Nanostructures and Nanomaterials: Characterization and Properties

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Lecture - 13
Introduction to Nanomaterials (C1)

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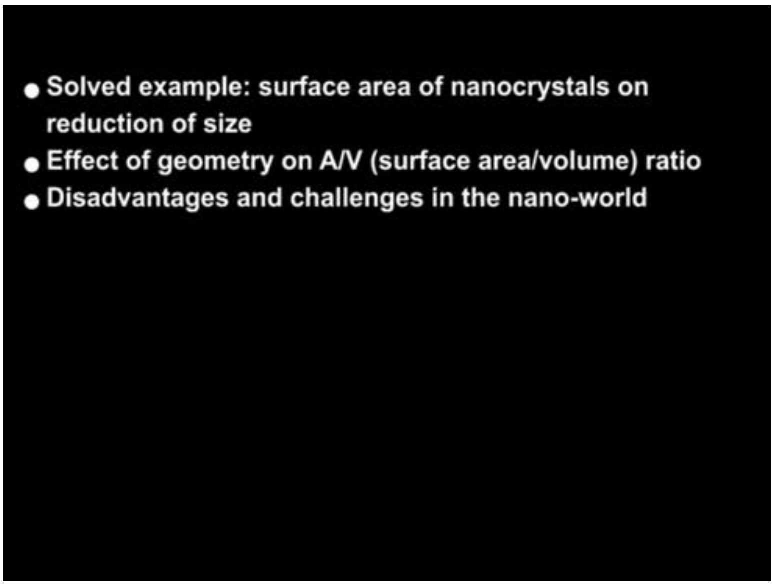

- Solved example: surface area of nanocrystals on reduction of size
- Effect of geometry on A/V (surface area/volume) ratio
- Disadvantages and challenges in the nano-world

We will solve an example to see one important effect, which we have been repeatedly mentioning that is the increase in area per unit volume of particle.

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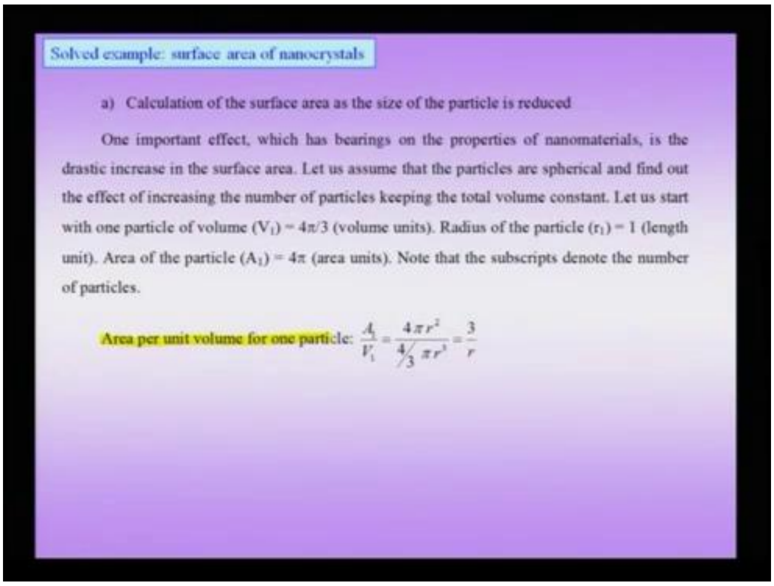

Solved example: surface area of nanocrystals

a) Calculation of the surface area as the size of the particle is reduced

One important effect, which has bearings on the properties of nanomaterials, is the drastic increase in the surface area. Let us assume that the particles are spherical and find out the effect of increasing the number of particles keeping the total volume constant. Let us start with one particle of volume (V_1) = $4\pi/3$ (volume units). Radius of the particle (r_1) = 1 (length unit). Area of the particle (A_1) = 4π (area units). Note that the subscripts denote the number of particles.

Area per unit volume for one particle: $\frac{A_1}{V_1} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}$

So, we said when you go to nano sizes at least one important effect is obvious, and which is expected is the increase in surface area. And we had noted that suppose instead of talking about only the external surface, and we are talking about a polycrystalline material and we are actually reducing the grain size, then the interface area which is the grain boundary area per unit volume of the material will increase as I reduce my grain size to very small dimensions. So, let us make a calculation to understand this effect so, that we have in perspective the kind of numbers involved and the effects we are talking about. At the outside there are two effects which you expect when you go down to small scales.

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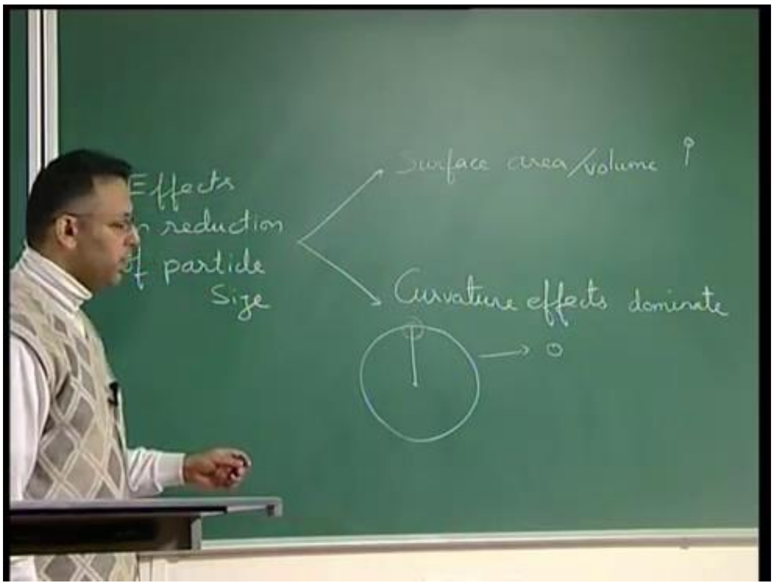

So, two important things we have to keep in mind when we are actually reducing the particle size, one is that the surface area per unit volume will increase and we will actually make a calculation to show this, but additionally we will notice that curvature effect start to dominate when you move on to small sizes. So, if we had a large size particle, this curvature here would be actually small as compared to a small size particle as you know curvature goes as the inverse of the radius of curvature.

Therefore, as we reduce the I reduce my particle size and make the radius smaller, the curvature effect will start to dominate because, now there will be more unsatisfied bonds on the with respect to the surface atoms here, as compared to the case where the curvature is small. So, these two important effects will start to dominate when I go down to small sizes and this example will particularly focus on the first one.

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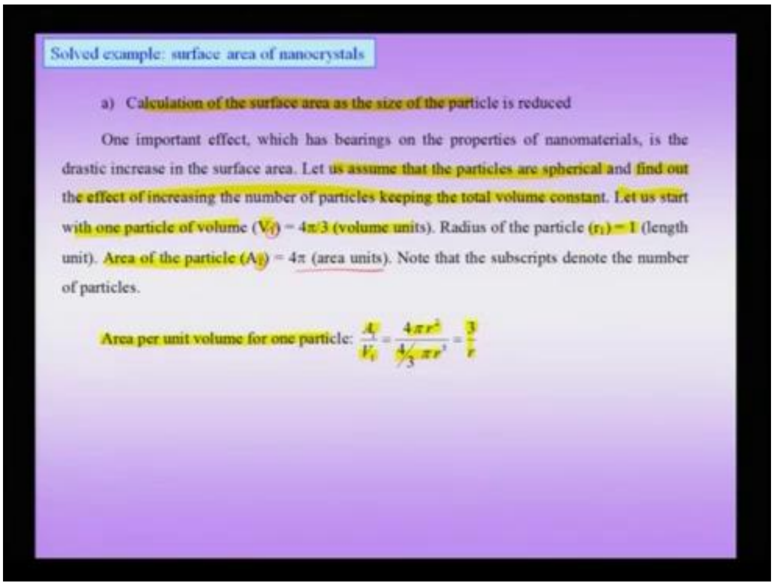

Solved example: surface area of nanocrystals

a) Calculation of the surface area as the size of the particle is reduced

One important effect, which has bearings on the properties of nanomaterials, is the drastic increase in the surface area. Let us assume that the particles are spherical and find out the effect of increasing the number of particles keeping the total volume constant. Let us start with one particle of volume (V_1) = $4\pi/3$ (volume units). Radius of the particle (r_1) = 1 (length unit). Area of the particle (A_1) = 4π (area units). Note that the subscripts denote the number of particles.

Area per unit volume for one particle: $\frac{A_1}{V_1} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}$

So, let us calculate the surface area as the size of the particle is reduced. Let us assume that the particles as spherical for now, and we will all later on take up a couple of more examples of what other possibilities exist, and find out the effect of increasing the number of particles keeping the total volume constant. Let us start with one particle of volume V 1, and if you assume as a radius of the particle to be one unit then the volume will be 4 by 3 pi one unit cube which is 4 by 3 pi.

The area of the particles if there is only one particle and the subscript here refers the number of particles so, the subscript in these cases refers to the number of particles at each stage of my what you mean to call a division and that will be 4 pi area units. The area per unit volume if I calculate is A 1 by V 1, and since I have only one particle at this stage it is 4 by pi r square by 4 by 3 pi r cube which is 3 by r, that means if I keep reducing my r then area per unit volume will increase. Now, what will happen if I divide this particle?

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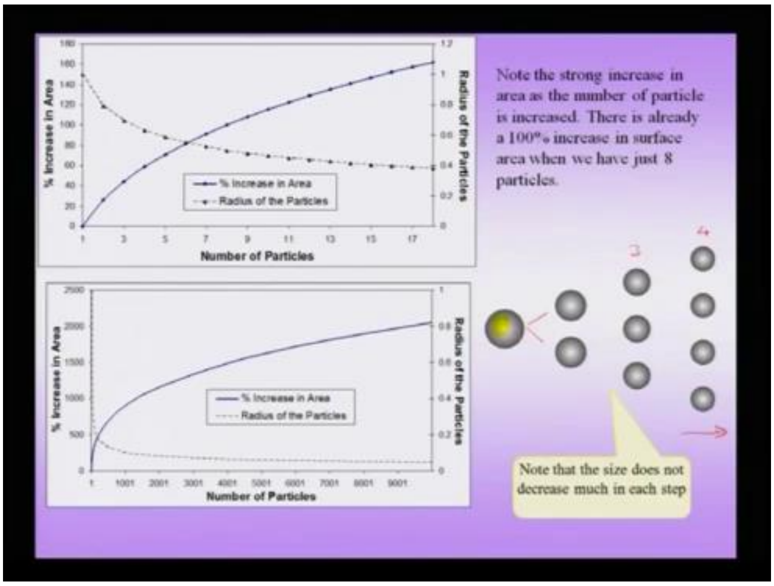

Note the strong increase in area as the number of particle is increased. There is already a 100% increase in surface area when we have just 8 particles.

Note that the size does not decrease much in each step

And here I am taking about a division like this where I take a single particle divided into two particles for the divide this particle into three particle in necessary and to four particles. So, there are three particles at this stage there are four particles at this stage and I keep on increasing the number of divisions, but at each point of time I keep my particles spherical. And I also keep the total volume that equal to the starting particle so, these are the two constraints I impose.

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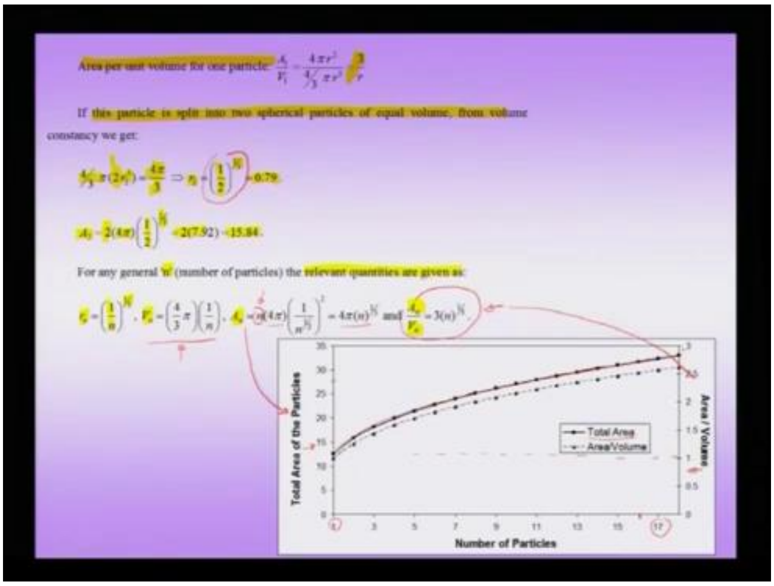
Area per unit volume for one particle: $\frac{A_1}{V_1} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}$

If this particle is split into two spherical particles of equal volume, from volume constancy we get:

$$\frac{4}{3}\pi(2r_2^3) = \frac{4\pi}{3} \Rightarrow r_2 = \left(\frac{1}{2}\right)^{1/3} = 0.79$$

$$A_2 = 2(4\pi)\left(\frac{1}{2}\right)^{2/3} = 2(7.92) = 15.84$$

For any general 'n' (number of particles) the relevant quantities are given as:

$$r_n = \left(\frac{1}{n}\right)^{1/3},\ V_n = \left(\frac{4}{3}\pi\right)\left(\frac{1}{n}\right),\ A_n = n(4\pi)\left(\frac{1}{n^{1/3}}\right)^2 = 4\pi(n)^{1/3} \text{ and } \frac{A_n}{V_n} = 3(n)^{1/3}$$

So, I had notice that the area per unit for one particle is 3 by r. If I split this particle into two spherical particles of equal volume from volume constancy we get that, 4 by 3 pi r 2 cube it is r 2 is being the radius of the smaller particle which is got from dividing the larger particle and there are two of these particles. So, the number 2 is coming from the fact there are two of these particles, then I 4 by 3 pi this implies and this is the original starting volume that means r 2 is 1 by 2 power 1 by 3 which is 0.79.

So, if I divide my one unit radius particle into two particles the radius of those particles will be 0.79 units. The area now is to a twice because there are two particles into 4 pi r square which is 4 pi into half power 2 by 3 because, we know now that r 2 is 1 by 2 power 1 by 3 therefore, I get 2 into 7.92 which is 15.84. So, I have 15.84 as the area in the second stage. Now, I would like to do this truncation repeatedly and therefore, I would write a formula for any number n general number n of particles.

And in that case I can calculate the relevant quantities as rn being the radius at the n stage of division. V n being the volume at the n stage of division An being the area at the n stage of division. And I can actually go ahead and calculate the area per unit volume at the n stage of division. So, let us see what are the relevant formulae here, rn is 1 by n power 1 by 3. So, at the second stage it will become 1 by 2 power 1 by 3 as you had as you had seen here in the case of the first stage of division. So, it this is the case for the two so, the suppose I am talking about the fifth stage of division it will become 1 by 5 power 1 by 3. The volume at the nth stage will be 4 by 3 pi r cube, r being 1 by n.

So, it is 1 by n power 1 by 3 cube so, it is 1 by n. Therefore, the volume at the nth stage is 4 by 3 pi into 1 by n. The area at the nth stage now we have n of these particles therefore, I am calculating the total area, here the volume I am referring to is the volume of the particle individual particle, and not the total volume which anyhow remains constant even if you divide into a number of particles because, we are starting with the given volume and dividing into smaller ones smaller volumes. Now, each of these particles will have 4pi r square which is 1 by n power 1 by 3 square, but then n of these particles will contribute n times that area and that is what I am writing down as An here.

So, it becomes 4 pi n power 1 by 3. The area per unit volume then goes to An by Vn is 3n power 1 by 3 so, if I now plot these quantities to get a feel how these things changes so, the plot is shown here this is the number of particles and initially I am starting with small number of particles like starting from 1, I go to about say fifth seventh particles here. And if I have two relevant quantities, the primary access it refers to the total area of the particles and the secondary area secondary access refer to the area per unit volume, which is this formula here. So, this is my secondary access and the total area of the particles is plotted as the primary access.

So, we notice that the total area of the particles starts from about if you look at the formula here it is about we start from somewhere around about more than 10. And this is the total area given by this upper line and you can see that the number increases and by the time we go to about say 16 particles, already the area as increased more than double. So, you can see that this number is of closed to double and we see that even when you are about more than 16 particles or we have divided the original part in16 and 16 times, the total area as gone more than double.

If you look at the area per unit particle, then this is now my secondary access you see that initial starting value with is close is 1 because, that is what my starting area per unit volume is. And then I see that it is gone to value of 3 so, there is three time increases approximately 3.

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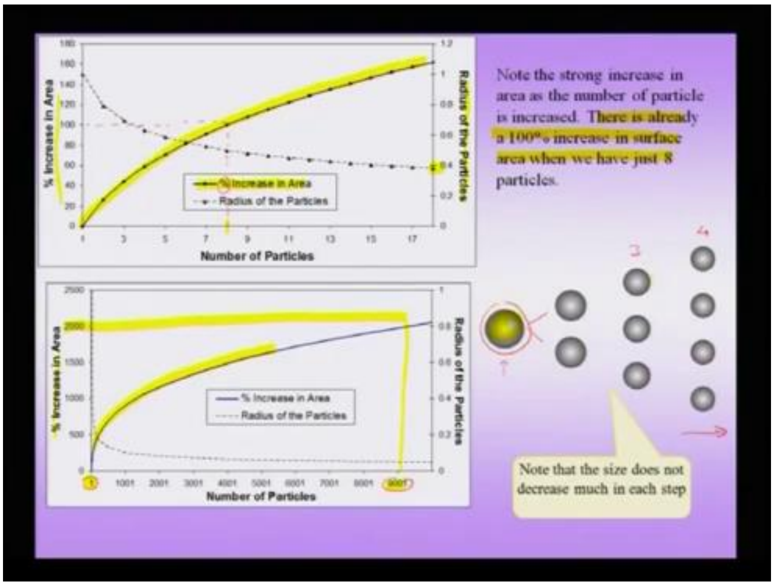

Note the strong increase in area as the number of particle is increased. There is already a 100% increase in surface area when we have just 8 particles.

Note that the size does not decrease much in each step

So, let us do this calculation little more and try to understand the impact especially when I go to large number of particles as shown in the bottom graph. So, you are starting with one particle and going something like a few thousand particles here we have shown about 9000 particles to see how these numbers change and how what is what will be the impact of this increase in number of particles.

Before we go to such large numbers, let us do our calculations in terms of percentages, because often it is very important to have a number that, if I reduce my particle size by a certain value, what is my overall percentage increase in area and especially what is the percentage increase in area for a given volume of material I start with. So, the percentage increase in area is the curve which is plotted on the top and which is referred to in the primary access.

So, the primary access refers to the percentage increase in area. So, initially of course, there is only one particle. And therefore, the percentage there is no increase in percentage we are calculating the increase in percentage with respect to this one particle where, the important point to note is that, when you are about for instance just about eight particles here you see that you already reached an 100 percent increase in area.

So, all I have to get is eight particles from one particle before I already see a 100 percent increase in surface area. This is a very important effect that means that as I go dividing more and more my percentage increase is expected to be more drastic and that is what is the usual goal of producing nano particles. Now, the radius of the particle is an important number to note here, you see that the radius of the particle is not changing much. If you refer to the previous calculations, when we had two particles the radius is 0.79 and this can be better seen in the figure like this, that at each stage these particles are not looking much smaller than the previous particle. The radius is not changing that drastically as compared to the surface area or percentage increase in surface area.

And you can see that even when you have divided your particle about 18 times the radius is come down to about only 0.4 starting from a radius of 1. That implies that though the radius is not decreasing drastically and of course, that is directly a consequence of way the function depends is 1 by n power 1 by 3. But my overall percentage surface area increases. So, let us see if I keep on dividing carry on this sub division at the one single particle into larger and larger number of particles. What kind of a reduction in area can I get? And we will later on carry the forward this calculation to see to represent these numbers in a slightly different way.

So, suppose I start with one particle and I go to for instance a number like 9000 particles, which is note which is a still a small number as compared to what is possible. And you would notice that the curve increases drastically, and by the time I am reaching the number like that, I can almost get a 2000 percent increase in the area. So, this is an important point to note that, if I take one particle and divide it into say about 9000 particles, I get 2000 percent increase in surface area which is meaning that I am not change the volume of the starting material.

That means, I have the same volume of the material, but I am just dividing the particle into sub particles and my overall surface area is going to increase drastically. Of course, as I pointed out that instead of starting with dividing the particle itself, I could actually talk about starting with the single grain material. This is single crystal and I can visualize this being divided at each stage into a number of grains. So, this could be for instance into two grains then, I can think of dividing this of course, I it is easier to start with the for instance it is spherical particle to see the effect so, let me do that.

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So, let me start with the single grain particle, and then I will divide into two grains then, I can divide it into three grains. And of course, I can keep on doing the sub division which I will get a particle in which there are very small grain sized material. In this case of course, this is a schematic division. In this case, it is the particle size is not reducing, it is actually the grain size which is reducing and this implies that my grain boundary area or my interface area is going to drastically increase.

Now, this is profound consequences like now, we are talking about if we are talking about grain boundary diffusion or I am talking about creep dominated by grain boundary diffusion. Then, these kind of effects will start to dominate when I reduce my grain size to these values.

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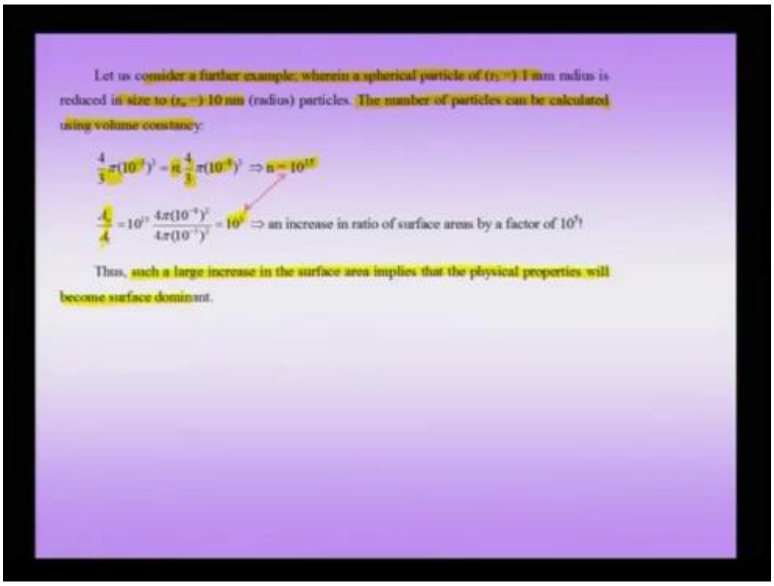

Let us consider a further example; wherein a spherical particle of $(r_1 =)$ 1 mm radius is reduced in size to $(r_n =)$ 10 nm (radius) particles. The number of particles can be calculated using volume constancy:

$$\frac{4}{3}\pi(10^{-3})^3 = n\frac{4}{3}\pi(10^{-8})^3 \Rightarrow n = 10^{15}$$

$$\frac{A_n}{A_1} = 10^{15}\frac{4\pi(10^{-8})^2}{4\pi(10^{-3})^2} = 10^5 \Rightarrow$$ an increase in ratio of surface areas by a factor of 10^5!

Thus, such a large increase in the surface area implies that the physical properties will become surface dominant.

Let us further extend the same example wherein, let us consider a spherical particle with radius equal to 1 millimeter. Now, this is now a tangible particle 1 millimeter in radius and reduce the size to 10 nanometers. That means now, I am starting with a tangible particle and reducing the size to the nano metric scale. The number of particles can be calculated using volume constancy like we did before that means, that 4 by 3 pi this is now my 1 millimeter particle cube is n times. Now, n is a number of particles I would obtain 4 by 3 pi into now, it is my 10 nanometer particle is 10 power minus 8 cube that means that n is 10 power 50.

Therefore, when I go to the nano metric length scale, the number of particles I was produced is ((Refer Time: 14:41)). So, this increase in area is one aspect of the thing, but also additionally we see that the number of particles is also huge. So, if I make an area ratio calculation I would notice that there is a 10 power 5 fold increase in area. And therefore, these two aspects go hand in hand and this implies that I do not need lot of material. If want to actually produce the large number of nano particles, it is just that I to have to keep sub dividing till I reach the relevant length scale for my problem.

And this is directly leading to what we have been reiterating many times that such a large increase in surface area implies physical part properties would become surface dominant. So, there will be a definitely a contribution from the surface in any one of the physical properties you are talking about let it be plasmon resonance, let it be absorption of gases, let it be creep in the case of a polycrystalline material all this we will get, will be dominated by surface or interface effects. Now, let us do a, instead of doing a top bottom down approach wherein, we are starting with a particle and actually cutting it down.

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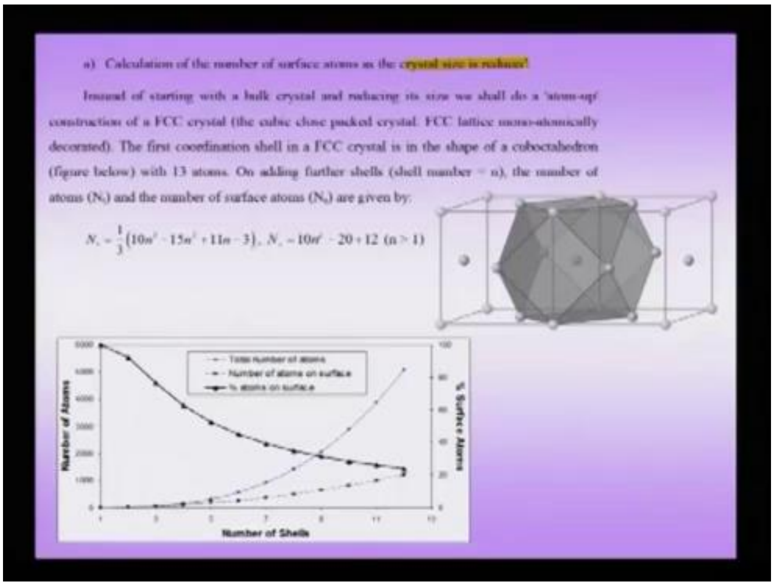

a) Calculation of the number of surface atoms as the crystal size is reduced!

Instead of starting with a bulk crystal and reducing its size we shall do a 'atom-up' construction of a FCC crystal (the cubic close packed crystal: FCC lattice mono-atomically decorated). The first coordination shell in a FCC crystal is in the shape of a cuboctahedron (figure below) with 13 atoms. On adding further shells (shell number = n), the number of atoms (N_t) and the number of surface atoms (N_s) are given by:

$$N_t = \frac{1}{3}\left(10n^3 - 15n^2 + 11n - 3\right),\ N_s = 10n^2 - 20 + 12\ (n > 1)$$

Let us start with something known as a bottom up approach and this bottom up approach will throw into light certain other concepts like when you take a nano crystal. Often it is not spherical, you may find that apart from it being non spherical there are certain magic numbers which appear. That means, certain magic number of atoms are stabilized.

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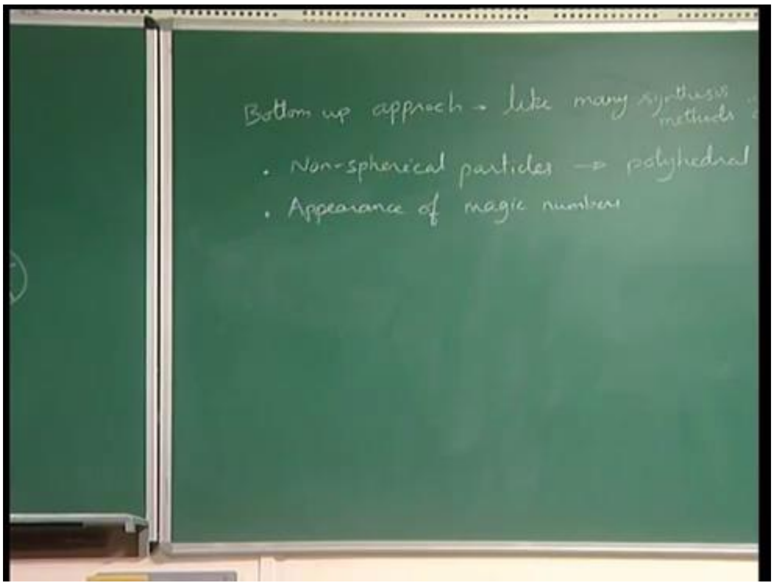

Bottom up approach → like many synthesis methods

- Non-spherical particles → polyhedral
- Appearance of magic numbers

So, here we are considering what you may call a bottom up approach and this is how many synthetic methods actually work, we do not start with the bulk crystal, but we actually construct the nano crystal starting from a few atoms or a few molecules. So, this is a very important method of actual synthesis and so, this is we should keep this kind of a technique in mind. The particles may be non-spherical in fact they could actually be polyhedral and if you are talking about roughening of shape.

That means, well defined shape surface if surface refusal affects the dominant then you will see that nano particles can easily assume that kind of a polyhedral shape. And there is an additional factor that there are magic numbers which appear. This magic numbers may be stabilized by electronic configuration etcetera. But here we will see that because of purely geometric reasons such magic numbers may appear.

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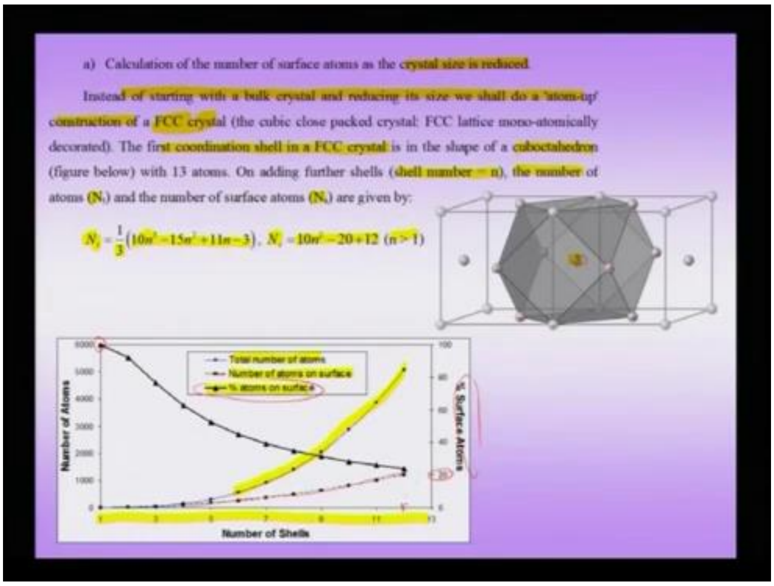

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So, instead of starting with a bulk crystal and reducing its size, we do an bottom of constructions and as an example let us take an cubic close pack crystal and here we take the first coordination shell of such a crystal. I have here what is known as a shape it is known as a cube octahedron which is between a cube and an octahedron and it is the coordination polyhedron in FCC. So, around each atom for instance I take a centralized atom I can have twelve other atoms around it which are in the shape of a cube octahedron.

Further, to this I may build the second layer around this central atom I may build the third layer and the fourth layer at each stage making sure that this kind of a polyhedron is maintained. Now, if I calculate the and now my shell number is n that means the number of atoms I am adding at the nth shell, the number of atoms N t and the number of surface atoms is what we are going to track. The total number atoms is given by N t the total the fraction of those atoms out of these which is n is being a subset of N t is the atom sitting on the surface.

At level when of course, we see that we of course, use this formula for n greater than 1, but currently we will ignore the central atom and we will take all the atoms on the outer shade. So, we will assume that at n equal to one all the atoms are on the surface. And as we increase the shell add more and more concentric shells we will see that only a fraction of these atoms actually sit on the surface and remaining interior atoms will be treated like bulk atoms.

So, if you now calculate the total number of atoms a formula like this can be derived. Wherein, if the number of atoms total atoms when I have a shell number n is 10 n cube minus 15 n square plus 11 m minus 3 one third of that and then number of atoms can be given by 10 n square minus 20 plus 12.

So, therefore, if I put n is equal to 1, I will see that the number of surface atoms is 12 which is the same as the number of bulk atoms, or if you want to add the central atoms the bulk atom will be one more in number. There will be one bulk atom and remaining will be surface atoms if I take it around the central atom also. So, now what happens if I track this number of total number of atoms, the number of atoms which sit on the surface and better still the percentage of the atom on the surface.

So, here I am making up what is known as a bottom up approach therefore, I track the number of shells here on the x axis so, I start with one shell two shell three shell and go up to a small number of shells say for this is about twelve shells. So, here I am maintaining a polyhedral shape at each stage. The first stage of course, is the what you might call the coordination polyhedron around the central atom in an cubic closed pack crystal which is cube octahedron. And when you go higher and higher up there are dissymmetry remains the same for the coordination shells. But you have more and more atoms being added, and at those stages you will see that the fraction of the surface atoms is going to reduce. Or a as we will plot here the percentage of the surface atoms is equal to reduce.

So, let us see first the total number of atoms which is given by this curve here and as you can see obviously it is a cubic function then it increases. Initially of course, you start with the number of atoms on the surface and I will mark this number of atoms on the surface by a red line. You see that the number of atoms on the surface is 0 of course, if I want to treat and you can see that the number of atoms on the surface is going to increase drastically. So, after a few truncations say for instance about 12 truncations. Now, if I see the number of percentage of atoms sitting on the surface, you see that the percentage actually decreases.

So, this percentage surface atoms is on the right hand side initially of course, when I have for instance just one layer, I could treat all the atoms and on the surfaces total number of atoms. So you will get 100 of atoms sitting on the surface of course, we initially take that the one atom is sitting inside the bulk. But you see that as we increase the number of layer, the percentage of the atoms comes down and only about 20 percent of the atoms are actually sitting on the surface by the time you are in 12 layers.

So, it is very clear that in the bottom up approach as I add more and more shells the percentage of atoms sitting on the surface is going to drastically reduce with the number of shells I add. And this implies that the effect of surface atoms is also going to reduce and the energy of their particle is correspondingly going to reduce. Because, now overall Gibbs free energy the surface contribution is going to be less and I will find the atom the this particle is more stable as I go to larger and larger sizes. Now, just to put these things in numbers.

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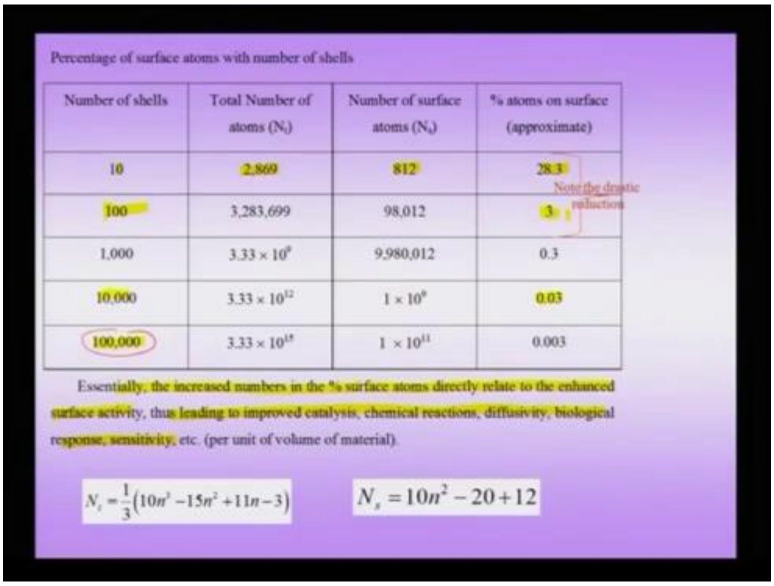

Percentage of surface atoms with number of shells

Number of shells	Total Number of atoms (N_t)	Number of surface atoms (N_s)	% atoms on surface (approximate)
10	2,869	812	28.3
100	3,283,699	98,012	3
1,000	3.33×10^{9}	9,980,012	0.3
10,000	3.33×10^{12}	1×10^{9}	0.03
100,000	3.33×10^{15}	1×10^{11}	0.003

Note the drastic reduction

Essentially, the increased numbers in the % surface atoms directly relate to the enhanced surface activity, thus leading to improved catalysis, chemical reactions, diffusivity, biological response, sensitivity, etc. (per unit of volume of material).

$$N_t = \frac{1}{3}\left(10n^3 - 15n^2 + 11n - 3\right)$$

$$N_s = 10n^2 - 20 + 12$$

If I have now and I am trying to go to large numbers here so, I am starting with about 10 shells which we had considered in the previous graph. I am going up to say about 10000 or more shells at when it is about 10 shells. The total number of atoms about 3000, number of surface atoms is about 812 or 800 and about more than 25 percent of the atoms are sitting on the surface, with the drastic fraction of the atoms which are sitting on the surface when I have 10 shells.

But you can see the reduction I got about 100 shells the fraction of percentage of the atoms sitting on the surface only 3 percent. And that was I am talking about 10000 atoms this fraction is very small and for many calculations related to energy etcetera. I may want to effectively ignore this surface contribution to energy. So, but this is not possible obviously when you are in the regime about 100 shells wherein, there would be a correction involved to the total number of atoms which are not having their bonds fully satisfied.

Essentially the increase in numbers in the percentage surface atom directly relate to the enhanced surface activity, thus leading to improved catalysis chemical reaction diffusivity biological response sensitivity etcetera. Therefore, it is very clear that many of the what you call the important effects which can come because we are using nano materials comes from this aspect of the what you may call the surface. And this can put this can be safely put into this category, which we had seen before in the classification.

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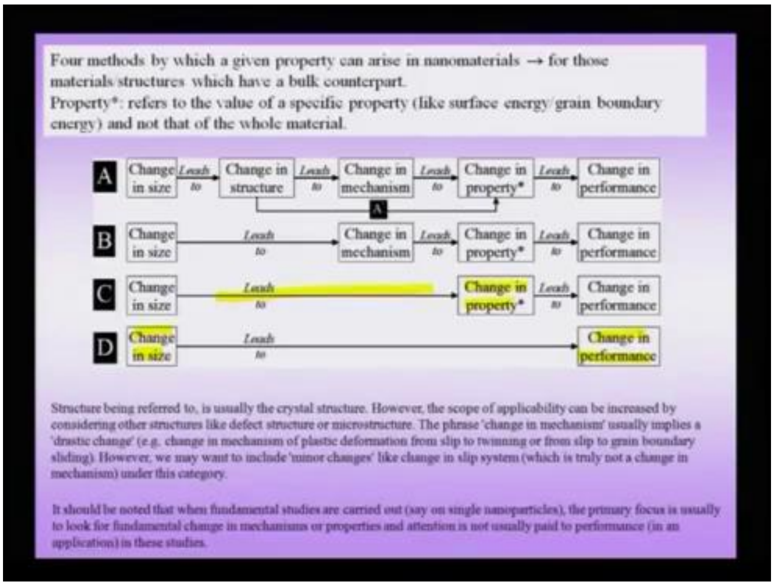

Four methods by which a given property can arise in nanomaterials → for those materials/structures which have a bulk counterpart.
Property*: refers to the value of a specific property (like surface energy/grain boundary energy) and not that of the whole material.

Structure being referred to, is usually the crystal structure. However, the scope of applicability can be increased by considering other structures like defect structure or microstructure. The phrase 'change in mechanism' usually implies a 'drastic change' (e.g. change in mechanism of plastic deformation from slip to twinning or from slip to grain boundary sliding). However, we may want to include 'minor changes' like change in slip system (which is truly not a change in mechanism) under this category.

It should be noted that when fundamental studies are carried out (say on single nanoparticles), the primary focus is usually to look for fundamental change in mechanisms or properties and attention is not usually paid to performance (in an application) in these studies.

As change in size can directly lead to a change in performance and this performance as we just now pointed out could be absorption of gases. But, here we are effectively ignoring the fact that when we are reducing the size. In fact, the specific surface energy could actually change and if there is a drastic reduction in the specific surface energy then, I may have to use this root C. Wherein, my change in size is going to lead to change in specific surface energy which will further lead to a change in performance.

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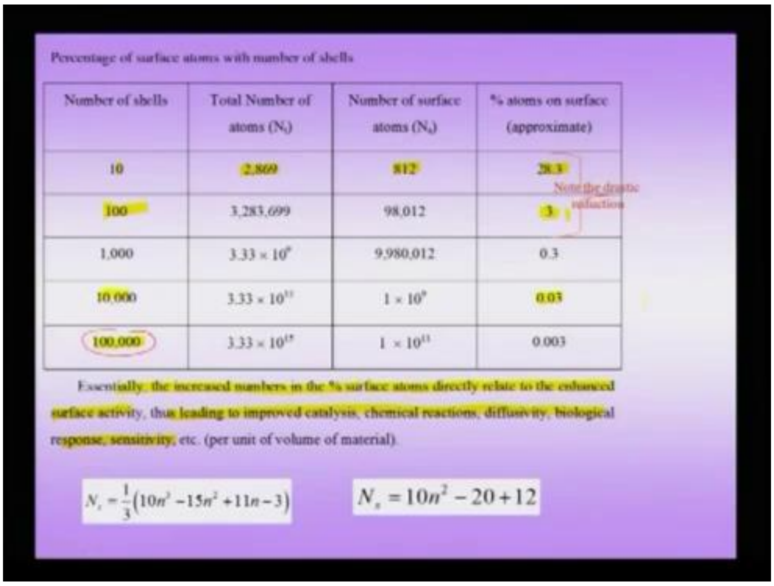

Percentage of surface atoms with number of shells

Number of shells	Total Number of atoms (N_t)	Number of surface atoms (N_s)	% atoms on surface (approximate)
10	2,869	812	28.3
100	3,283,699	98,012	3
1,000	3.33×10^9	9,980,012	0.3
10,000	3.33×10^{12}	1×10^9	0.03
100,000	3.33×10^{15}	1×10^{11}	0.003

Note the drastic reduction

Essentially, the increased numbers in the % surface atoms directly relate to the enhanced surface activity, thus leading to improved catalysis, chemical reactions, diffusivity, biological response, sensitivity, etc. (per unit of volume of material).

$$N_t = \frac{1}{3}\left(10n^3 - 15n^2 + 11n - 3\right)$$

$$N_s = 10n^2 - 20 + 12$$

So this is at least two of this classes are nicely explained by the fact that when you make the volume calculation or the number of particles calculation, we see that there is a drastic change.

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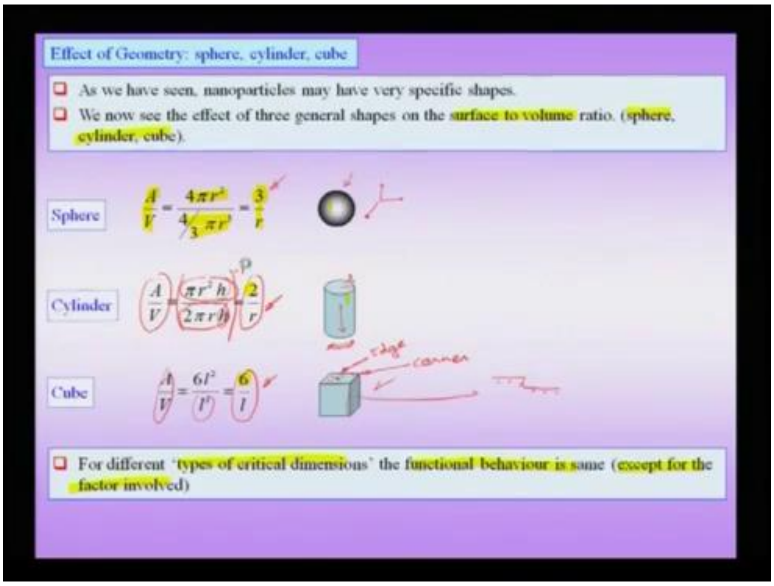

Effect of Geometry: sphere, cylinder, cube

- ❑ As we have seen, nanoparticles may have very specific shapes.
- ❑ We now see the effect of three general shapes on the surface to volume ratio. (sphere, cylinder, cube).

Sphere $\frac{A}{V} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}$

Cylinder $\frac{A}{V} = \frac{\pi r^2 h}{2\pi r h} = \frac{2}{r}$

Cube $\frac{A}{V} = \frac{6l^2}{l^3} = \frac{6}{l}$

- ❑ For different 'types of critical dimensions' the functional behaviour is same (except for the factor involved)

Now, so far we have considered for instance two geometries which is the geometry a spherical particle or the geometry of what you might call a polyhedral particle which we had considered was a cube octahedral kind of starting shape. In general of course, we will we have seen when we classified nano particles, we said that they can come in very many different kind of geometries, they can be nano flowers, nano bows, nano strings, nano rods etcetera.

So, three of these general shapes I have taken up here and obviously, this is not an exhaustive kind of a list out here. But I want to see that, what can be, what can happen when I have these three kind of general kind of shapes with respect to their trend lines as you reduce the particles? And here they are of course, we are interested in the area per unit volume.

So, the shapes you consider here are sphere, cylinder and cube and we are tracking the surface to volume ratio. For the case of a sphere, the area is given by 4 pi r square and the volume is 4 by 3 pi r cube. And therefore, we have already seen that the area per unit volume is 3 by r that means, it is an 1 by r kind of a dependence for a cylinder. And now, I am talking about reducing the diameter of the cylinder. Of course, we can also cut the cylinder in its length, I may take a cylinder and to produce the nano dimensional particle. I am actually do cutting at various stages, I may cut here, then I may cut here, then here, then cut here.

And therefore, I will obtain a disk which is now, nano metric in thickness, but that is not what I am doing here? I am actually reducing the radius and therefore, the critical parameter I am talking here is the radius. And now, I am seeing how does the area per unit volume change as I am reducing. So, the h remains constant in this case so, my area is given by 4 pi r square h, the volume is 2 pi r h and therefore, the cylinder would have A by V as 2 by r. For a cube, there are 3 dimensions and of course, I am still maintaining it as a cube as I am reducing the dimension. I am not changing its geometry, and I can track my A by V and I can see that the area is 6 l square.

Because now I have 6 of this surface, the volume is l cube and therefore, it is a 6 by l. So, it is clear by considering these three geometries that, if I am talking about different kind of critical, the various types of critical dimensions, and of course, when I mean various types here I am talking about the radius of the cylinder. The radius of the sphere and here is the edge of the cube the functional behavior is very similar. Of course, we can clearly see that the factor involved is very different here it is a fact of 6, here it is fact of 2, here it is the fact of 3. But for these simple geometries which I have considered here, the functional behavior is very similar.

But just because the functional behavior is similar, I should not conclude that the enhancement in property or any one of these things is going to be similar because of some reasons which we are obviously if I am looking even at this geometries here for instance, the number of dimensions in which the curvature is increasing is just one. So, the curvature is increasing in one dimension effectively the curvature is flat on the other dimension.

Therefore, more and more bonds will be unsatisfied in the direction of the curvature, but to this curvature by the other direction it would be a flat kind of a dimension. But in the case of sphere, the curvature is increasing in all three dimensions. So, as a particles size reduced, there is more and more bonds of the atoms sitting on the surface which is going to be unsatisfied. And therefore, the energy of this particle and the reactivity of these particles may be bore.

In the case of a cube, as you can see there is no change in curvature involved because all surface phases happened to be flat and they continues to be flat and. But the important point to be noticed here is that the topology of this kind of an object tells you that there are certain lower dimensional entities to be taken into account when you are dealing with the cube, like for a cube has an edge. An edge atom sitting on the edge obviously have bonding much worse than that of a atom sitting in the phase.

So, and the other main point to be noted is the corner, and bonding of atoms sitting is on the corner is going to be worse than that of the atom sitting on the edge. And therefore, if I have a single cube, I can have only of course, 8 corners, but I am suppose I am not reducing the dimension of the cube, but splitting this cube then, I will notice that more and more atoms will actually sit in. The corner and therefore, just by merely looking at the functional dependence, I cannot conclude that all the properties changes will be identical.

The property changes will obviously depend on the specific geometry. I am considering and as you can see, here the geometry puts in additional parameter which I need to consider for instance the dimension in which the curvature is going to change the number of lower dimensional entities in the object like for instance edge or a corner. And for instance in more complicated situation, even a surface may have additional entities like led gent and surfaces led gent and king we for about which we will talk about in an upcoming lecture.

Therefore, the summary of this slide is that I need to talk about not only a reduction in particle size, I need to talk about various geometries which can lead to my nano particles. For instance I may take a nano wire and actually split it into make a nano particle and the it is the effect of a specific property coming from specifically these kind of a reduction in dimension. One small era of course, in the case of cylinder is that actually the formula has got inverted now, we have actually this is the volume of the cylinder. And therefore, I need to invert this formula to get my functional dependence which is now 2 by r.

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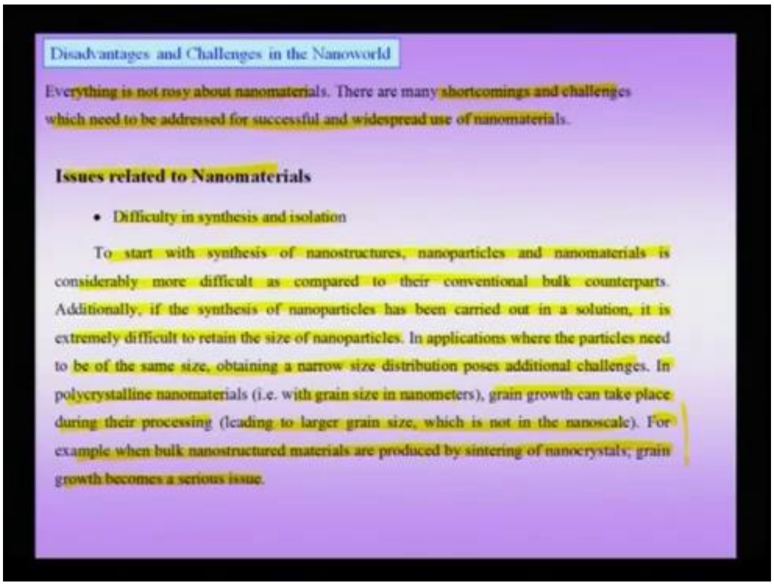

Disadvantages and Challenges in the Nanoworld

Everything is not rosy about nanomaterials. There are many shortcomings and challenges which need to be addressed for successful and widespread use of nanomaterials.

Issues related to Nanomaterials

- Difficulty in synthesis and isolation

To start with synthesis of nanostructures, nanoparticles and nanomaterials is considerably more difficult as compared to their conventional bulk counterparts. Additionally, if the synthesis of nanoparticles has been carried out in a solution, it is extremely difficult to retain the size of nanoparticles. In applications where the particles need to be of the same size, obtaining a narrow size distribution poses additional challenges. In polycrystalline nanomaterials (i.e. with grain size in nanometers), grain growth can take place during their processing (leading to larger grain size, which is not in the nanoscale). For example when bulk nanostructured materials are produced by sintering of nanocrystals; grain growth becomes a serious issue.

Now, you have seen some of the advantages some of the beautiful things about the nano world, but would like to list comprehensively or as far as possible the disadvantages and challenges which faces when we are entering the nano world. These are as important as actually knowing about the advantages and as we shall soon see that more often than not in the excitement of a new discovery. You may actually miss some of the problems which are associated by this which can actually be potentially harmful in the longer. So, everything is not rosy about nano materials there are many short comings and challenges which need to be addressed for successful and widespread use of nano materials.

So, what are these challenges will let us list them? So, the issues related to nano materials are, first and foremost difficulty in synthesis an isolation. To start with synthesis of nanostructures, nano particles and nano materials is considerably more difficult as compared to their conventional bulk counterparts. This is of course, needless to say because, here we are talking about a dimension which is extremely small. And therefore, we are actually going to put in considerably more effort in actually synthesizing nanostructure and nano particles.

Additionally, if the synthesis of nano particles is been carried out in a solution it is extremely difficult to retain the size of the nano particles. So, once having synthesized it often becomes the challenge that we have to retain size and retain the size of course, during synthesis and later on of course, as we shall see during the service of the actual nano particle in certain intended application. In applications where the particles need to be of the same size obtaining a narrow size distribution poses additional challenges.

More of them not we do not want particles of various sizes to co-exist because, if I am depending on for instance absorption of a specific wavelength or I am talking about a certain other kind of a property which is now going to be dependent on the grain size. If I have too wide grain size variation, or too many particle size is involved, then I will obviously not get the specific property enhancement which I am looking for.

Therefore, I want to get a narrow sized distribution and this is definitely a challenge when it comes to a nano materials. In polycrystalline materials example, for instance I am talking about the grain size in nanometers grain growth can take place during their processing. So, as we already said, if I am talking about a nano poly crystal then the interface area is very large the grain boundary is very large this automatically implies that the diffusion is going to be very large along the interface and grain growth can also take place.

This means that even though I have synthesized the nano material before I even put it into application, I would see that the grain size would have increased and I am no larger having a nanostructure material, but I would be having a grain size which could have already increased to a micron size. And this would imply that the nano scale has been destroyed for example, when bulk nano structured materials produced by sintering of nano crystals grain growth becomes a serious issue. There are many synthesis techniques and alternate lectures may talk about them in this course.

Wherein, I have not produced a bulk nanostructure materials, but I have actually produced powder which has a either the powder grain size itself. It is the grain size is in a nanometers or the particle size is in a nanometers. And when I want to synthesize a bulk material out of this, I need to sinter the material. And when I am trying to sinter obviously I am exposing the material to high temperature. So, this will lead not only to sintering of the particles, but also it may lead to for instance loss of nanostructure. And this means that certain conventional techniques may not be suitable for making nanostructures materials.

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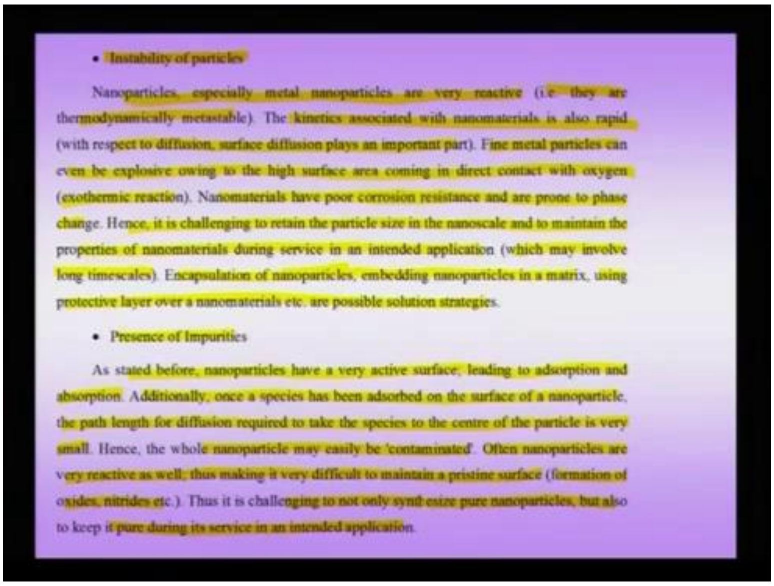

- Instability of particles

Nanoparticles, especially metal nanoparticles are very reactive (i.e they are thermodynamically metastable). The kinetics associated with nanomaterials is also rapid (with respect to diffusion, surface diffusion plays an important part). Fine metal particles can even be explosive owing to the high surface area coming in direct contact with oxygen (exothermic reaction). Nanomaterials have poor corrosion resistance and are prone to phase change. Hence, it is challenging to retain the particle size in the nanoscale and to maintain the properties of nanomaterials during service in an intended application (which may involve long timescales). Encapsulation of nanoparticles, embedding nanoparticles in a matrix, using protective layer over a nanomaterials etc. are possible solution strategies.

- Presence of Impurities

As stated before, nanoparticles have a very active surface, leading to adsorption and absorption. Additionally, once a species has been adsorbed on the surface of a nanoparticle, the path length for diffusion required to take the species to the centre of the particle is very small. Hence, the whole nanoparticle may easily be 'contaminated'. Often nanoparticles are very reactive as well, thus making it very difficult to maintain a pristine surface (formation of oxides, nitrides etc.). Thus it is challenging to not only synthesize pure nanoparticles, but also to keep it pure during its service in an intended application.

The second issue I have to deal with is the insatiability of the particles, nano particles especially metal nano particles are very reactive. In fact in some cases they could be so reactive that they can even lead to an explosion. So, there are safety issues also involved here I they are that is they are thermodynamically metastable, and as we are we just made a calculation we know that this is an increase in surface area. And with the increase in surface area, the number of atoms who are poorly bonded increase thus making my nano particle very reactive.

The kinetic associated nano materials also rapid like we have already seen with respect to diffusion surface diffusion plays an important part. Fine metal particles can even be explosive owing to the high surface area coming direct contact with oxygen which is now an exothermic reaction. So, when I am dealing with this nano particles, the reaction need not be slow. It can even be explosive, nano materials have a poor corrosion resistance and are prone to phase change.

We already seen that when you reduce the particle size then, actually a different kind of crystal structure may be stabilized and additionally because of the size large surface area they are poor in corrosion resistance. Hence, it is challenging to retain particle size in the nano scale and to maintain properties of the nano material during service in an intended app, and I mean you are talking about an application this may actually involve long time scales.

So, we are talking about actually a component in service and therefore, we are really talking about large time scales. The next issues related to nano materials is the presence of impurities, as started before nano particles are very active surface leading to adsorption and absorption, and I am talking even of gases. Additionally, once a species has been adsorbed on the surface of a nano particle the path length for diffusion required to take the species to the center of the particle is small. Even this aspect we have talked about before that means, that the entire nano particle be easily contaminated.

And this is the serious issue because, the species being adsorbed on the surfaces is soluble in the material, it will be taken to the center of the nano particle and the entire particle will now be contaminated with respect to the impurity which might have obviously a deleterious effect on the properties I am considering. Often nano particles are very reactive as well, thus making it very difficult to maintain a pristine surface. And when I am talking reactive actually there could be formation of oxides, nitrides etcetera on the surface.

And hence, it is not only challenging to synthesize pure particles, but also to keep it pure during service intended application. So, this is a very serious issue with regard to nano particles that I have to protect it in somewhere from allowing impurities to come on the surface and this is not only to be done during synthesis. But also during an intended application which could involve long time scales.

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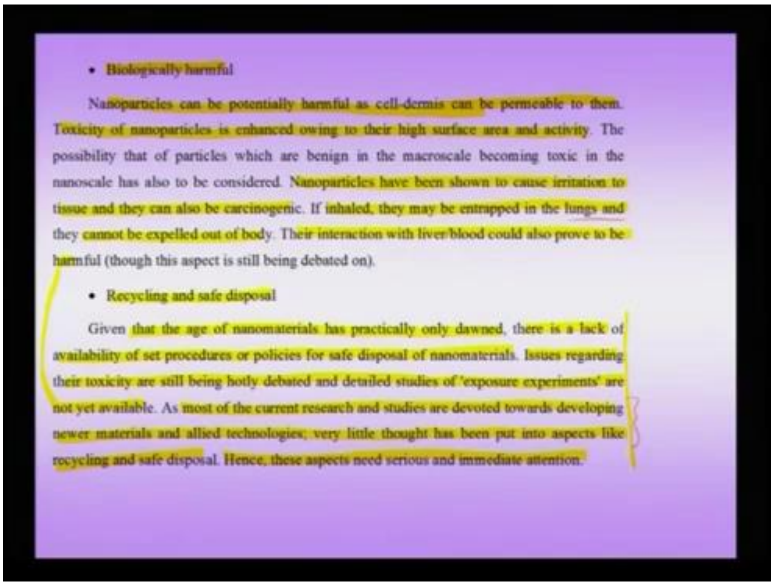

- Biologically harmful

Nanoparticles can be potentially harmful as cell-dermis can be permeable to them. Toxicity of nanoparticles is enhanced owing to their high surface area and activity. The possibility that of particles which are benign in the macroscale becoming toxic in the nanoscale has also to be considered. Nanoparticles have been shown to cause irritation to tissue and they can also be carcinogenic. If inhaled, they may be entrapped in the lungs and they cannot be expelled out of body. Their interaction with liver/blood could also prove to be harmful (though this aspect is still being debated on).

- Recycling and safe disposal

Given that the age of nanomaterials has practically only dawned, there is a lack of availability of set procedures or policies for safe disposal of nanomaterials. Issues regarding their toxicity are still being hotly debated and detailed studies of 'exposure experiments' are not yet available. As most of the current research and studies are devoted towards developing newer materials and allied technologies; very little thought has been put into aspects like recycling and safe disposal. Hence, these aspects need serious and immediate attention.

The next issue is that many of the biologically, many of the nano particles of nano materials having a nano entity could actually be biologically harmful. Nano particles can be potentially harmful as cell-dermis is permeable to them. These size is being so small then actually get into the human cell or a cell of an animal or a cell of a living being and there may be no natural defense to the penetration of these particles into the biological system.

Toxicity of nano particles is enhance to their high surface area and activity. Here of course, I am talking about two kind of particles which are of course, ((Refer Time: 39:25)) in the micro scale, but become somewhat toxic when you go to the nano scale those other particles which are toxic anyway in the macro scale. Therefore, when you go down to the nano scale they may tend to become even more active and therefore, even more toxic.

Hence, nano particles have been shown to cause irritation an example of these kind of bad effects is one of these is that nano particles have been shown to cause irritation tissue and they can even be carcinogenic. If inhales they may be entrapped in the lungs and they cannot be expelled out of the body their interaction with liver blood could also prove to be harmful.

So, there are lot of studies which need to be carried on further to actually establish the toxicity of these particles interaction with various kind of cells in the body. They not only short terms acute effects, but also the chronic effects coming from repeated exposure to these nano particles. And this area of biological, but may call the effect of nano particles of course, originally not intended even to be like it is not a drug delivery particle or one of those particles, which is originally intended to be put into a human system or an animal system their effects is I studies on this aspects barely begun.

And therefore, and especially the chronic studies are studies are no were near complete and therefore, we will do not know that what wrong could go what wrong could happen. If some of this particles are somehow entrapped in the human system, like we said in the lungs of a human being, as we had pointed out and more importantly how much of such a material could be tolerated by the body is also not known. Therefore, this biological aspect needs lot more of study and we need to characterize various kind of nano particles that we are producing for totally different applications in terms of their, for instance effects on a human system or an animal system.

Another area which is again lacking constable study is the recycling and safe disposal, given that the age of nano materials has only just dawned. That mean, we are just parallelly scratched the age of nano materials. You are newer kinds of nano materials are been discovered virtually every day and hence, there is a lack of availability of set procedures or polies fore safe disposal of nano materials.

Often initially of course, these nano materials are just made in a milligrams or even a smaller quantities and therefore, nobody is really worrying about what will happen if this kind of a material where you know produced in a larger quantity. Wherein, we have to worry about issues like recycling or even issue of how do we dispose of this particles once. Of course, my research or my intended testing is over. Issues regarding the toxicity as still being debated and detailed studies of exposure experience are not yet available and this we has cited as an example when you talk about a biological effects.

As most of the current research and studies are devoted towards developing newer materials and allied technologies, very little thought has been put into aspects like recycling and safe disposal. So, the current shortcoming is not that we cannot study them, but most of our efforts are not going in this direction we are just trying to develop new materials. We are trying to put them into newer applications and we are never there is no what you meant by question? Cause and question being asked that, what if such materials we are to come into human contact or in contact with over living organisms?

And hence, these issues need serious and immediate attention. So, this is one of the areas where it is almost imperative that we do lot of research. We do lot of studies regarding safe disposal, regarding recycle, recycling and also regarding the effect of nano materials on various kind of living beings. So, unless this aspect is conclusively proven that there is a beneficial effect without what you might call much of deleterious effect. And if there is deleterious effect then, how do I deal with it? The age of nano materials can fully never be beneficial. So, there are some challenges, which we need to address before nano materials can find wide produce.

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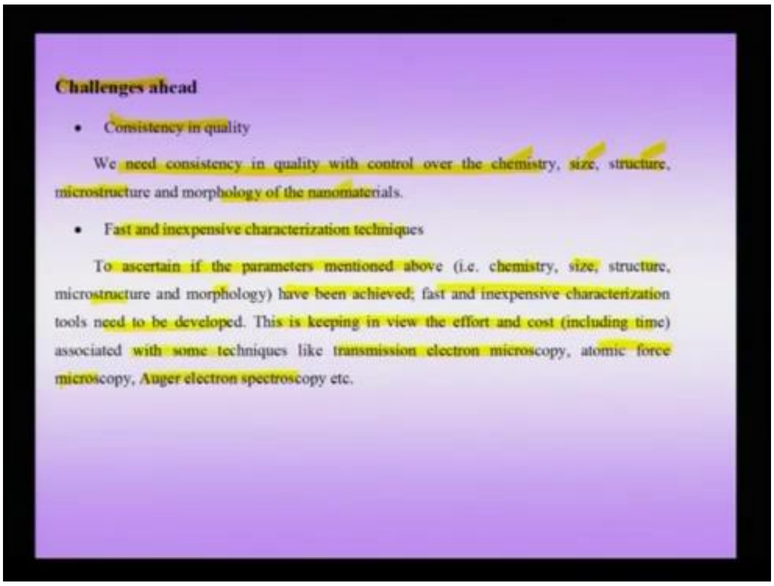

Challenges ahead

- Consistency in quality

We need consistency in quality with control over the chemistry, size, structure, microstructure and morphology of the nanomaterials.

- Fast and inexpensive characterization techniques

To ascertain if the parameters mentioned above (i.e. chemistry, size, structure, microstructure and morphology) have been achieved; fast and inexpensive characterization tools need to be developed. This is keeping in view the effort and cost (including time) associated with some techniques like transmission electron microscopy, atomic force microscopy, Auger electron spectroscopy etc.

And these challenges which are basically coming from some of the issues which already stated are consistency in quality. We need consistency in quality and control over chemistry, size, structure, microstructure and morphology the nano materials. So, variety of these nano materials have been produced in small quantities, but you know when we try to scale up the production. We need a control over quality of these nano particles or nano materials and we need to control over their chemistry, we need a control over their size, we need to control over their structure and microstructure and finally, the morphology.

When we will we begin to say that ok we have understood the all aspects of you know nano structured materials. We need fast and inexpensive characterization techniques at the research stage. It is of course, there is not a problem at all I may actually use techniques like transmission electron microscopy. Wherein, you know it is a time consuming costly kind of procedure which I am using or an atomic force micro scope or auger electron spectroscopy which are very costly equipments very, what you might call. Involving lot of at times lot of specimen preparation before material can be put for testing, but in the long run I need fast and inexpensive characterization technique.

To ascertain if the parameters mentioned above like chemistry, size, structure, microstructure and morphology have been achieved fast and inexpensive characterization tools need to be developed. So, I when a factory production line for instance I cannot use any of these tools to characterize my materials which is coming out of the assembly line. And therefore, I need some newer techniques or modified version of some of these techniques which will give me a fast characterization a fast hand on all these various properties and parameters which I need to control.

This is keeping in with the effort and cause associated with some other current techniques. So, there is the capital investment the specimen preparation time the amount of material which can be tested at a single time. All these are poor in some of these techniques. And therefore, definitely we need some inexpensive characterization technique which can give me quick results and quick results, I mean sometimes even when the assembly line is rolling.

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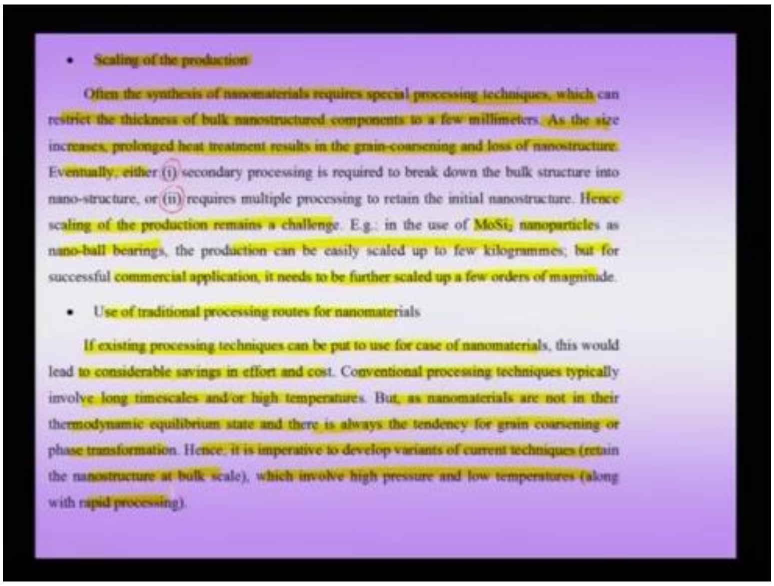

- Scaling of the production

Often the synthesis of nanomaterials requires special processing techniques, which can restrict the thickness of bulk nanostructured components to a few millimeters. As the size increases, prolonged heat treatment results in the grain-coarsening and loss of nanostructure. Eventually, either (i) secondary processing is required to break down the bulk structure into nano-structure, or (ii) requires multiple processing to retain the initial nanostructure. Hence scaling of the production remains a challenge. E.g.: in the use of $MoSi_2$ nanoparticles as nano-ball bearings, the production can be easily scaled up to few kilogrammes; but for successful commercial application, it needs to be further scaled up a few orders of magnitude.

- Use of traditional processing routes for nanomaterials

If existing processing techniques can be put to use for case of nanomaterials, this would lead to considerable savings in effort and cost. Conventional processing techniques typically involve long timescales and/or high temperatures. But, as nanomaterials are not in their thermodynamic equilibrium state and there is always the tendency for grain coarsening or phase transformation. Hence, it is imperative to develop variants of current techniques (retain the nanostructure at bulk scale), which involve high pressure and low temperatures (along with rapid processing).

So, further challenges which we need which to address is the scaling of production, often synthesis of nano materials require special processing and techniques which can restrict the thickness of bulk nano structured components to a few millimeters. As the size of the as the size increase prolonged heat treatment results in grain coarsening and loss of nanostructure.

Eventually, either secondary process is required to break down the bulk structure into nanostructure or we require multiple processing to retain the initial nanostructures. Hence, scaling of production remains a challenge for example, if I have had to use MoSi 2 nano particles as a nano-ball bearings, the production can easily be scaled up to a few kilograms. When I say easily of course, I do not mean very easily, but definitely with some effort we can actually scale it up to few kilograms, but for successful commercial application this needs to be scaled up a few orders of magnitude.

So, it is very clear that in some mess applications where I need very small quantity of material nano materials are already achieving quite a bit considerable amount of success. But for a large what you might say widespread application of nano materials, it is clear that I need to have a scaling of production. I may be talking about tons of materials being produced and each of these tons or batches actually has somewhere at its heart a nanostructure or a nano material or some length scale which is nano. And each one of them obviously is going to have some special property.

And either during my synthesis or during further processing to actually take the material and make the component I should not have a loss of nanostructure. So, these are some of the challenges which are very serious and have to be addressed before we see that nano materials and can be used in a day to day life in a widespread manner. If as we had noted before that most of the time nano materials and nanostructures are not produced by the usual routes used for producing bulk components.

Suppose, I were to produce for instance a bulk component I may use something like an injection molding or a simple casting or some kind of a forging. But we would notice that, when we wanted to produce nano structured materials for instance suppose I want a grain size in the order of nanometers, I may use some severe plastic deformation techniques. And when I am talking about the severe plastic deformation, then I am limiting myself. I am introducing a new processing technique and not relying on my conventional processing which I have used over the years for conventional production.

So, one way is to coup these techniques the conventional methods in a new form to actually produce nano materials. If existing processing techniques can be put to the use in the case of nano materials this would lead to considerable savings in effort and cost. Conventional processing techniques typically involve long timescales or high temperatures. But as nano materials are not thermodynamic in the state of non-thermodynamic equilibrium, there is always a tendency for grain coarsening or phase transformation.

Hence, or in other words a loss of the nanostructure in the general sense. Hence, it is imperative to develop variant of current techniques which involve high pressure and low temperatures and which also will give me nano structured bulk material in a short timescale. So, a not only do I have to scale up the production using the new techniques I have developed, but also try to somehow co-opt the existing technique by modifying the processing in parameter, by modifying various processing steps so, that I can use them as well in the in production of nano structured materials.

The obvious advantage would be that I can use my existing production lines, I can use my existing capital investments with of course, modifications to them therefore, I would have a considerably saving in terms of my overall integration of the new technology in to an existing production line or an existing industry. So, this is another challenge which remains in front of us and very few people are actually what you might call working on these areas where they are trying to use an existing processing methods to get nano structured materials.

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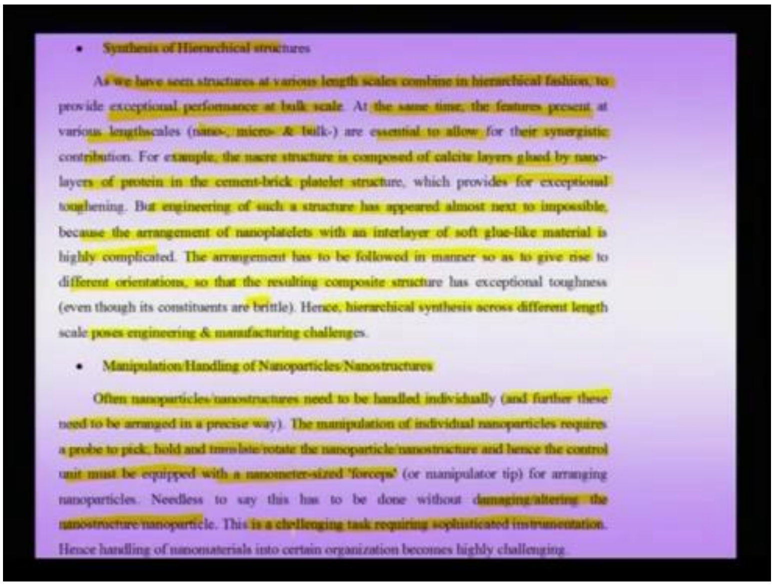

- Synthesis of Hierarchical structures

As we have seen structures at various length scales combine in hierarchical fashion, to provide exceptional performance at bulk scale. At the same time, the features present at various lengthscales (nano-, micro- & bulk-) are essential to allow for their synergistic contribution. For example, the nacre structure is composed of calcite layers glued by nano-layers of protein in the cement-brick platelet structure, which provides for exceptional toughening. But engineering of such a structure has appeared almost next to impossible, because the arrangement of nanoplatelets with an interlayer of soft glue-like material is highly complicated. The arrangement has to be followed in manner so as to give rise to different orientations, so that the resulting composite structure has exceptional toughness (even though its constituents are brittle). Hence, hierarchical synthesis across different length scale poses engineering & manufacturing challenges.

- Manipulation/Handling of Nanoparticles/Nanostructures

Often nanoparticles/nanostructures need to be handled individually (and further these need to be arranged in a precise way). The manipulation of individual nanoparticles requires a probe to pick, hold and translate/rotate the nanoparticle/nanostructure and hence the control unit must be equipped with a nanometer-sized 'forceps' (or manipulator tip) for arranging nanoparticles. Needless to say this has to be done without damaging/altering the nanostructure/nanoparticle. This is a challenging task requiring sophisticated instrumentation. Hence handling of nanomaterials into certain organization becomes highly challenging.

One class of materials which we have seen which are very interesting, but are equally difficult to synthesize are the hierarchical structures. Biology as we has noted is a bound with some of these hierarchical structures, but when it comes to production of these this definitely is a big challenge. As we have seen that structures at various length scale combine in a hierarchical fashion to provide an exceptional performance at the bulk scale, at the same time features represent these individual features represent various length scale like nano, micro and bulk are essentially to allow for their synergistic contribution.

So, this various length scales give rise to a synergistic contribution for example, we have seen a macro structure is composed of calcite layers glued by nano layers of protein in a cement-brick platelet structure, which provides for its exceptional tough toughness or an impact resistance. But hearing such a structure as appeared almost next to impossible because the arrangement of nano platelets with an interlayer of a soft material like glue like material is highly complicated.

Further it is not that I am just going to arrange these layers in a one localized region, but I need to arrange them in a larger length scale so, has to give rise to different orientations that allow retaining this composite structure with exceptional toughness in spite of the constants be being brittle. Hence, hierarchical synthesis across different length scale poses even more serious engineering and manufacturing challenges.

So, when it comes to normal nanostructures materials, where we have a single length scale to deal with it is difficult enough. But I am, when I am talking about a hierarchical structure these issues are compounded the manufacturing issues the issues of you know even making it in a lab scale becomes even more difficult. So, it is very clear that in spite of the exceptional properties I get from hierarchical structure they if I have to see them used in a real industrial scale then I have to worry about much more serious issues.

Many of you must have been exposed to the fact that I need to manipulate nano particles and nanostructures. So, this manipulation is itself an issue, often nano particle nanostructure need to be handled individually and further these need to be arranged in a précised way. And here of course, I am not talking about those kind of nanostructures and nano materials which are called comes under the class of self-assembled nanostructures.

Therein of course, in the case of self-assembled nanostructures there is a propensity for the material itself to arrange in a particular configuration given a certain kind of a processing condition. And there of course, I have do not have to worry about arranging these nano particles in an external way. But here in normal cases I may want to arrange them, and I may want to manipulate them I want arrange them in a very précised configuration may be in two dimension some time even in three dimensions.

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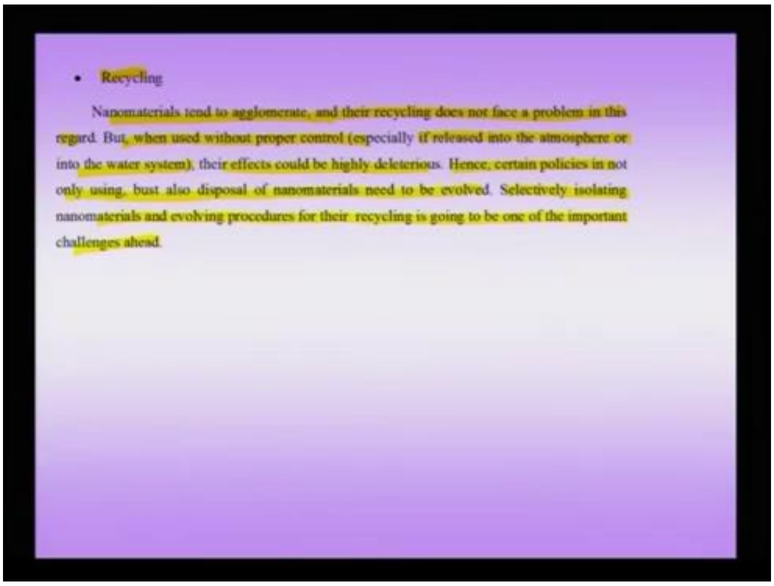

- Recycling

Nanomaterials tend to agglomerate, and their recycling does not face a problem in this regard. But, when used without proper control (especially if released into the atmosphere or into the water system), their effects could be highly deleterious. Hence, certain policies in not only using, bust also disposal of nanomaterials need to be evolved. Selectively isolating nanomaterials and evolving procedures for their recycling is going to be one of the important challenges ahead.

The manipulation of individual nano particles requires a probe to pick then to hold and translate rotate the nano particle nanostructure and hence control the control unit structure must be equipped with a nanometer sized forceps like structures. So, I need some kind of a manipulator which is nano sized which can hold this particles, translate it, rotate it if necessary and locate it in a precise position in my assembly. And of course, this has to be done without damaging or altering the nanostructure nano particle so, I have to obviously keep my nanostructure pristine while the entire processing.

This is a challenging task requesting sophisticated instrumentation and hence, handling on nano material into certain organization becomes highly challenging. And needless to say that, when I am actually dealing with single nano particles being arranged in an array, obviously the process is going to be time consuming and this is not what you might call unable to mass scale production. So, we have to come up with newer techniques wherein, I am able to actually do such a process in a fast timescale so, that I am able to produce many of these components which is done by a precise arrangement of these nanostructures or nano particles.

Perhaps we had already talked about this aspect when we said that we need recycling and save disposal, but we just re-hydrated the aspect here, the recycling still remains a serious issue. Nano materials tend to agglomerate and their recycling does not face a problem in this regard, but when used without proper control especially if released into the atmosphere or into the water system their effects could be highly deleterious. And especially in this regard the important problem remains that there are not enough studies to conclude that if they are even deleterious or not.

So, this aspect is not even been studied in the case of nano materials. Hence, certain policies not only using, but also disposal of the nano materials need to be avoided. So far, there are what you might say, there are no strict what norms for using them, there are no norms for recycling them. There are no policies in the record to government that what kind of nano materials can be released in the atmosphere, what kind of nano materials need to be protected what kind of nano materials to be agglomerated before they are released. And what kind of other procedures we need to especially we need to have all with regard to nano materials.

Hence, now we are talking about policies extending across countries which is what is lack currently lacking. Selectively isolating nano materials and evolving procedures for their recycling is going to be one of the important challenges ahead. So, the challenges is one of scientific importance and also one of as I said governmental policies which is now going to play a very important role in the coming years, when we are talking about widespread use of nanostructures and nano materials.

Thank you.