brownian motion. Similarly, this nanoparticle assembly in this colloidal dispersant they are doing random Brownian motion now, if I sign a laser light on this nanoparticle, so light will be scattered by this nanoparticle.

And we can measure this scattering intensity and from there by using some mathematical equation, we can find out the size distribution of this nanoparticle and that is the principle behind this dynamic light scattering or DLS and then there can be like you know, I mean transmission electron microscopy method which is an imaging method where you allow the your light to pass through you nanoparticle system.

And in the detector, you get an image of the nanoparticle, then there are scanning electron microscopy method, is the another imaging technique which looks for the backscatter electron and then there can be scanning tunneling microscope, again like you know if you have a very, very thin sample and the very, very thin nanoparticle layers, so you can use scanning tunneling microscope to get a very nice image of the nanoparticle assembly.

Then one can get a surface morphology, topography, surface roughness by doing atomic force microscopy again, here you use a laser beam like you know we scan the sample surface and whatever the laser light which have been deflected from the top surface that have been collected by detector and from there, we can find out by doing some analysis what is the topography of this surface.

Then, there are these FCS methods, then there are NTA methods, there are several methods like you know to characterize the size distribution of the nanoparticle. Then, to look for the chemical bonding like you know what kind of chemical bonding exist in here, so one can do either a FTIR or one can do an X-ray spectroscopy, okay. Now to know that aggregation or disaggregation or to know that whether this is a real dispersion or whether it is a suspension or whether it is a solution to know that, we can again do the dynamic light scattering; DLS to measure the polydispersity index.

We can do FFF, we can do UV Vis spectroscopy and then some imaging technique like TEM, SEM, STM, AFM as well as NTA, it is another a DLS based techniques. To know the fractionations that means how many of them has been fractionised to what percentage we can get ICP or we can get HPSEC, to measure the surface charge on this nanoparticle we can do an electrophoretic mobility, we can measure the zeta potential or the surface charge again by this DLS method.

So, these are all like you know characters and techniques of the nanoparticle, one needs to know their size, one needs to know their size distribution, one needs to know their aggregation, one needs to know their chemical bonding, one needs to know their surface charge etc., and these are the experimental techniques one can find out that.

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Detection and characterization

- Sample Preparation (Filteration, Centrifugation)

- Imaging (TEM, SEM, AFM)

- Separation (HPLC)

- Characterization

Now, the detection and characterization they depends upon the sample preparation like filtration and centrifugation, imaging technique like TEM, SEM AFM, separation; one can do the separation by HPLC technique and then finally, some characterization like optical characterization, electrical characterization etc.

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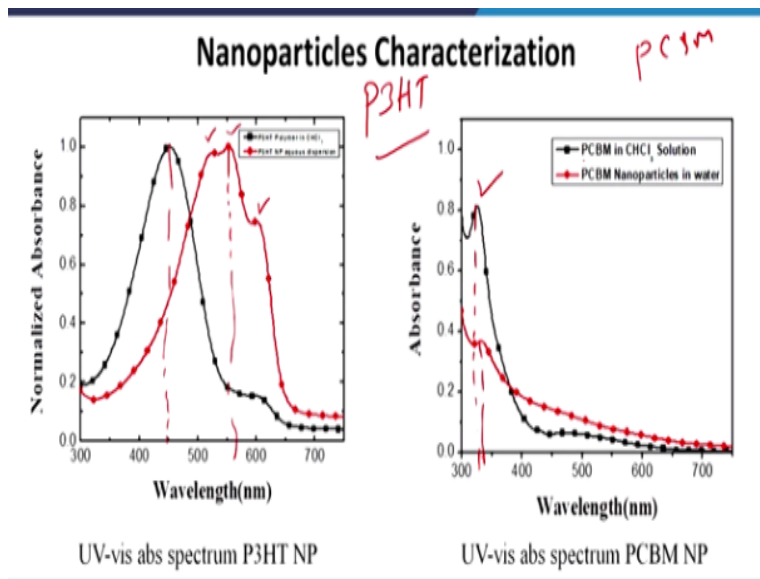
Now, let us look at first the optical characterization for a very common example for example, we have taken a polymer called P3HT okay, this is a polymer which have been commonly used for making organic solar cell, right and this polymer organics, this P3HT has been dissolved in chloroform, okay and then we have taken an absorption spectrum of this polymer.

So, you see that y axis is the normalized absorptions, normalized absorbance and the x axis is your wavelength so, for a polymer you can see this black curve, this is absorption spectrum but when you make a nanoparticle in an aqueous dispersion, you get this red colour graph as its absorption spectrum. So, what is the difference between them 2, so there is a peak shifting happens.

So, the maximum absorbance polymer happens around this 450 nanometer but the maximum absorption happen here around 550 nanometers, so there is a huge big shift happen and also you see that nature or the dynamics or the nature of the peak distribution is different in these 2 case, here you see only one peak but here you see one peak here, one peak here, there is a solar here.

And also I mean, the way this has been distributed here it is also different and very interestingly, if you take this polymer and make a thin film of the polymer and heat that film at 120 degree Celsius and take an absorption spectrum, that absorption spectrum will matches with this nanoparticle across dispersion. So, I repeat that if I take this polymer in some kind of organic solvent like chloroform and if you make a thin film of the polymer.

And if you record the absorption spectrum that will mimic the absorption spectrum of this nanoparticle, so what does it mean that this nanoparticle dispersant absorption spectrum resembles like a thin film absorption spectrum and that is kind of expected because once you have a nanoparticle dispersion although, it is in a colloidal suspension, it resembles or mimics a solid state system.

Now, everything in a close vicinity now, in a thin film what will happen like you know you actually arrange the random motion of the polymer chain in a solvent, so that is why the interaction between the polymer chain enhance there, so similarly like you know once you make a nanoparticle dispersion, so what will happen now the distance between that two polymeric chain has been enhanced.

Because of that the interaction between the chain, chain has been increased that is why although a polymeric nanoparticle in a dispersant system it resembles the same spectrum like a polymer thin film spectrum and if we take even a small molecule like PCBM, if you take

PCBM which is a small molecule you observe the similar trend, this is the PCBM small molecule absorption spectrum in chloroform.

And the red colour graph is the nanoparticle dispersion in the water, so you see that the peak shifting happened in the case of the nanoparticle things, so that means this nanoparticle dispersion can be straightforwardly used for fabricating devices because for making devices, you do not make the devices with the solution basically, what you take a polymer in chloroform we take PCBM in chloroform then we mix them together.

And from the mixture, you make a film, then you heat the film and then it deposits the electrode on the two different side to make the devices but here the dispersion itself mimic the same properties of the film, so that means if we mix these 2 dispersant together and then if we disperse them or if we self-assemble them on ITO substrate and then if we deposit the electrode basically, we will have a device and that was the purpose behind doing this organic nanoparticles things in the solar cell.

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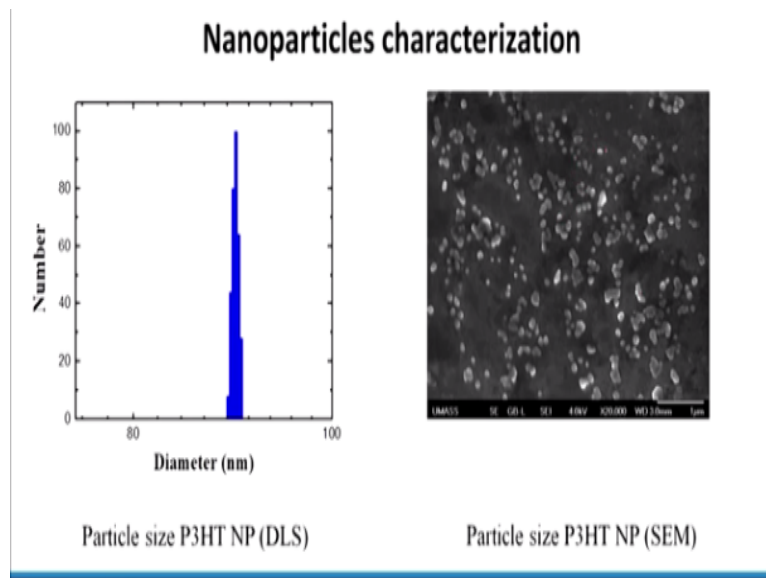
Now, to go one step further to characterize their size, so we said that this nanoparticle size distribution can be calculated or can be determined by dynamic light scattering, so this is a dynamic light scattering data so, in the y axis you have the number and the x axis you have the diameter and you see that from the histogram, this particle size is kind of mono dispersed and they are somewhere around 90 nanometer in size.

And the same features one can pick up by doing some SEM analysis here, so for example here we are showing some scanning electron microscope and you can see that this P3HT nanoparticle dispersion although, there are some aggregates there and that is because of the like you know some surfactants is there and this is possible that some aggregation happens.

But many of the times, we can see that very isolated, very nice nanoparticle distribution in the SEM image.

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Tapping mode AFM image of an annealed P3HT NP:PCBM NP film

IPCE
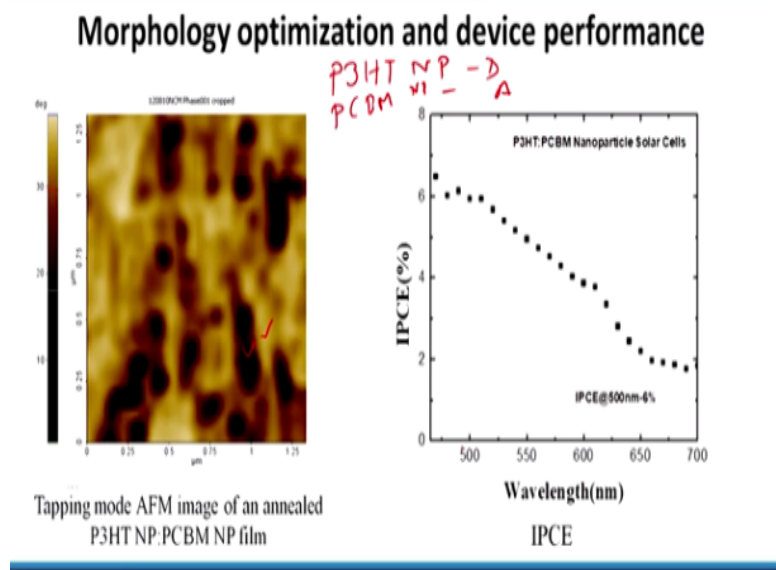
Then, the next step is that we have these nanoparticles; donor nanoparticle and acceptor nanoparticle, we have this P3HT, nanoparticle and we have made the PCBM nanoparticle, one is the donor, another is the acceptor and both of them in the water okay, so now we mix both of them so, in one of the beaker we have the donor nanoparticle, in another beaker we have acceptor nanoparticle.

So, we mix both of them and from the mixture, we made a film, so we coat the film with from the mixture and then we allowed the mixture to dry or we can also heat the mixture a little bit like 100 or 120 degree Celsius okay. So, what will happen? So, now we have the spherical nanoparticles inside the dispersion now, once we make a thin film out of that they will self-assembly according to their pre energy distribution.

So, we have picked up the self-assembly distribution by doing an AFM image which you have shown here and if you see this image, you can see 2 different colours; one is this very dark colour; black colour and other is this yellowish colour okay, so this dark colour; this

dark black colour that is the donor phase that is the donor P3HT nanoparticle phase and this yellowish colour which is the acceptor PCBM nanoparticle phase.

So, you remember that in the previous time when we talked about P3HT nanoparticle and PCBM, when you talk about the polymer P3HT and acceptor PCBM, we said that we need a phase separated by continuous percolated network and we have seen in one of the diagram that there is a donor phase, acceptor phase; donor phase acceptor phase, so that is a by continuous percolated network and phase separated.

So phase separated by continuous percolated network and we exactly observed the same thing here in nanoparticle assembly, you see there is a donor phase acceptor phase, donor phase acceptor phase okay so, the tapping mode AFM image of an annealed P3HT, PCBM nanoparticle films also show the same kind of topography as a bulk system, so that means this kind of system provides a phase separated by continuous percolated network.

That means, it can be used for making devices, let us proceed to make some devices and that is what we have done so, what we have done like you know we have self-assemble this P3HT and PCBM nanoparticle in one mono layer and the one mono layer device shows an efficiency of 6% at the peak absorption wavelength. This graph is called the internal photo current conversion efficiency.

This is the number of electron generated per incident absorbed photon, so y axis is my IPCE percentage and x axis is my wavelength, so you can see this IPCE spectrum or what is the number of electrons has been generated per incident photon from there, we can find out that the peak absorption wavelength, the efficiency is 6%, so that is a tremendous improvement over the bulk system, this is for a one mono layer.

So that means if we make a multi stack or multi-layer, so there is a room for efficiency enhancement or we can make an efficiency more than 8% by suitably optimizing this thing and by suitably changing some of the protocol. Well, there are a lot of disadvantages or there are lot of things has to be optimized for example, like you know we are using a surfactant right, so surfactant is like an insulator.

And we try our best to use the surfactant as much as possible, we use like molecular cut off filter so, the purpose of using molecular weight cut off filter is that to eliminate certain molecular weight and to allow certain molecular weight to stay in the system. So, let us say for example, if the surfactant has a molecular weight of 20,000 kilo Dalton so, if I use like a molecular weight cut off filter which cuts up 20 kilo Dalton and beyond that.

So that means, only so it will remove the surfactant from the dispersal and allows the polymer of the small molecule provided they have a molecular weight lesser than that inside the system so, we can choose the molecular weight cut off filter and we can do the centrifuges and again and again and washing, so that we can make sure that whatever the loosely bound surfactant removes from the system but still there will be some surfactant in the system and that acts like a trap state or as like a defect state.

So that is one of the disadvantage in this process now, just like a bulk structure assembly here the nano structure assembly can also be generated in 2 different ways.

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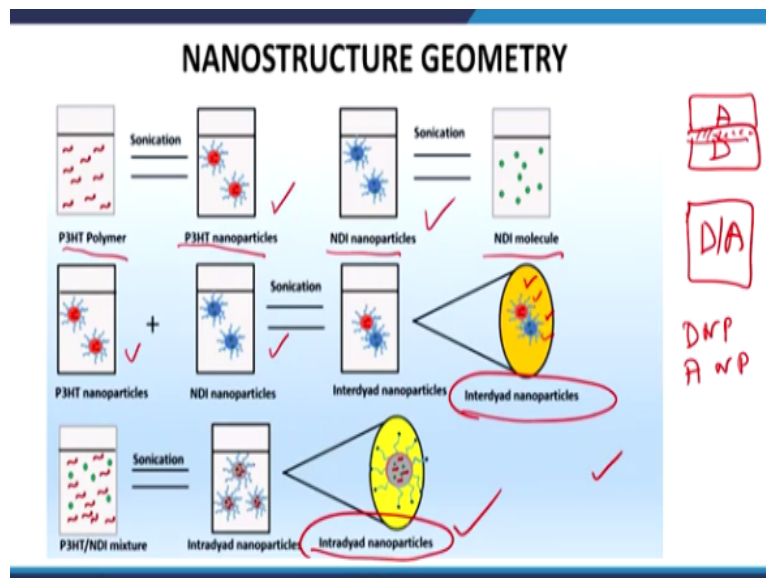
So, you remember when we talked about the organic solar cell, we said that if this is a donor system and this is the acceptor system, we can assemble them by layer by layer or in a single layer, we can mix donor and acceptor and we can mix them and mix a combine thin film out of that. We can do the similar thing here also, we can take a donor nanoparticle, we can take an acceptor nanoparticle and we can make a layer by layer film or we can mix them together.

And from mixture, we can make a mixture film in that that is have been done here, we started here from the P3HT polymer and we made a nanoparticle of the P3HT and we started with another small molecule called NDI; naphthalene dimide, from there we made a nanoparticle; NDI nanoparticle so, this is your donor nanoparticle, this is your acceptor particle.

Now, both this donor and acceptor nanoparticle they are physically mixed with each other to make this kind of assembly. Now, one thing has been done here when we make the donor nanoparticle, we use their negatively charged surfactant, so that means the surface charge of this donor nanoparticle is negative and when we make this acceptor nanoparticle, we make positively charged surfactant.

So that means the surface charge of the nanoparticle is positive okay, so this is negatively charged, this is positively charged now, what will happen if we mix them together? They will electrostatically bind with each other and that is what has been shown here so, if you take a magnified view of this assembly, you see that this donor assembly and the acceptor assembly they are bound by electrostatic attractions, okay.

And we call them as an interdyad nanoparticles, on the other hand what we can do; we can mix the polymer and the small molecule in the same time together in an organic solvent and from the mixture we can make a nanoparticle, so a magnified view of this nanoparticle source that here the donor phase and the acceptor phase now stays in the same matrix but here you see that donor phase is different, acceptor phase is different.

We have attached them by physical interaction, by electrostatic interaction but here both the donor and acceptor phase this taste together inside this assembly and that is called intradyad nanoparticle, so this is basically a bulk hetero junction analogue and this is basically a layer by layer analogue. So, now we wanted to see that whether this is better or whether this is better.

Now, our bulk polymer chemistry that teaches us that the bulk hetero junction solar cell is better than layer by layer and what was the reason behind that; see if I take a donor and acceptor because of the small diffusion length of the donor of the charge carrier, so only those charge carrier which is at the interface which is a close proximity to the interface, they can contribute to the charge conduction.

So, to overcome that, we mix them together to make a phase separated by continuous percolated network. Similarly, if here like you know we electrostatically attach them together, the distance between the donor and the acceptor is higher than if we mix them together where the probability of seeing the acceptor by the donor is much higher than the interdyad case.
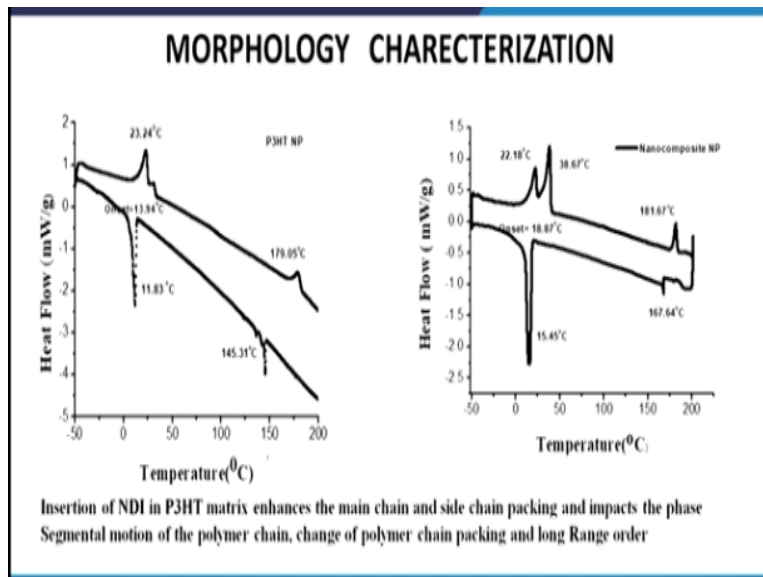
So, the consequence is that not only the morphology by the self-assembly but the charge transport dynamics will be completely different in here than here and by doing some sophisticated experiment just like transient PL spectroscopy, we have found that or by doing some like you know time correlated single photon counting experiment TCS, PCE which is basically nothing but a transient spectroscopy to look at the decay of the charge carrier what we have found that 2 different kind of charge conduction mechanism works in these 2 different cases.

In one of these cases, the electron transfer in other case, the energy transfer, one of the case you call it as a fluorescence resonance energy transfer or FRET, and other case you call as a dexter electron transfer. In the case of the solar cell like you know for a bulk polymer case, if you take a P3HT polymer and if you gradually add the acceptor molecule, you will see that the fluorescence from the P3HT polymer will be quenched.

So that means, there is an electron transfer from the luma of the P3HT to the luma of the PCBM, so similarly the similar kind of phenomena has obtained in the case of intradyad nanoparticle, so here because of the close proximity of the donor and acceptor, it is possible that the electron can transfer from that donor lumo level to the acceptor lumo level but whereas in this case, which is physically attached with each other, there is not an electron transfer mechanism is possible but an energy transfer mechanism is possible.

So, what it teaches us that this kind of system is more efficient for fabricating solar cell device than comparison to these kinds of devices. So, when we proceed to do some more advantage or more advanced characteristic or more advanced like in experimental techniques to characterize the system, we found our this speculation or this like you know observation.

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MORPHOLOGY CHARECTERIZATION

Insertion of NDI in P3HT matrix enhances the main chain and side chain packing and impacts the phase Segmental motion of the polymer chain, change of polymer chain packing and long Range order

For example, here we are showing the differential scanning calorimetry or DSC data of this nanoparticle assembly and this DSC data which actually plot the heat flow versus temperature, it shows that like different kind of packing or different kind of long range order exists in the intradyad system as well as in interdyad system. So, in intradyad and interdyad system, 2 different kind of long range order and packing exists.
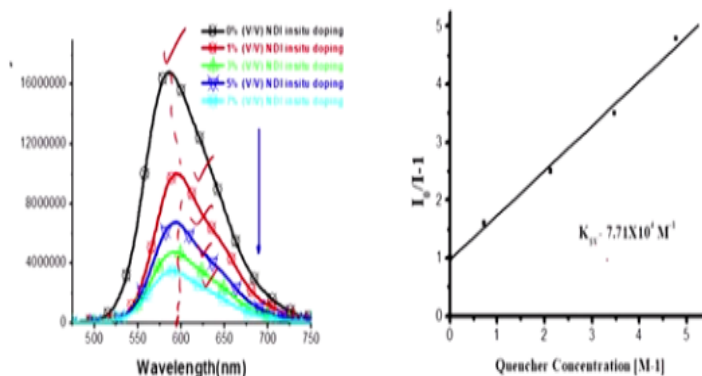
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OPTICAL CHARACTERIZATION
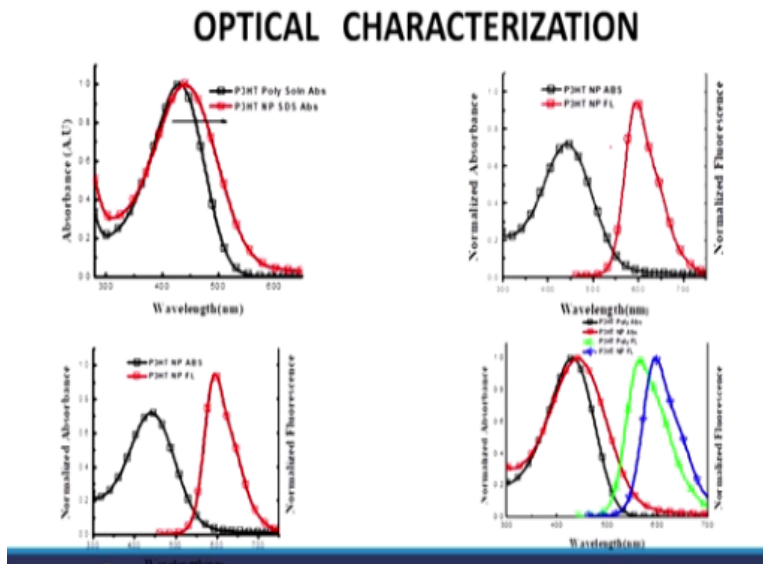
So, for the optical characterisations, like this polymer and for the small molecule also prove us the same phenomena.

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STEADY STAE PHOTOPHYSICS

Now, whenever we do the fluorescence experiment with this nanoparticle system, we observe the similar phenomena like in the case of a bulk polymer counterpart in an intradyad case. So, this is the fluorescence from the P3HT nanoparticle okay, when we do not have any acceptor doping but if we gradually increase the acceptor doping, nanoparticle fluorescence gradually decreased.

So, if I take the intensity decrease of the fluorescence, if I plot that on the y axis and if I plot in the x axis, the acceptor concentration we get the so called Stern–Volmer plot and the slope of the Stern–Volmer plot is very, very high which tells that the systems will be an efficient system for fabricating the device, not only that the energetics; the positions of the homo and lumo energy level also matches in this nanoparticle assembly.

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ENERGETICS

Electron Transfer Mechanism
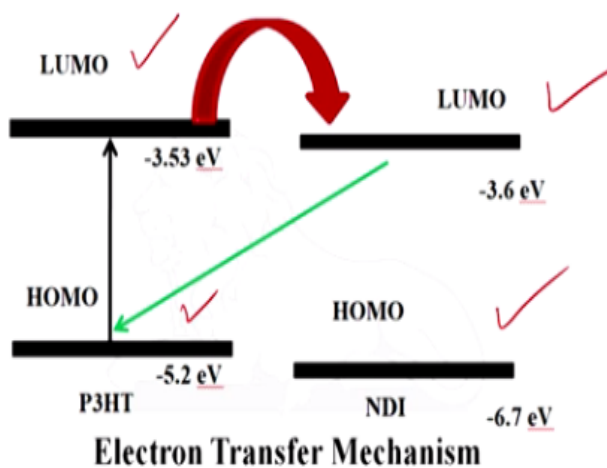
You take a lumo energy level of the P3HT, you take a home energy level of the P3HT, you take a lumo energy level of the NDI and take a home energy level of the NDI, so basically their energy is such that the electron can be injected from the lumo of the P3HT to the lumo of the NDI, so that means the system is also good for fabricating device. So, guided by this idea like you know what we have learnt that this kind of nanoparticle assembly satisfies all the basic criterion for fabricating a device.

The first criterion was that like to fabricate to maintain the energetics or the positions of the homo lumo energy level that is maintained in here, the second criterion was that in the presence of the acceptor, the donor level fluorescence will be quenched and that also we have observed there, if we gradually increase the concentration of the small molecule NDI, so we have observed the P3HT nanoparticle fluorescence is reduced.

And not only that what you also have observed that comparison between the interdyad and intradyad case, in the case of the intradyad, where we have both the donor and the acceptor nanoparticle together in the same system, the charge carrier dynamics is completely different than in the interdyad case, where you have a physical mixture. So, in the case of the intradyad, we see a dexter electron transfer whether in the case of the interdyad case, we have seen that fluorescence resonance energy transfer.

Now, we need an electron transfer for a sufficient donor acceptor pair or for an effective donor acceptor pair to have exists for making in a optoelectronics devices, so that kind of criteria is also satisfied in this geometry, so that is why this kind of systems will be very, very useful for fabricating organic nanoparticle solar cell where you can circumvent the fundamental problem of the exciton diffusion length in a bulk polymer system.

So, you see that even by the discovery of the best low band gap polymer, the efficiency of an organic polymer solar cell is limited to 8 to 10% but this kind of approach can easily increase the efficiency of solar cell beyond 15% and now there are lot of research is on-going where people have been trying to use the low band gap polymer for fabricating this nanoparticle and different kind of like geometry, different kind of self-assembly they are taking out for fabricating the devices.

And by this continuous process, we are hopeful that very soon the efficiency of this organic nanoparticle solar cell will reach to the efficiency of a silicon solar cell. So, in today's class we have learned that what are the different methods or the procedures of fabricating the organic nanoparticles, how to characterize the organic nanoparticles by different experimental methods and while to fabricate a device, whatever the cross tactics of the organic nanoparticle we should keep in mind.

And how a particular class of organic nanoparticle assembly is advantageous to use over the other and we have also seen that this kind of nanoparticle assembly satisfies all the criteria for fabricating an efficient solar cell device and we are hopeful that this kind of organic nanoparticle device very soon we level to beat the efficiency of a silicon solar cell. Thank you so much.