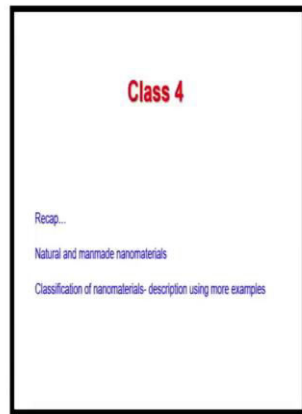


**Nanomaterials and their Properties**  
**Prof. Krishanu Biswas**  
**Department of Materials Science and Engineering**  
**Indian Institute of Technology, Kanpur**

**Lecture - 04**  
**Nanomaterials: Hierarchical Nanostructures (Part-II)**

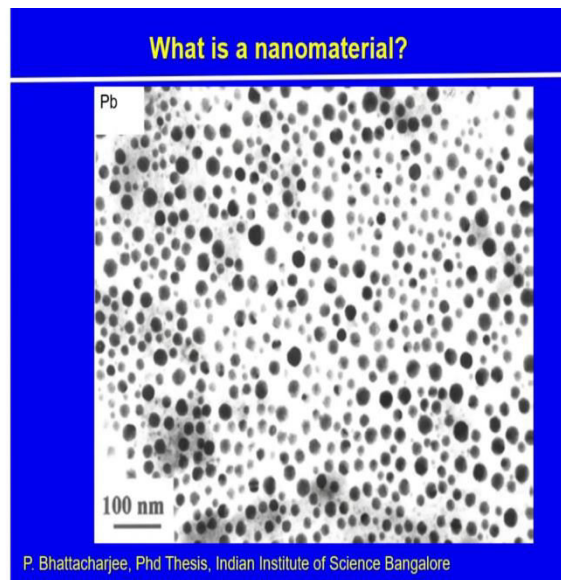
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Students we are going to learn something new in this class that is class 4. First, I like to have some recap of what we have done so far. As you know we have talked much about natural and manmade nanomaterials and then at the end of the last lecture I talked about some classification and as well as examples from that and finally, I talked about something about carbon-based nanomaterials. So, let us first discuss about these aspects then we will go ahead with other things.

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As you know this is something which I will again and again tell you that nanomaterial is something which is a material with one of its dimensions in the nanometric design or nanoscale.

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### What is a nanomaterial?

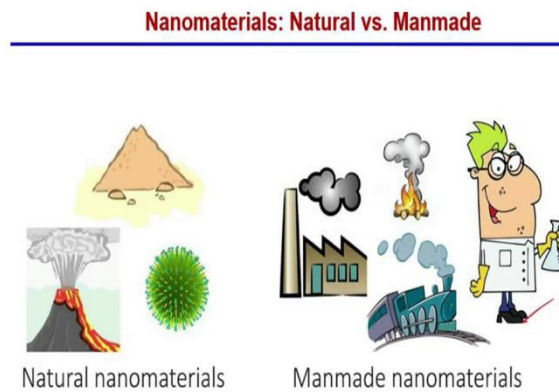
- **nanoscale:** size range from appr. 1 nm to 100 nm
- **nano-object:** material with one, two or three external dimensions in the **nanoscale**
- **particle:** minute piece of matter with defined physical boundaries
- **nanoparticle:** **nano-object** with all three external dimensions in the **nanoscale**
- nanoplate, -fiber, -tube, -rod, -wire, quantum dot

M.F. Ashby et al. , Nanomaterials, Nanotechnologies and Design, 2009

What is that? That is the size ranging from 1 to 100 nanometers. So, you can have nano objects, nanoparticles and nanoplates, fiber, tubes, rods, wire even quantum dots, but remember these aspects I have been telling you again and again every lecture. So, these something which students likely to forget instead of nanometers

they will add micrometers. So, that is why the size ranges from 1 to 100 nanometers is very important.

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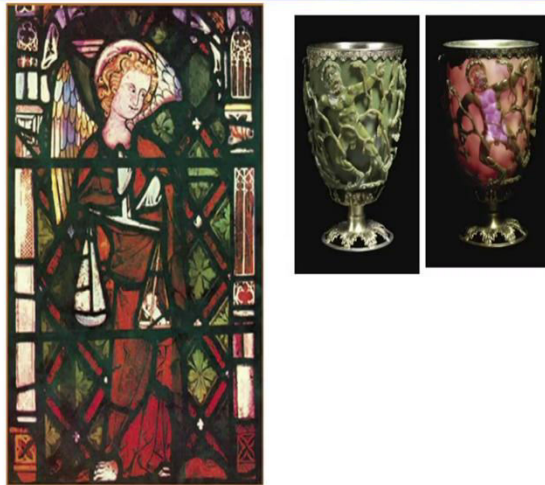
<https://niniithi.wordpress.com/nanomaterials/>

So, as you know there are naturally available nanomaterials like you have virus which is going on for the last 6 months then you can have you know volcanic smoke containing nanomaterials, you can also have nanomaterials in natural world like in tree leaves in case of you know other nanostructures I have discussed for the different animals actually what I have talked about it ok like silk, spider fine.

Then there are hundreds, thousands of different times of or not 100 thousands maybe or different types of manmade nanomaterials. We can burn some coal or something can produce fine scale particles which are dangerous for health like pollutions, then you can have also factory exhaust you can have exhaust from the automobile and you can even create in the lab right.

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### Painting



M.F. Ashby et al. , Nanomaterials, Nanotechnologies and Design, 2009

So, you can have different types of nanometers we discussed. Man made nanomaterials important applications which I talked about is painting using gold, silver especially gold nanomaterials and you know you can think about this as thousands of thousands of years ago, humans started using. And then I talked about this you know cup or the mug actually which is been given to Pajjan time king.

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### Mayan Civilization



[en.wikipedia.org/wiki/Maya\\_civilization](https://en.wikipedia.org/wiki/Maya_civilization)

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### Mysterious Maya Blue formula



And then I talked about something about Mayans and their paintings the blue color which I discussed about that the blue formula in their paintings is basically because of nano structure clay.

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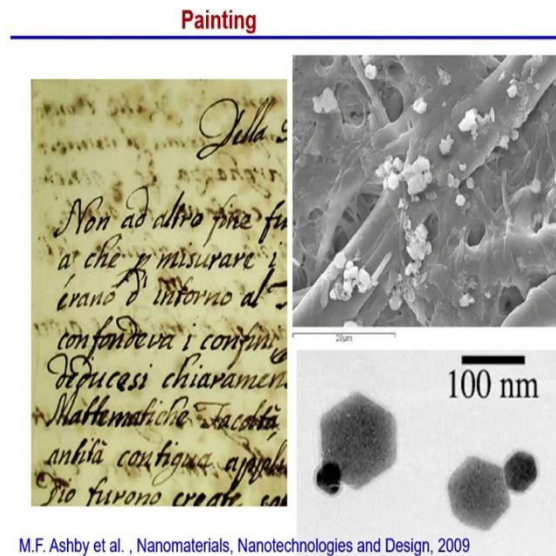
### Painting



M.F. Ashby et al. , Nanomaterials, Nanotechnologies and Design, 2009

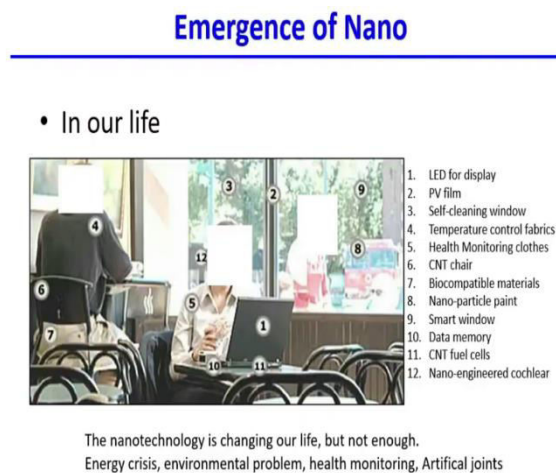
Not only that some of the Mayans painting also have gold and a particles which you have seen it or sorry silicon dioxide nanoparticles present in that.

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Well, you know these you know the for the conservation of the paintings or script, text, you can use nanomaterials also like clay ok and that can go inside and then protect these kind of things.

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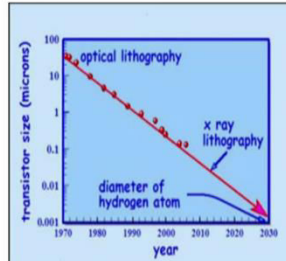


So, nanomaterials emerge in our life as an important aspect. You can have nanomaterial in every sector of life that is why you need to know about it.

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## Emergence of Nano

- Moore's Law



Moore's Law plot of transistor size versus year

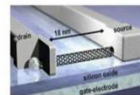
To meet the Moore's Law, the size of transistor should be decreased



Original contact transistor  
1947  
~1cm



Transistor  
in Integrated circuit  
Nowadays  
~1micrometer



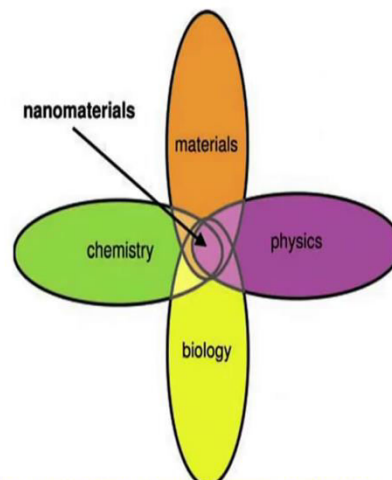
CNT Transistor  
Future  
~1nanometer

M.F. Ashby et al. , Nanomaterials, Nanotechnologies and Design, 2009

And you know Moore's law is almost reaching its law limit. You can you? You can no longer put transistors. So, as smaller than about say 10 nanometers or so, it is impossible now to go down this limit. So, we are slowly reaching that. You can see 2030 is what is the predicted limit by X ray lithography and so we have gone to that. So, therefore, we need to go to now atomic scale lithography that is not yet achieved.

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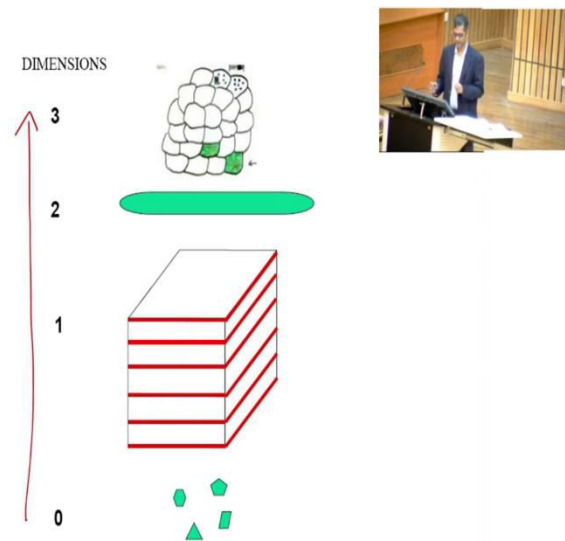
- Interdisciplinary Investigation



M.F. Ashby et al. , Nanomaterials, Nanotechnologies and Design, 2009

So, that is something which is you need to know, but the on the other hand nanomaterials actually to understand nanomaterials you need to understand the interface between chemistry, physics, biology and materials that is why the difficulty comes in picture for most of us. So, we need to learn lot of new things, how all these subjects are making an interplay in determining this materials world is something which is new to all of us.

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Ok. So, now, let us come back to the discussion which you are going to do. So, that must be a way to classify nanomaterials right because we are seeing plethora of nanomaterials available in the natural world and manmade world, but if you have to classify them if you have to categorize them, how you are going to do? The best way of doing is by using a concept called dimensions which I have discussed in the last lecture.

What is that dimension? Well, it means in a nanomaterial, it indicates the number of dimensions which number of basically in dimensions in x, y, z if you consider three x u x is x, y, z. So, number of dimensions which are not a nanometric design right which are beyond whose dimension is beyond 100 nanometers ok that is what is the way we define dimension is.

So that means, if it is 0 dimensions; that means, out of x, y, z, three important three dimensional dimensions all of them are in the nanometric scale that is what is that is



nothing but a nanoparticle. Then one-dimensional means one of the dimensions are not in nanometric regime right. Two dimension means two of the dimensions are non-nanometric regimes. Three dimension means all three are non-nanometric regimes.

So, you must be surprised why do we call them as a nanomaterial. We will discuss more detail about that. First let us start from zero dimension that is what is important. So, I hope you understood it right. The important aspect is this numbers 0, 1, 2, 3 this numbers as you go along this direction these numbers, they indicate the dimensions out of three x, y, z which is not in nanometric scale that is what it is. So, that is you must remember.

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**Classification**

- Classification is based on the number of dimensions, which are not confined to the nanoscale range ( $<100 \text{ nm}$ ).
- (1) zero-dimensional (0-D),
- (2) one-dimensional (1-D),
- (3) two-dimensional (2-D), and
- (4) three-dimensional (3-D).

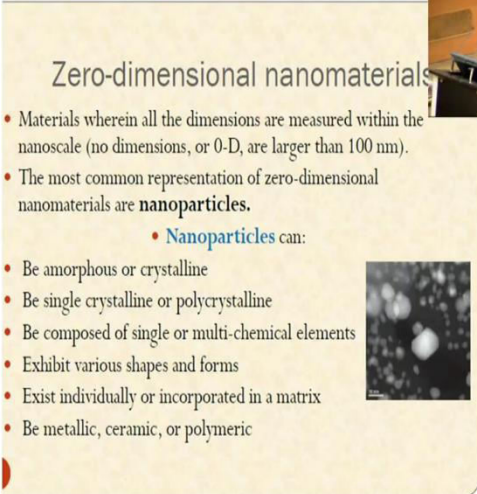
**0-D**  
All dimensions (x,y,z) at nanoscale  
 $d \leq 100 \text{ nm}$   
Nanoparticles

**1-D**  
Two dimensions (x,y) at nanoscale, other dimension (z) is not  
 $d \leq 100 \text{ nm}$   
Nanowires, nanorods, and nanotubes

**2-D**  
One dimension (z) at nanoscale, other two dimensions (x,y) are not  
 $t \leq 100 \text{ nm}$   
Nanocoatings and nanofilms


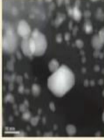
So, you know that is what is written. Classification is mostly based on number of dimensions which are not confined to nanometric or nanoscale design ok 0, 1, 2, 3.

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**Zero-dimensional nanomaterials**

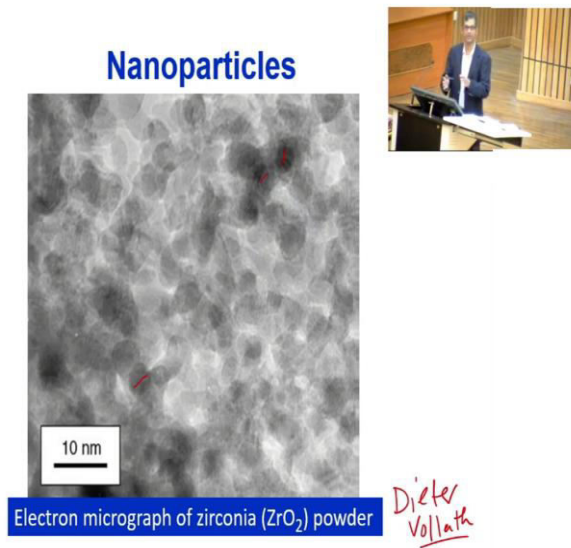
- Materials wherein all the dimensions are measured within the nanoscale (no dimensions, or 0-D, are larger than 100 nm).
- The most common representation of zero-dimensional nanomaterials are **nanoparticles**.
  - **Nanoparticles** can:
    - Be amorphous or crystalline
    - Be single crystalline or polycrystalline
    - Be composed of single or multi-chemical elements
    - Exhibit various shapes and forms
    - Exist individually or incorporated in a matrix
    - Be metallic, ceramic, or polymeric



Now, what is zero dimensions? Materials in where in all those dimension measured within nanoscale all the dimensions  $x$ ,  $y$ ,  $z$ , they are called zero dimensional that is like a nanoparticle. But you have to understand it can be amorphous or crystalline, it need not be only crystalline materials. It can be single crystalline or a polycrystalline it can be composed of single elements or multi elements.

It can have different shapes and forms. It can exhibit individuality or incorporate in a matrix in a something which these particles can be incorporated. It can be obviously, metallic, ceramics or polymeric anything is possible.

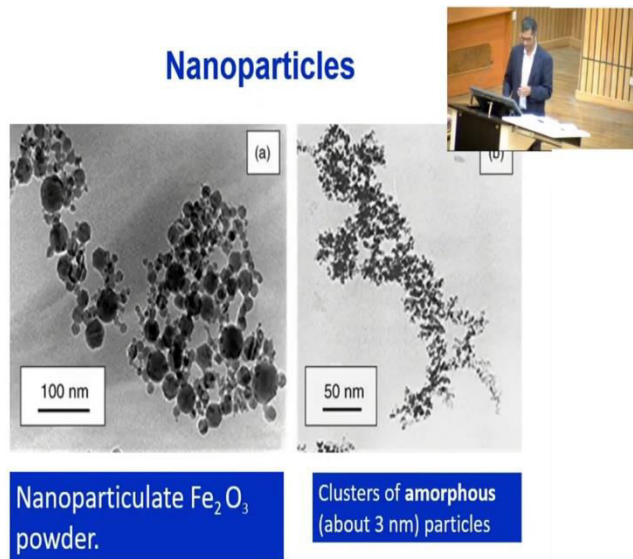
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Well, let us see that. This is an electron micrograph of ZrO<sub>2</sub> that is zirconia nanoparticles powder. See you can see some of these particles all the image is not very distinct and clear. This picture is again taken from the book of Vollath ok. Hope you have seen the book already or you have not seen the book Dieter Vollath this is taken by taken from that.

So, this indicates there are a lot of zirconia oxide nanoparticles which are dimension less than 100 nanometers, but because in the nanoparticle mostly spherical. So, it has only one dimension that is the diameter of the nanoparticle in the sphere that is in nanometer regime. So, you do not need to bother about other two dimensions like theta and phi. We do not care about in determining the dimensions of nanoparticle of those aspects.

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Well, you can also have other things like nanoparticulate of hematite  $\text{Fe}_2\text{O}_3$  right. You can see that hematite crystals they are less than about 100 nanometer small or big. You can also have amorphous like nano materials amorphous crystals you can see that. So, you can have both crystalline amorphous nano materials present. So, therefore, all of these are zero dimensional nano particles.

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### One-dimensional nanomaterials

- One dimension that is outside the nanoscale.
- This leads to needle like-shaped nanomaterials.
- 1-D materials include **nanotubes, nanorods, and nanowires**.
- **1-D nanomaterials** can be
  - Amorphous or crystalline
  - Single crystalline or polycrystalline
  - Chemically pure or impure
  - Standalone materials or embedded in within another medium
  - Metallic, ceramic, or polymeric



Now, let us talk about one dimensional nano particles. What are these one dimensional nano particles? Well, one dimensional nano particles are if one of the

dimensions are outside the nano scale. So, if you understand if your one dimension is outside the scale; that means, one dimension can be much longer than other two dimensions, what you can get is a needle like needle shape like crystals ok.

So, like nano tubes and rods, nano wires they are all one dimensional. It can be also again amorphous crystalline or other all parameter like single crystalline, polycrystalline, chemically pure or impure they can be stand alone or putting on a substrate and obviously, metallic ceramics and the polymeric.

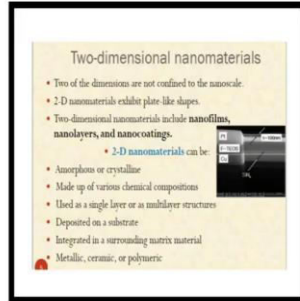
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Giving an example ok, let us look at ZnO nano rods ok. These are again taken from Dieter Vollath ok. So, this is a secondary electron image object zinc oxide nano rod zinc oxide is also very important nano materials. It a lot of dopamine oxide, but it is also has lot of interesting properties multi properties functionality. So, they are actually rods you can see.

So, if you look at rods this is like a this kind of things. This dimension z is not a nanometric scale they are much longer than an nanometrics. On the other hand this dimension diameter is in nanometric regime. So, imogolite nanotubes also comes in this picture ok they are also very long needle like. So, you understand that.

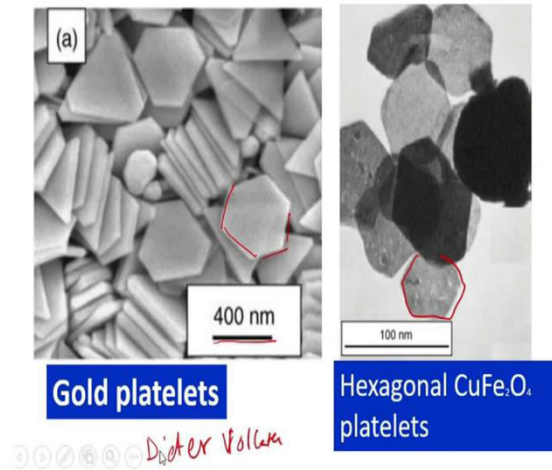
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Now, let us look at 2D nanomaterials. What are they? Two of the dimensions are not confined to nanoscale only one that is suppose either of x, y, z only one is confined on a scale. And they obviously, they will look like a plate, if you understand that they look like a plate. Two dimensional nanomaterials will be thin films on a substrate nano layers nano coatings even other things also.

Give a example of silicon nitride coatings on a copper substrate you can see that or you have a platinum and FET FETOs coating on the copper substrate. So, they are all very thin layers ok less than nanomaterials 100 nanometer thickness.

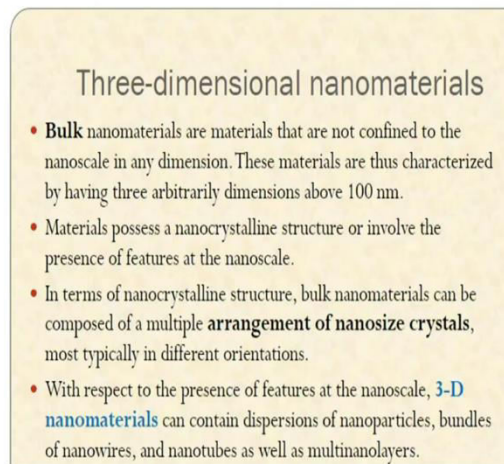
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To give you some more aspect let us look at gold platelets. You can see hexagonal separate gold platelets ok. Their only thickness is less than 100 nanometers, but other dimensions even these dimensions they are pretty big this is at 400 nanometers they also like that. So, that is true. Not only that if you look at copper fluoride  $\text{CuFe}_2\text{O}_4$  they are also like that.

You can see the picture with 100 nanometers, so; that means, these dimensions are much much bigger than 100 nanometers ok, but thickness is less than 100 nanometers. So, this is again also taken from Dieter Vollath books oops ok.

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### Three-dimensional nanomaterials

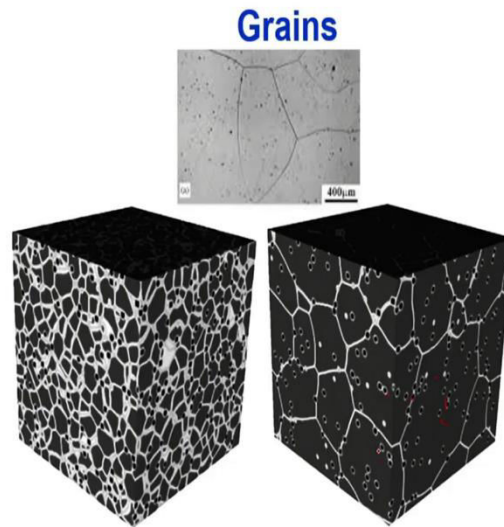
- **Bulk** nanomaterials are materials that are not confined to the nanoscale in any dimension. These materials are thus characterized by having three arbitrarily dimensions above 100 nm.
- Materials possess a nanocrystalline structure or involve the presence of features at the nanoscale.
- In terms of nanocrystalline structure, bulk nanomaterials can be composed of a multiple **arrangement of nanosize crystals**, most typically in different orientations.
- With respect to the presence of features at the nanoscale, **3-D nanomaterials** can contain dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multilayers.

3D nanomaterial that is what the most of the discussions will concentrate. Bulk nanomaterials are 3-D nanomaterials. Why? Because these materials dimensions x, y, z they are not confined to nano scale in any dimensions ok. Material possesses in nanocrystalline structure ok in terms of, it can have multiple arrangements of nanocrystalline materials.

Even with respect to the features 3-D nanomaterials can contain dispersion nanoparticles bundles some nanowires nanotubes or even nano layers. We will see that multi nano layers you will see that actually. So, they are nanomaterial because of their internal structures ok not external dimensions that is what you must remember.



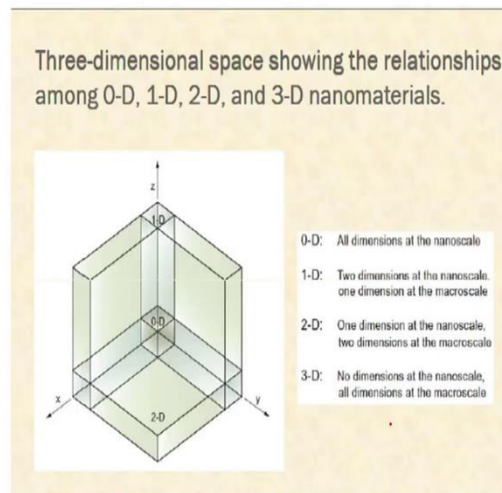
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Let us look at the grains actually. If you look at these grains very clearly you can see these grains are pretty big in 2-D as well as 3-D I am showing ok. So, but it has something inside these grains they may be poor or there may be something else. Nonetheless their dimensions if they are less than 100 nanometers then we call them as a nanomaterials, but they are 3-D all the grains are bigger than 100 nanometers, but they are called 3-D nanomaterials.

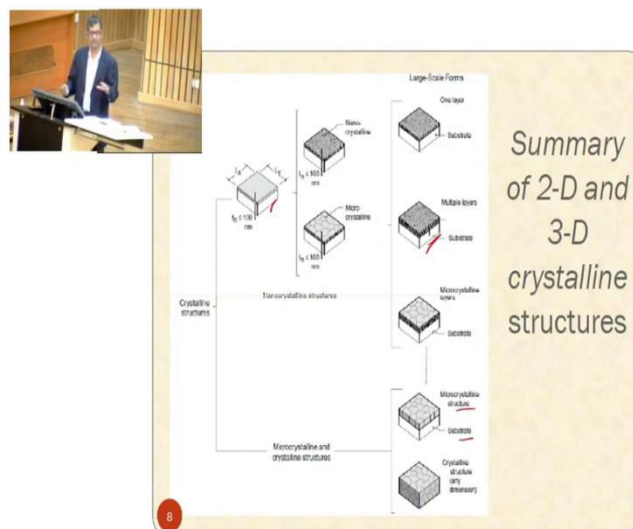
This is you something which you must remember that because this is something which is very difficult to understand or take in the minds ok.

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So, if I have to put everything together 0-D means all the dimension x, y, z are in nano metric design. 1-D means only two, 2-D means only one and 3-D means none right that is why 3-D does not comes into picture of that. Different shapes are also shown. You can see 1-D has a rod like shapes, needle like shapes, 2-D has a plate like things, 0D has a particle shapes and 3-D is not actually a nanomaterial.

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Well, you know in terms of structural things let us also discuss something like this. So, if we deposit a thin films on the substrate and thickness of a thin film is less than

100 nanometers we call them a nanostructure-one dimensional nanostructural materials. Obviously, other two dimension z and sorry y and x can be very very large right.

So, but even within the there are now comes to the point. Suppose I have this thin films on the substrate you can see that here. Now then I look at the grain structure of these thin films. If the grain structure can be nano crystalline or microcrystalline if the thickness of this thin film is less than 100 nanometers it does not matter whether the grain structure is nano crystalline or microcrystalline, we will have to call them as a nanomaterial.

Let us suppose thickness is more than 100 nanometers ok then none of the dimensions of these in nanocrystalline regime or nanoscale, but still we can call the material nano material if the grain structure inside this thin film is nano crystalline. Remember this, this is very important right. So, we need to know internal structure of these thin films to say this is a nano or not nano.

You can also have multiple layers instead of single layers right. Suppose you have a this structure substrate and then you have put a multiple layers and each layer is thickness is less than 100 nanometers then we call them as nanomaterials. Now, within each layer you have grain structure that can also be microcrystalline or nanocrystalline depending how you deposit that.

So, my question is this to you how many different ways you can create this kind of nano structures. Please do it yourself and find it out that is very important exercise that will give you a thought process clear ok. Otherwise, you will forget it very easily that is very something which you have to remember and then in exams you may not be able to put it.

So, microcrystalline structure you see you have a substrate, thick film less than more than 100 nanometers microcrystalline grains correct. You have a substrate, multiple layers each layer has nano crystalline grains. You have a substrate multiple layers each layer is thickness is less than 100 nanometers, but the grain structure is microcrystalline. Different different combinations you can do it and see it at your own disposal right that is not easy.

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Materials: Classes and Fundamentals

1-D  
Two dimensions ( $x, y$ ) of nanoscale, other dimension ( $z$ ) is not  
 $d \leq 100$  nm  
Nanowires, nanorods, and nanotubes

2-D  
One dimension ( $z$ ) of nanoscale, other two dimensions ( $x, y$ ) are not  
 $l \leq 100$  nm  
Nanosheets and nanofilms

3-D  
No bulk dimension of nanoscale  
 $l_x, l_y, l_z$   
Nanocrystals and nanocomposite materials

M.F. Ashby and others

Well to give examples of better quality pictures ok, this all taken from again the book by Michael Ashby and others. So, you can see that this is a nanoparticle mostly gold and its dimension is less than 100 nanometer because this is 2 nanometers. So, you must be able to read now, this is a linear scale. You can measure this scale and measure the dimensions of the particle.

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Materials: Classes and Fundamentals

1-D  
Two dimensions ( $x, y$ ) of nanoscale, other dimension ( $z$ ) is not  
 $d \leq 100$  nm  
Nanowires, nanorods, and nanotubes

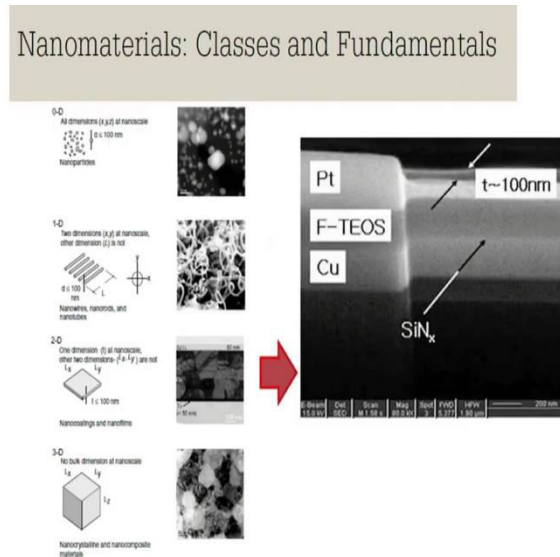
2-D  
One dimension ( $z$ ) of nanoscale, other two dimensions ( $x, y$ ) are not  
 $l \leq 100$  nm  
Nanosheets and nanofilms

3-D  
No bulk dimension of nanoscale  
 $l_x, l_y, l_z$   
Nanocrystals and nanocomposite materials

50 nm

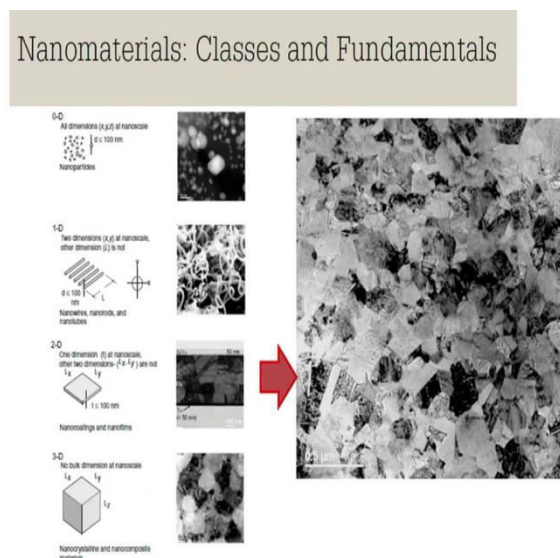
You can also have 2-D like this one which is basically nano rod you can see that, but bent and other things happened that is ok, but it is bent. So, it is very 1-D not 2-D, one of the dimension is long, the other 2 dimensions are basically nanometric scale.

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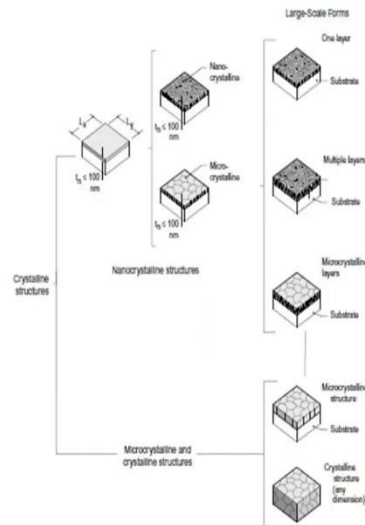
You can also have thin film. I have already shown you no need to discuss about it.

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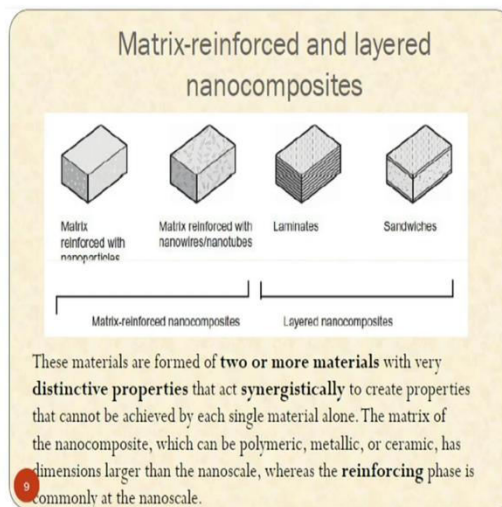


Or you can have grain structures which I have shown you, this 3-D nanomaterials.

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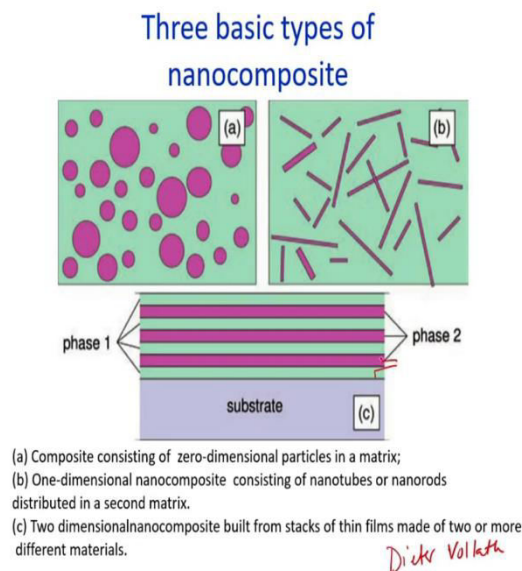
Now, as I told you 3-D nano materials can be created in many ways. Let us see some of the examples of that taken both from the book of Michael Ashby and as well as from Dieter Vollath. See you can have a matrix whose grains are very big. Let us say matrix with a large micron size grain and then you can put reinforcement particles like precipitates in the matrix. An aluminum copper alloy I gave you the example do not forget that that is a classic examples in metallurgy.

Then you have a matrix reinforced with nanotubes, nanowires you can also have laminates. The thickness of each layer is less than 100 nanometers then you can create a matrix you can create a material 3-D material or you can also have sandwiches. Very simple like sandwich means two pieces of bread intimacy of something either meat or vegetarian food right.

So, same thing can be done also. You can put two pieces of same material within each one other material can be kept and one of dimensions of these materials can be nanometric then you can call them nanomaterial right. So, these materials are basically formed by two or more materials not a single material and they have this each material has distinctive material property.

And when you put them together they actually act together synergistically to create properties that cannot be achieved by a single material. Matrix of nano mat composites can be polymeric metallic or ceramics has dimensions; obviously, more than nanoscale, but mostly in a reinforcing phase will be at nanoscale that is something we should remember. So, by putting different reinforcing phase you can create these 3-D nanostructure materials in many many many different ways.

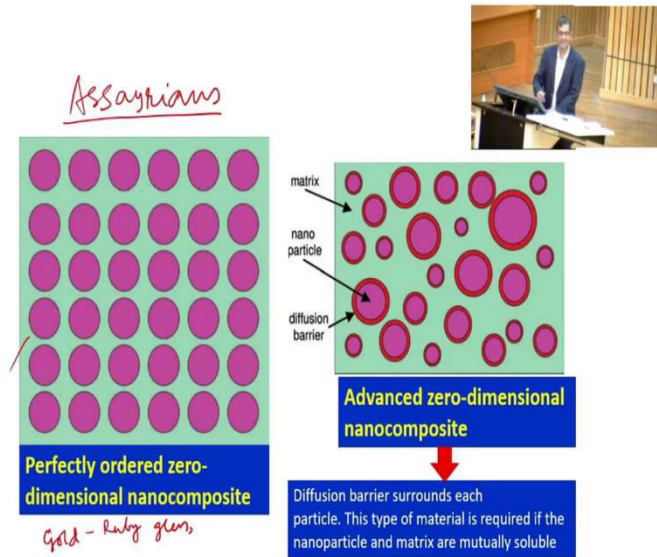
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Let us see that. There are three basic types of nanocomposites ok. One is you put zero-dimensional particle in a matrix, that is a this is taken from Dieter Vollath ok you can see that. You can also have one dimensional nano composite consisting of

nanotubes or nano wires this is with the second matrix you can see that or you can have two-dimensional nanocomposite built the stacks of thin film. You can see one phase and second phase the stack on each other.

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So, you know very interestingly this is something which was discovered, but which was there in the you know earlier world. I will tell you who has done that. As you know the oldest and most important nanocomposite is which has more or less spherical nanoparticles spherical gold nanoparticle actually. Example is gold ruby glass, this is gold ruby glass.

What is that? A ruby matrix you are putting spherical gold by nanoparticles well order. Can you imagine this material was made by a made in you know long back in 7th Century BC ok by Assyrians and they actually mastered the art. Later on, it was made in Germany also in 17th Century, but look at it, 7th Century BC somebody is making such a kind of nanomaterials is really a masterpiece.

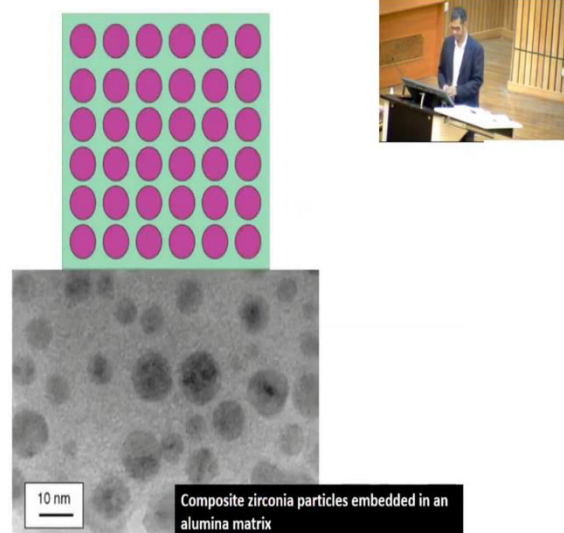
Well as you know it is the goal in ruby glass they may not interact ok or that means, they may not interpret each other there will be no diffusion. If there is an problem of diffusion happening you can also put a diffusion barrier layer around it which is you know widely used in various surrounds each nanoparticles and it is required if nanoparticles matrix are mutually soluble.



That is possible actually. You can put a polymeric layer on the metallic nanoparticle before you embed in a metallic matrix because most of the many metals actually have good solubility to each other. This is done actually, but then the stability of a nanoparticle will depend on stability of this layer which you are putting around it, but Assyrians are very very clever.

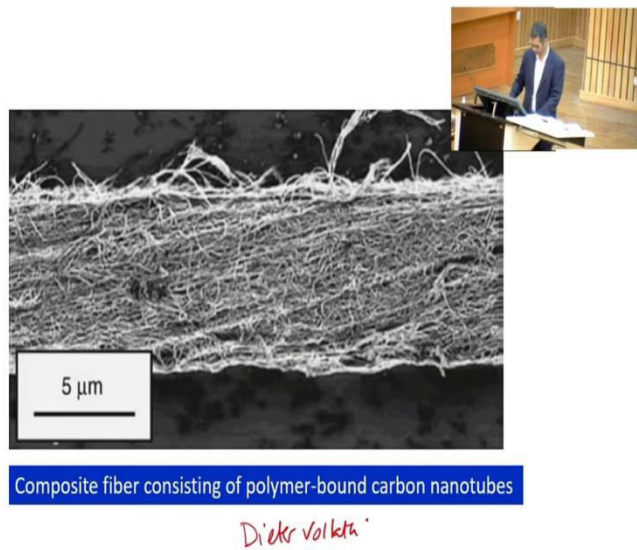
They put gold in ruby glass there is no solid solubility between ruby and the gold and that was a classic material which can be used for many purposes. Well so, that is something which you should know ok and because there are many ways you can create this. Now, the ruby matrix has a grain size which is much much bigger than 100 nanometers. So, they are not in nanoscale.

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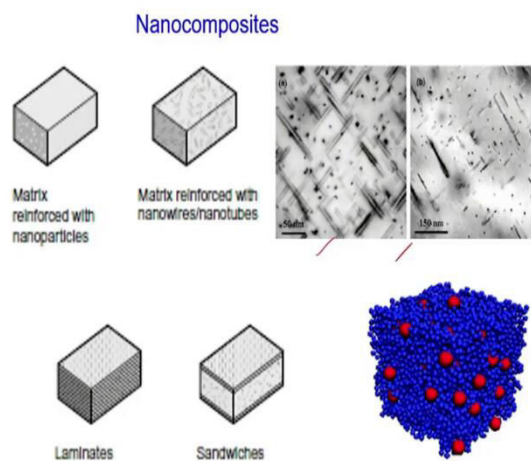
Well to give you examples, zirconia particle embedded in an aluminum matrix. Although it is not well order you can see that, but they are there at different sizes also it is possible to create such a kind of structures, ok. But zirconia aluminum have solid solubility. So, therefore, you have to be worry about diffusion barrier that is something which is not easy to design.

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Well, you know also you can see composite fiber or consisting of polymer bound carbon nanotubes. You are putting carbon atoms in polymer matrix in a very staring or something then put it that is also a nanocomposite is polymeric; that means, nanotubes in a polymer matrix, this is also taken from Dieter Vollath.

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Well so, in a nutshell before I stop this part of my lecture. So, you can have a matrix whose 3-D matrix whose grain size is much much bigger than 100 nanometers they

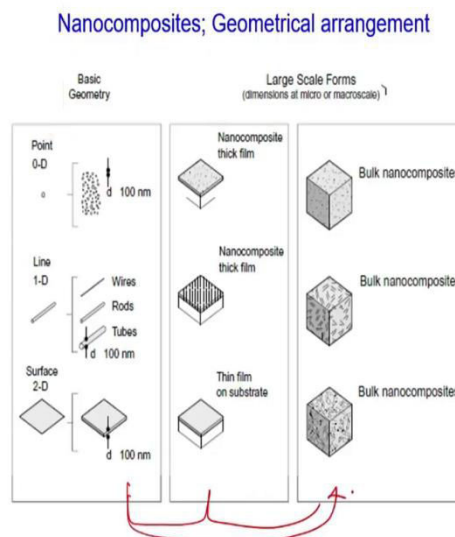
can be even microns 5 to 10 or 20 microns, 50 microns within each you can put the reinforcements.

Like you can put nanoparticles you can put nanofibers, nanowires, nanotubes or you can have laminates or you can have sandwiches you have seen that and you know these are the examples of real world. These are the you know copper aluminum copper alloys ok in which nano precipitates can be needle separate or plate separate precipitates are formed or you can also have particles also depending on the heat treatment which you provide correct.

So, that is how you can create this 3-D nano structure materials. So, in a nutshell you know I talked about lot things on 2-D and 3-D, how to create different 2-D and 3-D nanomaterials in case of thin films on the substrate and in case of nanocomposites. Please study well, look at the books and even think about it. You should be once you listen the lecture listen it bits and pieces. So, that it goes into your mind and you do not forget it in your lifetime that is what you should do it.

Well, you know that is my first part of my lecture. So, I have discussed about different types of nanomaterials.

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So, basic geometries, nanoparticles, nanowires and a rods and a tubes, thin films and substrates right then you can create different kinds of structures, 2-D or 3-D from

these structure that is what I discussed. You can see that these connections from here to there and then here to there ok, that is possible actually.

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### Nanomaterials : Class and Dimensionality

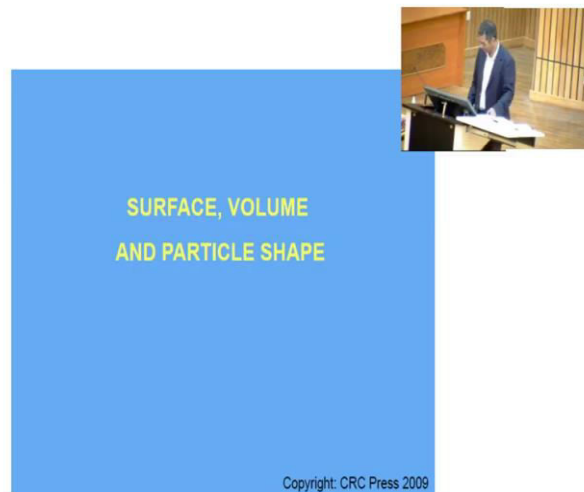
		Classes		
		Class 1 Discrete nano-objects	Class 2 Surface nano-featured materials	Class 3 Bulk nano-structured materials
Dimensionality	0-D All 3 dimensions on nano scale	Nanoparticles (smoke, diesel fumes)	Nanocrystalline films	Nanocrystalline materials Nanoparticle composites
	1-D 2 different dimensions on nano scale	Nanorods and tubes (carbon nano tubes)	Nano interconnects	Nanotube-reinforced composites
	2-D 1 different dimension on nano scale	Nanofilms, foils (gilding foil)	Nano surface layers	Multilayer structures

Well in a nutshell, if you have to talk about class and dimensionality class is discrete nano particles like smoke, diesel fumes. Nano rods tubes examples carbon nano tubes, nano thin films, foil like glide gilding oil foil or something which glitter.

Class 2 is surface nano featured materials like nano crystalline, thin films, nanocrystalline interconnects or nano surface layers and class 3 is a bulk things. You can create nanocrystalline materials like nanoparticles composites, nanotube reinforced composites and multi layer structures ok.

So, these are we can divide 2-D 2-D, 1-D and 0-D right you can create that using those things you can create this kind of 3-D or bulk nanostructure materials. So, that is my part 1 on lecture today and next 20 minutes or so, I am going to talk about something new right. Let us see that.

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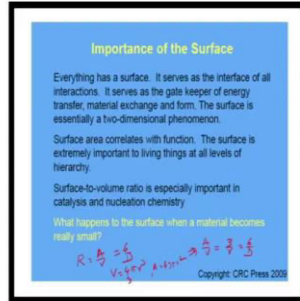


As you know this is something which you should understand. Why nano materials are so, important? Because of the high surface area to volume ratio that I have discussed to you again and again. Now, we have to put in perspective side. So, that you understand it you do not forget it. Well, this is something I should share with you. I have seen in my life here. Most of the students actually not to for all ok only for some of the students.

They just listen to the lectures take the exam and then in the next semester they forget everything, nothing remains in their brain they erase out everything very interesting capabilities they have. It is very difficult to forget something right in life which you are new learning, but I do not know this new breed of students they seem to be mastering the art of erasing out from their brain.

So, they have something like a memory in your memory stick. You just copy it and after some time you completely format it right that is possible which I did not know. So that means, human are slowly going to the machine like behavior that is funny right. If human become computer then the senses will be lost. Well, let us not discuss much about that. So, this lecture is taken from some many of these books outside this.

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But this is there from the Vollath Dieter Voollath's book chapter 2 I think in Dieter Vollath books talks about these aspects surface as this nanomaterials chapter book. You know nanomaterials surface, basically from a sharp interface between a particle and the outside world or between a particle and the matrix.

Now, you understand what is matrix right, I have already told you about the matrix. So, this in surfaces basically a sharp interface between a particle and the surrounding matrix a surrounding atmosphere rather or interface between a precipitated phase and the parent phase. The free surfaces in case of particles materials or grain boundaries ok in the bulk material, nanomaterials have large surfaces correct as you know, the fact which can be demonstrated very easily.

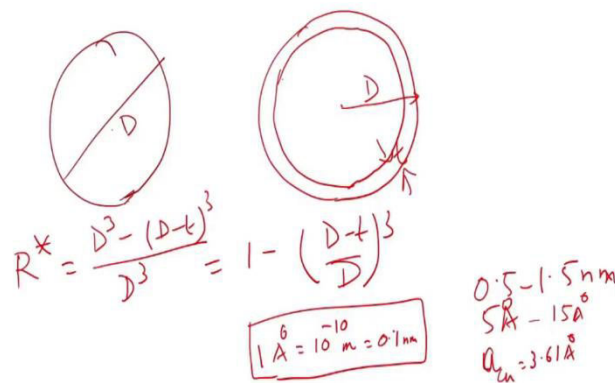
You know if you talk about spherical particles ok. The volume to say the what is that? Ratio between surfaces at a volume ok this is something,  $R = \frac{A}{V} = \frac{6}{D}$ . How do you get it? Very simple. For a sphere,  $V = \frac{4}{3}\pi r^3$  and  $A = 4\pi r^2$ .

So, if you clearly see it is basically  $\frac{A}{V}$ , if I can consider these two relationships,  $\frac{A}{V} = \frac{3}{r} = \frac{6}{D}$ . So that means, it is inversely proportional to diameter of the particles. As you decrease the particle size diameter decreases, r increases that is very important, but that is mathematical right that is means we are talking about very thin layer of surface which is not correct ok.

Practically every material has a thin surface layer. How do you define that surface layer? Well, it is these atoms sitting on the surface which are interacting with the surroundings. Bulk atoms are not interested. They are sleeping ok, just like many of you sleep in the class.

So, they are not interested to interact as they remain cool calm only that layer of band of atoms they interact with the surrounding matters. So, now, that is such a finite dimension right. Let us suppose the dimension is thickness is  $t$  right.

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Let us suppose that ok. So, what I do is I consider a spherical nanoparticle right. Let us suppose this is a dimension of  $D$  diameter of  $D$ . Now, I am talking the surface let us consider surface this is not a mathematical entity. Surface is physical entity that is obvious and that means in this nanoparticle if I draw again this picture ok this does not look good right. Let us erase it out ok. So, I just draw it again much better way.

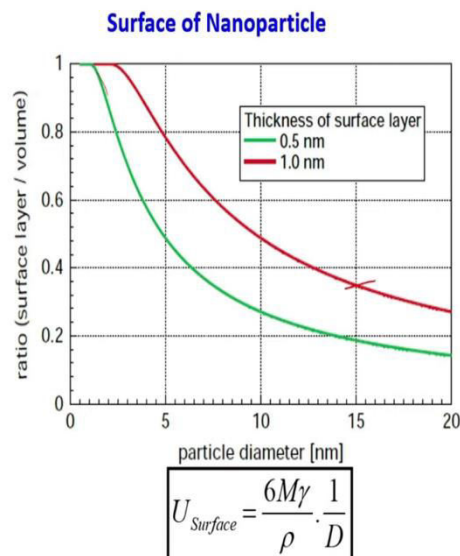
So, now I am saying that there is a finite thickness of the surface layer. Let us suppose this is the thickness  $t$  right and this is the center, this is the earlier diameter. So, now, if I have to consider, what is the number of atom sittings the fraction of atoms sitting in the surface. So, I can always consider this  $R^* = \frac{D^3 - (D-t)^3}{D^3} = 1 - \left(\frac{D-t}{D}\right)^3$

Now, if I this t is a variable here. Depending on the type of material this t will change. Normally t changes from 0.5 to 1.5 nanometers; that means 0.5 is 5 Angstrom. You know 1 Angstrom right.  $1 \text{ \AA} = 10^{-10} \text{ m}$  that is equal to 0.1 nanometer and to about 15 Angstrom that is ok.

So, what is the lattice parameter of copper? Lattice parameter of copper is lattice parameter of copper is 3.61 Angstrom. **5 n micron means almost like a 2 n close to 2 layers 2 and a one half layers of copper.** And 15 angstrom means almost like a 4 layers of copper that is not much right. If I have a copper nanoparticle is expected, therefore, 2 to 3; 2 to 4 layers will be interacting with the surrounding matrix. It is logically correct.

So, now if I plug in these values of this t from 0.5 to 1.5 nanometers, what do I get? Let us go back to that plot.

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So, now signals of the surface layer as a function of these ratio R star what have I done it just now surface layer to volume. As you see if it is 0.5 nanometers thickness then this as a function of particle size, this is how these things changes. And you can clearly see as about 5 nanometers or less the huge rise of this ratio; that means, then the surface effects us significantly large compared to bulk.



And below about say about 15 nanometers higher than 15 nanometers these effects are not large. What happen if I increase the size of this thickness? Then the effect is pretty strong something about say 15 nanometers. You can see that very pretty strong it is about 35% to 40% atoms are sitting on the surface.

Only when its goes down to about say 30, 40 nanometers then you do not see. So, that is the effect you understand you have to remember. The thicker the surface layer, larger will be the particle size, one which this effect will be prevalent right. So, thinner the layers less will be lower will be the size of the particles on which these effects will be significantly felt that is the thing which I wanted to tell you.

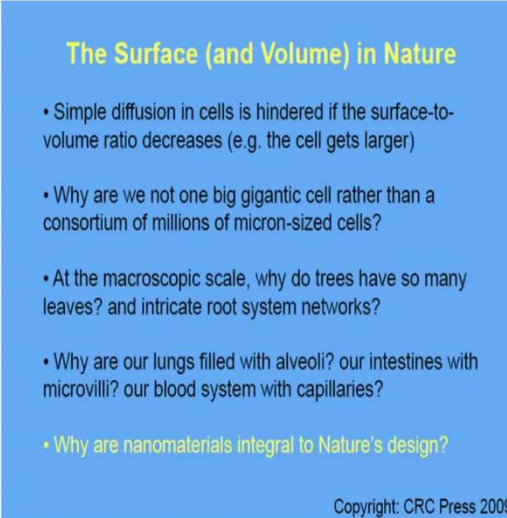
So, most of the mathematical treatments do not consider these aspects. They always consider a finite size whether; that means, a sharp interface kind of things. There is only one layer of surface atoms then surface then the surrounding comes into picture there is absurd and that are absolutely not correct at all. So, please understand that in all your mathematical treatments which you will be doing this must be built in.

But unfortunately, I may not be able to do all the analysis like this way thickness consideration, but you can do it at your home task or homework assignments something like that. So, let us come back to it now. So, what is the importance of the surface then that you understood, right.

It serves as an interface of all kind of interactions; reactions, interactions everything right. It serves as a gatekeeper of energy; transfer, material exchange and also all kinds of formations. Surface is nothing but a two-dimensional phenomenon right. Surface area is correlates with functions of surface extremely important for living things right very important right. You mean some corona virus you get infected right.

Surface to volume ratio is especially important in catalysis and nucleation. What is happen to the surface becomes materials when the material become very small ok. That is the question we are dealing with.

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**The Surface (and Volume) in Nature**

- Simple diffusion in cells is hindered if the surface-to-volume ratio decreases (e.g. the cell gets larger)
- Why are we not one big gigantic cell rather than a consortium of millions of micron-sized cells?
- At the macroscopic scale, why do trees have so many leaves? and intricate root system networks?
- Why are our lungs filled with alveoli? our intestines with microvilli? our blood system with capillaries?
- Why are nanomaterials integral to Nature's design?

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Simple diffusion in cells is hindered if the surface to volume ratio decreases, cells become larger ok. Why we are not big gigantic cells rather than consortium of millions of micron sized cells? That is the question many people ask. Why cannot they have one gigantic cell everything is controlled? You know it is basically micron sized cells assembled properly to make a human being.

At the macroscopic scale why do trees have so, many leaves and intricate root system networks? Why our lungs filled with alveoli? Our intestines are microvilli, our blood systems are with capillaries? Why do nanomaterials integral to nature's design, that is the very fundamental questions one is to know ok.

They are integral to the fundamental design concepts they cannot be removed. So, in each of these things we have nano structures built in, that is main ideas to increase the surface rate of volume ratio.

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### Singular Surface Area and the Surface-to-Volume Ratio

When we refer to singular surface area, we refer to the surface area of a single nanoparticle.

Area is a function of a dimension squared, e.g.  $d^2$ ,  $x^2$  or  $r^2$ .  
Volume is a function of that dimension cubed, e.g.  $d^3$ ,  $x^3$  or  $r^3$ .

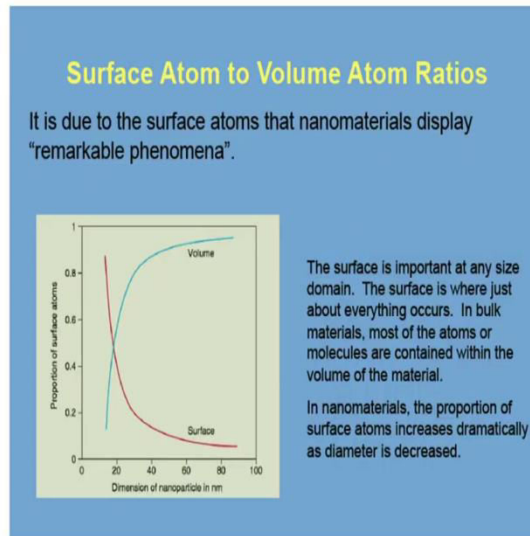
Surface-to-volume ratio ( $d^2 / d^3$ ) scales as the inverse of the dimension: e.g.  $d^{-1}$ . In other words, as the dimension approaches smaller and smaller limits, the surface-to-volume ratio scales as the inverse of the dimension.

Well, when we refer to single surfaces singular surface area, we refer to a surface area of a single nanoparticles right. As you know area is a function of always  $d^2$ ,  $x^2$  or  $r^2$ . Volume is a function of cubed like  $r^3$ ,  $d^3$ ,  $x^3$ .

And now, obviously, this is  $\frac{1}{d}$ , the surface at the volume ratio. In other words, the dimension appears smaller and smaller limits. The surface to volume ratio scales as inverse of a dimension. This people know it long long back maybe even olden days also 2000 years ago, people knew it very well.

That is why they could create all kinds of structures in the olden days even before Christ or may be 3000 years ago also well.

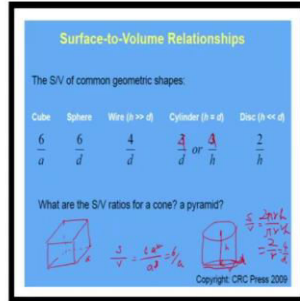
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So, let us see it. Let us plot it. This is something I showed you. It is because of the surface atoms that nanomaterial display remarkable phenomenon. Surface is important at any size domain, but not in a bulk ok. Because surface area is very small in a bulk material, they do not make much difference to the properties.

Surface is what we just about everything occurs. If bulk materials most of these atoms are molecules are contained within the volume only a fraction very small less than maybe 2% or 3% of the atoms sitting on the surface they do not make much difference. In nanomaterials it is the other way which we have been discussing again and again.

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Well, so, I will not talk about much to that. So, I will just want to share you that this you need to do with this maths very clearly. If we consider cube what the surface area to volume ratio is  $\frac{6}{a}$ ,  $a$  is the dimension of the cube. I can do it here also very easily. In a cube ok how many faces are there? 6 right and in a cube basically each side has a dimension of  $a$ .

So, then volume of the cube is  $\frac{S}{V}$ , So, volume of the cube is  $a^3$  we know that. So, what is the surface area of the cube? Each surface area =  $6a^2$ . So,  $\frac{S}{V} = \frac{6}{a}$ . So, here I have already done. Why are you have to do it yourselves it is  $\frac{4}{d}$  when  $h$  is very large. Cylinder is very easy. All of you should do that. How do you do it cylinder? Ok.

Cylinder is like this. You have a two dimension. One is the height  $h$  other one is your diameter  $d$  right. So, surface area to volume ratio, what is the volume?  $\pi r^2 h$ ,  $r$  is  $\frac{d}{2}$  right. This is  $r$ . And what is surface area,  $2\pi r h$ ? So, it is become just  $\frac{2}{r}$  right, that is a cylinder. So, it is  $\frac{2}{r}$ . So, now, you put it is  $\frac{4}{d}$  yes, it is not  $\frac{3}{d}$  it is  $\frac{4}{d}$  ok.

I mean  $h = d$  then it will be  $\frac{4}{h}$ . I am sorry about it. This we will have  $\frac{2}{h}$  right. So, that is why you should do it for all kinds of geometry like this you can plate you can do it for even a cone you can do it for many things it is possible.

Well so, I think I should stop here. So, with this discussion, next class we will talk about what is the evolution of surface energy. Actually, I start this definition of surface energy and then I will go into the surface energy of these nanoparticles. Something I am showing you here. You can see the surface energy also scales with  $\frac{1}{a}$ , right. So, we will see that actually.

So, this up something which you should read it well and try to understand. There is a new thing which I am talking about it surfaces and interfaces surface energy how they built in and how actually the important in nanostructural materials. Remember these are actually generalized discussions.

So, they are valid for any kind of materials which you can think about it. And, lastly, I would like to tell you that you know the as I am talk giving a video lecture to you know I am not asking you any questions, or you are not asking me any questions right. So, the most of the lectures will be pretty packed up.

So, whenever you see this lecture, you should see in pieces like ok. I am trying to make it pieces, but if sometimes I may not be able to do it, you can actually see it and stop it and again come back and see it. So, that watch it. So, that its gives you a good feeling of the lecture.

Thank you.