Nano Structured Materials-Synthesis, Properties, Self Assembly and Applications

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Module - 3
Lecture - 25
Core Shell Nanostructures - II

Welcome back to this course on nanostructured materials synthesis, properties, self assembly and applications. Today, we are going through the module 3 lecture 11 and we are discussing a core shell nanostructures and this is the second lecture of the three lecture series on core shell nanostructures. So, module 3 lecture 11 on core shell nanostructures.

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TiO_2 shell

TiO_2 shell is a promising material for various applications such as photoelectrochemical activity, solar energy conversion and photocatalysis

Ag@TiO_2

The core Ag displays unique activities in the field of biological and chemical sciences.

titania shell over metal nanoparticle leads to enhanced optical and catalytic properties due to photoexcitation of electron from the TiO_2 shell to silver core

Now, we already introduced what are core shell nanostructures in the last lecture and we discussed quite a bit on silica based shells on various types of particles. So, we took examples of silica on metals on semiconductors oxides and chalcogenides and discussed what the different types of core shell structures that you can make on metals and other things based on silica shell. Now, you can also have shells other than silica like titania Ti O 2 is a very interesting material, it is a biocompatible, it is nontoxic, it is available in plenty.

Hence, like silica, titania or titanium dioxide is also very promising material for various applications such as photo electrochemical activity solar energy conversion and photo catalysis. Let us look at one core shell structure where silver nanoparticles form the core and titanium dioxide forms the shell here silver the forms the core and we displays unique activities with the applications in both biological and chemical sciences. Now, the titania shell leads to enhanced optical and catalytic properties a especially photo catalysis, this is due to photoexcitation of electron from the titania shell to silver core.

So, when light falls on the this core shell structure, where you see this is the silver core and the shell is formed of titanium dioxide, then this light generates electrons and holes and the electrons migrate from the titania shell towards the silver core. Hence, the electron and hole are separated, which is a very important aspect of any photo catalytic reaction and even in photovoltaics, where you separate electrons and holes, this kind of core shell nanostructures are very useful in that regard.

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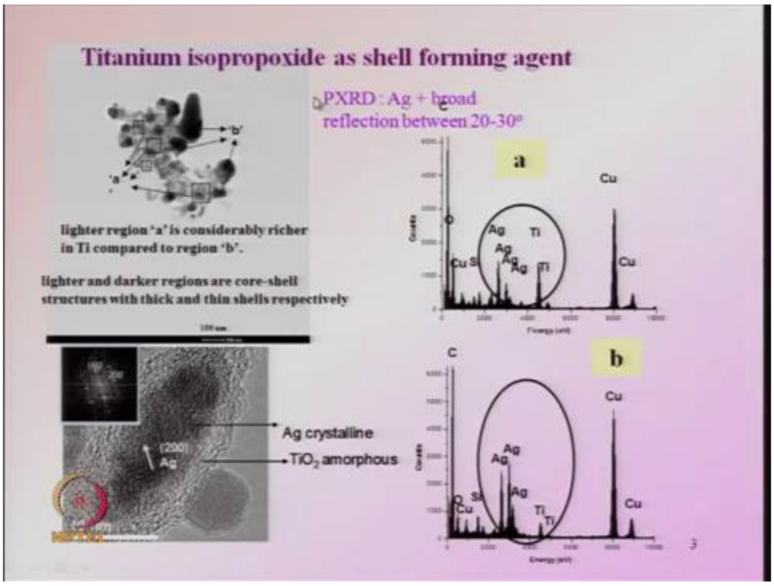

Titanium isopropoxide as shell forming agent

PXRD : Ag + broad reflection between 20-30°

lighter region 'a' is considerably richer in Ti compared to region 'b'.

lighter and darker regions are core-shell structures with thick and thin shells respectively

Now, how do you make these titanium Ti O 2 based core shell structures, we discuss little bit on earlier on silica based shell on metal particles and there we started with an alkoxide of silicon. Here, you have to start with an alkoxide of titanium, titanium isopropoxide is the most commonly used chemical reagent, which is used as the shell forming agent. So, using this people have made silver titania and under the transmission electron micrograph you can see bunch of dark and light shades and the dark particle is richer in titanium compared to the region band.

The lighter one is actually where it is richer in titanium because silver has more electron. So, scattering by electrons from silver when the electron beam hits will be more from silver reach regions and the contrast will be more where silver is present. So, if you look at this high resolution picture, it is clearer where you can see inside this is the silver nanoparticle on top of which there is this core which is made up of titanium dioxide. So, we had yesterday discussed how you can identify what is the core and what is the shell that is by doing and edacs analysis of the core and the shell.

So, similarly here if you look at the core, that is you pass the electron beam from the core you can get region where there is more predominantly silver, so here you see silver is there because you also see titanium.

However, here you see there is more silver than titania, so the silver peaks are enhanced, so this is coming from the core region and this edacs spectrum is from the shell region. So, you have a high density of silver in the core and we suggest this is a typical core shell structure. From the lattice fringes which you can see, you can estimate this fringe width and can find out the corresponding lattice planes of silver particles and this distance corresponds to the 2 0 0 reflection plane of silver.

You can also do electron diffraction at this point from these particles and find out the reflections which correspond to silver particle. So, this shows you how to characterize a silver a titania core shell structure where silver is in the core and titania is in the shell.

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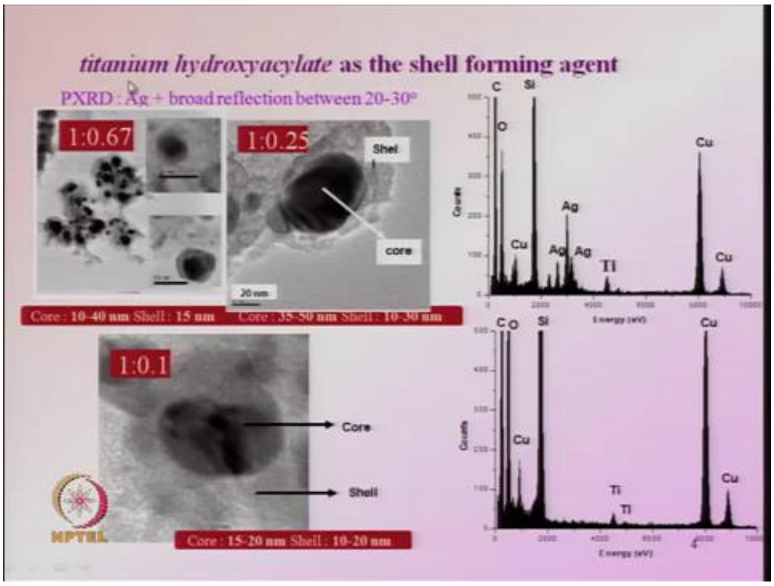

titanium hydroxyacylate as the shell forming agent

PXRD : Ag + broad reflection between 20-30°

Core : 10-40 nm Shell : 15 nm

Core : 35-50 nm Shell : 10-30 nm

Core : 15-20 nm Shell : 10-20 nm

Now, here you had started with titanium isopropoxide as the reagent for the shell and you can change that reagent, now you see this example is based on titanium hydroxyacylate. This is another starting material which you can make using acetic acid in some titanium based starting material and you get this titanium hydroxyacylate. You have to generate this and that you can use as the shell forming agent and you can see this dark region is the core which belongs to silver abd this light region is the shell.

If you change the concentration of the titanium hydroxyacylate like from 0.67 to 0.25, you are decreasing the amount and you can see the change in the shell thickness. So, from 0.67 to 0.25 to 0.1, you can change the concentration and you can vary the thickness of the core with respect to the shell and you can do the edacs again. You see in this case here, if you pass the electron beam through the core because on top of this, you will have the titania.

So, you will see titanium and in the core you have silver cores both titanium and silver can be seen in these edacs spectra, whereas if you pass the electron beam from the shell you can see only spectra due to titanium. You do not see any silver peaks here of course,, you may have copper because of the grid and silicon comes from the detector which is used to analyze the X rays which are coming out due to the electron bombardment of these particles.

So, as we discussed earlier, the carbon is comes to due to some impurities and their copper is due to the grid. Hence, what silicon comes from the detector and your material is here, it is silver and titanium coming from the core and only titanium being seen in the shell and of course oxygen is there which can be seen in the core as well as in the shell. We are passing the beam from the top, so the shell is on top of the core, so you will see oxygen also.

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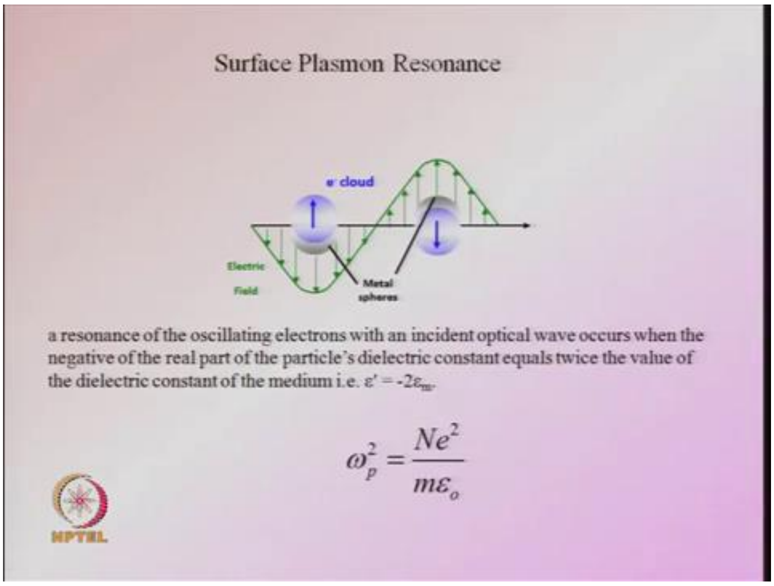

Surface Plasmon Resonance

a resonance of the oscillating electrons with an incident optical wave occurs when the negative of the real part of the particle's dielectric constant equals twice the value of the dielectric constant of the medium i.e. $\varepsilon' = -2\varepsilon_m$.

$$\omega_p^2 = \frac{Ne^2}{m\varepsilon_o}$$

Now, another property which comes out very much in metal core based species a especially when you have nano size metal you come across of phenomenon which is called surface Plasmon resonance. Now, this surface Plasmon resonance of nanoparticles can be module modulated or modified based on some thickness of some other material and you can modulate the type of SPR band that you get. So, what is a surface Plasmon resonance, now Plasmon the term especially means quantized oscillations of conducting electrons.

Now, it happens because when you have an optical wave passing through a medium and you have these electron clouds of these nanoparticles. Then, these oscillating electron cloud interacts and when there is a resonance between these two, then you get what we call as a surface Plasmon resonance. So, it occurs at a particular frequency or a particular wavelength, now the Plasmon frequency can be related by this equation to the dielectric constant.

Other things are of course related to some specific constants like the charge of the electron and mask of the electrons etcetera. So, when do you get this condition of resonance of the oscillating electrons with the optical wave that precisely happens when the dielectric constant of your particle, which may be silver or gold or nickel.

Each one of them will have a different dielectric constant, so when this becomes the negative of this dielectric constant becomes equal to twice the value of the dielectric constant of the medium through which the optical wave is passing. Then, you get a condition of resonance and that is when you see an SPR band. So, surface Plasmon resonance is a very important phenomena in metal nanoparticles and you can modulate this by using a shell around the metal nanoparticle.

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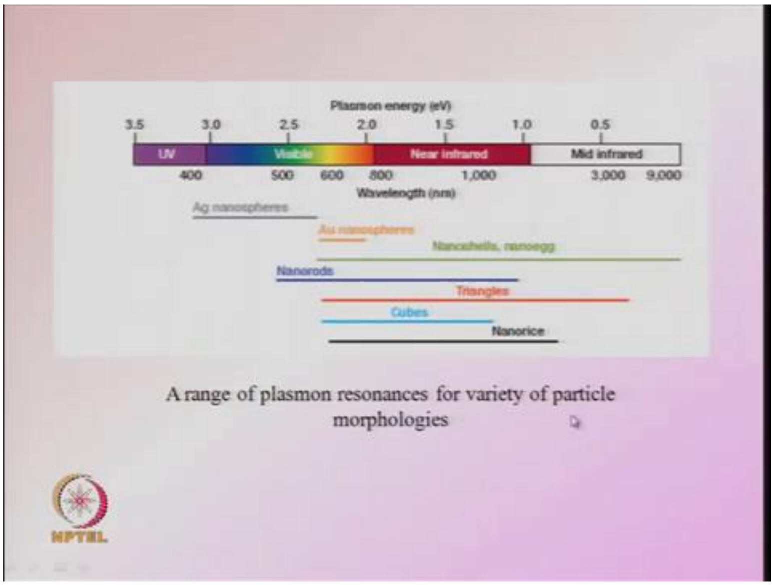

A range of plasmon resonances for variety of particle morphologies

So, you can see a range of Plasmon resonances for the same a metal, for example, you have gold, now gold depending on the shape whether it is a spear or it is a shell or it is a rod, you will have different region of the Plasmon band in the electromagnetic spectrum. So, this is an electromagnetic spectrum where at this you have the UV somewhere around 300 nanometers. So, if you are in 400 nanometers or below, you are in the UV region most of the particles that you know you see them a having a surface Plasmon band in the visible region.

So, this is your visible and you see most of them lie in the visible or near infrared region, of course sometimes you can stretch it to the mid IR region also by changing the structure by the shape of the particle.

So, for example, gold spears of a particular size can have a surface Plasmon resonance band SPR band around 600 to 800 nanometers, which lies from the orange to the red region. That is what you see normally, gold particles a in the orange red region, whereas if you make gold nano rods, you can tune depending on the aspects ration of the nano rods. You can tune them from the green to somewhere in the near in infrared, so the surface Plasmon absorption the band can be varied depending on the particle morphology.

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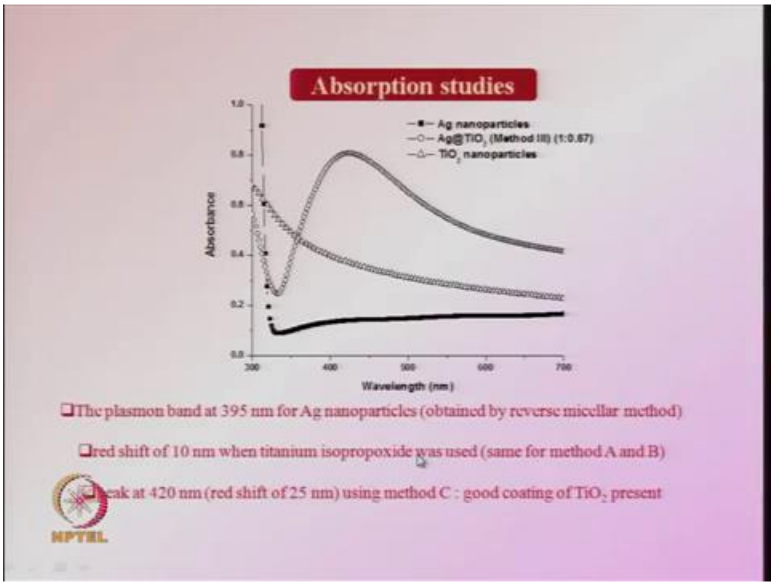

Absorption studies

❑The plasmon band at 395 nm for Ag nanoparticles (obtained by reverse micellar method)

❑red shift of 10 nm when titanium isopropoxide was used (same for method A and B)

❑eak at 420 nm (red shift of 25 nm) using method C : good coating of TiO_2 present

Here, what we are discussing now is what happens to the SPR band or the surface Plasmon resonance band of silver nanoparticles, when it is covered with Ti O 2. So, when Ti O 2 is formed a shell on a silver nanoparticles, what happens to the surface Plasmon band. So, if you see that pure silver nano particles of the kind which was prepared in this particular study, it has this type of band and that band is around 395. Somewhere, you can see that there is a band which can be attributed to the Plasmon band at 395 nanometers.

Now, these silver particles where obtained by the reverse micellar method or the micro emulsion method of synthesis, now when you make shell of titanium dioxide on top of the silver particles.

Then, what happens this you had this band of pure silver particle when you put titanium dioxide on top of silver particle you see you have a very pronounced band and this absorption is centered on more than 400 nanometers. So, it is around 420 nanometers, so there is a shift towards the higher wavelength, which is called a red shift and this shift is around 25 nanometers and this was synthesized using a particular method, where a good coating of the titanium dioxide was present.

Now, if you use some other methods you can see the shift may be different, so you can have various types of shifts depending on the type of shell. The type of shell thickness is if you have uniform coating of the particle core particle by the shell, you have a larger shell. So, these three plots show you the absorption bands of silver particle of titanium dioxide pure titanium dioxide and a silver particle coated with titanium dioxide and that shows a red shift of around 25 nanometers when the shell is formed on top of the silver particle.

You can change this while changing the thickness and a homogeneity of the shell on top of the particle the shift in the wavelength from 395 are to higher wavelengths can be modified by changing the thickness and uniformity of the shell. So, this is another detailed plot, where you are seeing that different compositions of silver is to titania have been used to and there surface Plasmon bands have been studied. So, you see the peak was broader when the molar ratio was a less and that shows better coating of Ti O 2 or the better coating of Ti O 2 was absorbed only when you use are much larger quantity of Ti O 2 of 0.67 is to 1, where 1 is silver.

When you used less quantity, the peaks start to broaden, so the best peak for 1 is to 0.67 is this diamond shape plot and which is this plot and it shows the maximum absorption and it also shows the sharpest band all the other bands are much broader. So, the concentration of the shell forming agent is important in finding out the position and the breadth of the band. Now, if you add two mercapto ethanol, now mercapto ethanol has a message groups and this sulfur of the thiol group will attach itself on top of the silver particle because silver and gold are they buy to the salver.

So, whenever you have this mercaptoethanol the sulfur group will bind on to the silver particle, so what will that do to the SPR band, so you have a damping of the surface Plasmon.

So, the surface Plasmon effect will be diminished when we you have any sulfide or any thiol because silver sulfide will form and the surface Plasmon is due to silver and when silver sulfide forms or silver sulfur bond forms due to the thiol. Then, the intensity of the original SPR band of the silver core particle will get diminished so that damping effect is because the metallic type of silver layers become demetalized because of the formation of silver sulfide or silver sulfur linkages on top in on the top layers of the silver nano particle.

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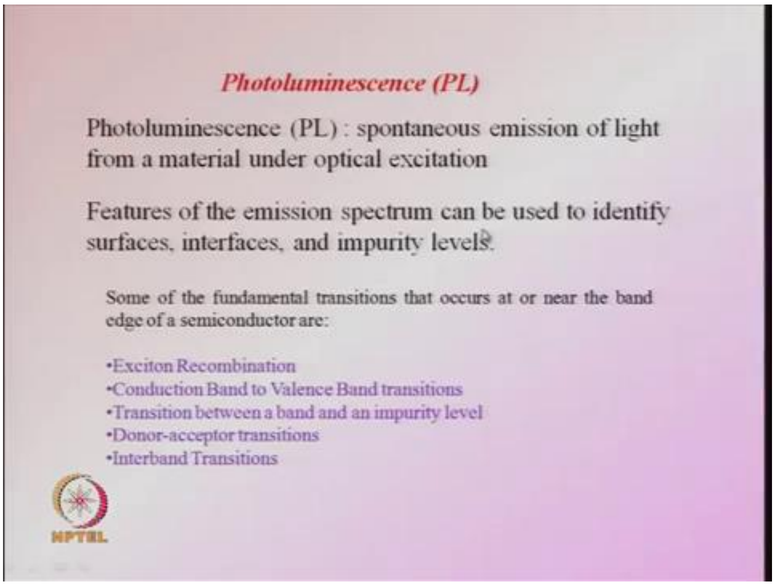

Photoluminescence (PL)

Photoluminescence (PL) : spontaneous emission of light from a material under optical excitation

Features of the emission spectrum can be used to identify surfaces, interfaces, and impurity levels.

Some of the fundamental transitions that occurs at or near the band edge of a semiconductor are:

- Exciton Recombination
- Conduction Band to Valence Band transitions
- Transition between a band and an impurity level
- Donor-acceptor transitions
- Interband Transitions

Now, coming to another property of core shell structures, previous one was on surface Plasmon. Now, let us look at the photoluminescence that is when something absorbs energy, then after some relaxation processes, it can emit energy and that emission can take place at a different wavelength. So, that is the photoluminescence and in photoluminescence, you have spontaneous emission of light under optical excitation the features of the emission spectrum can be used to identify surfaces interfaces and impurity levels.

So, some of the fundamental transitions that occur at or near the band edge of a semiconductor are exciton recombination band to band transition that is from conduction and to valence band and transition from a band to an impurity level. Then, transition from a donor to an acceptor and then inter band transitions, so some the PL could be from any of these transitions.

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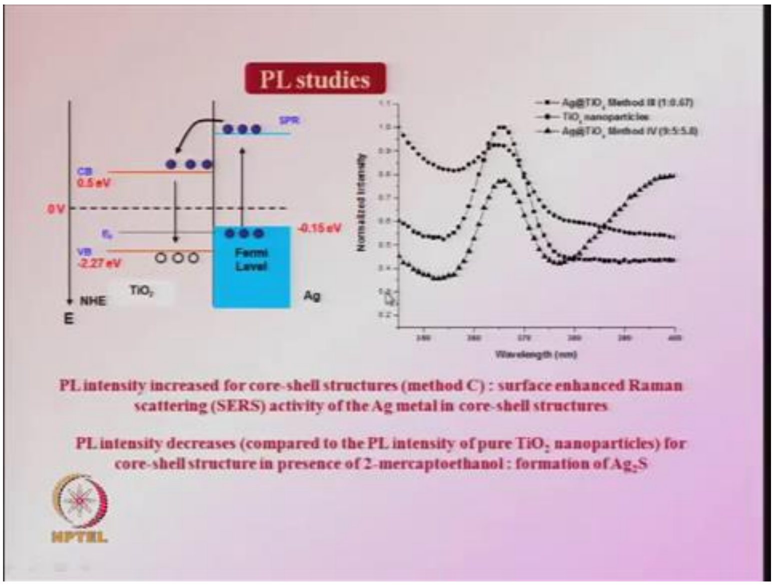

PL studies

PL intensity increased for core-shell structures (method C) : surface enhanced Raman scattering (SERS) activity of the Ag metal in core-shell structures

PL intensity decreases (compared to the PL intensity of pure TiO_2 nanoparticles) for core-shell structure in presence of 2-mercaptoethanol : formation of Ag_2S

So, let us do on example of silver, which is coated by Ti O 2 as we discussed earlier what happens to its photoluminescence. So, if you look at the silver particle with the titanium dioxide particle and look at their band diagrams. So, the band diagram of titanium dioxide which is a semiconductor is shown here, it has a valence band and the conduction band and for the silver which is a metal particle you have the fermi level here and the SPR band.

This SPR band is due to this absorption for the fermi level to this level and when the electrons are exited in the silver particle, they can be transferred to the conduction band of Ti O 2 which is lower than the SPR energy level of silver nanoparticle. So, effective electron transfer can occur from silver to Ti O 2 and then you can have an emission from this excited state or the conduction band here to the valence band, so this way you can get the photoluminescence. This kind of enhancement of the photoluminescence is called can be due to what is called the SERS activity or surface enhanced Raman scattering activity of the silver metal in core shell nanostructures.

So, you can see that if you look at the intensity of the PL, this is the photoluminescence plotted with wavelength. So, you can see the highest intensity is for the silver Ti O 2 core shell structure, now for bare Ti O 2 bare Ti O 2 is somewhere here this is the bare Ti O 2 and this is the core shell structure. So, this enhancement in the PL can be explained by the surface enhanced Raman scattering activity of the silver metal in core shell nanostructures.

The PL intensity will decrease in presence of mercaptoethanol like we discuss the effect of silver sulfur linkages. If it is present, it leads to de metallization of the silver particle and that would lead to a decrease in the surface Plasmon band intensity and also it will lead to lowering of the PL intensity.

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Coupling of excitons (Semiconductor) and plasmons (metal): attractive opportunities to design new materials for photonic applications.

Now, looking at another example, so now let us couple a core and a shell which has the coupling of semiconductor and a metal. So, we are coupling excites on in semiconductor and Plasmons of a metal and this kind of coupling of two materials which have different types of particles excite on Plasmon gives us several opportunities to design new materials for photonic applications.

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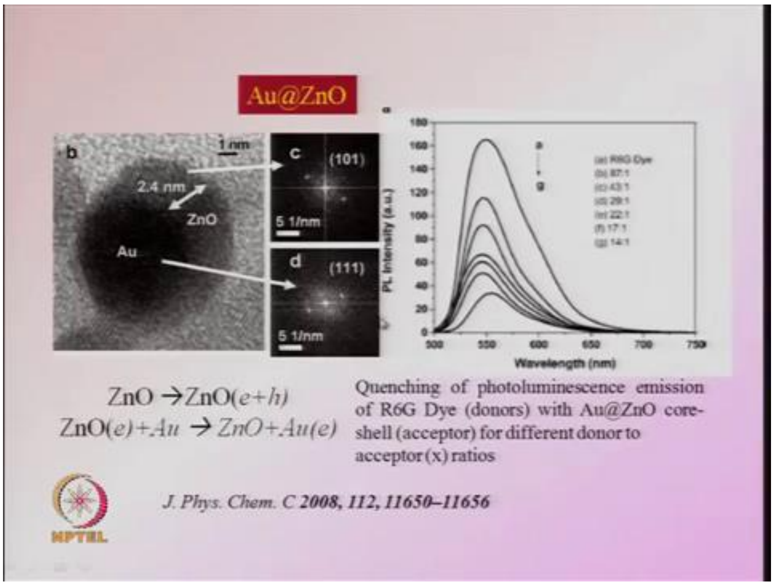

Au@ZnO

$ZnO \rightarrow ZnO(e+h)$

$ZnO(e)+Au \rightarrow ZnO+Au(e)$

Quenching of photoluminescence emission of R6G Dye (donors) with Au@ZnO core-shell (acceptor) for different donor to acceptor (x) ratios

J. Phys. Chem. C ***2008, 112, 11650–11656***

So, the example here is gold and zinc oxide, so gold has a Plasmonic band because it is a metal nanoparticle and zinc oxide is a semiconductor. So, it will have an excite on and this is the high resolution transmission electron micro graph of a gold core surrounded by a semiconductor, which is zinc oxide the shell thickness is around 2.4 nanometers. You can identify as discussed earlier using transmission electron microscopy and their electron diffraction, so if you do the diffraction from the shell region you will get a pattern which is corresponding to zinc oxide.

When you take a diffraction from the gold from the center, you get a pattern electron diffraction pattern or which is called the fast Fourier transform of this image. Then, you get a diffraction pattern which corresponds to the gold nanoparticle and the one reflections have been identified. Now, this kind of core shell structure with the metal particle surrounded by a semiconductor which is zinc oxide, what will happen when it is exposed to light. Then, the shell which is zinc oxide will produce electron and a hole together which is called an excite on. So, zinc oxide will have the electron and hole and then the electron will move to the gold which is at the core so the electron gets trapped in the core and the hole remains in the shell.

This was exactly what we discussed earlier in the case of silver Ti O 2, where when you shine light on Ti O 2 then electron and the hole are generated, and the electron is transfer to the metal core which is the silver particle and the titanium dioxide retains the whole.

So, there is so charge separations exactly similarly, here the metal gold gets the electron from the electron hole pair generated in the semiconductor which is zinc oxide and the electron gets in the gold particle.

The hole is retained by the zinc oxide, now when you do a reaction of this kind of particles with something where you have a donor a dye like rhodamine 6 g. So, this is the dye and you study the photoluminescence of this dye, then what happened that as there is quenching of the photoluminescence emission from the dye, so in the absence of any core shell particles, the dye shows the PL intensity which is shown by this. Now, if you increase the content of this core shell particles, then they will trap electrons because the zinc oxide is has got holes because the electron is now trapped in the gold nanoparticle.

So, electrons from the dye which act as donors will be transfer to the zinc oxide which acts as the shell, which act as the acceptor and the intensity of the photoluminescence will go down because the electrons, which were supposed to be a emitted. Now, they are getting transfer on to the zinc oxide shell, so this can be clearly seen in this photoluminescence intensity that drop in intensity as you are increasing the concentration of the core shell particle with respective to the dye.

So, here is the dye is the 87 and the particle concentration is 1 and then you decrease 43 is to 1 29 is to 1. So, the concentration of the dye is decreasing with respective to the core shell particle right and then you see a decrease in the photoluminescence intensity. So, this shows how when you have a Plasmon that is a metal particle giving in a Plasmonic band and a zinc oxide a semiconductor which is has on excitonic band when they to come together what kind of photoluminescence changes can occur.

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Coupling
of
two semiconductors

Now, again coupling two semiconductors, earlier we coupled one metal and one semiconductor now we couple two semiconductors.

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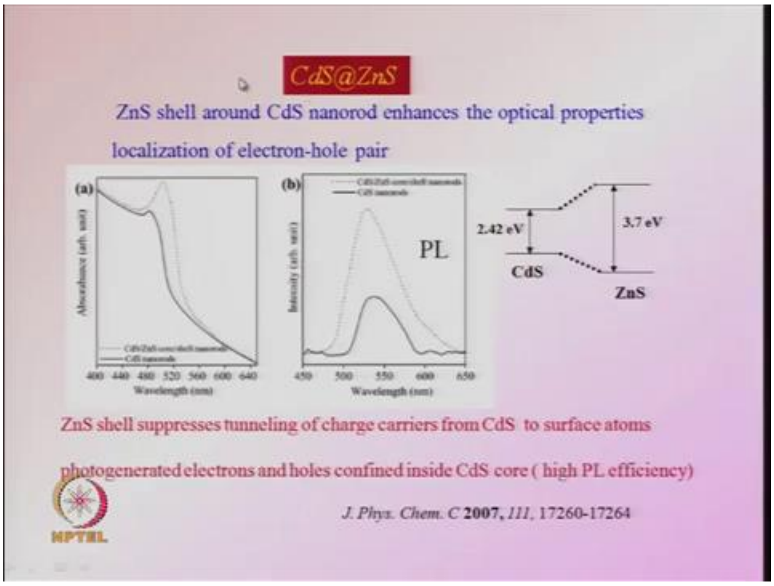

CdS@ZnS

ZnS shell around CdS nanorod enhances the optical properties

localization of electron-hole pair

ZnS shell suppresses tunneling of charge carriers from CdS to surface atoms

photogenerated electrons and holes confined inside CdS core (high PL efficiency)

J. Phys. Chem. C **2007**, *111*, 17260-17264

So, what happens you have two semiconductors one is cadmium sulfide which has a 2.42 electron volt band gap and that forms the core and you have another semiconductor, zinc sulfide which has a larger band gap. So, you have a small gap band gap material which is at the core and it is covered with the large band gap material, which is the shell and then you try to understand what happens to the photoluminescence. So, this zinc sulfide shell around the cadmium sulfide nano rods, so the core here is not spherical, but it is rod shape, it enhances the optical properties by localization of the electron hole pair.

So, the zinc sulfide shell suppresses tunneling of charge carriers from cadmium sulfide to surface atoms and for the photo generated electrons and holes are confined inside the cadmium sulfide core. So, the zinc sulfide which is at the shell does not allow the charge carriers from the cadmium sulfide because the charge carriers are generated by them in the cadmium sulfide. Now, of this particular band gap 2.42 electron volts and zinc sulfide is outside the cadmium sulfide.

Now, when the charge carrier created, they are not allow to go to the surface, but are confined inside and that leads to high PL efficiency because of this photo generated electrons and holes being present and that you can see here. So, the dark lines these dark lines this absorption and this is the photoluminescence, so you can see the dark one is pure cadmium sulfide with no shell.

It has this kind of intensity; the intensity is here where as when you put a shell on top which is zinc sulfide the dotted line you see an enhanced signal. So, it has enhanced from this value to it has gone to this value and for cadmium sulfide covered with zinc sulfide, so the p l efficiency has been enhanced because you localize the electron hole pair inside the cadmium sulfide nano rod.

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Stimuli responsive
Core-shell

Now, let us take an example of a core shell particle which is responding to some change in it is environment. So, you have a particle in a say a solution and there is some change in the solutions say either the pH changes or the temperature changes or there is an electric filed or magnetic field. Then, what happens to the core shell particle, does it change anything, so if it happens, then we call this a stimuli responsive core shell, the stimuli is the external perturbation which we are giving.

So, that perturbation can be in the form of a pressure a temperature it can be in the form of pH or ionic charge some kind of influence of the environment and what happens to the core shell in response to this change in stimuli. So, those kinds of core shells which do respond are very useful for some applications where if you apply a temperature change you can cause a change in the core shell properties. You can cause a change in the core shell properties by changing the pH around the system.

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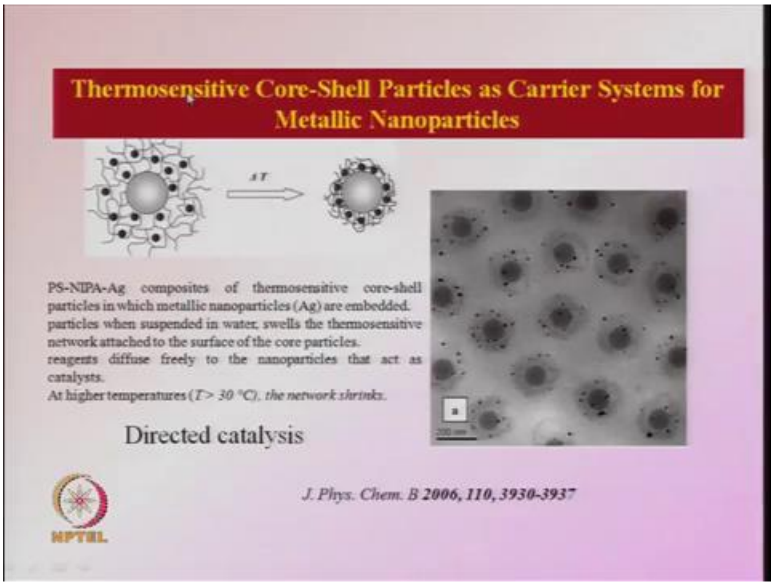

Thermosensitive Core-Shell Particles as Carrier Systems for Metallic Nanoparticles

PS-NIPA-Ag composites of thermosensitive core-shell particles in which metallic nanoparticles (Ag) are embedded.
particles when suspended in water, swells the thermosensitive network attached to the surface of the core particles.
reagents diffuse freely to the nanoparticles that act as catalysts.
At higher temperatures (*T* > 30 °C), *the network shrinks.*

Directed catalysis

J. Phys. Chem. B **2006, 110, 3930-3937**

So, let us look at an example, this is a thermos sensitive core shell particle and is being used as a carrier for metallic nanoparticles. So, what you understand by thermos sensitive core shell particles thermos sensitive means something which is sensitive to temperature. This is the core shell particle and it will be used to carry metallic nanoparticle, so what is this particular example, so you can see these kind of change. So, this is kind of polymer and this polymer is polystyrene and nipa which is some an isopropyl acrylamide and you have got silver nanoparticles along with that.

So, you have this kind of composites where you have a core shell, so this core shell of a specific kind can release silver particles at a certain temperature. So, suppose you change the temperature, you can see here the network is very open when you increase the temperature it becomes very tight. So, this kind of change in the rigidity of this composite as a function of temperature makes this a thermos sensitive core shell particle. So, what happens here it is holding the silver particles here it is going to make the silver particle accessible to something else suppose something else wants to react.

So, this silver particle then be able to react here it is being held very tightly, so the silver particles will not be able to react. So, this kind of assembly of core shell particles with a polymers for example, can be used in the presence of water its swells the thermos sensitive network attached and reagents can defuse freely to the nanoparticles. Then, the silver particles which can act as catalyst will react on them this is very important for photo catalysis by silver or some other catalysis to kill bacteria etcetera. So, we can call this directed catalysis because only when you want that is under some condition of temperature you can release it or you can hold it.

Hence, these are called thermos sensitive core shell particles and they can used as a carrier system for metallic nanoparticle. So, this is TEM picture where you see this particle the core shell particle can be seen the dark one in the light shell and you can see that black dots those are the silver particles. So, you can make them very release them like they are here or you can close them by changing the temperature and the silver particles then will not be amenable for reaction. So, this is very interesting for many applications where the core shell particles are thermally sensitive.

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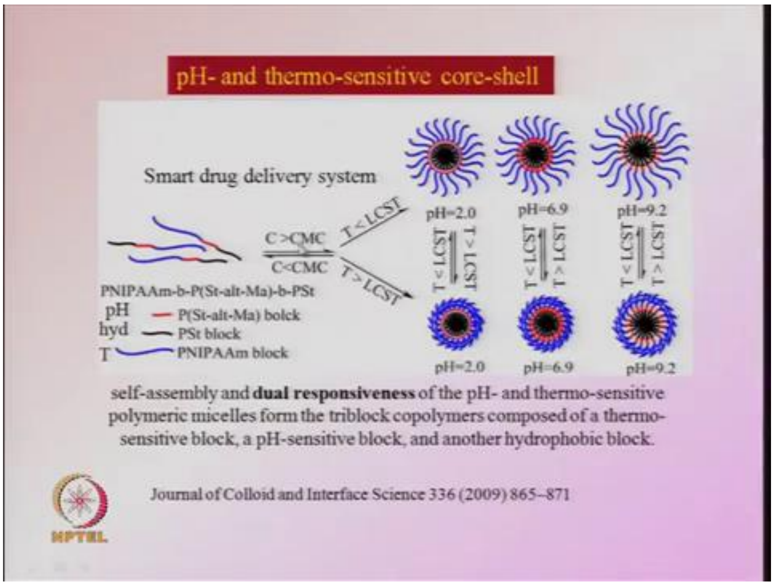

pH- and thermo-sensitive core-shell

self-assembly and **dual responsiveness** of the pH- and thermo-sensitive polymeric micelles form the triblock copolymers composed of a thermo-sensitive block, a pH-sensitive block, and another hydrophobic block.

Journal of Colloid and Interface Science 336 (2009) 865–871

Similarly, you can have other examples where you can have both pH and temperature sensitive, so thermos sensitive as well as pH sensitive core shell it is a same material, but it can act under both pH changes as well as thermal changes. So, this particular example you can see is made up of a try block copolymer, so three polymers one black one red and blue. You can see and these have different properties, one of them is pH sensitive one is temperature sensitive, the other one is the third one is more hydrophobicin nature. So, a combination of this if you take and you increase the concentration beyond a certain concentration, which is called the critical micellar concentration.

Then, this change agglomerate and form this kind of self assembled structures, now you can see in the self assembled structures the black ones are inside and then the red ones are formed a middle layer and then the blue ones around the outside. So, under certain concentration, this try block copolymer each having a particular property self assemble to form this kind of a structure. Not only it is dependent on temperature, the structure because here the temperature is some temperature which is lower than what we called the critical solution temperature.

So, when the temperature is lower than the lower critical solution temperature, it is kind of in the dissolve state we say the critical solution temperature is the temperature when you are in the kind of a dissolved state. Then, above the critical solution temperature, it starts to agglomerating, so these are terms more commonly used in liquid crystals etcetera, but here it is been used for an assembly of try block copolymers. So, you have this kind of structure at a temperature below the LCST, the lower critical solution temperature, so also called the lower consulate solution temperature.

Now, when the temperature becomes larger than the LCST, then you see the structure has become more constricted these chains which were looking outside have now become constricted. So, there is a change in the structure and the total size of this particle will become smaller. Now, this is one chain that with change in temperature at lower temperature you have this at higher temperature you have this now not only that this can change with pH. So, this particular shape that you are seeing is seen at pH 2, but if you keep the same temperature and you increase the pH 2, 7 or 6.9. Then, you see the structure changes slightly and what has changed from here to there is the red region, the one which changes due to pH, it is pH sensitive.

So, the red part you see there is a slight change in the structure compare to this part, so keeping the same temperature if you change pH the red part which is pH sensitive this part of the polymer is changing its shape. If you change the pH further to 9.2, it has further opened out and the overall size of this particle is now much larger than what you started with when the pH was 2, this is all at a temperature. All these three are at temperature larger than LCST, if you do all these pH changes at temperature below LCST, then you will have three different structures like this.

So, you have these open chains of the blue block, which is basically a temperature dependent block, but since all of them have the same temperature this blue part is not showing much changes. They are all similar except the red part which as we saw at the low temperature case will change with pH. Here also, the red part changes with pH, so you have six different type of structures because you have playing with two parameters which is pH and temperature and you have a try block co polymer which has dual responsiveness.

That means it gets affected by two parameters both pH as well as temperature, so it is a very well designed a smart drug delivery system, you can put a drug inside and you can vary the pH and temperature and you can get release of drag at a particular pH. It is planned or designed in such a way that you want to deliver the drug around pH 6.9, which is close to the pH of the living cells.

So, that is what is designed here and similarly, many such combinations of sensitiveness like here we discussed pH and temperature two properties to which these block copolymers are sensitive. You can combine to other properties like something which is responding to magnetism, then you will have a magnetic particle combine with say a pH sensitive particle. So, such combinations of properties will give you advanced and smart materials for the future.

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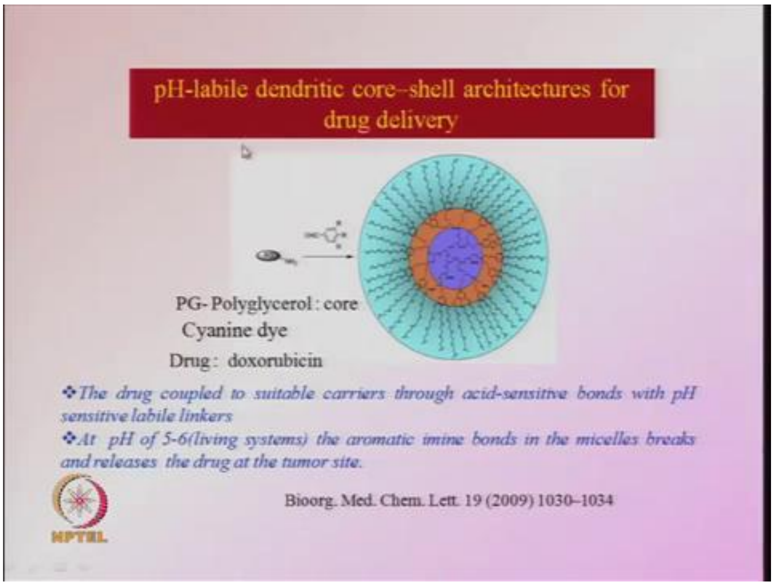

pH-labile dendritic core–shell architectures for drug delivery

PG- Polyglycerol : core
Cyanine dye
Drug : doxorubicin

- *The drug coupled to suitable carriers through acid-sensitive bonds with pH sensitive labile linkers*
- *At pH of 5-6(living systems) the aromatic imine bonds in the micelles breaks and releases the drug at the tumor site.*

Bioorg. Med. Chem. Lett. 19 (2009) 1030–1034

This is now another example of a pH labile dendritic core shell architecture for drug delivery pH labile again means pH sensitive. So, it is sensitive to pH at 1 pH, it has one structure at another pH it has another structure and one of them is a kind of a close structure. The other is a more open structure which can release the drug, the idea is to deliver the drug at a point of your choice at where the pH is what you know where the drug should go. So, this is planned as a combination of a polyglycerol moiety, so you have a poly glycerol here which is amine functionalized and you have this aromatic aldehyde with three long chains alkyl chains.

Now, if you combine these two, then you get a structure like this where this three alkyl chains are seen, so this alkyl chains are on the outer periphery and the CHO has interacted with the amine group to form an imine bond. So, you get the imine the carbon nitrogen double bond, which links the poly glycerol to this aromatic aldehyde and you get a core shell structure like this, where the drug can be encapsulated in the core. What happens at a certain pH at pH around 5 to 6, which we said is present in the living cells? In the living systems, the imine bond actually breaks when the imine bond breaks, then the drug which is in the core is released.

So, the drug is released at the tumor site where the pH is around 5 to 6, so this particular example took a drug which is doxorubicin which is an anti cancer drug. It also incorporated a dye, cyanine dye so that you can see where the drug is going where the tumor cell is going.

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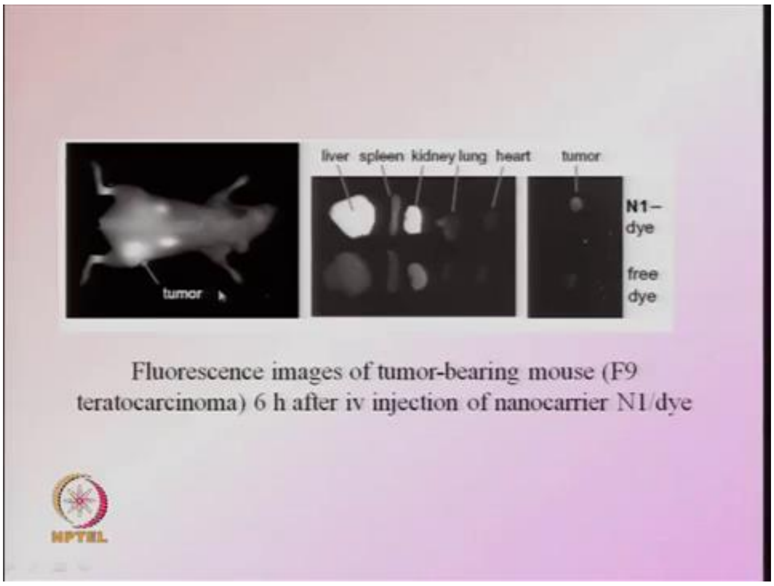

Fluorescence images of tumor-bearing mouse (F9 teratocarcinoma) 6 h after iv injection of nanocarrier N1/dye

This you can see in this picture, so the tumor cell you can see here and you can see in this liver in the kidney and when you have the dye with that nanocarrier we call n 1 is the nano carrier and it has the dye. Then, you can see the tumor cell much more easily when you have only the free dye, then it is not so clear, it is not very clear, but when the dye is along with the nano carrier, then it is much more easily visible.

You can then even release the drug at the particular point by targeting the nano carrier since the dye is going there the drug will also go there. You can target the tumor cell this is in mice in the laboratory where you can target the nano carrier along with the dye and the drug and you can kill the tumor cells specifically.

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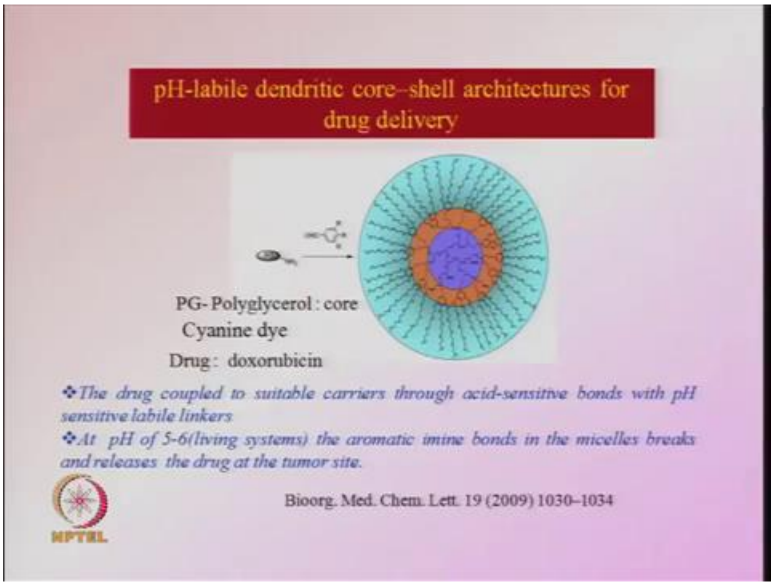

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So, this is an application where the pH change has brought about the release of the drug. So, this is the pH sensitive nano carrier, which has been designed in combination with two molecules generating a bond which will break in the presence of conditions which are present in the tumor cell.

Then, the bond will break and the drug will be released and the drug will be released at the point where the pH is 5 to 6 that is in the tumor cell and so the tumor cell with will be neutralized. So, the normal or the healthy cells will not be affected, so this is a smart drug delivery system a designed to for tumor, cancer treatment.

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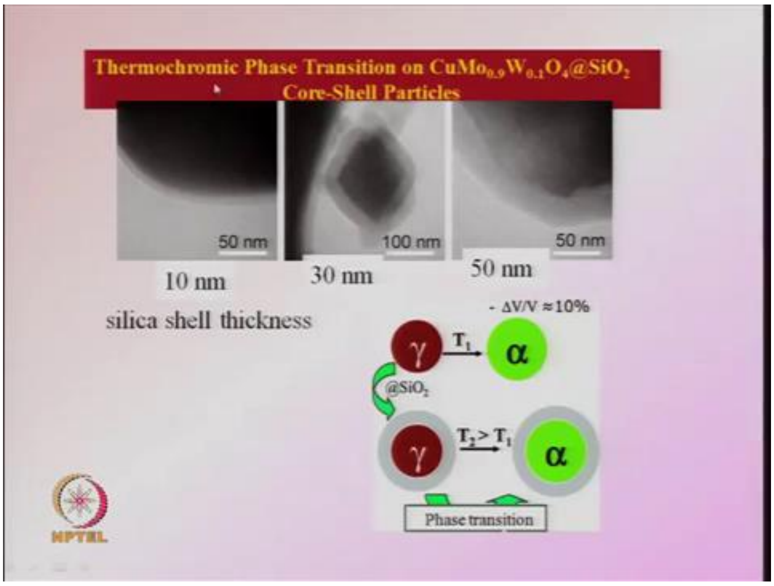

Thermochromic Phase Transition on $CuMo_{0.9}W_{0.1}O_4@SiO_2$ Core-Shell Particles

Now, you can also a think of more material kind of example not towards biology or not to for medicine, but you can look at properties. For example, can you stabilize some particle by making a shell on top of it, so the mechanical property or the thermal property of the particle can be enhanced, you can stabilize a particle by forming a shell. So, this is an example of a kind of oxide which has got primarily copper and molybdenum and a small amount of tungsten. So, it has got this kind of stoichiometry and this is forms the core this oxide of copper molybdenum tungsten forms a core and the shell is formed by silica.

So, this is a core shell particle and shell thickness can be varied, so you can see here it is a thin shell. So, inside you have got this copper molybdenum tungsten oxide is inside and the silica is the shell and this is a thin shell of around 10 nanometers and you can enhance the thickness and this is around 30 nanometers here. You can further enhance to 50 nanometers, so you can vary the shell thickness that is the thickness of the silica shell on top of this oxide nanoparticle. Now, one property of this particle the core particle the copper molybdenum tungsten oxide is that it is normally stable in what is called the gamma type of structure.

When you heat it up this structure changes to what is called the alpha structure, so this oxide is stable in two forms the gamma form and the alpha form depending on the temperature. Now, the temperature or the transition temperature because it is undergoing a structural transition, so it is a phase transition which we can call it is a first order phase transition because the structure is changing. So, this gamma to alpha this transition taking place at temperature t 1 in the particle, which has no shell. So, it is there is no shell around it, now if you add a shell on top of the particle then the gamma particle now has a shell which is of silica.

So, you make a now a core shell structure, now this if you heat at t 1 it does not transfer to form alpha. So, what you have done by making the shell is you have made the gamma form more stable, so it does not change to alpha form at temperature t 1, you have to go to much higher temperature that is t 2, which is much greater than t 1. Then, this gamma form changes to alpha, so this phase transition will occur at a much higher temperature t 2 compare to the particle, where there was no shell. That was at a lower temperature t 1, so you can stabilize the particle by forming a shell on top of this.

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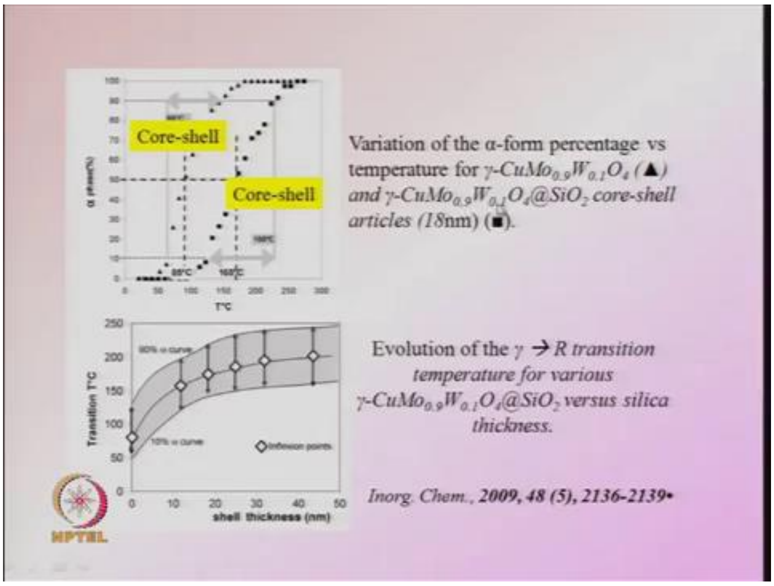

Variation of the α-form percentage vs temperature for γ-$CuMo_{0.9}W_{0.1}O_4$ (▲) and γ-$CuMo_{0.9}W_{0.1}O_4@SiO_2$ core-shell articles (18nm) (■).

Evolution of the $\gamma \rightarrow R$ transition temperature for various γ-$CuMo_{0.9}W_{0.1}O_4@SiO_2$ versus silica thickness.

Inorg. Chem., **2009, 48 (5), 2136-2139**

This you can measure, so this is the same thing, but now in numbers, so you see the amount of alpha phase at low temperature alpha phase is 0. There is no alpha phase everything is gamma phase if you increase temperature for the bear particle, this is not core shell this is only core and this is core shell. So, this you take it this a mistake here this is core and this core particle changes into alpha form as you increase temperature. So, as you increase temperature it is going over to the alpha form and becomes 100 percent alpha when you are say at around 175 or 165 degree, whereas if you make a shell on top of the core, then it becomes alpha only after you go to higher temperature.

So, there is a shift of nearly 100 degrees, so there is a shift from this temperature, which was 165, 170 or 1 to something like 240. So, there is a large shift in temperature between these two this is the pure core structure, this is the core shell structure and there is an enhancement in the temperature at which the transition from the gamma phase to the alpha phase occurs. This can be plotted in the other way that if you increase shell thickness, what happens in the transition temperature? So, the transition temperature keeps increasing as you increase the shell thickness these are plotted from the 90 percent of this curve.

So, this is 100 percent, this is 90 percent if you take this value of the temperature, then you take this curve and if you take 10 percent 10 percent is here. So, if you take this temperature or this temperature, then you are on this part of the curve, you can take either of them both of they show that the transition temperature changes as a function of shell thickness. So, what you learn from this is that if you make a shell on top of the core the stability of the core has been enhanced by the shell and core transforms at a much higher temperature than it would if it did not have the shell.

So, today we will stop our discussion on core shell nanostructures here, we will continue our discussion on core shell structures in our next lecture of this three part series. So, today was the second lecture and you will have one more lecture on core shell nanostructures and the applications of core shell nanostructures.

So, thank you and see you in the next lecture.