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

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Module - 2
Lecture - 6
Synthetic Methodologies (Contd.)

Welcome to the fourth lecture of module II. Earlier we have done in model II lectures on the Sol-gel method of synthesis, and the last lecture, which was the lecture 3 of synthetic methodologies was the beginning of the topic of micro emulsions and micro emulsions based synthesis of nano structured materials. Today is the second lecture, which is a continuation of the synthesis using micro emulsions of nanostructures, and basically today we will be studying about how we use micro emulsion technique for the synthesis of different sizes and shapes of various variety of nano structured materials. In a typical synthesis of nanostructures, first you have the nucleation stage.

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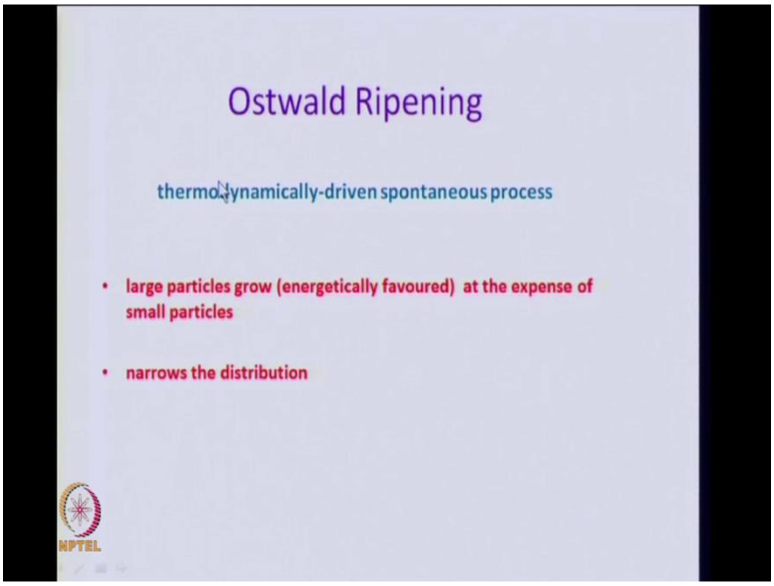

Ostwald Ripening

thermodynamically-driven spontaneous process

- large particles grow (energetically favoured) at the expense of small particles
- narrows the distribution

So, small embryonic nuclei form and then these nuclei grow to form the nano crystals.

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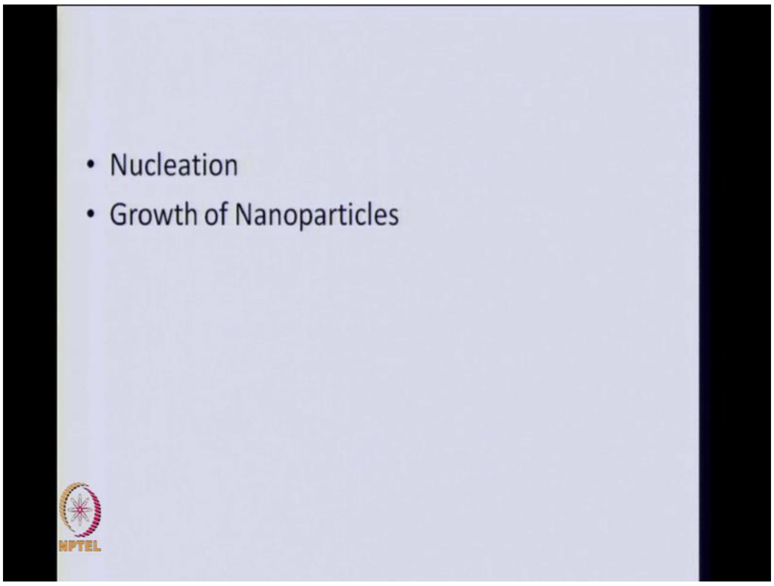

- Nucleation
- Growth of Nanoparticles

So, there are two major steps in any crystallization. You have first nucleation and then these nuclei grow to form the nano crystals or nano particles, and the important thing is how to control the size of the nano particles depends on how you control the growth of these nano particles. So, to understand the methodology of controlling the size of nano particles, we have to understand the thermodynamics and kinetics of these two processes which is nucleation and growth of these nano crystalline materials.

So, one of the mechanisms by which these nano crystalline form and grow is by what is called the Ostwald ripening method. In the Ostwald ripening method, it is basically considered to be thermodynamically driven spontaneous process. In this process, large particles grow at the expense of small particles. These large particles are energetically more favored, and hence the small particles in the vast number of nuclei which form change into or grow into these large size particles. So, they attach themselves to the larger size particles making them even larger and by this, they reduce the surface energy because smaller sized particles have more surface energy.

So, the larger sized particles are energetically more favored, and this is the thermodynamically driven process. Spontaneously whenever there is a growth, it happens through the Ostwald ripening process. Since, it is what is defined by thermodynamics and energetically, you will have growth of larger particles and less number of smaller particles will stay till you reach equilibrium. So, if you look at the formation of a large number of nuclei of small size, as time grows the number of particles with a particular size which is larger than the initial size of the nuclei will become larger. There will be more particles with largest size, and hence the distribution of particle size will become very narrow and you will have most of the particles at one size which is reasonably large size of particle.

So, initially you will have particles of very small size and then you will have particles of various sizes and at equilibrium, you will have a majority number of particles at one particular size which is a large size and the size distribution will become very narrow as time goes on. This is the Ostwald ripening process and as I said earlier, this is the thermodynamically driven process and it will occur spontaneously in any system unless you give some external input, external driving forces, which may be in the order of salts or other chemicals or some electric field or magnetic field. Then you can go to a process which is kinetically stable and not thermodynamically driven process like which is guided here through the Ostwald ripening process.

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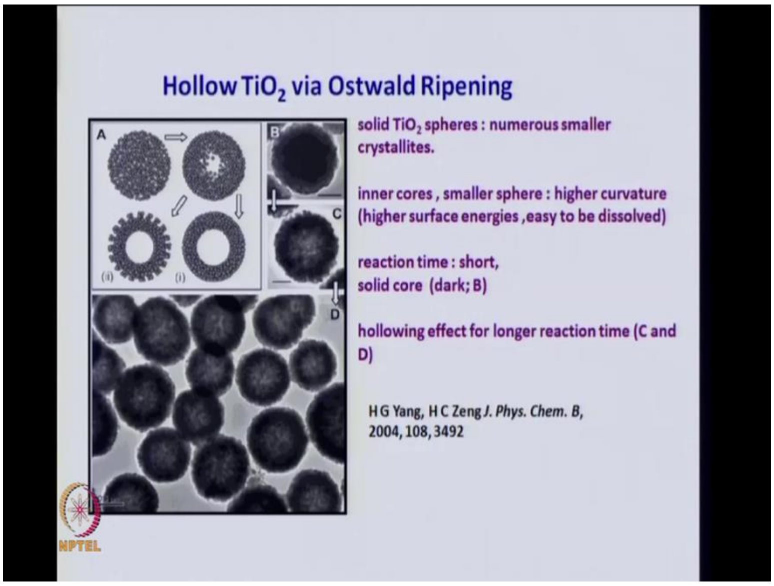

Hollow TiO_2 via Ostwald Ripening

solid TiO_2 spheres : numerous smaller crystallites.

inner cores , smaller sphere : higher curvature (higher surface energies ,easy to be dissolved)

reaction time : short,
solid core (dark; B)

hollowing effect for longer reaction time (C and D)

H G Yang, H C Zeng *J. Phys. Chem. B*, 2004, 108, 3492

So, this is an example of hollow titanium dioxide which is forming through the Ostwald ripening process. So, you see solid TiO2 spheres, initially there are large number of numerous small crystallites which you can see here in this model. As the time goes on, the inner cores, which are smaller spheres, they have higher curvature higher surface energies, and they are dissolved and you get more large particles towards the edge. So, the core particles which have higher surface energy compared to the particles on the surface on the exterior of these large group of particles, so that will grow inside the particles which have more courage, and higher surface energy will be lost. This is a model of what is happening in TiO2, how hollow TiO2 is forming and these are real pictures where you see that the outer part of these large agglomerates of particles is becoming darker, and the interior is becoming lighter. This is the hollowing effect, which you observe because of Ostwald ripening at longer reaction time.

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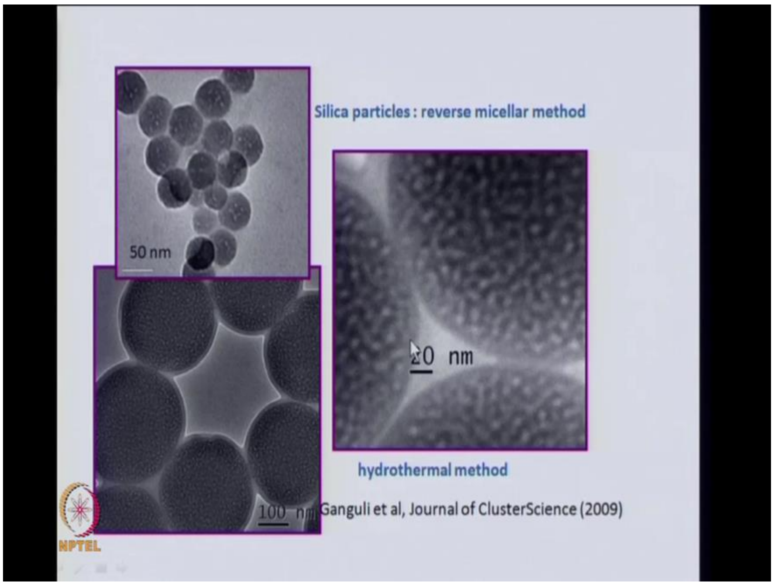
Silica particles : reverse micellar method

hydrothermal method

Ganguli et al, Journal of ClusterScience (2009)

We have also observed in many other systems for example, in silica particles, which we have made using micro emulsions. You can see these pores and with time you can increase the size of these pores. This is typically what you see in the last case as we discussed in TiO2, where Ostwald ripening will increase these pores and will lead to more dense outer structures.

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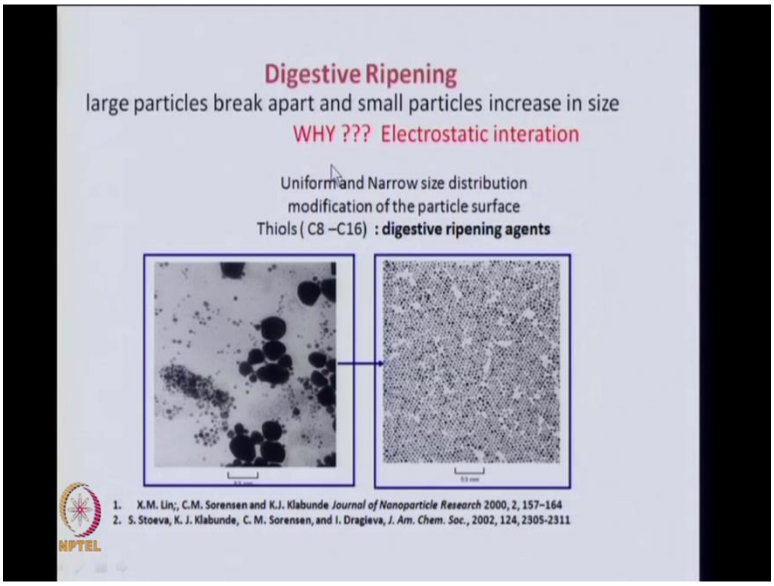

Digestive Ripening

large particles break apart and small particles increase in size

WHY ??? Electrostatic interation

Uniform and Narrow size distribution

modification of the particle surface

Thiols (C8 –C16) **: digestive ripening agents**

1. X.M. Lin;, C.M. Sorensen and K.J. Klabunde *Journal of Nanoparticle Research* 2000, 2, 157–164
2. S. Stoeva, K. J. Klabunde, C. M. Sorensen, and I. Dragieva, *J. Am. Chem. Soc.*, 2002, 124, 2305-2311

The other alternative to Ostwald ripening is what is called the digestive ripening. This is not the thermodynamically driven process, this is against the thermodynamically driven process where large particles break apart and small particles increase in size. So, this is just the opposite of Ostwald ripening. In Ostwald ripening, you have small particles getting removed from the system and the larger particles growing. In this case, large particles break apart and small particles increases in size. Why does this happen? This is due to some external influences.

For example, if you add some Thiols, some long hydrocarbon chain thiols, which have say 8 carbons to 16 carbons, these kinds of thiol molecules bring about this kind of digestive ripening through some electrostatic interactions. And these kinds of materials or these kind of molecules are called digestive ripening agents which help in this process, where instead of having large and small particles, the larger particles break to become uniform. A small sized particle as seen here in this particular case, which is published in these two journals and you get a very uniform homogeneous distribution of particles, a very small size through this digestive ripening process.

This process is not thermodynamically driven. It is kinetically driven and this process is helped by the presence of molecules like thiols which act as digestive ripening agents and this kind of work has been shown in the literature by Klabunde Etal, and these are some other publications where details of the digestive ripening process, the kinetically driven process is explained in detail.

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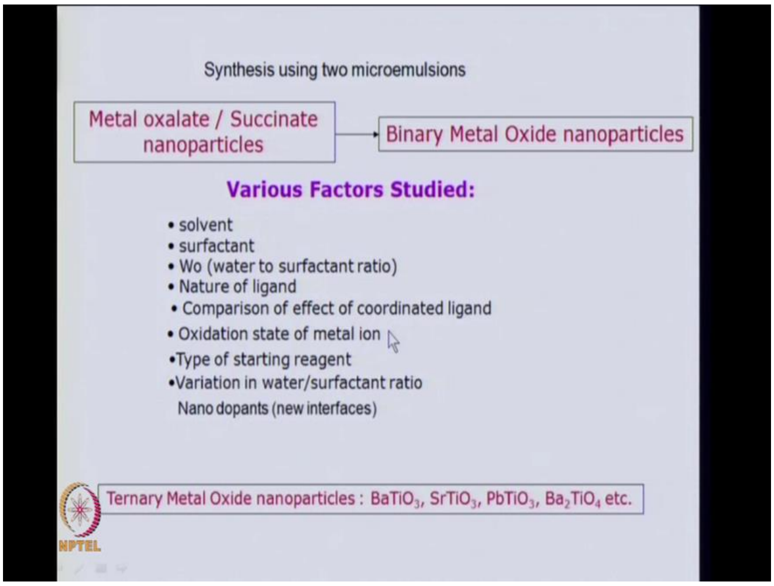

Synthesis using two microemulsions

Metal oxalate / Succinate nanoparticles → Binary Metal Oxide nanoparticles

Various Factors Studied:

- solvent
- surfactant
- Wo (water to surfactant ratio)
- Nature of ligand
- Comparison of effect of coordinated ligand
- Oxidation state of metal ion
- Type of starting reagent
- Variation in water/surfactant ratio

Nano dopants (new interfaces)

Ternary Metal Oxide nanoparticles : $BaTiO_3$, $SrTiO_3$, $PbTiO_3$, Ba_2TiO_4 etc.

Now, typically how you synthesize nano structured materials? So, we will study how we synthesize using two micro emulsions by which we get metal oxalates or metal carboxylates and then generate binary metal oxide nano particles. You know in earlier lecture, we discussed that whenever we have to make a nano material using micro emulsions, we start with 2 or 3 or 4 micro emulsions depending on whether we want binary oxide, binary chloride or ternary material or quaternary material. Depending on that, the number of micro emulsions that you take increases.

So, in this case, we will be taking binary metal oxides. We want to synthesize binary metal oxide. That means one metal and one oxide oxygen species. So, you need two micro emulsions to start with one micro emulsion you will have your metal ion say cobalt or nickel or iron. In the other micro emulsion, you will have the oxalate are succinate or any carboxylate by which you will precipitate the metal carboxylate and then using this metal oxalate or carboxylate, you slowly decompose it to get binary metal oxide nano particles.

So, these nano particles we can control using the micro emulsions. The size and shape of these nano particles can be used by effectively choosing the various parameters, which govern these micro emulsions. So, what are these parameters? These parameters are like the solvent. What is the non-aqueous medium? For example, it can be benzene, it can be toluene and it can be heptanes. What is the surfactant? As we discussed in the previous lecture, you can have surfactant like a cationic surfactant, you can have an anionic surfactant, and you can have surfactants with one tail that is a hydrocarbon chain or two chains or three chains.

So, you can vary the nature of the surfactant, you can vary the head group. What is the charge on the head group whether it is positive or negative, then you can change the w naught parameter which is the water to surfactant ratio. That will also control the type of the size of the micro emulsion. That is fun. The nature of the ligand is important. What kind of ligand you want to attach to the metal? For example, is it that a carbonate ligand, Is it an oxalate ligand or succinate that will affect the dynamics during the mixing of the micro emulsions. They are effects of the ligands. There the oxidation state of the metal ion may be important because it depends on the celebrity product of the metal ion with the ligand, and that will vary whether it is iron plus 2 or iron plus 3, you will have to worry about what is just starting agent whether you are taking ferrous chlorides or ferrous nitrate. Then variation in water surfactant ratio we already discussed will affect.

So, all these parameters have a role to play in the type of micro emulsion that you get and can be varied to get a large variety of metal oxalates or carboxylates. It can be extended to other systems like metal sulfides, metal selenides and metal phosphates. So, here we will discuss first the synthesis of metal oxalates using two micro emulsions and then we can enhance this instead of from two my promotions we can take three micro emulsions and get ternary phases. Then we get ternary oxide materials like barium titanate, strontium titanate where you have 2 metals and 1 oxygen. So, it is a ternary system. This is also a ternary system. So, starting first from a binary to micro emulsion system, we can discuss how we can go to three micro emulsion systems and get ternary oxide phases which are very important for several applications.

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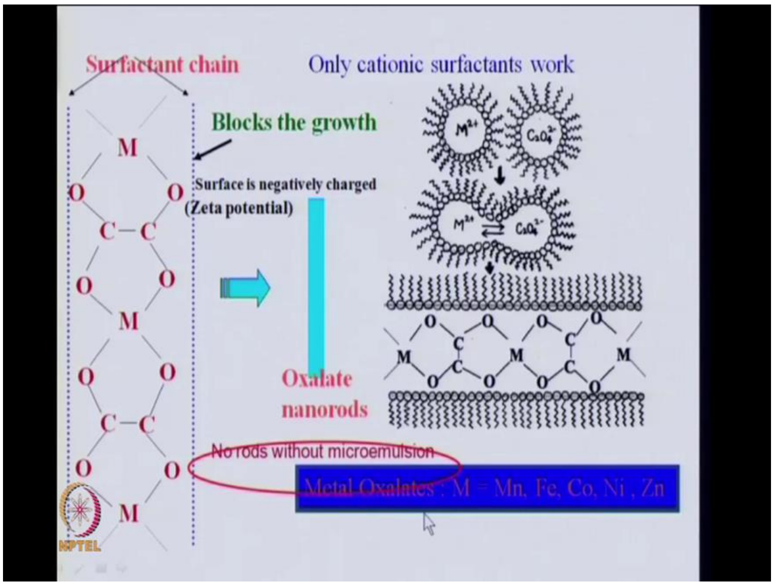

Surfactant chain

Only cationic surfactants work

Blocks the growth

Surface is negatively charged (Zeta potential)

Oxalate nanorods

No rods without microemulsion

Metal Oxalates : M = Mn, Fe, Co, Ni , Zn

So, this is one example where we have taken cationic surfactant, and when we take a anionic surfactant, what we observe is that when you have the metal precipitates with the oxalate, then it might form these kind of chains and we find that in our microscopic studies. We can explain why metal oxalate nanostructures form this kind of linear chains because it can be explained. These oxygen ions which have negatively charged will attract the polar head group which is positive in case of CTAB which is the cationic surfactant.

So, the cationic surfactant will be aligned along these surfaces and hence, growth will be more amenable along this axis, but not on this axis. This is one of the mechanisms that have been proposed for the formation of and isotropic nano structures in metal carboxylates, especially when you take cationic surfactants. The reason as we said is because the surfaces are these rods will be negatively charged and that can be measured using a technique which is called zeta potential measurements. And you can measure the surface, these rods and since, they are negative, there they will attract the positive head group of the cationic surfactant like c CTAB, and the growth will be along this direction. You will end up with nano rods of these metal oxalates if you do not use surfactant.

That means, if you would know if you do not use micro emulsion, then you will not get rods and this is you can take any type of metal like iron, nickel, cobalt, zinc, manganese, all of them from metal oxalates. And they form rod like structures, because of this positive cationic surfactants which make them aligned along these two sides and allow for growth of the rod around one dimension.

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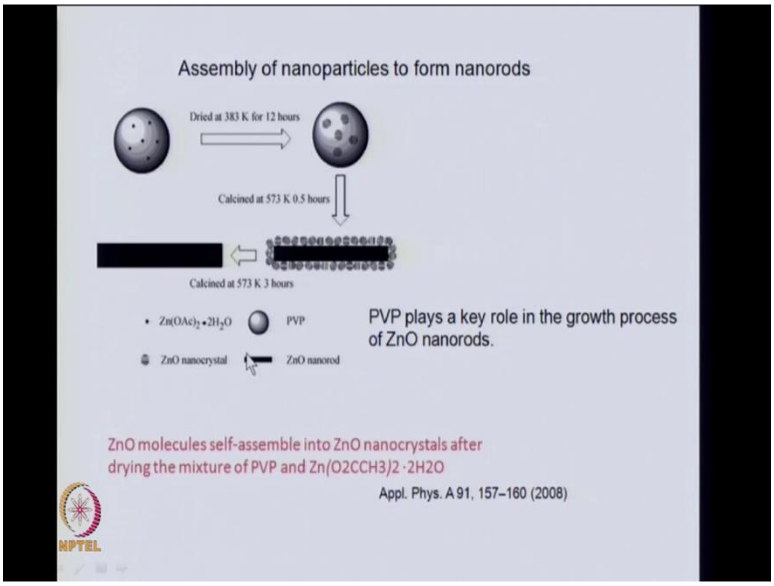

Assembly of nanoparticles to form nanorods

PVP plays a key role in the growth process of ZnO nanorods.

ZnO molecules self-assemble into ZnO nanocrystals after drying the mixture of PVP and $Zn(O2CCH3)2 \cdot 2H2O$

Appl. Phys. A 91, 157–160 (2008)

Now, there are generally the mechanisms by which other rod formation take place is through what is called assembly of nano particles to form rods, nano rods. So, here if you have for example zinc acetate particles and inside this is a polymer like PVP. PVP plays a very important role here for formation of the nano rods. So, in this case, if you have these kinds of zinc acetate particles along with the polymer, and you try this at 383 Kelvin. This is an optimal temperature for this polymer PVP and then you see these particles becoming larger from here.

If you heat for a higher temperature for some more time, then you will see this rod like growth on top of the surface. You see these particles are aligning themselves that assembling on the initial rod, which forms, and as time goes on at that temperature, these particles coalesce on these rods and you get a larger nano rod. So, this is one of the methodologies. How you get nano rods from nano particles? By self assembly during the drying up of the polymer along with the metal ion solution. So, this is very well known technique now by which nano rod formation can be explained.

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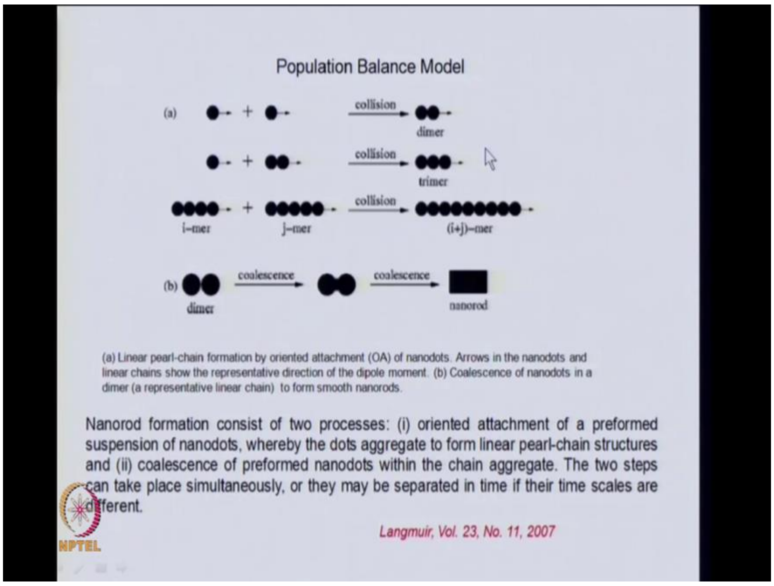

Population Balance Model

(a) Linear pearl-chain formation by oriented attachment (OA) of nanodots. Arrows in the nanodots and linear chains show the representative direction of the dipole moment. (b) Coalescence of nanodots in a dimer (a representative linear chain) to form smooth nanorods.

Nanorod formation consist of two processes: (i) oriented attachment of a preformed suspension of nanodots, whereby the dots aggregate to form linear pearl-chain structures and (ii) coalescence of preformed nanodots within the chain aggregate. The two steps can take place simultaneously, or they may be separated in time if their time scales are different.

Langmuir, Vol. 23, No. 11, 2007

Now, the other way that this rod formation is explained is that you have these nano particles. This is called the population balance model of nano rod formation is that you have these nano particles which are colliding, and they form this kind of dimers and then further collision to give you trimers and then it continues to form tetramer and pentamer etcetera. Now, when they can farm two pentamers may collide and form 10 or deccamer and this continues and then these particles start coalescing. So, these are like a pearl string where each are aligned next to each other in a linear fashion and after some time, they coalesce and as they are coalescing, they form this neck formation and finally, they give the nano rod.

So, this kind of linear pearl chain formation is happening through the oriented attachment of nano dots. So, these nano dots whenever there is a trimer, one more nano dots can come and align itself ahead. So, this is called the oriented attachment mechanism and this basically, first there is a oriented attachment and the second stage is the coalescence of the aligned nano particles to give the final nano rod. So, the oriented attachment of the particles and then coalescence together give you the mechanism for the rod formation in these systems.

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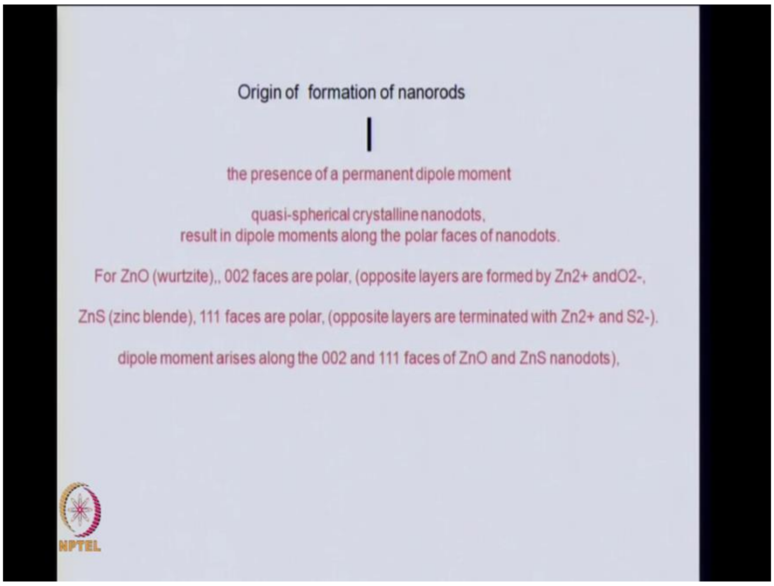

Origin of formation of nanorods

the presence of a permanent dipole moment

quasi-spherical crystalline nanodots,
result in dipole moments along the polar faces of nanodots.

For ZnO (wurtzite),, 002 faces are polar, (opposite layers are formed by Zn2+ andO2-,

ZnS (zinc blende), 111 faces are polar, (opposite layers are terminated with Zn2+ and S2-).

dipole moment arises along the 002 and 111 faces of ZnO and ZnS nanodots),

There is another reason for this oriented growth. If you have a permanent dipole moment, then many of these spherical what we consider spherical nano crystalline particles are actually not spherical, they are quasi spherical. That means there is some distortion of the sphere and that distortion or the quasi spherical nature or these crystalline nano dots that will result in dipole moment along with the polar faces of these nano dots.

Now, whenever you have these dipole moments, so there is some positive and negative dipole charges or opposite faces or opposite layers. Then the fresh ions, which are positively charged ions will then come closer to the negatively charged faces and the negatively charged ions will come closer to the positively charged faces. So, if you look at a zinc oxide for example, the wurtzite structure of zinc oxide in that 002 faces are polar faces. That means, they have some polarity and the opposite faces, 002 faces 2 opposing 002 faces have zinc 2 plus ions on the surface and oxide 2 minus surface on the ions on the other surface.

So, one surface of the 002 is positive and the opposite 002 surface or face is negative now. So, the next zinc 2 plus ion will come closer to the 002 phase which is negative, that is which is having oxide ion terminating on the surfaces. And this way the process is continued by oriented attachment led by this permanent dipole moment which are represented in this polar systems in zinc sulfide or zinc blende structure which has the zinc blende structure, the 111 faces is polar. So, in this case opposite 111 layers will have either, positive or negative charges and accordingly, the subsequent ions say the sulfide ions will come and attach to the surface which has the positive charge, which is terminated by zinc 2 plus ions.

Similarly, the zinc 2 plus ions will come and attach to the surface, which is terminated by sulfide ions and this way, the crystal growth will take place in a very oriented manner and you will have this nano rod formation. So, the dipole moment along the 002 face of zinc oxide and the 111 face and zinc sulfide is important for the growth of nano rods in this system.

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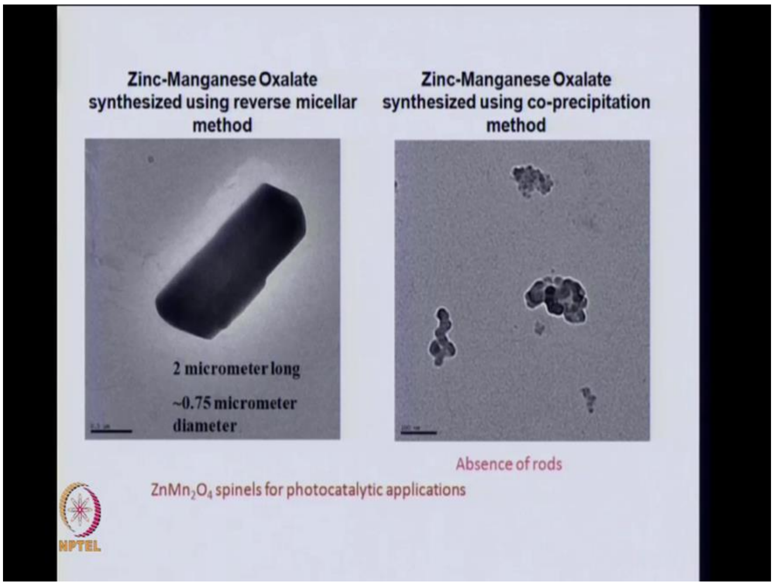

Zinc-Manganese Oxalate synthesized using reverse micellar method

Zinc-Manganese Oxalate synthesized using co-precipitation method

Absence of rods

ZnMn$_2$O$_4$ spinels for photocatalytic applications

Now, to give you an example that the micro emulsion is important for the nano rod formation here, we show on the left panel a nano rod of dimensions may be few the length of several microns, maybe 4 microns, 5 microns and the diameter may be around 300-400 nanometers or may be larger. This nano crystal is of or submicron sized crystal is of zinc-manganese obsolete which has been synthesized using reverse micelles that is using micro emulsions on the right side. We have used the same conditions for making the same compound using the co-precipitation method, where we do not have any surfactants or micro emulsion.

As you see this micro emulsion process containing cationic surfactant gives a nano rod kind morphology whereas, in this case where we have not used any surfactants or micro emulsions, you can see that there are no rods or isotropic structures. They are more or less spherical agglomerated particles of zinc manganese oxalate. If you take the x-ray diffraction of both of them, they will have the same x-ray diffraction telling you that in both the cases the product is the same. However, the morphology is very much dependent on the methodology how you have obtained them.

So, if you use reverse micellar method, you get these rod shape structure. If you do not use reverse micellar method, no micro emulsion. When you get these spheres like structures, of course these materials are important and they belong to a structure called the spinel structure and are useful for photocatalytic applications. So, this is one example, but there are many examples we can show, where the metal oxalates synthesized using micro emulsions show and isotopic rod like structures compared to a spherical or irregular structures if you do not use the micro emulsions containing a cationic surfactant.

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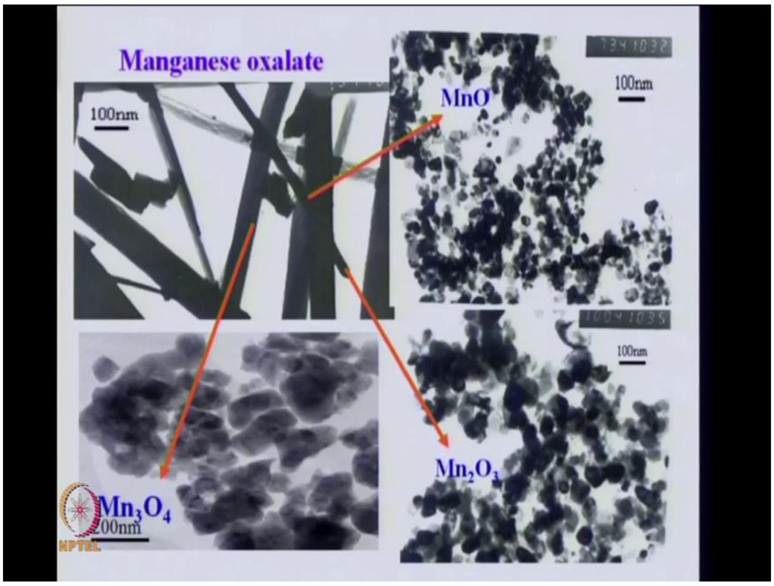

Manganese oxalate

So, this is another example where we have made manganese oxalate rod like structures using micro emulsions with a CTAB as the surfactant and you see as explained earlier, we have rods which have diameter of around 78 nanometers and lengths of several microns. And if you decompose this manganese oxalate rods under some condition that is you can heap this in air or oxygen or nitrogen depending on the environment in which you decompose these manganese oxalate rods, you will get different oxide nano particles like MnO, manganese oxide, manganese 2 oxygen 3 and Mn3O4.

All these three oxides are of size in the nanometer dimensions. Some are smaller say 20-30 nanometers and some are larger say in Mn2O3, we get sizes around 50-70 nanometers and in Mn3O4, we can have sizes around 100-200 nanometers. So, you can get different oxide materials under different conditions of synthesis like the decomposition, temperatures and the environment in which decomposing is important, and if you have more oxygen in the environment, you will get more oxidized species of manganese. Manganese here is divalent and here manganese has an average oxidation state of 3 by 2, right. Here it is 2 and here, we have 6 charges for oxygen and manganese here is trivalent and it is divalent and here, it is trivalent and here is a mixture of divalent and trivalent. So, depending on the conditions, if the more we oxidize, the species will need higher the partial pressure of oxygen during decomposition. All these oxides are very important, because nano structured manganese oxides have lot of applications in battery materials.

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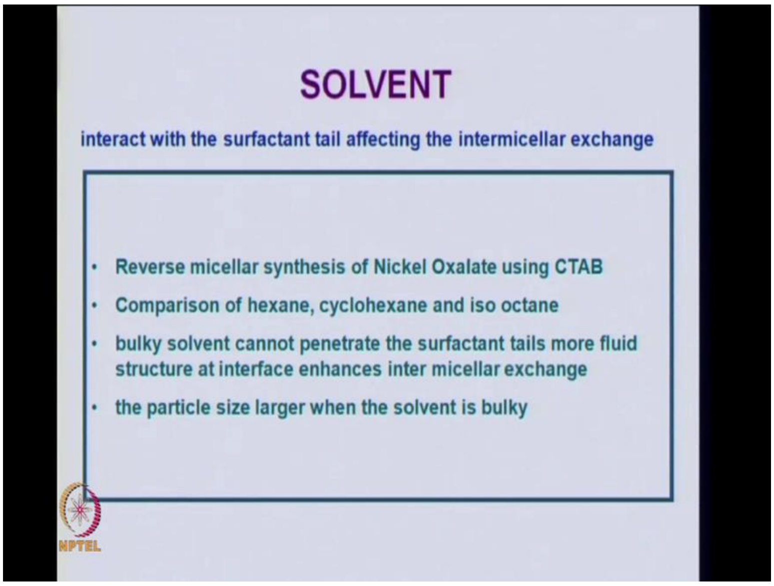

SOLVENT

interact with the surfactant tail affecting the intermicellar exchange

- Reverse micellar synthesis of Nickel Oxalate using CTAB
- Comparison of hexane, cyclohexane and iso octane
- bulky solvent cannot penetrate the surfactant tails more fluid structure at interface enhances inter micellar exchange
- the particle size larger when the solvent is bulky

Now, let us give you an example how the solvent affects the shape and size of these nanostructures. So, solvent molecules interact with the surfactant tail because the surfactant tail is hydrophobic, and the solvent is on aqueous medium in these cases. So, the surfactant tail will interact with the hydrophobic solvent and that will affect the exchange of the ions between two micelles during interactions. So, for example, we choose just this system of the synthesis of nickel oxalate using a CTAB surfactant and then we compare different solvents, different hydrocarbons, hexane, cyclohexane and isooctane.

Now, all these three are hydrophobic and will intractable with the surfactant tail. Of course, the hydrophobicity will vary with different kind of solvent. Now, if you have a bulky solvent, it cannot penetrate the surfactant tails at the interface of water and oil that is water and non-aqueous medium. The surfactant will be aggregated and the bulky solvent which is outside this interface cannot penetrate the surfactant tails and hence, the interface becomes more fluid and whenever the interface becomes more fluid, then that enhances intermicellar exchange. In other words, whenever you have bulky solvent molecules, you have more fluidity at the interface and you have enhanced intermicellar exchange. When you have enhanced intermicellar exchange, the particle size will be larger and hence, particle size is larger when the solvent is bulky.

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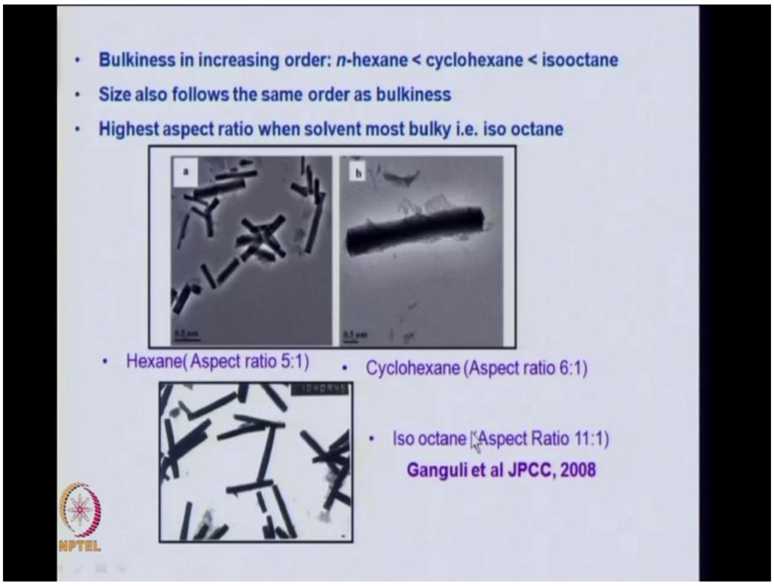

- Bulkiness in increasing order: *n*-hexane < cyclohexane < isooctane
- Size also follows the same order as bulkiness
- Highest aspect ratio when solvent most bulky i.e. iso octane

- Hexane(Aspect ratio 5:1)
- Cyclohexane (Aspect ratio 6:1)
- Iso octane (Aspect Ratio 11:1)

Ganguli et al JPCC, 2008

So, what we have discussed, we can see in experiments. So, if you choose three solvents, hexane, cyclohexane and isooctane, the bulkiness increases like this. So, a hexane has the least bulky and isooctane is more bulky. It has 8 carbons, it has 6 carbons and you can find out that the highest aspect ratio you obtain is when you divide the length with the diameter, you get the aspect ratio. So, the aspect ratio becomes larger as the solvent becomes larger or bulkier. So, hexane is the smallest in size and the aspect ratio is 5 is to

1 whereas, cyclohexane and isooctane, the aspect ratio increases to 6 is to 1 to 11 is to 1. So, you can enhance the aspect ratio and the size as you increase the bulkiness of the solvent.

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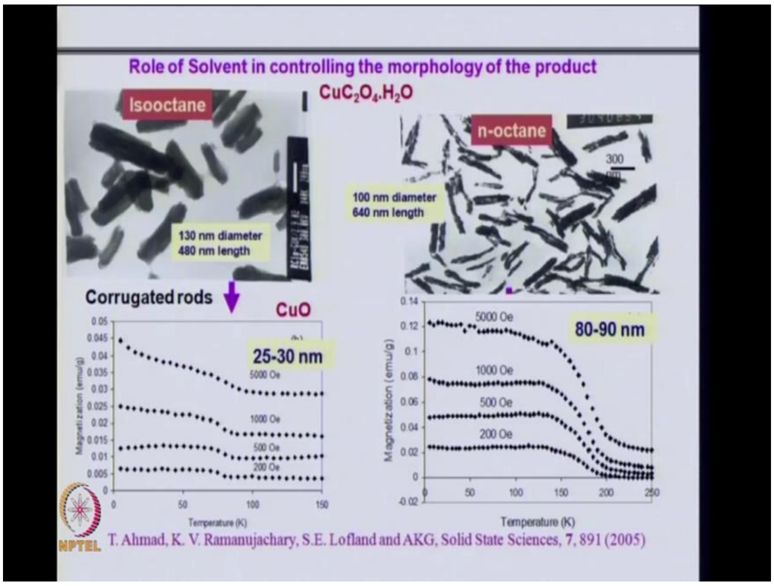

Role of Solvent in controlling the morphology of the product

$CuC_2O_4.H_2O$

T. Ahmad, K. V. Ramanujachary, S.E. Lofland and AKG, Solid State Sciences, 7, 891 (2005)

Now, you can see the same thing in another example. So, this was the example of nickel oxalate. When you have one micro emulsion having nickel and other micro emulsion having oxalate and then you can take another example where you have the solvent is isooctane and n octane. You are comparing two solvents and you are keeping other things constant. So, you are taking the same surfactant CTAB and we are taking in one solution copper, and in another solution obsolete ions. And you are mixing them and inert micellar exchange occurs, and copper obsolete hydrate forms as crystals and in isooctane, you see a much larger particles like this in n octane, you see a much lesser diameter here is much larger the aspect ratio is larger here.

These kinds of effects in controlling the morphology can be seen in all such nano structured materials. Of course, if you decompose these copper oxalates at around 400-500 degree centigrade, you get copper oxide and the copper oxide that you get from this is different in size is 25-30 nanometers, while the copper oxide that you get from normal octane has the size of 80-90 meters and that brings about difference in their magnetic properties. So, this is an example how the size can be controlled through the obsolete precursors and that is difference in size 25 nanometers and 80 nanometers will bring about a difference in the magnetization which is plotted on the y axis compared to the magnetization in the other case, and the difference in these two is just the size of the particles. So, you see that there is some transition here around 80 Kelvin and that transition in this these nano particles is around 100 and 90 Kelvin. So, this change in the particle size brings about the change in the magnetization in copper oxide.

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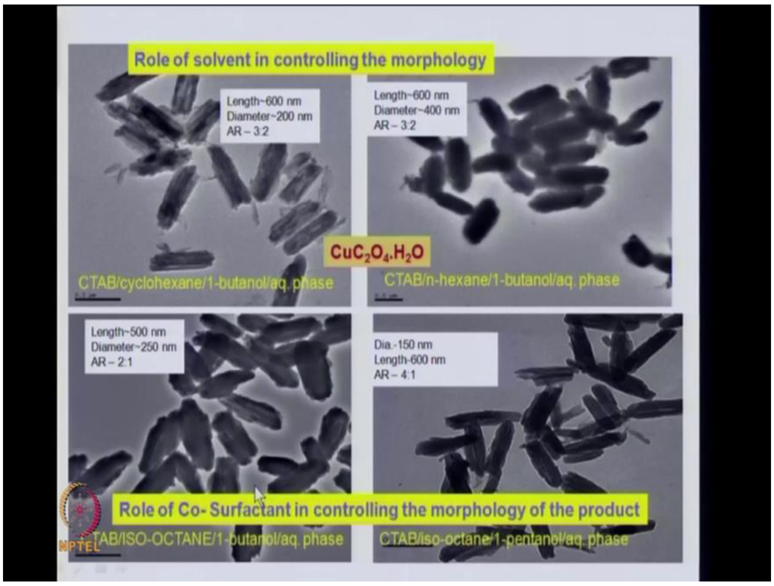

Role of solvent in controlling the morphology

Role of Co- Surfactant in controlling the morphology of the product

Now, you can see the same thing, the solvent is controlling the morphology. So, you are changing from cyclohexane that is the solvent here to hexane to isooctane, right and in this case, we have changed from butanol which is co-surfactant to pentanol which is a bigger co-surfactant. So, the top to show you change in the dimensions or the nano structured materials when you change a solvent and the bottom to slides show, what happens to the morphology when you change the co-surfactant. The co-surfactant normally is an alcohol. So, in this case we have taken butanol and in this case pentanol.

So, we have increased the length of the hydrocarbon chain from 4 carbons to 5 carbons which brings about some changes in the morphology. So, you can bring about changes in the morphology from changing the solvent, the surfactant as we discussed earlier and the co-surfactant. Now, if you want to monitor the effect of one parameter, keep all the others constant. For example, keep the surfactant same like CTAB and keep the solvents same like isooctane and then change the co-surfactant in this case. In this case, you keep the co-surfactant same, but the solvent has been changed. So, you see the effect of the solvent on the aspect ratio, the size of the nano rods of copper oxalate.

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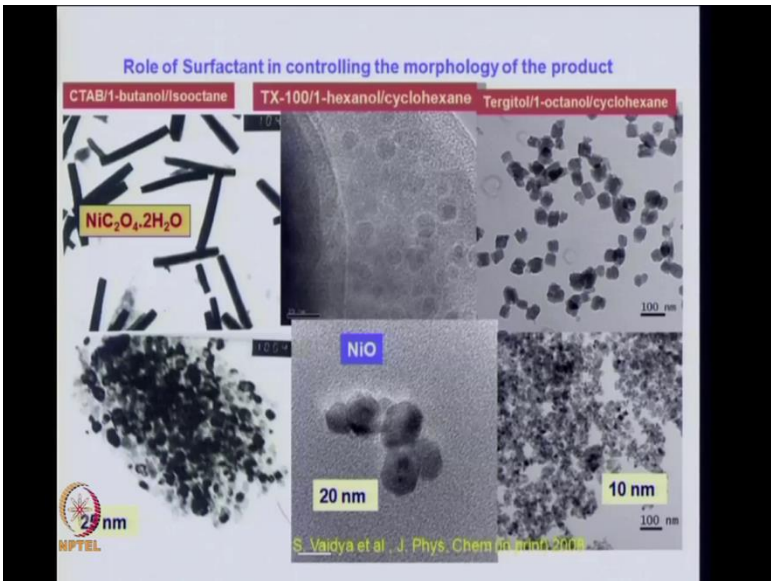

Role of Surfactant in controlling the morphology of the product

S. Vaidya et al., J. Phys. Chem (in print) 2008

This is another case, where the surfactant we have changed from cat and cationic surfactant, we always get rods. As we discussed in the previous slides, if you change the cationic surfactant to TX-100, this is triton X-100. It is a neutral surfactant of some molecular weight, some size. We get spherical particles, not rods like you get in cationic surfactant. This is nickel oxalate dehydrate. In all the cases, you will get same x-ray diffraction pattern telling you all of them are nickel oxalate dehydrates, but when you look at them, some of them are rod like some of them are spherical particles and some of them have cube like shapes. That is because you have changed these surfactants from CTAB which is cationic surfactant to a neutral surfactant like TX-100 to another neutral surfactant of a different size which is tergitol, and you get different shapes of these oxalates. If you decompose them, you of course get nickel oxides of different size particles. You have 25 nanometer particles, 20 nanometer particles and 10 nanometer particles based on the precursor that you use, the precursor size you have controlled using this different surfactants in each case.

So, this is another example of controlling the size and shape using surfactants. Earlier, we showed nickel oxalate. This is cooper oxalate, where you are changing the surfactant from CTAB which is cationic surfactant to AOT, which is anionic surfactant and then this is again cationic, but it has a restricted rotation because we have a pyridinium group here. So, this is cetylpyridinium bromide whereas, this is a cetyl triniethyl alkyl bromide and you see the shape of these particles are not so rod like. Compare it here, they are more spherical. However, if you use another surfactant like TTAB say of different dimensions, different chain length, you get again rod like structures. So, the surfactant has a very important role in controlling the shape of these particles and the size of these particles.

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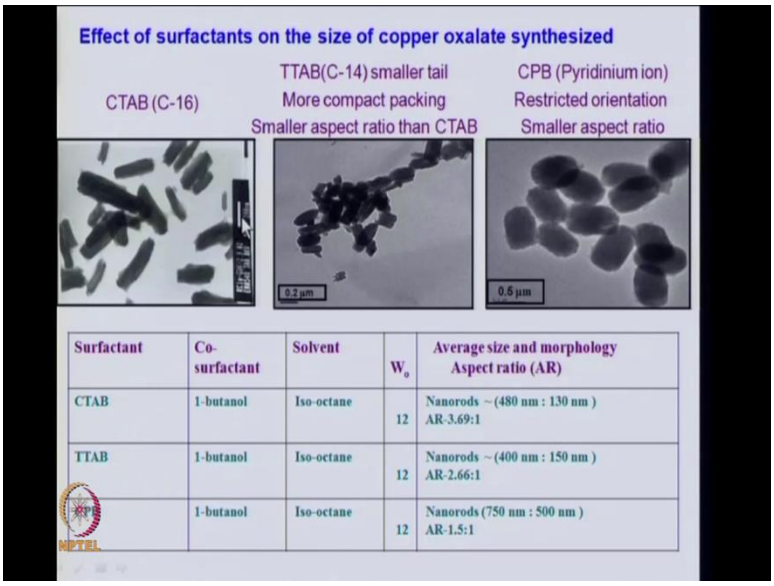

Effect of surfactants on the size of copper oxalate synthesized

CTAB (C-16)

TTAB(C-14) smaller tail
More compact packing
Smaller aspect ratio than CTAB

CPB (Pyridinium ion)
Restricted orientation
Smaller aspect ratio

Surfactant	Co-surfactant	Solvent	W_o	Average size and morphology Aspect ratio (AR)
CTAB	1-butanol	Iso-octane	12	Nanorods ~(480 nm : 130 nm) AR-3.69:1
TTAB	1-butanol	Iso-octane	12	Nanorods ~(400 nm : 150 nm) AR-2.66:1
	1-butanol	Iso-octane	12	Nanorods (750 nm : 500 nm) AR-1.5:1

So, this is more or less what we discussed already. If you have C-16 carbon, C-14 carbon, this is a larger tale hydrocarbon chain, the smaller hydrocarbon chain, more compact packing. There is a small aspect ratio if you have CPB which is pyridinium ion. You have restricted rotation and you get smaller aspect ratio. So, these numbers we have tabulated when CTAB or another surfactant TTAB. So, you are wearing this surfactant keeping the co-surfactant same. The solvent is the same, the W naught parameter is the same.

So, only variation is in the surfactant and you get variation in the average size, and morphology or the aspect ratio which is the ratio of the length is to breath, and that changes like going from 3.7 is to 2.7 is to 1-1.7 is to 1 by changing the dimensions of the surfactant and this is the surface charge, the charge of the surfactant. So, you have positive charge in CTAB and you have a neutral charge in TX-100 and tergitol which are non-ionic and here, you see isotropic growth, whereas in the cationic surfactant, you see more an isotropic. So, there more the aspect ratio is nearly 1 cubic in nature whereas, the aspect ratio is here 3 is to 1.

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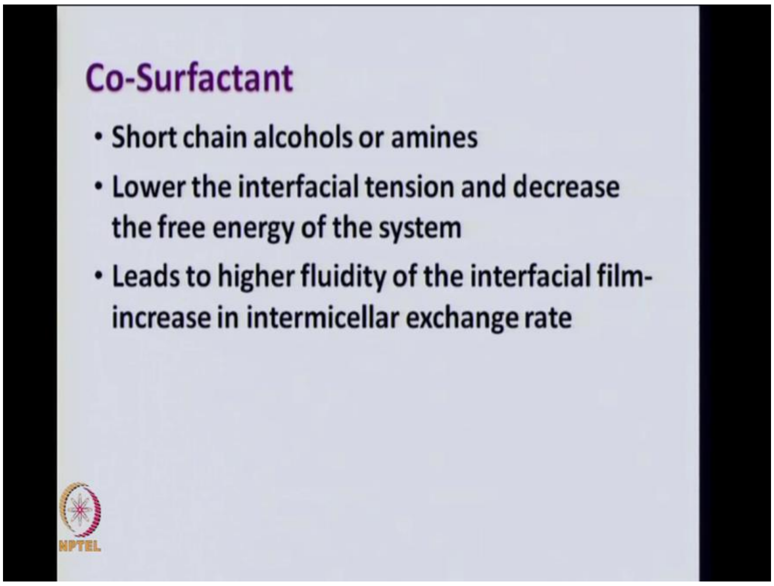

Co-Surfactant

- Short chain alcohols or amines
- Lower the interfacial tension and decrease the free energy of the system
- Leads to higher fluidity of the interfacial film-increase in intermicellar exchange rate

So, the co-surfactants I already discussed co-surfactants have short chain alcohols or amines. They help the surfactant to lower the interfacial tension and they lead to higher fluidity of the interfacial film and increase in intermicellar exchange rate. So, the co-surfactants basically like we have used butanol or pentanol etcetera help in decreasing interfacial energy between the water medium and the non-aqueous medium, the solvent which we are taking which may be isooctane or heptane etcetera.

Now, so this role of co-surfactant we can see more in detail. So, here you have butanol, pentanol, hexanol and octanol. So, you are varying everything else is saying you have CTAB as surfactant. In all these cases, only the self co-surfactant is varying and you can see a variation in the diameter and length of these particles. So, if you go from butanol to hexanol, you see the aspect ratio is changing and then beyond hexagonal, the aspect ratio comes back. It becomes cubes. So, there is an optimal chain length of the co-surfactant and it appears to be 6 carbons is an optimal size.

We have seen that if you increase beyond hexanol, then you get aspect ratio of starting to become less and then they become in octanol and decanol, which are very large chain co-surfactant 8 carbons and 10 carbons. They become more uniform and nano-cubes and nano particles start forming. So, you start with 5 carbons, 6 carbons, 7 carbons, 8 carbons, 10 carbons and up till says 6 or 7, you see an isotropy and beyond that you see it becomes more uniform particles. And this we have tried to explain that beyond c6, the carbon chain in the co-surfactant starts interacting with the surfactant tails because the co-surfactant tails are hydrophobic and the surfactant tails are also hydrophobic. They start interacting with each other and hence, it affects the inert micellar exchange and it actually prevents decrease in the intermicellar exchange and hence, it reduces the size of the particles which are formed.

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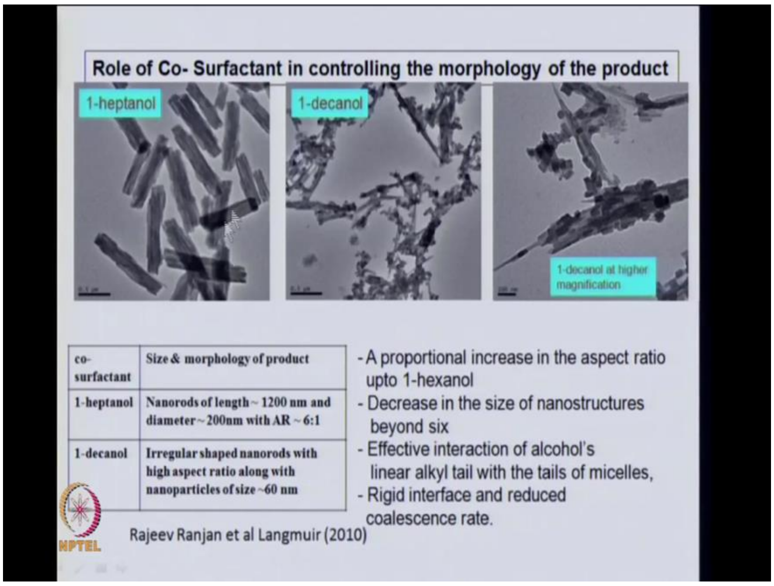

Role of Co- Surfactant in controlling the morphology of the product

co-surfactant	Size & morphology of product
1-heptanol	Nanorods of length ~ 1200 nm and diameter ~ 200nm with AR ~ 6:1
1-decanol	Irregular shaped nanorods with high aspect ratio along with nanoparticles of size ~60 nm

- A proportional increase in the aspect ratio upto 1-hexanol
- Decrease in the size of nanostructures beyond six
- Effective interaction of alcohol's linear alkyl tail with the tails of micelles,
- Rigid interface and reduced coalescence rate.

Rajeev Ranjan et al Langmuir (2010)

So, this is already what we discussed in heptanol and decanol. We can see that the morphology changes and up till 6 carbons in the co-surfactant, the size of the particles increases.

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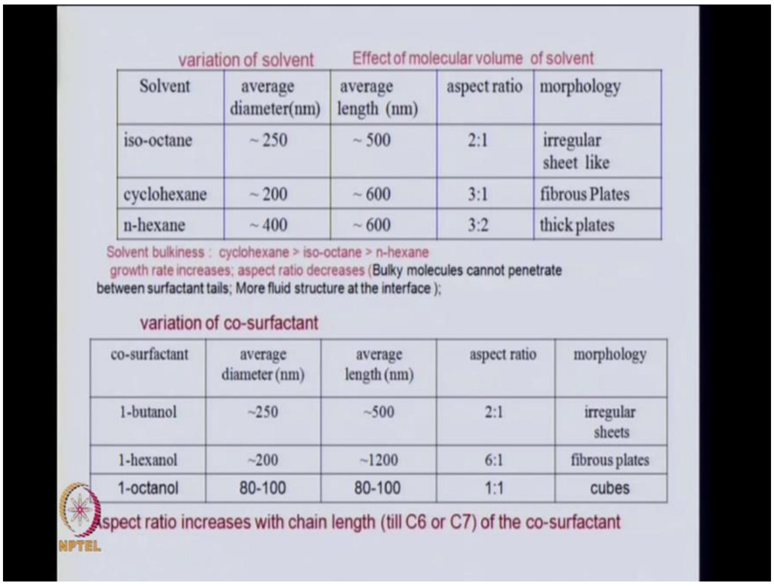

variation of solvent Effect of molecular volume of solvent

Solvent	average diameter(nm)	average length (nm)	aspect ratio	morphology
iso-octane	~ 250	~ 500	2:1	irregular sheet like
cyclohexane	~ 200	~ 600	3:1	fibrous Plates
n-hexane	~ 400	~ 600	3:2	thick plates

Solvent bulkiness : cyclohexane > iso-octane > n-hexane
growth rate increases; aspect ratio decreases (Bulky molecules cannot penetrate between surfactant tails; More fluid structure at the interface);

variation of co-surfactant

co-surfactant	average diameter (nm)	average length (nm)	aspect ratio	morphology
1-butanol	~250	~500	2:1	irregular sheets
1-hexanol	~200	~1200	6:1	fibrous plates
1-octanol	80-100	80-100	1:1	cubes

Aspect ratio increases with chain length (till C6 or C7) of the co-surfactant

So, to compare all of them, we have made this table where we are seeing variation of solvent isooctane, cyclohexane and hexane. You can see the average diameter and the average length and the aspect ratio and the morphology is changing depending on the type of solvent, and we explain that as the solvent bulkiness is decreasing or increasing. In this case, cyclohexane is greater than isooctane and is greater than normal hexane. So, the growth rate increases and the aspect ratio decreases, and this we already explained because bulky molecules will give more fluid interface because they cannot interpenetrate and hence, intermicellar exchange will increase and the size of the particles and aspect ratio increase. Now, in the variation of co-surfactants, we saw that till C6 or C7, the chain length will increase after which it will start decreasing.

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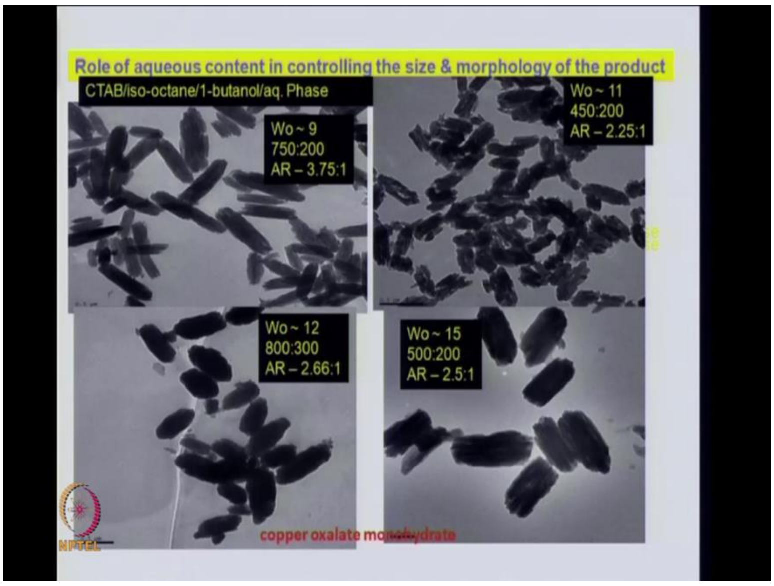

Role of aqueous content in controlling the size & morphology of the product

CTAB/iso-octane/1-butanol/aq. Phase

copper oxalate monohydrate

So, this is kind of example that where we are showing what happens when you change the water to surfactant ratio which is the W naught parameter. So, if you keep the surfactant, the solvent and co-surfactant same in all these four cases, the surfactant and the solvent are not changed. Only thing which is changed is W naught parameter. So, the W naught parameter is here which is the water is to surfactant ratio is 9 and here, it is 11 and then here it is 12 and 15.

So, the W naught parameter is changing and the shapes of these rods are changing, and this is an example of copper oxalate monohydrate. You have taken one micro emulsion of copper ions and other micro emulsion of oxalate ions with this surfactant CTAB with isooctane as the solvent and one butanol. So, co-surfactant with the varying W naught parameter and you are getting different aspect ratios. So, what we find is as the W naught parameter is increasing, the aspect ratio is decreasing from 3.75 is to 1 to 2.5 is to 1.

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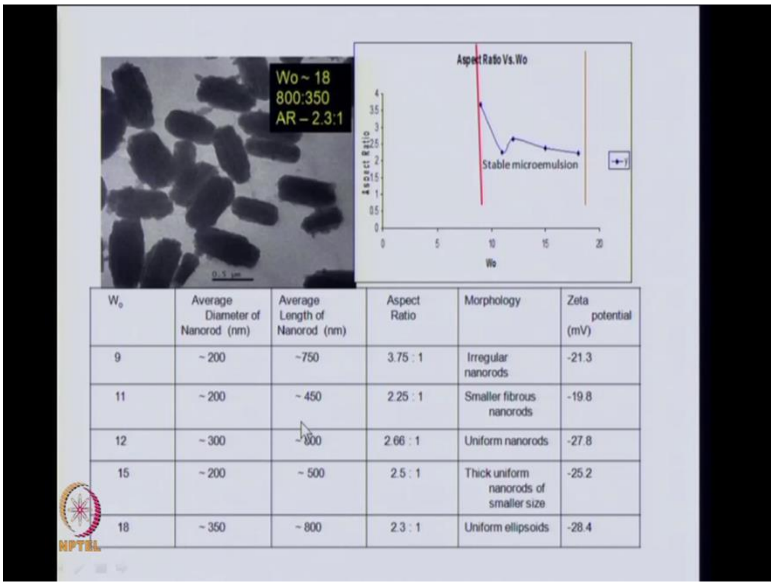

W_o	Average Diameter of Nanorod (nm)	Average Length of Nanorod (nm)	Aspect Ratio	Morphology	Zeta potential (mV)
9	~200	~750	3.75 : 1	Irregular nanorods	-21.3
11	~200	~450	2.25 : 1	Smaller fibrous nanorods	-19.8
12	~300	~800	2.66 : 1	Uniform nanorods	-27.8
15	~200	~500	2.5 : 1	Thick uniform nanorods of smaller size	-25.2
18	~350	~800	2.3 : 1	Uniform ellipsoids	-28.4

So, this is another case of W naught 18. So, this was 15 and this is 18, and it further decreases. So, more or less if you plot the aspect ratio versus the W naught parameter, it appears to decrease as a function of W naught. So, larger the W naught, the aspect ratio is smaller and this is again shown in the variation W naught, and the aspect ratio is shown here. It decreases more or less with same fluctuation here as the function of W naught parameter.

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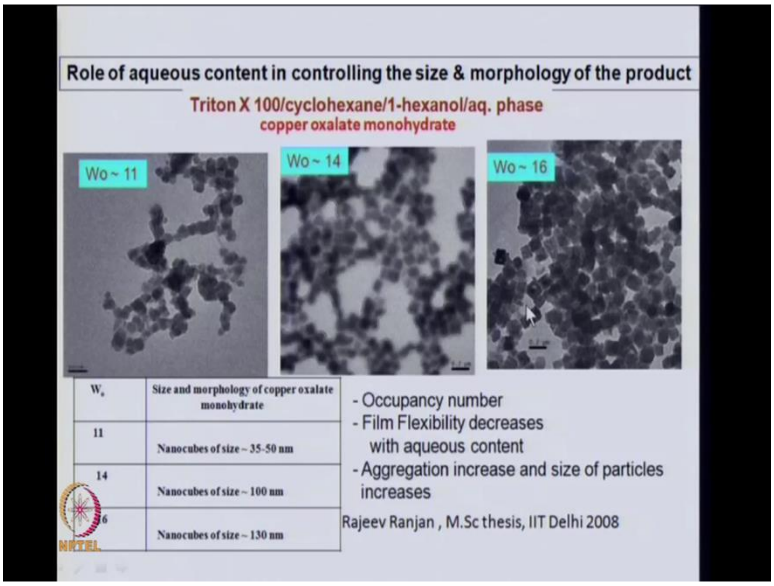

Role of aqueous content in controlling the size & morphology of the product

Triton X 100/cyclohexane/1-hexanol/aq. phase
copper oxalate monohydrate

W_o	Size and morphology of copper oxalate monohydrate
11	Nanocubes of size ~ 35-50 nm
14	Nanocubes of size ~ 100 nm
6	Nanocubes of size ~ 130 nm

- Occupancy number
- Film Flexibility decreases with aqueous content
- Aggregation increase and size of particles increases

Rajeev Ranjan , M.Sc thesis, IIT Delhi 2008

Now, you can further see this in the case of another surfactant that was with CTAB. If you use another surfactant like triton X-100 and you vary the W naught parameter from 11, 14 to 16, so in this case what happens is you are changing the W naught parameter. The size of the particle is increasing, because you have more water, more crystallization. The reverse micelles are larger in size and you get the size of the particle increases. So, this is for case, where you have taken a neutral surfactant, you get uniform particles cube like particles and not rod like particles.

In the earlier case, we had taken CTAB as the surfactant, which gives rise to anisotropic structures. And in this anisotropic structures as we increases W naught, the aspect ratio continues to decrease which is in a way tells you that the size of the particle, the spherical particles or the cubic table particles will increase as the W naught parameter increases whereas, the anisotropic will decrease as the W naught parameter will increase. So, in a more constrained reactor and more constrained reverse micelle, the anisotropy is higher.

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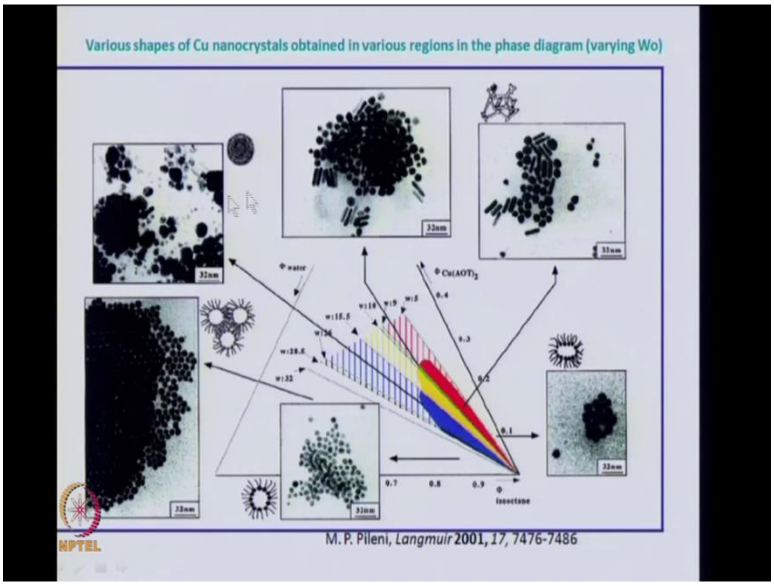
Various shapes of Cu nanocrystals obtained in various regions in the phase diagram (varying Wo)

M. P. Pileni, *Langmuir* 2001, *17*, 7476-7486

So, this is another example of how using different W naught parameters, this is for a copper nano crystals. We were showing in earlier slides copper oxalate or nickel oxalate, these kinds of nanostructures. This is a slide where you see just copper nano crystals with varying W naught and you see different types of size and shape. So, you have spheres for W 32, and you have these kinds of particles when your W naught equals to

28 and when you have W naught equal to between 9 and 10, you seem to get this kind of rod and particle type of mixtures for copper. When you are in this range which is around 6-7, W naught is equal to 6 or 7; you get more anisotropic structures and spheres. So, this is a steady on copper nano crystals reported earlier.

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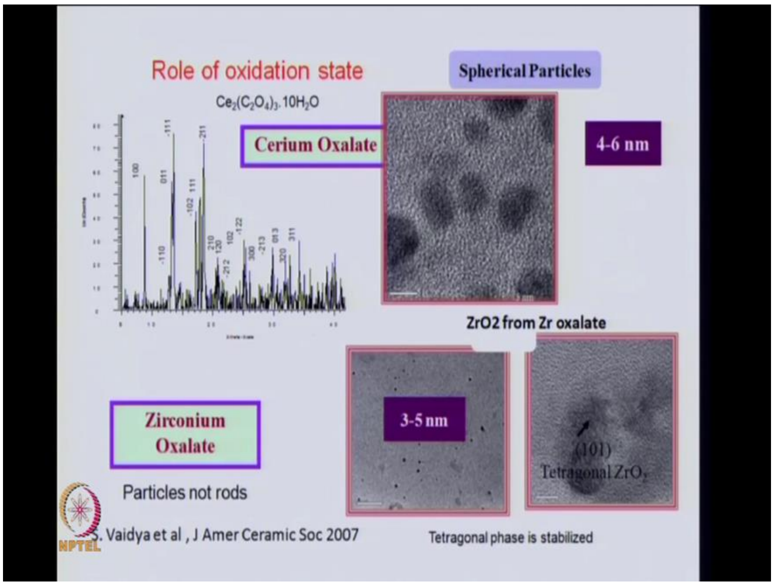

Role of oxidation state

$Ce_2(C_2O_4)_3.10H_2O$

Cerium Oxalate

Spherical Particles

4-6 nm

ZrO2 from Zr oxalate

Zirconium Oxalate

3-5 nm

Particles not rods

S. Vaidya et al , J Amer Ceramic Soc 2007

Tetragonal phase is stabilized

Now, we also see that the role of oxidation state plays a part because if you see that whatever a metal oxalate dogs, we discussed in that always we had metal in the divalent oxidation state like cobalt 2 plus nickel 2 plus reacting with oxalate ion in the micro emulsions gives you rods with CTAB as a surfactant cationic surfactant. However, if you choose the same system like CTAB based cationic surfactant and the synthesis of cerium oxalate or zirconium oxalate, we get particles and not rods, although we are using a CTAB as a surfactant, which is cationic surfactant.

So, it suggests that the oxidation state is important because cerium here is not divalent. It is trivalent and zirconium here is tetravalent and not divalent. So, it appears that the 1 is to 1 ratio oxalate ion is di-negative and the metal ion if it is di positive. And they have same charge of course opposite, then it forms anisotropic nano rods in a CTAB based micro emulsions whereas, when the oxidation state is larger say 3 or 4. Then they are giving rise to spherical particles of zirconium or cerium oxalate and zirconium oxalate because they again can be decomposed to give you zirconia or ceria depending on the conditions.

In this case, we stabilize a tetragonal ZrO2 phase which normally is stable only under certain conditions. So, you can make metastable phases using the micro emulsion process.

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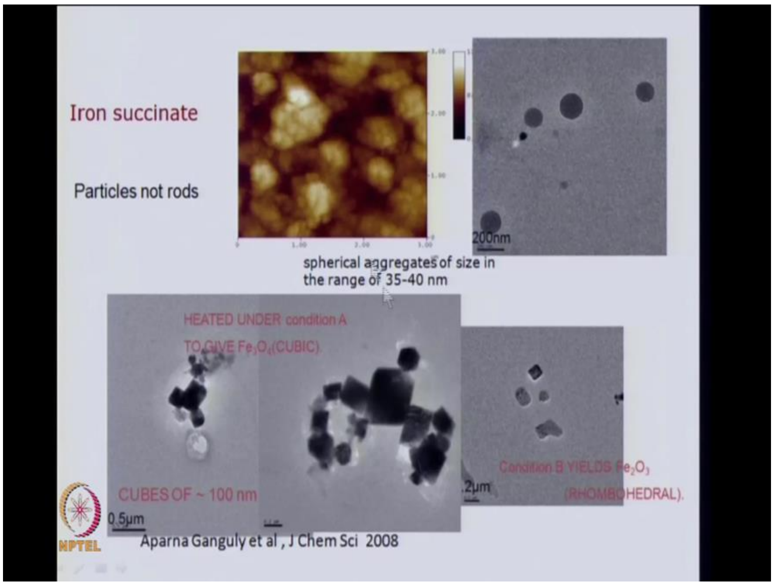

Iron succinate

Particles not rods

spherical aggregates of size in the range of 35-40 nm

HEATED UNDER condition A TO GIVE Fe_3O_4 (CUBIC).

CUBES OF ~ 100 nm

Condition B YIELDS Fe_2O_3 (RHOMBOHEDRAL).

Aparna Ganguly et al , J Chem Sci 2008

You can choose. Instead of oxalate, you can choose succinate and then what we find is, we do not get those rods; we are getting particles. So, the anion is also important. In all the earlier cases, we chose oxalates as anion and we got rods in the presence of CTAB. Here we see although we have chosen CTAB as the surfactant, everything else is the same except we have changed the succinate from the oxalate, you get particles and not rods. So, that means, the ligand is also very important as is one of the important parameters of the formation of anisotropic structures.

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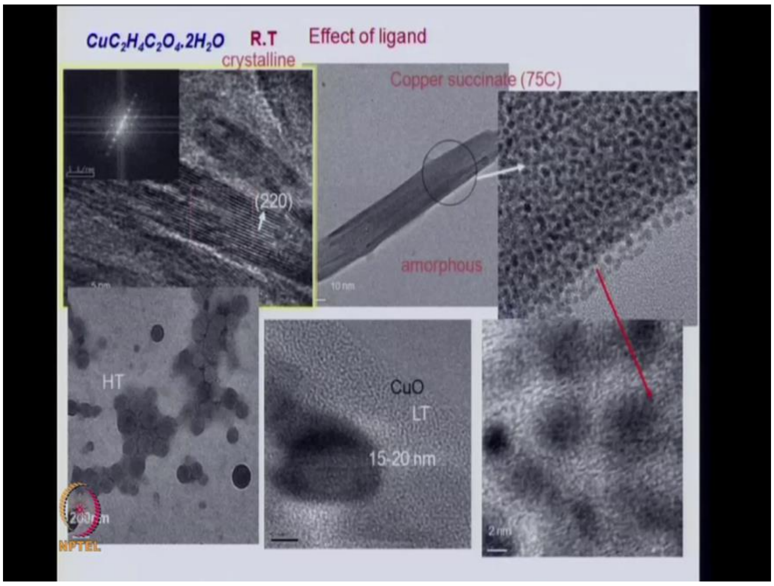

$CuC_2H_4C_2O_4.2H_2O$ R.T Effect of ligand

Here we see that this is cooper succinate. In this case depending on the ligand, we can get crystalline anisotropic structures under certain cases, and you can change it to amorphous structures and that amorphous structure can again give rise to particles like this and on heating can give rise to the oxides. So, this is iron succinate, where it was the trivalent iron use. So, trivalent iron was not giving any rods whereas, divalent cooper gave us anisotropic rods with succinate ion also, and some we can transform them to at room temperature. They are crystalline rods as you can see from the transmission electron microscope and if you heat it, it becomes amorphous. The crystallinity disappears, and if you look carefully you can see these particles and these particles when under a high resolution can show you this lattice fringes and decomposition.

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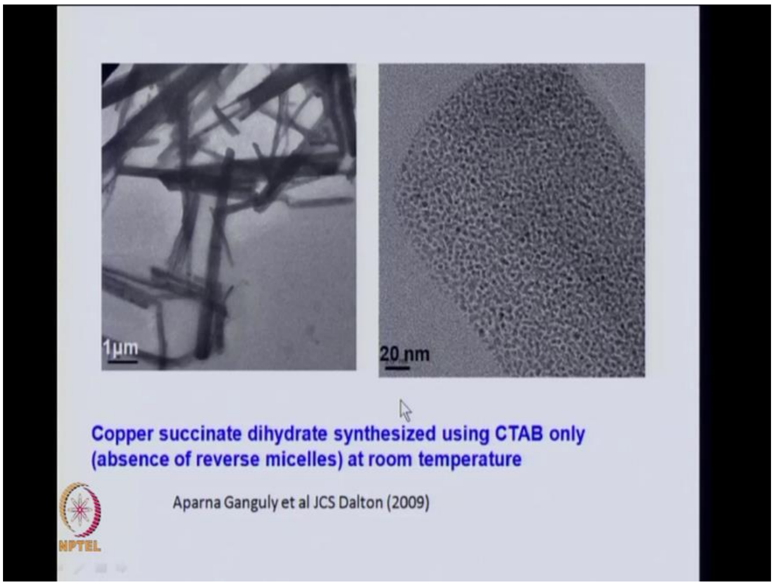

Copper succinate dihydrate synthesized using CTAB only (absence of reverse micelles) at room temperature

Aparna Ganguly et al JCS Dalton (2009)

They will give you copper oxide like they can be obtained from copper oxalate. So, again we show you the same copper succinate dihydrate synthesized using CTAB in the absence of reverse micelles at room temperature, and they are slightly different. And if you use the reverse micelles, you are getting this crystalline rods, whereas you can change the morphology of these rods by choosing whether you want to do in reverse micelles or in the absence of the reverse micelles.

So, by this we come to an end today of the various examples of synthesizing nano structured materials using micro emulsion. So, I hope we have learnt some basics of micro emulsions, and that technique to make nano structured materials and how to control this shape and size of these nano structured materials using micro emulsions. So, we meet next time for a new methodology.

Till then thank you and goodbye.