Nano structured Materials-Synthesis, Properties, Self Assembly and Applications
Prof. Ashok K Ganguli
Department of Chemistry
Indian Institute of Technology, Delhi

Module - 4
Lecture - 38
Optical Properties – II

Welcome back to this course on nano structured materials, we are in the module 4 and we are discussing optical properties of nano materials. This is the lecture number 10 of module 4 and we have 12 lectures in total in this model, this is going to be the second lecture on optical properties of nano structured materials. So, in the previous lecture on optical properties we discussed some of the basics of what happens, when a particle size decreases, what happens to its optical properties, what happen to it is color and why those changes in color take place.

Specifically, we discussed about the nature of bands and the different discrete levels which can be incorporated within the energy gap by impurities, which can cause different the low energy absorption, which can cause a two photon absorption and emission. Then the change in the shape of the density of states versus energy plots how you can continuously change the density of states and energy where in a bulk solid, which you cannot in say a nano well or a nano wire or a nano dot that is a quantum dot.

So, what happens when you change a bulk particle to a nano sized particle and how it changes with the dimensionality; whether you lower the dimension to nano size along only one dimension or two dimension or all three dimensions will give rise to different changes in the density of states. Versus energy and that will bring rise to changes in the a absorption of energy and the excitation of an electron from a valence band to a conduction band.

And what are the different types of properties which you can expect in a semiconductor like cadmium selenide, which we saw how it gave different types of colors in colloidal solutions of cadmium selenide having the same material, but having different sized particles. That was one example and then we looked at different other types of optical transitions, the fluorescence and phosphorescence in these systems. And what happens when the size decreases to the nano dimension, so let us continue on that and on the second lecture.

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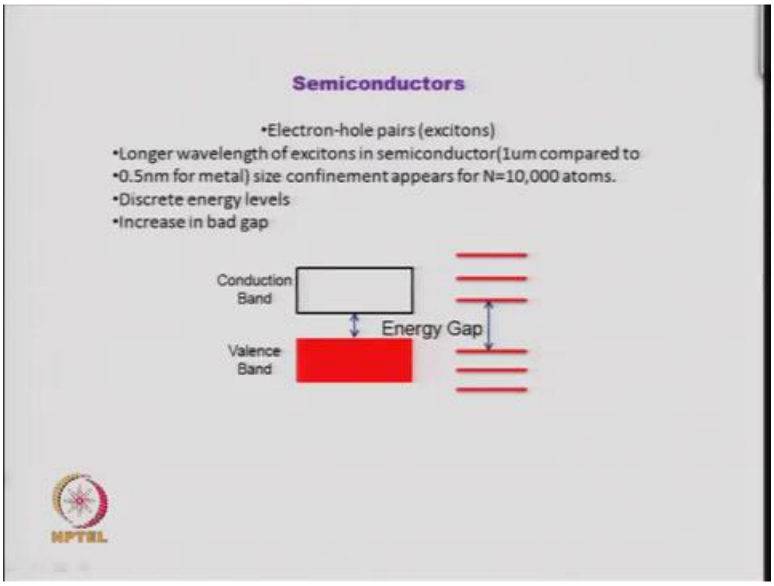

So, in semiconductors you have a conduction band and you have a valence band as discussed earlier and you have an energy gap and when you make small size semiconductor particles, then you have more discretized energy levels. Instead of a band, where you have a continuum of a available energy states, now you have discrete energy states. Of course, the band gap is there and the band gap is enhanced this is much larger than the band gap in a bulk semiconductor.

So, that band gap also increases along with discretization of the energy states. So, this effect is also called quantum confinement, because you are confining the electrons and because the energy gap is becoming higher and electron cannot be excited easily unless you give higher energy. So, increase in the band gap and confinement appears for particles with around 10000 atoms and that maybe the size of like 0.5 nanometer particle and when compared to a bulk particle which is around 1 micron.

Now, when you have an electron, which moves from the ground state, which is the valence band to the excited state, which is the connection band. So, you have a hole left behind and that hole is positively charged, because it is the absence of the electron which went into the conduction band, now this pair of electron and hole, together because in this semiconductor.

Now, you have an electron in the conduction band and a hole in the valence band together, these two particles will be called an electron hole there and it is also called as an exciton. So, what is an exciton, an exciton is an electron and whole pair and that has been created, because the particle has absorbed energy which has been given and that energy is larger than the band gap. And so an electron is excited and it leaves behind a whole in the balance band and together the electron and hole pair is called an exciton. So, this is the basics of absorption of radiation creating excitons.

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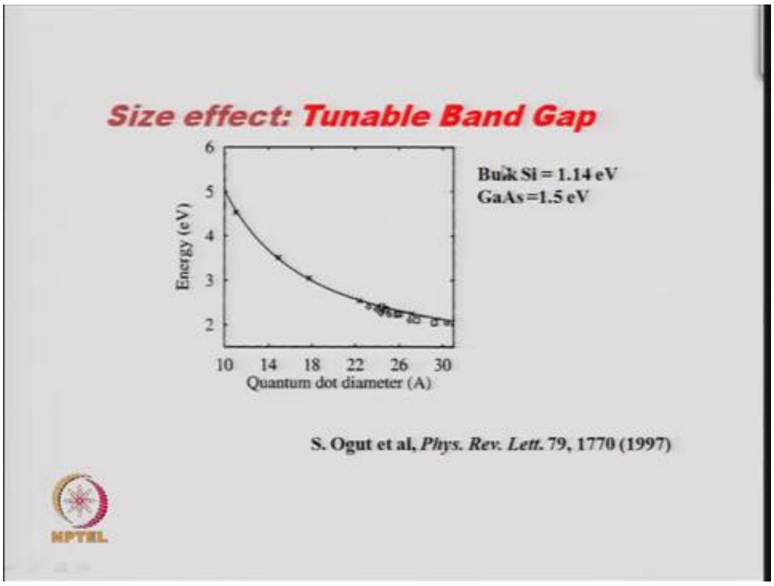

Now, what we discussed earlier also what happens as the size decreases, as a size decreases the band gap changes. So, we can tune the band gap it is called the tunable band gap in semiconductors and this has been plotted for several semiconductors. And for bulk silicon for example, you have a value of 1.14 electron volts and for bulk gallium arsenide, you have a value of 1.5 electron volt, now these values can change depending on the size of the nano particle.

So, here you have the some quantum dot which has a band gap of around 5 electron volts, when it is very small around say 10 angstroms or 0.1 a nanometer and then it is like 30 angstroms. So, 30 angstroms, 1 angstrom is like 0.1 nanometers, so 30 angstrom is like 3 nanometers, so if you do this study then you can see the band gap varying from 5 e V to around 2 e V. When you are changing the size of the quantum dot, the diameter of the quantum dot is changing from say 1 nanometer, because 10 angstroms is 1 nanometer and this is in angstroms. So, 1 nanometer particle has a band gap of 5 electron volts and 3 nanometer particle as a band gap of around 2. So, you can vary a considerable amount say around 3 electron volts in this particular semiconductor a whereby just varying the size of the diameter of the particle.

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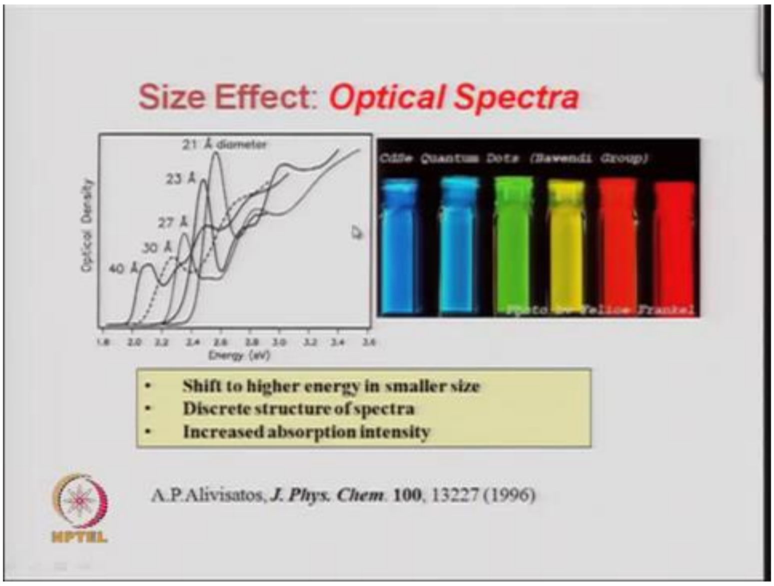

Now, this change in the diameter and the band gap reflects it into in its color, so if you plot the optical density with a energy for particles of the same kind. So, you have cadmium selenide particles, these are quantum dots and these are having different diameters. So, you have 21 angstrom, so it has an absorption at around 2.6 electron volts, when you go to hire particle size say 40 angstrom which is 4 nanometers, your band gap is now close to 2.01 or 2.02 electron volts.

So, from 2.02 electron volts at 4 nanometers which is a larger particle, if you decrease the size of the particle to around a 21 nanometer, the band gap has increased to around 2.56 electron volts and this shift in the band gap can show the variation in colors. So, a large particle will have a smaller band gap and will have a color which is towards the red.

If it absorbs and this shift to higher energy in as the size of the particle become smaller, we are shifting to a higher energy, this is typical of size effects, quantum size effects and also it shows you the discrete structure of the spectra. In addition, you also see that the intensity of the absorption, so it becomes more intense, more sharp and more intense as the size of the particle is decreasing. So, if when it is 21 angstrom is much sharper and when it is 40 angstroms, it is little broader.

So, not only the wavelength or the energy shifting, but the intensity also changes as you change the size of the quantum dots of the size of the semiconductor and this can be a cadmium selenide, it can be studied in other quantum dots as well. Now, this so far we were looking at semiconductors which have a valence band and which have a conduction band and there is a band gap and you are changing the band gap of the semiconductor by changing the size up the particle.

So, that is about semiconductors in metals what happens because in metals you do not have a band gap. So, the color of a metal nano particle normal bulk metals are normally black in color or very shiny and but when you make nano sized metal particles colloidal solutions you will see colored solutions even for metal particles. So, but the absorption phenomena is not the same as in semiconducting nano particles, because metals do not have a bad gap, whereas semiconductors have a bang gap, so what is this color in metals due to.

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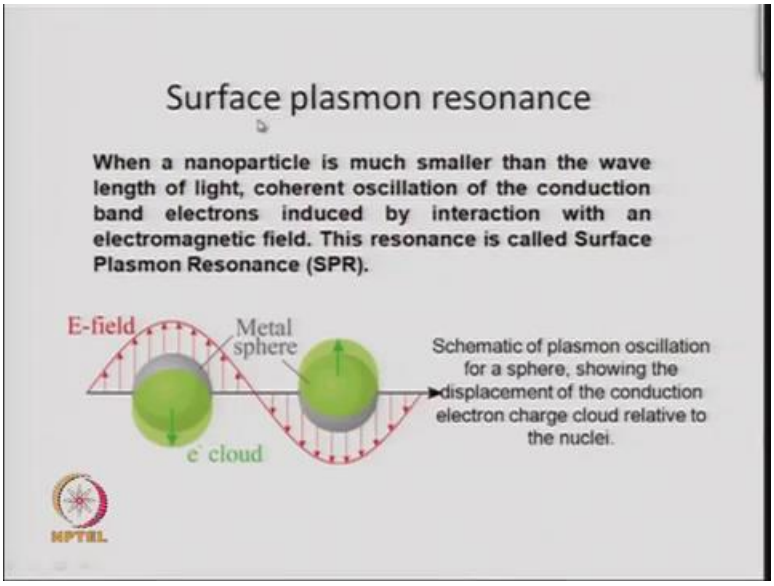

So, if you look at metal nano particles there is this property of surface plasmon resonance which occurs especially, if your nana particles are metals. So, in this what happens when, if you apply an electromagnetic field, the electromagnetic feild is like a light with also electromagnetic field, so whenever you shine light, there is an electromagnetic field. And, if that a nanometer sized particle, the size is smaller than the wavelength of the light which you are passing.

In that case there can be an oscillation of the conduction electrons because, in metals you have conduction electrons the electrons are present in the conduction band. So, these electrons can have coherent oscillations, if the size of the particle is much smaller than the wavelength of the light which you are passing. So, if the wavelength of the electromagnetic radiation which we are light here is much smaller than the size of the metal particle.

Then, the conduction electrons of the metal article can oscillate coherently; that means, in phase with the conduction band electrons and this is basically due to the interaction with the electromagnetic field. And, this is called surface Plasmon resonance, Plasmon is basically quantized oscillations of a conducting electrons or their conduction band. So, all the metals will have conduction electrons and if they oscillate as light false on it then you will have surface Plasmon resonance.

So, this is the schematics where you have this metal particle and that this is the electric field and this shows the oscillations and this electron cloud. So, this the electron cloud can oscillate along with the electromagnetic radiation which is light, if the particle size is much smaller than the wavelength of the incoming light beam. So, wavelength up the incoming light beam is of this length, because you have one crest and one trough makes the wavelength and you see the particle is much smaller than the wavelength of the light coming.

Suppose, the particle had been this big and this is the wavelength, then you will not see this Surface Plasmon Resonance. So, this you can see when the size of the particle is much smaller than the wavelength the light and then you will see these oscillations of the conduction band electrons and that is called the Plasmon’s.

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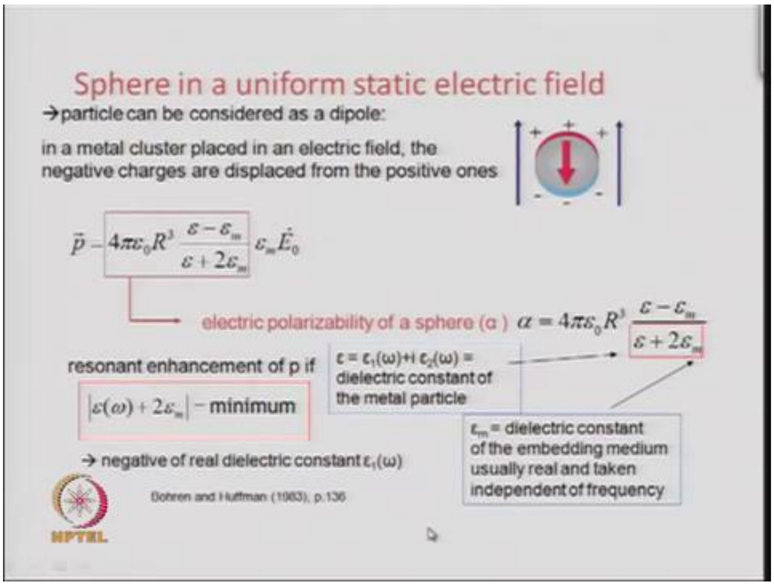

Now, when you have this kind of particle, which you considered as a dipole, so can have in a dipole a positive and negative a arrangement creating a net dipole moment. If there is a shift in the electron density, then you can write the equalization for the dipole moment as a function of the dialectic constant and the applied electric field. So, if the metal cluster, that is placed in an electric field, because the electromagnetic radiation or light is associated with the oscillating electric field.

It also has oscillating magnetic field, the light has a oscillating electric field, so; that means, whenever you have light, you have an electric field and the metal particles are now in the electric field. So, the negative charges will be displaced from the positive ones, in the presence of an electromagnetic field and then you can write this equation, where this is a electric polarizability. This whole quantity, where Epsilon is the dialectic constant of the particle and Epsilon m is the dialectic constant of the medium.

So, and E naught is that plied electric field from the electromagnetic radiation, so if this entire term is the electric polarizability alpha. Then, you can write alpha is equal to this and then you see in that if you want to make alpha very large, then you need this to be very small. Now, this can be very small or you can make this whole thing go to infinity, when this goes to 0, now here this will go to 0.

When, Epsilon plus 2 Epsilon m becomes equal to 0 and that can happen only when Epsilon is equal to negative of 2, twice of the Epsilon of the medium. So, that is what is it in a different way that if the magnitude of this term which is in the denominator becomes a minimum, then this will become very high. So, you want to know when alpha will be high, that is when will the electric polarizability be very high, if this is high then this will be high.

So, now here there are two things, one is the electric, the dielectric constant of the particle and the dialectic constant of the medium and these two have to be taken into consideration. And, depending on the numbers you can find out when this will become huge value and that is when make call surface Plasmon resonance to occur or SPR to occur, when this value will become a very high and that will happen.

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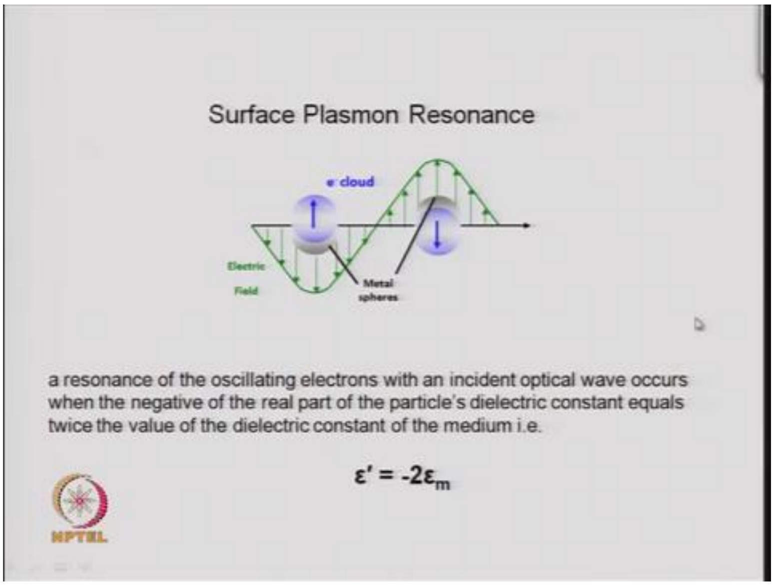

So, you will have surface Plasmon resonance, when Epsilon prime becomes equal to negative of 2 Epsilon m that is because of this equation that this is in that denominator and you want to make this whole term very large. So, that will happen only when Epsilon plus twice Epsilon m, becomes equal to 0 and this Epsilon of the nano material is can be written as the Epsilon 1 and Epsilon 2 with the Epsilon 1 is the real part and Epsilon 2 is the imaginary part of the complex dielectric constant up the matter.

So, similarly you can write the dielectric constant of the medium in which you have these metal particles embedded. So, what you basically want is this equation that is the real part of the dialectic constant of the metal should be equal to negative of twice of the dielectric constant of the medium. And then you will have a resonance up the oscillating electrons, so this is the oscillating electron clouds.

So, it is up there and down there and that will a oscillate the such that there will be a resonance between the incident light wave, optical beam and that can happen, exactly when this value matches. So, this is the criteria for Surface Plasmon Resonance to occur and that depends on the dielectric constant of the metal and the dialectic constant of the medium in which the metal has been impregnated or supported and the medium through which the light is being passed.

Now, according to the Drude model, we cannot rewrite the real part of the dielectric constant and the imaginary part of the dielectric constant using these equations where we incorporate the dialectic constant at infinite or very high frequency. And, we incorporate the plasmon frequency omega p and there is a dielectric relaxation frequency omega d. And so using these equations you know the relation between the real part of the dielectric constant to the plasmon frequency.

Similarly, the complex part other plasmon of the dielectric constant can be written in terms of the plasmon frequency and the relaxation of the damping frequency. Now, you can ultimately find out that the plasmon frequency of the metal is related the number density of the electrons, at the velocity of the electrons, at the Fermi energy and the mean free path of the conduction electrons.

So, the plasmon frequency you can kind of understand, if you know the mean free path of the conduction electrons and the velocity of the electrons at the Fermi energy which is called V F. If you know that then you can determine the omega p which is the plasmon frequency and that is related to these numbers here. So, here this is the various constants are there the electronic charge, the mass and the dielectric permittivity of free space.

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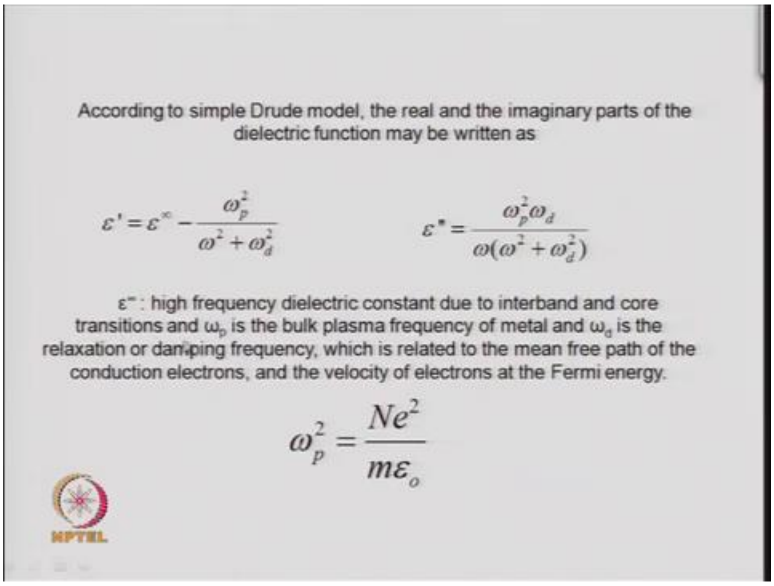

So, if you know the plasmon frequency of course, you know the plasmon energy from that one can find out what kind of particles will show what kind of plasmon frequency or plasmon energy. And from that you can find out, if the plasmon frequency or energy is lying in the visible region or not, if it lies in the visible region, then due to this surface plasmon resonance you will see a color, if it does not lie in the visible region we will not see the color.

So, if you look at that if you calculate the plasmon frequency of different metals and with different sizes, then you can calculate you cannot see which one will be red in color, which one will be blue in color etcetera. So, in this chart you can see that if the plasmon energy goes from say 3.5 electron volts, there to around 0.5 electron volts, you scan the region from ultra violet to the infrared.

And here different particles with different morphology have been have do show different colors which has been represented here for example, if you have silver nano spheres. So, if you make silver particles of a particular size, then you will be having a color which is in around blue in color, but it may also have green color it depending on the size of the nano particles.

So, there is a broad range of plasmon energies for similar nano spheres from starting from around 400, 10, 400, 20 nanometers to around approximately 580 nanometers. So, it is a big energy region; that means with silver nano spheres, you can get different energies from the green to the violet by changing just the size of the nano spheres of silver, however if you have gold, gold shows much more variety and much more range.

So, if you have gold nano spheres, you can vary the plasmon energy and the color associated with that plasmon energy from say 600 nanometers to something around 780, 760 nanometers. Just by changing the diameter of the gold nano spheres, you can get all these colors from the yellow orange to that red using gold nano spheres. But you cannot get blue color with gold nano spheres as shown using surface plasmon, if you have a structure which is not a sphere, but made of gold and it is in the form of nano shells.

So, it is like is a strip of gold particles in a circular fashion with the certain thickness without anything filled inside. So, that is like and nano shell or a nano egg, if you can make it can vary from 600 nanometers to 9,000 nanometers, this is a very large range. So, changing the shell thickness and changing the diameter of the nano shell, you can have all kinds of colors from green, yellow, red, brown and even colorless, those particles which have a plasmon energy in the mid infrared say 3,000 nanometers.

We are already in the infrared, very large wavelength, very small energy you can get colorless particles of gold, so you can not only get brown color, red color you can get colorless particles of gold as shown in the figure. Then, you can get using nano rods you can get from nearly bluish in color to up till brown color with nano triangles gold can be also made in triangular form not only as a disc, not only as a sphere, not only as a nano rod, gold can also be made as a tangle.

So, these triangles are very useful because see where they absorb these triangles can absorb in the infrared mid infrared, whenever you can have anything absorbed in the infrared; that means, you can heat that material. So, if you have gold nano triangles in your body say you inject gold nano triangles, somewhere people have shown how then it real heat up to cell around it. So, this is using the near i r or mid i r energy which gets absorbed by these nano tangles of gold, it can heat the surroundings the by the by picking up energy.

So, a range of energies are possible for the same material, if you change the day mentions or you change the shape, you can get very large range of energies using the SPR band. So, this is very particular for metal nano particles, this is not for semiconductor nano particles, this is for metal nano particles, for semiconductor nano particles of course, you can change color, but then you have to worry not about surface plasmon. But you have to worry about the band gap and how what is the bandwidth, how discrete are the levels etcetera. So, that is for semiconductor nano particles and this is for metal nano particles, where the color can come from the Surface Plasmon Resonance.

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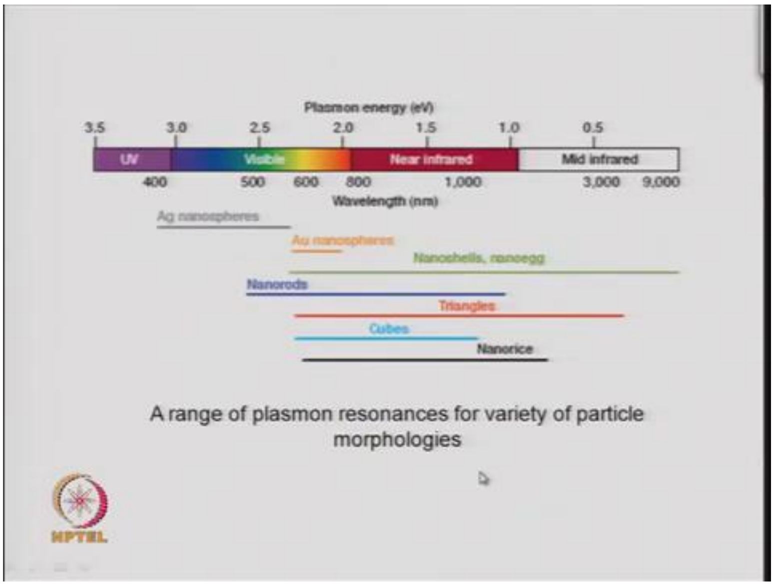

Now, this plasmon oscillation is basically, the density fluctuation of the free electrons or free electrons means, those electrons which are in the conduction band, in the conduction band the electrons are not held to the core tightly and so the electrons are supposed to be free to move. So, they may be called as free electrons in metals many times to use that term free electrons, basically they are electrons in the conduction band and they can a supposedly move around; that means, delocalized over all that different atoms in the cluster or in the nano particle.

So, if you have a density fluctuation of free electrons which are present in a metallic solid, then you can have what is called the plasmon oscillation. So, the plasmons oscillate at the plasmon frequency which is related to the free electron density and the effective mass, Now, if you confine these plasmons, this was in the bulk that they are oscillating with the plasmon frequency, when you confine the plasmons to surfaces which can interact with light.

So, if you have a wave which is going through the material and the material can interact with this light, then it can form what is called a propagating Surface Plasmon Polariton.

So, that is called a SPP band Surface Plasmon Polariton and that happens when plasmons are confined to surfaces, they are not present in the bulk, they are only confined to surfaces and then this kind of surface polaritons can form.

And that results, if you have confinement; that means, if you decrease the size of the particle, then this Surface Plasmon Polariton modes they get affected. So, earlier if you look in the bulk, the plasmon frequency is related to the free electron density and the effective mass in this fashion. Where in the nano particles, where you observe the Surface Plasmon Polaritons, where confinement is there, because now you cannot have the plasmons in any way in the bulk they are only in the surface.

So, confinement effects are there in this polaritons and this equation of the plasmon frequency changes and now you see a factor 1 by 3 has come in the in finding out the frequency of the nano particles. When, it is showing resonant SPP modes or resonant Surface Plasmon Polariton on modes, so different, whether the plasmons are confined or they are in the bulk, you will have different plasmon frequencies, that is what is being told and hence you will have different colors. Because, the frequency will be related to energy being absorbed and that will be related to the colors which are may given out or which you see for the different nano particles.

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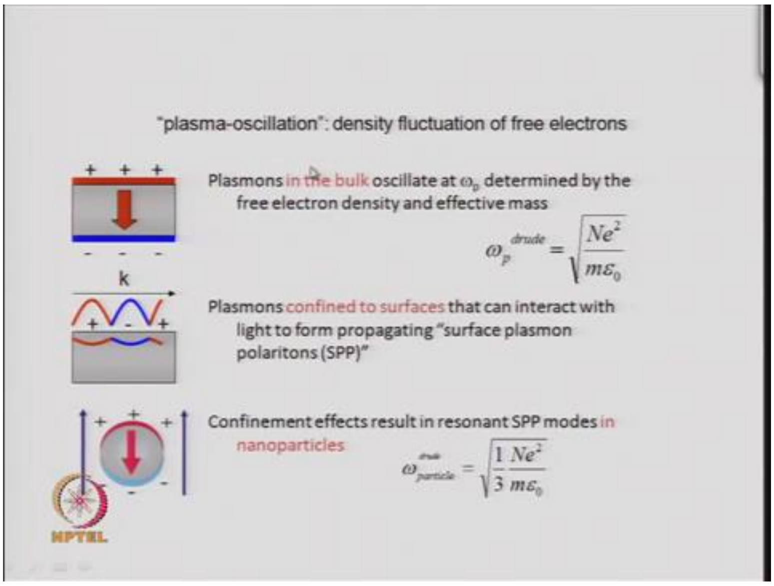

Now, a Michael Faraday as discussed earlier was the first to report the synthesis of colloidal metal particles and in this case the colloidal metal was gold. So, it was gold particles which are kept hear in this solution and you can see there is stable even today. Particles do not settle down, it is a clear looking solution is basically made up of gold, nano particles in this colloidal solution and a long back in 1908, Mie tried to explain the phenomena of the color of these metallic colloids.

And, that he did by solving Maxwell's equation and he predicted that for homogeneous metal particles, you will have optical extinction. Only, when the size of the particle here it is written 2 r that means twice that radius that is the diameter of the particle is much smaller than the wavelength or the light, which you are using to see the particles. So, Mie predicted that this kind of optical extinction, extinction involves scattering as well as absorption

So, there is an incoming beam there will be an intensity of the incoming beam and when it gets scattered or it gets absorbed, then that intensity gets lost and that is also you can say is called extinction. So, Mie tried to explain this extinction based on scattering and absorption and he predicted that this kind of extinction will be valid, when the size of the particle is much smaller than the wavelength of the light.

And, that is what we discussed earlier also, that you will have these oscillations of the conduction electrons of the metal particles, when this size of the particle is much smaller than they have length of the light. So, the wavelength of light is this big and the size of the particle is only this big, so the size is much small then you see this SPR band and then you can see colors of metals in collides as seen by Michael Faraday.

Long back around 1856 and 1857 and that is remarkable, that it is contribution not only in other fields of electromagnetism and laws of electrolysis policies, but also in nano science, where the first metal nano particle was synthesized in the laboratory by Michael Faraday as gold nano particles. So, this is the solution of gold nano particles and the color explained by means theory based on an extinction due to scattering and absorption for particles which are much smaller than the wavelength of light.

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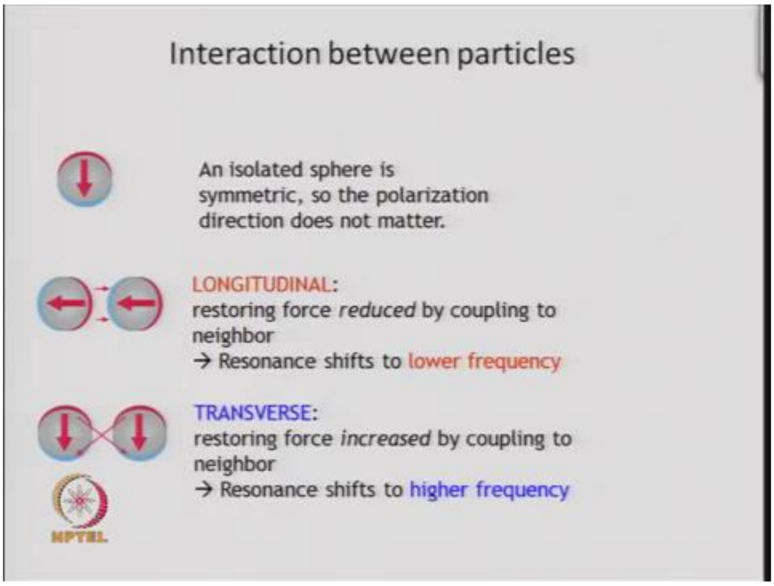

Now, when you have at two metal particles how will these plasmons interact, so will there be a shift in the surface plasmon band. So, or if we try to understand the interaction between particles and the fields around these particles and isolated sphere or a particle, the polarization direction does not matter, whether vector is pointing this way or that way. But, when there are two particles, it will matter in which way these dipoles are being shown and how they are present.

If they are present in say in the same direction, then the interaction will be in one way and in this case it will be in a different way. So, this is a longitudinal coupling of the two metal particles to the oscillations of the conduction band electrons and the two particles and this coupling results in a shift of the SPR band to lower frequency. So, the restoring force in a longitudinal coupling is actually reduced, when this one couples to this one.

So, that is because they produce a resultant which is opposing the original plasmon vector, so the restoring force is reduced by coupling to the net neighbor and the up SPR the band shifts to lower frequency. The force is reduced if shift to lower frequency and if it has a transverse component, so there are these two particles metal particles and these other vectors and if they have a transverse interaction, transverse coupling, then the restoring force is increased by coupling.

So, the resonance will shift to higher frequencies, so there are two possibilities of coupling of a two metal nano particles. The coupling bit a can be longitudinal and then longitudinal means the two dipoles are kind of arranged in the same direction and they have a restoring force which reduces tries to reduce the coupling. So, basically the resonance SPR band will shift to lower frequency or lower energy, whereas in the transverse case.

The SPR band will shift to higher frequency, this is that the interaction of particles, because in many systems nano particles will not be alone. They will have neighbors and so particle interaction will be there, between these metal nano particles and one has to understand what happens to the plasmons, the polaritons, when the coupling takes place.

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So, the size dependence that is say gold particles, we say while gold is yellow in color and then we decrease the size of the particles all kinds of colors can be seen. Now, all these colors a different size are the gold particles are not coming due to one reason, there are two reasons why you see color in gold particles, one is that the geometric factor, the blue, the purple. The large size particles, the color is explained by Mie theory, where the particle acts as a scatterer, so light scattering by the metal sphere is used to explain by Mie theory which gives rise to the gold blue and purple colors.

These colors for large particles, this is a when the metal nano particles is larger than approximately 30 nano meters. Then, these particles the reason because of this large particles having colors is that some of the electrons which are oscillating with the field are not in phase. So, some electrons get behind phase and this is called phase retardation or retardation effect and for that the color can change.

So, this change in color for the larger nano particles of metals is explained by Mie theory, where the light scattering by the metal spheres involves electrons. But all the electrons are not oscillating with the light, in phase some electrons are lagging in phase and this phase retardation can cause these colors. The subsequent at the small size level, when below a certain size say 5 nanometers, 3 nanometers, 4 nanometers at that size the changes in color a which is more towards reddish brown to range.

And then finally, it becomes colorless at very small size those are due to quantum size effects which we had discussed earlier and in quantum size effects, we had discussed as you reduce the size of that particle. The band gap is increasing, the energy states become more discreet and this is called the quantum size effect and the color change is associated with that or the changes in optical properties associated with these small particles less than 5 nanometer particles is due to quantum confinement.

And can also be said is due to the quantum size effect; however, the color changes at large sized particles at 30 nanometers, 25 nanometers etcetera is explained by Mie as due to scattering from a scattering of light. Leading to its resonance with the conduction band electrons, which is called the SPR, but all the electrons are not resonating in phase, some electrons because of the large size of the particle are lagging and hence it causes a shift in the color in the large sized particles.

Whereas in the quantum regime, when you are talking a very small particles the variations in the color are due to quantum effects, are due to changes in the density of states with energy or changes due to the band width or the discretization of the energy levels. So, there are two different areas, two different phases by which you can explain the color, so the color, the range of size or particles depends on the color.

Depends on the range of size of particles in one range, the higher range, the color can be explained by the Mie theory and at lower dimensions the color changes can be explained using the quantum confinement or quantum size effects. So, at very small size the colors are basically reddish brown to orange or colorless and those are due to quantum size effect, but at large size this blue violet and red at this size you can explain using light scattering by a sphere by as explained by the Mie theory.

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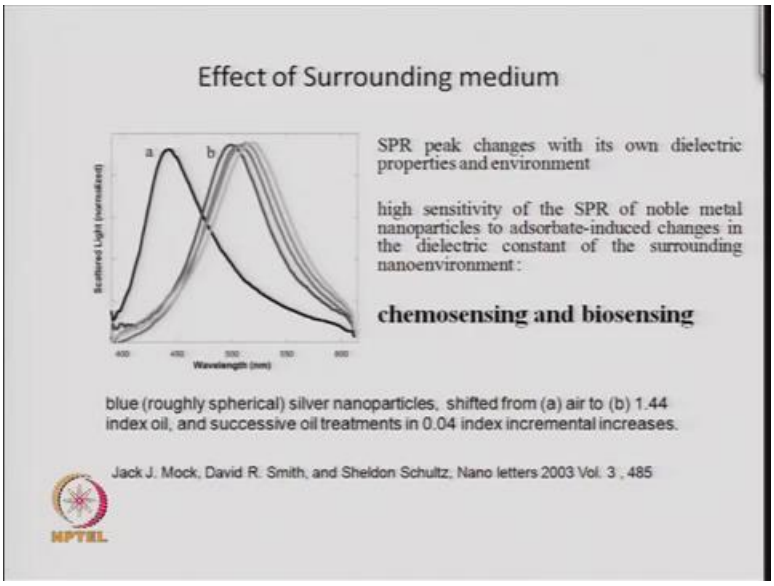

Now, what is the effect are the surrounding medium, if you have a metal particle and you have some solvent molecules say water or ethanol or a cyclohexane, how does the surface plasmon band or the SPR peak which is shown here, like how does this change as a function of the environment. So, here you can see that you have spherical silver particles and these spherical silver particles have an absorption around 440 nanometers, so this is the absorption of the spherical silver nano particles.

Now, if you move them from suppose, they were in year, now if you move the air remove the air and add some other liquid which has a refractive index of say 1.44, then you get the plot b. So, from which has a maxima at 400, 40 nanometers you now get b which has a maxima around 500 nanometers. So, this is a shift of 60 nanometers by changing the environment from air to some liquid which has a refractive around 1.44 and then further change can be observed.

If you change the refractive index of the medium from 1.44 to 1.48 you will get the next plot and like that there is a continuous shift in the maxima of the absorption of this energy due to the Surface Plasmon Resonance by the change in the environment. So, it is highly sensitive the SPR band is sensitive to the environment and this sensitivity of the SPR band for metal nano particles especially of gold silver etcetera can detect adsorbate induced changes in the dielectric constant of the surrounding an environment.

So, the sensitivity of the SPR band can be utilized for a device, which can sense what is happening in its environment, if you make any changes in its environment it can immediately detect because it will change its absorption of the Surface Plasmon law. So, suppose a pure SPR band for gold nano particle is at 440 nanometers, if you add some liquid around the gold nano particles and it shifts to 460 nanometers. Then, we are sure that the environment is doing something to change this SPR band so it is a sensitive tool.

And, if properly applied you can make it a chemosensing that is sensing molecules of different types or biosensing which is again sensing molecules of different type, but of biological relevance; that means, of relevance to life and medicine. So, you can use the SPR band very effectively in biological applications in medical applications for chemosensing and biosensing.

So, this particular example as I mentioned was for silver nano particles and the particle size, the particle size has fixed what you change is the environment around the particles. And, as you change the environment of the particles that is you change the liquid in which the particles are present and change the refractive index of the liquid. Then the absorption the surface plasmon band changes and you can follow these changes very effectively.

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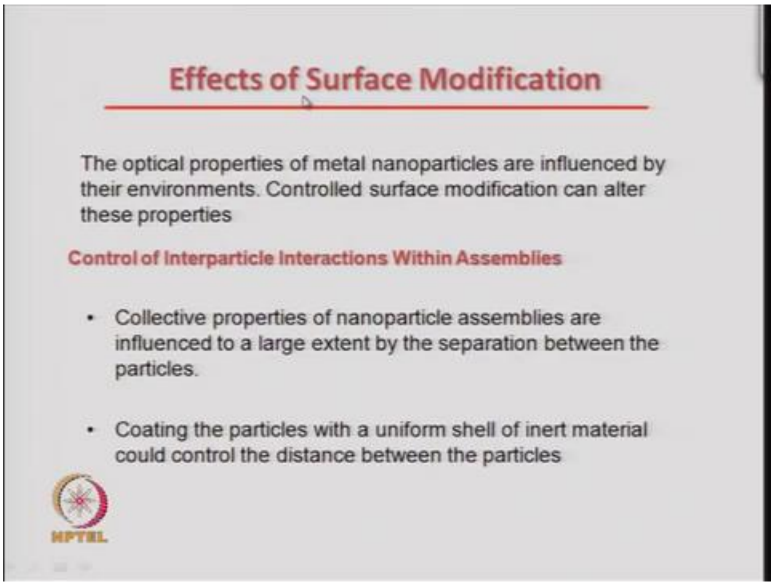

Now, one thing is about environment, the other is about surface modification, what about if you put some molecules or some functional groups on the surface of these a gold particles. So, there will be what is called surface modification and the optical properties of metal particles like gold particles or silver particles etcetera are influenced by their environment. And, if you change using a controlled manner the surface, you can alter their properties in a very controlled manner.

So, you can do controlled properties of nano particle assemblies, by the separation between the particles that is how much distance that two interacting particles should be if you can control by using some methodology. Then, there will be a very interesting approach towards a biosensing by controlling the interparticle interactions within these assemblies of metal nano particles. Also, you can coat these metal particles with a uniform shell of inert material like silica, titania etcetera you can cover them.

These metal particles with silica, titania etcetera and control the distance between the particles, so the two metal particles will be separated even, if they try to touch each other since there is a outer shell. They will be away from each other by at least twice, the thickness of the one shell or some of the shell thickness of the shells, form that on the two particles. So, you can control interactions by controlling the distance like keeping the particles at different distances. Chemically or physically or by introducing shells around the particles with particular shell thicknesses which will allow one to keep the particles at specific distances and hence control the surface plasmon.

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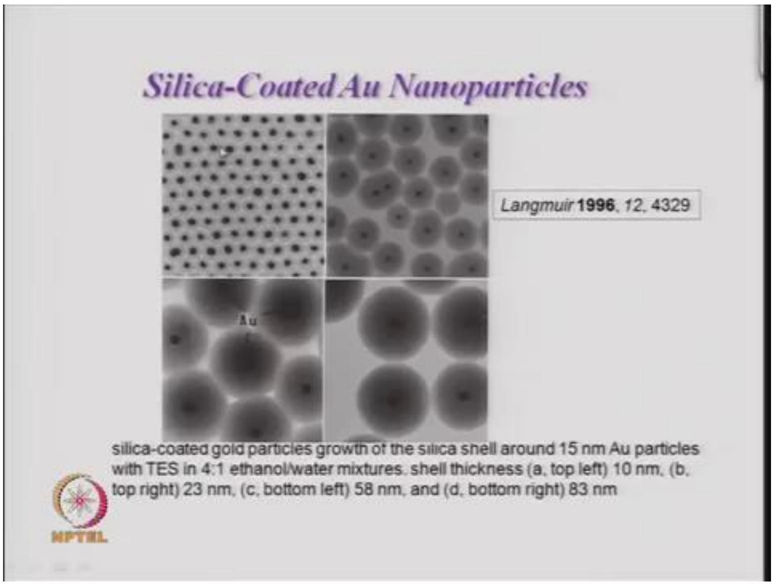

So, to that this is an example of silica coated gold nano particles, so you have got gold nano particles here and these gold nano particles have been covered with silica. So, that is what I was telling that, if you consider this particle inside and this particle inside they may have important interactions. But, those can be controlled by varying the shell thickness of silica on gold particles, so different types of thicknesses can we formed and what is given is you can make particles with 10 nanometers, 23 nanometers with 58 nanometers and with 83 nanometers.

Different size of particles and the gold coated with different shell thicknesses the particle size is not varying the shell thickness and in this case the particle is small of say 15 nanometer and the shell thickness is also similar order of around 10 nanometers. So, this is mostly uniform here of course, the particle size the core has increased although the thickness has been kept constant in all of them of 15 nanometers.

So, this type of silica coated gold nano particles are of importance for many applications and their thickness of the shell can be monitored and controlled. And that will control when you try to bring the particles together, the metal particles will come to some close distance and that distance can be controlled by controlling the shell thickness that is the amount of silica around the gold particles.

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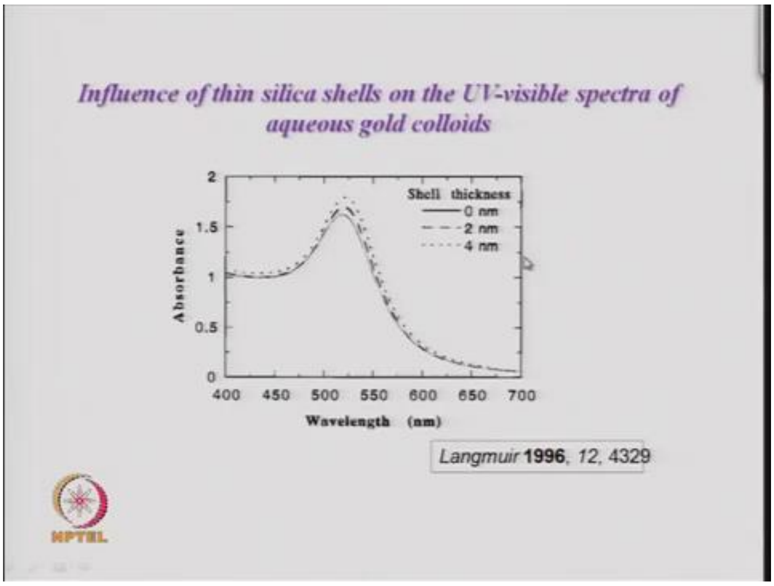

Now, what happens to the spectra, that is the adoption, now when you have these kind of shells around the gold particles. So, this is a plot of the absorbance of these gold colloids which have been coated with silica and you see the dark bold line is the surface plasmon band of the gold particles with no silica shell. So, there is this is the surface plasmon band which is coming around 520 nanometers approximately, now that has zero shell thickness.

So, there is no silicon top of these gold particles, but when you add or make a 2 nanometer thick shell around this gold particle, you see that the intensity has gone up and there may be a slight shift in the peak of this gold silica core shell nanostructures. When, it is 4 nanometers, you can clearly see the shift in the surface plasmon as well as the intensity will get affected.

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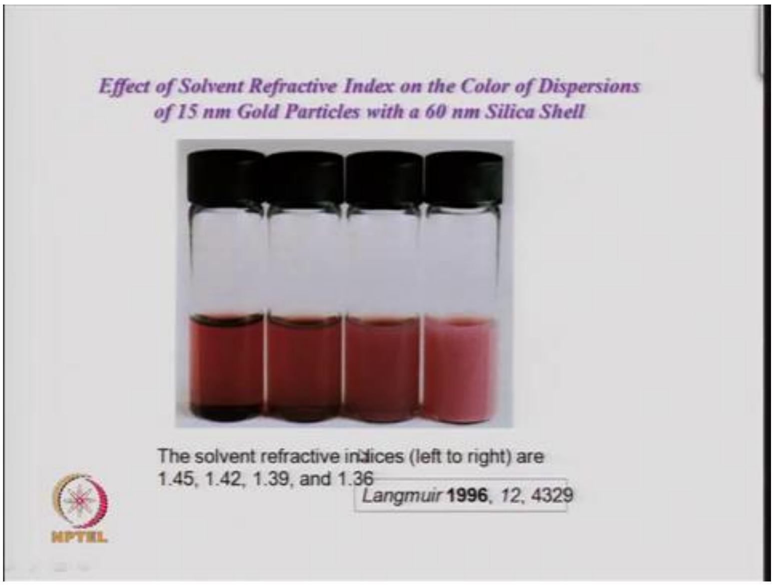

And this is the pictures of these particles of gold with different silica with a 60 nanometers silica shell and what has been changed is the refractive index of their liquid in which these particles have been dropped. So, you have the gold particles which are covered with 60 nanometer silica shell and you put them in some liquid which has a refractive index of 1.45, 1.42, so you are varying the refractive index of the liquid of the medium.

And you see the shift in a color using the same nano particle, 15 nanometer gold particles and 16 nano nanometer thick silica shell on top of the gold particles and you are adding the same particles to four different solvents. And, what is different in these solvents is the refractive index of these solvents and you can see variation of these gold silica nano particles in the depending on the environment and this has lot of importance in future applications.

So, with that we come to an end to today's lecture and this was the 10 th lecture of the module 4 and the second lecture on optical properties. And in our next lecture, we will complete our study on optical properties of nano structured materials and that will have be our 11 th lecture and then the last lecture will be the 12 th and last lecture of the module. And, the last lecture of the course which will be on mechanical properties of nano structured materials.

So, thank you very much and we will meet for the next lecture.