

**Nanomaterials and their Properties**  
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**Lecture - 03**  
**Nanomaterials: Hierarchical Nanostructures (Part-I)**

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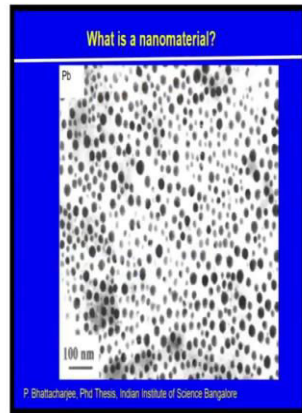


Welcome to the 3rd class my dear students. So, in this class, we are going to discuss about mostly on classification of nanomaterials. Let me just tell some time for discuss about what we have already done. So, in the very 1st lecture, we discussed mainly about the course followed by some discussion on the natural nanomaterials and then in the 2nd lecture, which was followed from that, we discussed about the more examples of materials, nanomaterials from nature.

I try to impress you upon the varieties of nanomaterial available in nature and their hierarchical structures and how these materials are been developed over the time scale to get idea about importance of nanomaterials. Obviously, there are few in manmade nanomaterials which are also important, which some of them I will discuss today's in the lecture.

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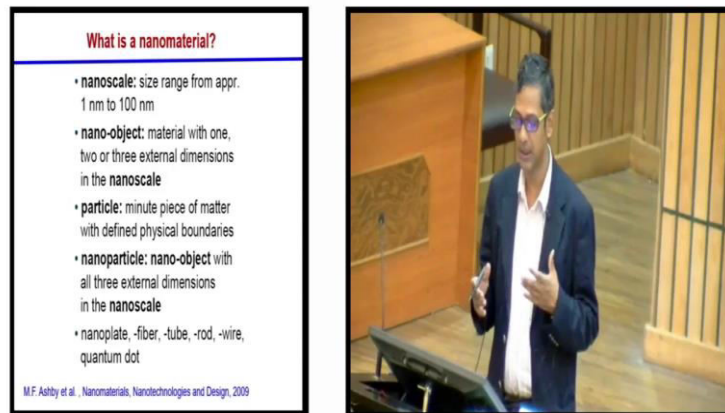
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So, let me just start with that, this is a picture I have been showing you for the last three lectures, just to impress you upon what is the nanomaterial mean. Nanomaterials means any material whose dimension in the x y z directions, all directions or one of the directions or two of the directions are below 100 nanometers or between 1 and 100 nanometers. This is a picture of laid nanoparticles, as you can see this is linear dimensions of 100 nanometers.

So, almost all the particles are less than that, the diameter of the particles; so that means the, these are all nanoparticles of laid mostly on this picture well.

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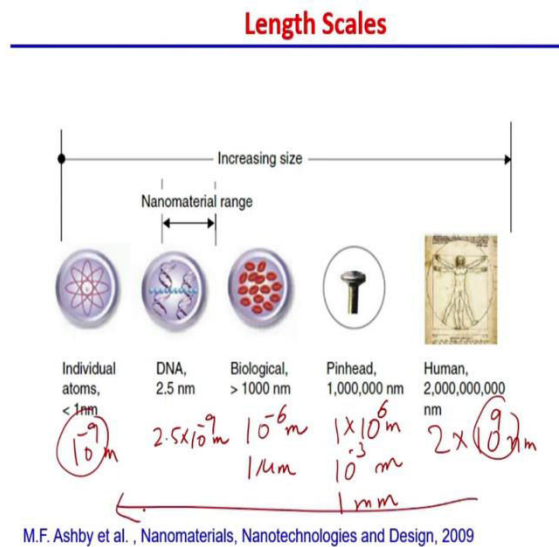


So, this is something which again and again I am telling you that, any things whose size is less than 1, less than 100 nanometers or it varies between 1 to 100 nanometers is called a nanomaterials, ok.

So, materials with one, two or three external dimensions having size in the nanometric domain or nanoscale domain are also called nano objects; you can have particles like minute piece of matter defined physical boundaries also nanoparticles, ok. Nano objects with all three external dimensions in nanoscale also that and lastly the nanoparticles nano objects can be different shapes like plates, fiber, tubes, rod, wire or dots, ok.

So, these are the various types of nanomaterials which are available.

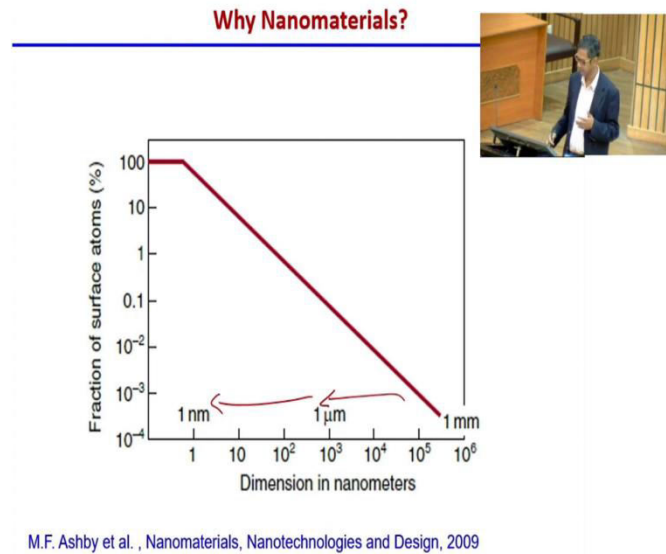
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So, now question is that as far as length scale is concerned, you can always compare with the height of a human being; the tallest human being will be 2 meters that is about  $2 \times 10^9$  nanometers. Pinhead is about  $1 \times 10^6$  nanometers; that is means about  $1 \times 10^{-3}$  meter, that means it is about 1 millimeter.

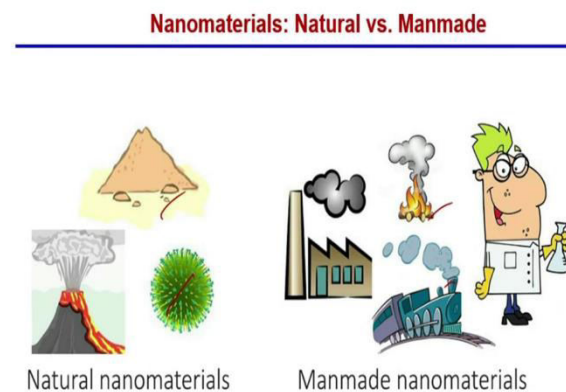
Red blood cells is of the order of micron that is  $10^{-6}$  meter, we call 1 micron. DNA is about 2.5 nanometers, that is  $2.5 \times 10^{-9}$  meter. And individual atom is about in the size of angstroms; so, therefore they are less than 1 nanometer, less than  $10^{-9}$  meter. So, you can see  $10^9$  to  $10^{-9}$  meter length scale variations can be seen in this picture.

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And you know why do we study nanomaterial? Because for small size particles and nano size materials, the large number of atoms sitting in the surfaces, the fraction of atoms sitting in the surfaces keeps on increasing as you go down from 1 millimeter to 1 micron to 1 nanometer and that is the reason we study nanomaterials, because this atom sitting in the surface provides provide you the good or the interesting properties and properties means performance, performance means applications. So, that is why we study nanomaterials.

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Well, nanomaterials can be naturally available or manmade, I have discussed this natural available nanomaterials is a virus; you know the first one ok, it is a corona virus. You can also have natural available materials coming from the volcanic eruptions, like ashes or dust or may be even crystals forming out of liquid or volcanic eruptions; you can also have dust particles sitting in the sand or something also nanomaterials.

There are many such things available in the naturally available things. But manmade (Refer Time: 05:01) more, you can also you can have you know soots coming out from factories, because of burning of woods or because of burning of fossil fuels in during train or the automobiles or you can prepare the nanomaterials in the lab; so but these are all mostly naturally available nanomaterials in the world. And I will not discuss about that, is ok.

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

So, now in the last lecture, I discussed about various types of naturally available nanomaterials, starting with the tree leaves, where the photosynthesis is actually done by the presence of sunlight. And then I started moved on to you know various other things like silk, the geckos, you know fingers or I discussed about the bone human bone hierarchical structures. But let me start with some very old, but manmade nanomaterials; all of you know about stained glass windows, right.

This is available in any church or even you know many important buildings in the western world or in India also. So, the stained glass actually are made to give you different colors of the, different colors because of the different kinds of materials presents, ok. But have you ever thought why these colors are originated from; how do you get these colors? Well, you can see in this picture, this picture is taken from some church which is depicting a phenomenon actually in the history of Christianity.

But its shows different colors, you can see the hues of red, you can see also the green, you can also see black, you can also see even white other colors also. But how do you get it? Well, this is mostly because of the embedded nanoparticles in the glass ok, but this nanoparticles are gold. So, let me just tell you why it so.

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You know as you know this picture many of you have seen; if you have gold nanoparticles or different sizes dispersed in the liquid, they shows photoluminescence. What is the photoluminescence?

So, if you disperse gold nanoparticles of different sizes from here to there ok, different sizes and just shine light on these, these nanoparticles shows different colors based on different sizes; it can also depends on orientation and size shape also, but let us not discuss about that thing now, we will come back to it later on when we talk about you know photo effects of light on the nano materials later on.

But for your understanding, this is something which is recent; you can prepare this gold nanoparticles in the lab, disperse in a liquid, it can be water, it can be non aqueous solutions and then shine light on it. Depending on the size of the nanoparticles, you can have different colors coming out of it. Why does it happens? That is because of what is known as a surface Plasmon resonance ok; these particles actually show a very critical resonance behavior, because of the surface Plasmon's.

Again because of the, you know large number of surface atoms on the surfaces of this gold, this thing is understood now. But think about this aspect, which is about 200, 300 or may be 400 years old. And in those days, there is no idea of understanding the subject.

What was known to the artisans or the artist who are doing this was that, this kind of materials available from certain mines. And in fact, if you read books of Michael Ashby and others, you will understand as these nanoparticles were basically used as a treasure or use as a very important aspects of the life of the artisans.

They used to collect them from these mines and then the technology or the you know way of applying these things on these glasses were only kept secret; it was transferred from one person to the other person of the family from one generation to other generation, this is very interesting, ok. And they did not know that these metallic or ceramic nanoparticles dispersed in a glassy matrix is or the, are they responsible for these different colors, they never knew it; but they knew that how to apply and which one to apply that they knew.

So, that means they knew that these nanoparticles are naturally available in certain mines, which they used to get it and then use it for their purpose, ok. This is, so there is no scientific understanding of the phenomenon at the time, not where the deliberate atoms to understand or even produce these nanoparticles. Early knowledge most relied on these craft based trial and error to achieve these effects.

It is known, for example, that introduction of certain materials by specific mines and accordingly you know empirically understood methods, did indeed produce rich colors in these aspects. And it was known to us long long time that, metallic compounds ok like cobalt oxides, silicon dioxides, or even various metals like gold, I told you silver, a nanometric domain obtained from different mines.



So, one of the mine is Bohemian Mines ok in Europe can lead to different types of colors, based on the size and type of materials that was known to them. But you know I would like to bring it to one of the most intrinsic or rather you know iconic pictures to show effect of nanomaterials, is this glass ok or you can say it is a basically a Roman era cup not glass ok and this is known as Lycurgus l y c u r g u s ok cup.

And you know this was all of you know that Constantine, who was a Roman king; in the late Roman era, he was a king of the all the Roman parts he is called Constantine 1 the Great, like Ashoka the Great. So, he could unify the Roman in the from the Europe to the some part of the Asia also is a large empire and during the war, one of the wars ok in 324 over Licinius ok **intress**, this cup was made and was by the additions and was given to him.

In fact, this indicates death of dinosaurs as you can see here; but most importantly what is intriguing of this cup is that or a goblet is that, if you shine light from outside, it shows some kind of a green contrast, but if you shine light from inside, it shows a red contrast. Why does it happen? Again this is mainly because of these nanoparticles embedded in the glass; because of presence of these nanoparticles, surface Plasmon resonance does occur and that leads to these different kinds of colors, ok.

And this is basically a very important example of surface Plasmon resonance utilized to give different colors. Remember this is something 324 AD something like about 2300, more than 2300 years and people knew it in those days that, how to use metallic ceramic nanoparticles to get such a kind of colors.

Well to give you much more perspectives of this ok, which is given in the, this book; analysis demonstrated that, the glass in this cup rather contains very very finest scale in a gold nanoparticle, something like 40 per million. These tiny metal nanoparticles suspended within the glassy matrix have diameters comparable to the wavelengths of light; you know that light it is wavelengths something like 400 to 700 nanometers.

So, you have a tiny gold nanoparticles, their dimensions are of the order of that dimensions, ok. Then what can happen? Then actually this lights as a consequence of these plasmonic excitation happens, the oscillation of these free electrons on the surface of the nanoparticle they get excited. And when they return back to the original

state, the light is emitted and this light is used to create such a kind of beautiful structures.

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### Mayan Civilization

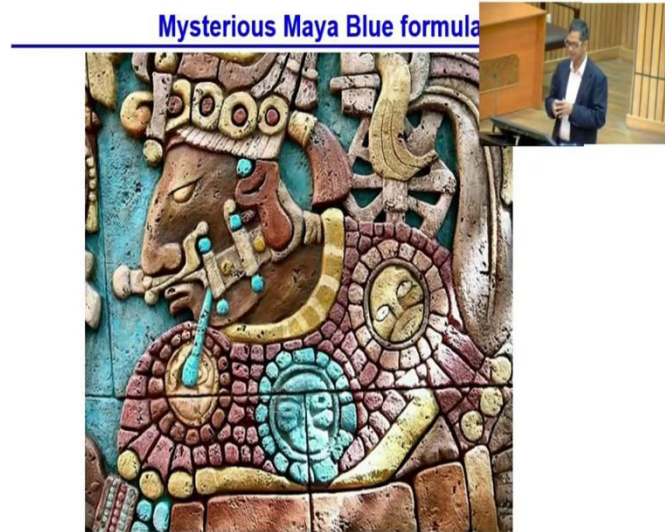


[en.wikipedia.org/wiki/Maya\\_civilization](https://en.wikipedia.org/wiki/Maya_civilization)

So, you understand the paintings were one of the best example of manmade nanomaterials. To give you more examples of that, go back even farther you know Mayan civilizations, which is very famous civilizations you know developed South of Mexico and some part of South America, Northern part of South America and Colombia, Honduras these different islands of that is ok. And this civilization is pretty old something like 2000 BC; that means 4000 years old to 250 AD, ok.

So, that is this is the variation of that; so that means it is about 2500 years almost, 2300 years almost long.

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So, they were you know very famous for creating this kind of paintings or this kind of structures on the walls, ok. And if you look at carefully these structures, there is a very typical blue color which is used in this. And you know that indigo, this is basically not a blue indigo color, which is present in many of these, you can see here, ok.

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You can see very clearly this indigo color here, here, there, ok. So, how do they develop this blue color, which was present even after 2000 years? And that was

surprising and that is why it is called Mysterious Maya blue formula, lot of research has been done. And you know Mayans they are very well developed you know civilizations; it was known to us, because it was something like you know thousands of kilometers away from the mainland Europe or of Asia, right.

But Mayans were very good at developing these aspects and those of you who are little bit in historical perspective that, this you know the movie by Harrison Ford what is known as Indiana Jones, the temple of the crystal skull is based on a Mayan civilizations. And there you can see that how Mayans were developed, Mayans who were very you know well developed society in terms of scientific knowledge, concepts, technology, ok.

So, let me come back to this origin of this blue ok, which you see here. You know Mayans used to use something different kinds of a blue dye, which is known as a neel, ok. You can see it has we call blue by Nil or Neel ok, n double e l in India and they used to use same kind of language probably, there is some similarity exist a neel and this dye was available often used to obtain from local plants you know in the pea Colombian textiles also, it is available.

So, now however, you know it is not acid resistance that is very important; because if you keep this model or the paintings or the you know wall paintings in open air because of pollution, pollution means lot of rain and pollution can really produce acidic things and that can damage this, this could not damage. So, why these things are available? Well, you know this mainly because this is you know, basically because they used to mix this with a kind of a things known as polygorskite.

It is a clay and this clay once it is mixed with the dye used to fired at about 1000 degree Celsius temperature and to retain such a kind of structures. Now, what used to happen is very interesting, that is what we should discuss now; you know within this clays actually there are lot of things improved is like iron, manganese, chromium everything is available and the host clay appeared to have originate in a mine, nearby mines actually.

They used to collect it that is what I said this artisan is to collect these things from the mines and to keep it within themselves and transfer from one generation to other generations. And then this whereas, the embedded impurities normally comes;

obviously it will come from the dye. So, the particular blue color is basically because of absorptions present in these kinds of things, which is the influence by exact size, shape and dispersion of these nanoparticles.

Now, the question is this, interestingly even you know minor amounts of these nanoparticles presents in you know in the impurities can be expected to significant effects on the optical properties. So, that is basically used to give this color, but they did not know that why these colors are coming from; they knew that this can be used to create a, such kind of colors.

Well, so scientific knowledge was absent; but we were using this naturally available materials to make different colors. Maybe once we understand thinking why not these are available in India? Well, one of the problem of this you know nanoparticles giving color is that, as you know if you shine light it produces; but even if you shine bright light like a flash of camera, the nanoparticle then lose their properties, Why? Because they can sinter themselves, they can become bigger or they can even get oxidized.

So, all these things can happen, that is what in our Indian monuments wherever these kind of objects are available in early days; because of the photographs taken in the dark by use of flashlights has completely damaged the color of the of these things. But it is known that these colors were existing in some of these paintings.

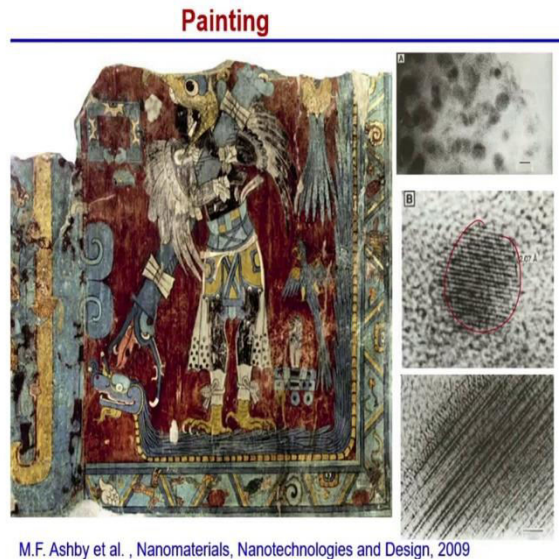
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#### Mysterious Maya Blue formula



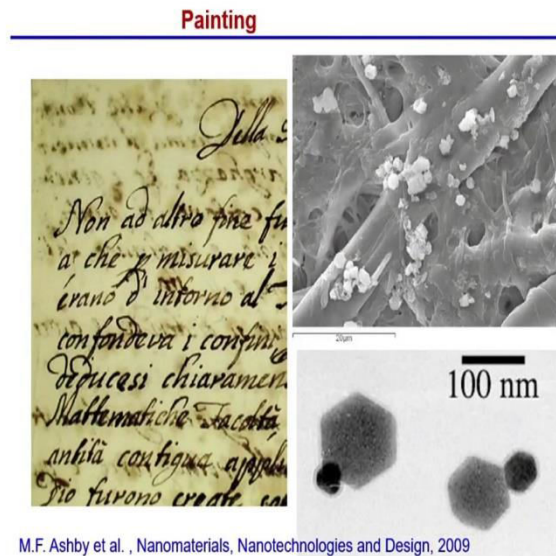
Well, so that is the about these aspects and you know this is something also known to you this you know this is a different color of blue ok compared to the one which is shown you and this is one of the mysterious pictures, which is not yet available.

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Well and people have done the M.F Ashby et al and others they have looked into it; you can see this kind of you know the clay, plate separate clay is available in these paintings and that is they are responsible for that. Very interestingly, when this clays are actually you know sinter or they burnt actually in presence of these dyes, that there are intercalation between these metallic atoms and these clay and that is probably the reason why they are not damaged by the acid attacks or they are not damaged by the environmental degradations things, which could have happened for the last thousands of years.

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Well, another important aspect of this, you know the diametrical console will be used to protect some of these things, which are available in the olden days; like one of these thing is the things text which are written on some piece of wood or something. So, they are what the people uses basically a calcium hydroxide, calcium oxide crystals and these crystals actually can lead to calcium, you know hydroxide crystals they can actually easily nanoparticles.

You can see them, they can actually; you can put it on the surface of these things and they can go inside it, because of the percolation and then they can create a layer. And you know sometimes this calcium hydroxide crystal can react with carbon dioxide available in the nature and create a pulpy kind of things and that is why they give the strength to these kind of a you know things which are only this text are available. And it is very important, nowadays to protect such a kind of text, things available on piece of wood or piece of you know leaves or something.

And this is this contain genuine information of the in the history. So, that is mostly about the aspects of painting and how to use it.

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## Emergence of Nano

- In our life



The nanotechnology is changing our life, but not enough.  
Energy crisis, environmental problem, health monitoring, Artificial joints

So, now, I will talk about little bit more on that, but let me stop it here for a moment. So, I have spent about 20 minutes, last 20 minutes to discuss about it; first 3 to 4 minutes I was talking about mostly the classes which I have done in the last two lectures and the next 15 to 17 minutes I talked about it necessarily available man made materials, ok.

I talk about naturally available, why? Because these materials are available in mines, they are not made in the labs or they are not generated because of the human action; they are all naturally available, but human understood it that these materials can be used for beautification purposes and then it was done to create paintings and other things. But you know what has changed; from 2000 BC to till today 4000 years, our life has changed.

If we look at typical things, nano has emerged all throughout soon. Look at your laptop, it has a LCD display, you know LED display rather ok and LED is basically a transistor based technology which is nanomaterials. You can have PV films on the on these glasses to block the different kinds of things like light and other things. Nowadays people talk about self-cleaning window, how do you clean the windows ok.

Windows are I already discussed about to you about nanoparticles, you can clean it use of using the light based or the photocatalytic reactions. You know there are fabrics not mine one, you can have it which is temperature control, ok. And this fabrics are



made use using nanomaterials. Clothes available especially carbon nano tube based clothes available which can monitor your health, like it can get your pulse, it can get you temperature, it can get your heart beats, you can even other many other basic parameters of that one can get it, ok.

You can also have chair made up of CNT, CNT is a stiff material; CNT is carbon nanotubes and these chairs which is shown here 6, they are CNT based. So, they will not bend you have to allow your body bent up your body because it is very stiff, that is way it can protect you from getting you know muscular pain. You can also have biocompatible materials, like many human beings can have you know bones broken or something to be replaced.

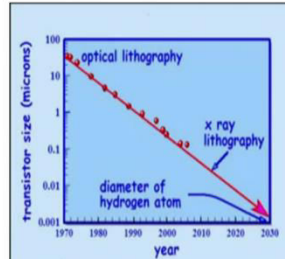
So, you can get a replaced by using artificially prepared bones, they are also nanomaterial many cases. You can have nanoparticle paints ok on the windows to get smart windows; depending on the intensity of the light outside, the color will change. Those of you travel in and the some of these planes by Boeing ok, they have these color changing windows, darkness changing windows rather, which is basically called smart window, they are also based on nanoparticles inside embedded in this glass.

Hard disk is basically data memory, where you are using nano; you can use is it a batteries in your laptop, you can use CNT fuel cells. You can also use you know nano engineer cochlear ok to creates many other structures. So, nano engine nano technology is changing our life, but it is, is it enough? You may say, no it is not enough; energy crisis, environmental problem, health monitoring, artificial joints, so many things to do and that is why actually nano can be used up.

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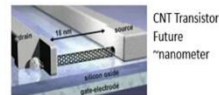
## Emergence of Nano

- 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



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

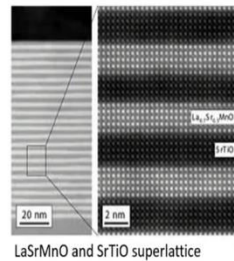
And it is this is a typical example here which always gives you, your devices which your using as a laptop or your mobile phone.

But it has you know transistors and Moore's law plots transistors size versus year from 1970s to 2030s; you can see we are going down to 1 nanometer. Is it possible to have? I am not sure 2020 is 10 years down the line, we have to wait and what and wait and watch, ok. Transistors have seen a sea chain from 1947 when it is discovered by Bardeen and you know Shockley and then it came into CNT transistors which is very thin and small.

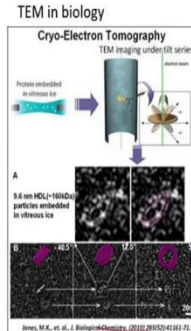
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## Challenges in Nano

- Atomic scale imaging



Understand and manipulate the target in nano scale



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

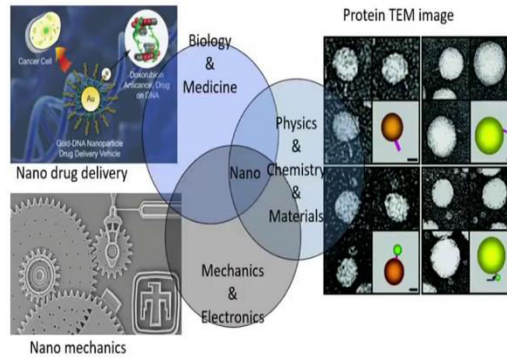
Well, there are many challenges, most important challenge is to seeing things in nanoscale what is known as atomic skill imaging. Can you see the atoms, that is the question you need to ask yourself? But that is why imaging techniques must improve and characterization has become a big tool in the world, ok. Now, this is poly inorganic materials or which are not alive, whatever bio you know; if you are looking at uses of nanomaterials in the biological aspects, you need to try electron tomography which is a new tool, which is coming in pictures, ok.

Those of you interested you can see this journal *Biological Chemistry* 2010 paper by Jones and it gives you perspectives of that, there are many challenges.

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## Challenges in Nano

- Interdisciplinary Investigation



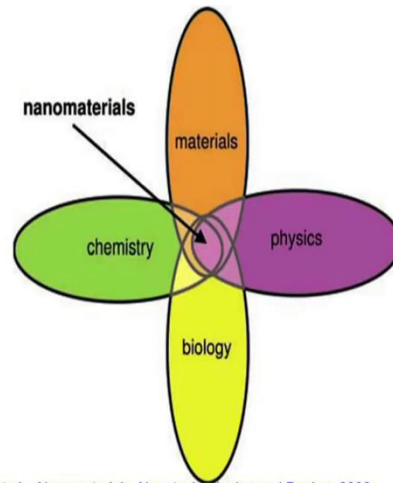
M.F. Ashby et al. , *Nanomaterials, Nanotechnologies and Design*, 2009

Another important challenge is this that, you know nanomaterial has become interdisciplinary, it is no longer a subject of metallurgy, material science; it is a subject comprising of many things, subjects from biology, mechanical engineering, chemical engineering, physics, chemistry, and material science and many others.

So, therefore, when you are working at the interface of these kind of interdisciplinary fields, it is very difficult to do something alone; you need to develop team to do that ok right, that is another important aspect which you should know, there are many such challenges.

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• Interdisciplinary Investigation



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

So, therefore, what I can see is that, mostly nanomaterials comes at the subset of four different fields physics, chemistry, biology, and material science. And therefore, one needs to know so much to understand nanomaterials, which is not possible for anybody studying the subject or one of these four, it requires lot of understanding of all the subjects.

Well, I will just go back now how to classify nanomaterials.

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### Classification

- Classification is based on the number of dimensions, which are not confined to the nanoscale range (<100 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  
 $d \leq 100$  nm  
Nanoparticles

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

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

So, well if you know that classification of nanomaterials is very important and this is something, which you will follow in next 15, 20 minutes time, ok. Why do you need to classify? That is the question which you first try to understand first.

You know we classify, why do you classify plants, why do you classify animals? To understand them better well ok, that is why we decide is. As you have seen there are variety of nanomaterials available natural, man-made; you know how do you discuss about themselves, their properties in a very interesting manner, so that everything's comes in one group and that is why the classification comes into picture.

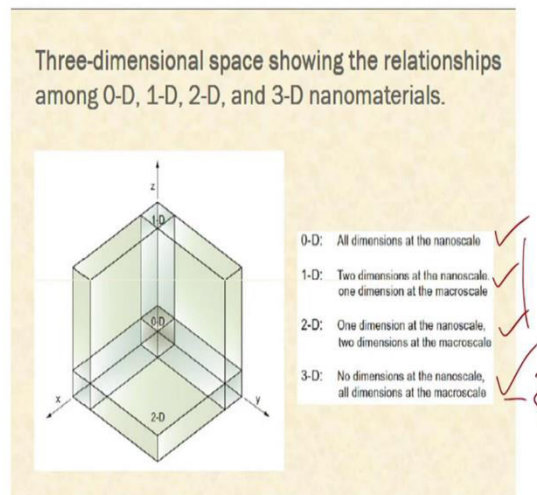
The classification is done in many ways, the most widely used one is what I discussed here; you know classification based on number of dimensions. As you know in real life there are three dimension x, y, z right, x o z, x and y, right. So, as I said for any material whose one of the dimensions x, y, z nanometric domain falls in nanometric domain, we call them nanomaterials.

Based on this idea we can divide nanomaterials into four different categories zero dimension, one dimension, two dimension, three dimensions. Very difficult to understand initially, it was is to happen to me also. You know what is the meaning of these zero dimensions very difficult right.

Well, you know we when you talk about dimensions here, we are talking about in a nanomaterials; how many dimensions are non-nanometric domain that means out of this x, y, z how many of the dimensions are beyond 100 nanometers.

That is the size of dimensions, one of the dimension is more than 100 nanometers that is used as a classification parameter. So, let me give you an example of that, ok. So, let us go back here.

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This is a nice picture, let us suppose whatever zero mean zero dimension; zero dimension means if one of the dimension  $x$   $y$   $z$  of a material falls below 100 nano meter is called zero dimensional nanomaterials.

If one of the dimensions are not falling into nanometric domain; that means one of the dimension is very big more than 100 nanometers its called 1 D. If two of the dimensions are very big more than 100 nanometer is called 2 D and all the three are beyond three dimensional nanometric domain is called 3 D.

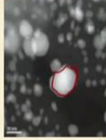
Well, so this is something which you should remember right; in 0 D all the dimensions are nanoscale that is what is given. In 1 D only two-dimensional nanoscale, one of the dimension is micron scalar, meter scale anything is possible. In two dimensional, only one dimension out of three are nanometric domain nanoscale, other two dimensions are the macroscale and 3 D all are microscale.

Now, all these three is to understand they will be nanomaterial. Why this one is nanomaterial? If none of the dimensions are nanometric domain, why the hell we call them as a nanomaterial? So, very surprising is it not, all of you should be surprised, well there are reasons for it. So, we will come back to it little later, first let us first discuss that, ok.

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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

A transmission electron micrograph (TEM) showing several small, dark, spherical nanoparticles of varying sizes. One nanoparticle is highlighted with a red circle, and a scale bar is visible in the bottom left corner.

As you know 0 D or zero dimensional nanomaterials are ones which all dimensions measured within a nanoscale that is why they are called 0 D. The most common representation of material is nanoparticle or what is known as a quantum dot; you can see this nanoparticle it has x y z dimensions, it is not a sphere ok even it is sphere, it will have x y z dimensions, ok.

It can be amorphous or crystalline, obviously nanomaterials definition by definition does not classify whether it has to be only crystalline, it can be amorphous or the crystalline; it can be single crystalline, polycrystalline, it can be one elements or multi elements, it can have different shapes and forms, it can exist individually or incorporate in a matrix, right.



Just like I do discussed about the Mayans blue color paintings; it can be metallic ceramic or polymeric. So, that means there is no restriction placed on these aspects; all the restriction placed this on the dimensions, all the three dimension will be nanometric that is what is discussed.



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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



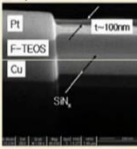
What about one dimensional, one dimension means one of the dimensional out of these three x y z are not in nanometric domain. Well, examples are nanotubes ok, nanotubes you have seen, I have shown you earlier right; it has diameters in nanometric domain length can be any dimensions. And, when the moment you talk about diameters ok, this is a nanotube, this is a diameter, this is a diameter, which is nanometric; but this length can be any size, it can be macro scale.

Again, it can be metallic, ceramic, polymeric; it can be pure, impure, it can be single crystalline, polycrystalline, it can be amorphous, crystalline or it can be standalone or it can be embedded in something all are possible that is something nano rods, nano wires, nano plate; nano plates are non, nano tubes, nano rods, nano wires remember these.

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### Two-dimensional nanomaterials

- Two of the dimensions are not confined to the nanoscale.
- 2-D nanomaterials exhibit plate-like shapes.
- Two-dimensional nanomaterials include **nanofilms, nanolayers, and nanocoatings.**
  - **2-D nanomaterials** can be:
    - Amorphous or crystalline
    - Made up of various chemical compositions
    - Used as a single layer or as multilayer structures
    - Deposited on a substrate
    - Integrated in a surrounding matrix material
    - Metallic, ceramic, or polymeric



2 D, well two of the dimension are not confined to nanoscale, ok. And any kind of plate structure nano, you know plates nanoplates or you know if you have a substrate on which you divide you deposit a thin films ok, that is very difficult to understand. Suppose this is a mouse, this is a substrate and I deposit something on the surface on these.

So, because mouse in the dimension has a dimension of in the macro scale, only a thin film which you deposited if that thickness is nanometric or nanoscale; then we call it a 2 D nanomaterial. So, nano thin films, nano layers, nanocoating all comes under 2 D nanomaterials. It can be also taken amorphous, crystalline, pure, impure, single layer, multi layers; you can develop different layers on the top of each other, this called multi layers.

It can deposited in a substrate, it can be free standing; you can integrate in a surrounding matrix, it can be metallic, ceramic, polymeric or anything possible, correct. So, you understood 0 D, 1 D and 2 D; this you must understand very clearly, do not forget it at all ok, because we are thinking it from the other side of that, right.

Here you are thinking how many of the dimensions are not in nanometric, based on that these dimensions are defined.

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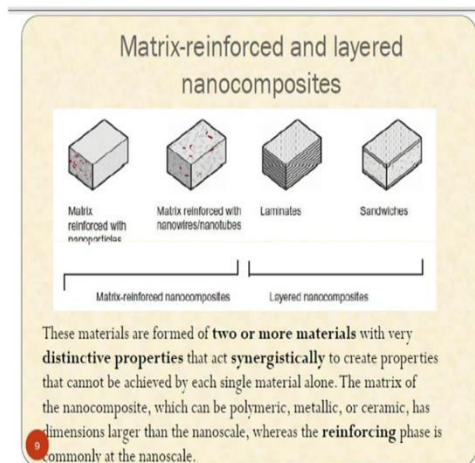
### Three-dimensional nanomaterials

- **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.

3 D bulk material, bulk nanomaterials are material that are not confined to nanoscale in any dimensions. These materials are thus characterized having three arbitrary dimensions more than 100 nanometers, correct.

Well, you must be surprised; why then do call them as a nanomaterials, they can be called micron scale, macroscale material? Well, that is because the last thing you see they can contain dispersions of nanoparticles, bundles of nanowires and nanotubes as well as multi nano layers; we will discuss using examples, let us talk about that ok, ok we will come back to later.

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Suppose you have a matrix, matrix can be anything, it can be metal ceramic polymer; but its dimensions are bigger, they are not a nanometric dimensions. And in which you are imposing nanoparticles, you see these dots here, they are nanoparticles. These nanoparticles are very small, all the dimensions will be nanometric domain; but they are embedded inside a matrix, whose dimensions are not a nanometric domain.

So, when you talk about these, this is a composite; composite between a matrix and a particle. We have it, I discussed you in the very first lecture, these you know precipitates in a matrix of aluminum used in duralumin and many other alloys those are useful materials nowadays. So, you can understand that, these composites are basically called 3 D; because only the precipitates are nanometric domain, matrix is not.

You can also have nanowires, nanotubes embedded inside it right. You can even have laminates, this is very interesting; you can have laminates, whose thickness in nanometric domain put one of the other. And if you put many layers of that laminates, the dimension of these things will be much bigger than 100 nanometers x y z right; because you are putting one on other, maybe you can put thousands of these laminates.

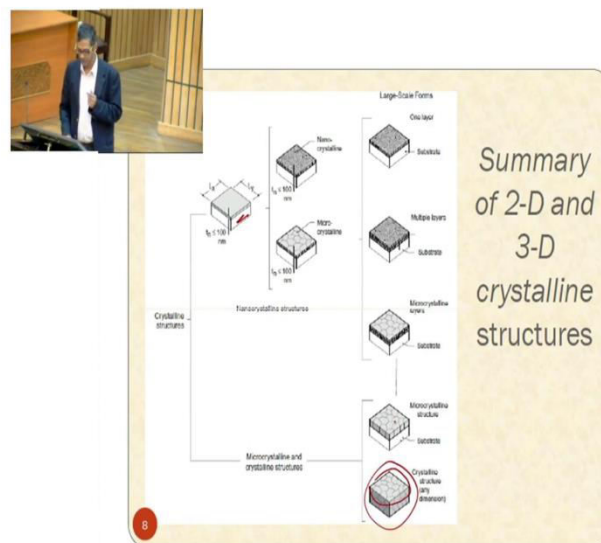
But each of the laminate thickness is nanometric domain; but when you put together, they are not a nanometric domain and that is why they are called 3 D. You can also

have sandwiches, all of you like to love to eat sandwiches you know whenever you go to a restaurants, somewhere even at home also; sandwiches are nothing, but two pieces of bread into inside which you have a something like something else like either veg or non-vegetarian food.

So, same thing can be done here; you can have two pieces of metallic or ceramic material, inside you can put a polymeric material. And this polymer material you have a nanometric thickness or any nanometric dimensions; but the whole thing is in microscale, that is always possible, right. So, you can see that 3 D nano materials are existing in the world and that is why this we have to classify them.

That is why we cannot throw them away, we cannot say no they are not part of nanomaterials.

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So, therefore, let us now discuss a little bit about this summary of these things. Nano crystalline structures can have crystalline, amorphous I told you. So, suppose you have a substrate, this is a substrate right and you deposit thin film; thickness of the thin film is nanometric domain.

But your grain structure may not have nanometric size, you are deposit a thin film those who appear for metallurgy, you know that, there will be grain structure inside

this, if it is not amorphous; it is the crystalline there will be grain structures. Now, thickness of the thin film is nanometric less than 100 nanometer.

But the grains which are develop in the thin film may not have nanometric sizes; they will have big size grains, still you will call it a nanomaterial, right. You can also have a thin film deposited on a substrate with thickness a nanometric domain and the grains are also a nanometric domain, grains are also a nanometric domain.

So, both are nanomaterials, you cannot say no; because in one case you have grains which are much bigger than 100 nanometer, you cannot call them nanomaterials, right. Just because this is you know third diameter, one of the dimensional nanometric domain the thickness, we have to call a nanomaterials, correct.

So, you know that size is what is important one of the sizes; it does not matter whether the size is microscopic or macroscopic, correct. Now, you know there are large scale structures, this is a crystalline structure ok; grains are also bigger, very big, whole structure is also very big, so you cannot call them nanomaterials. You can also have substrate on which this whole thing; suppose you cut a piece of it which dimension is nanometric, cut a piece from the top, thickness is low 100 nanometers and put it on the top of the substrate, you call it nanomaterials.

If you cut a piece of that whose side is micron scale or bigger than 100 nanometers and put it on the top of the substrate, you do not call a nanomaterial, ok. So, therefore, depending on, but then another way you can do it; you put a thin layer 100 nanometer less than 100 nanometers of this thing and then you keep on putting one over the other.

That means you create multi layers that is because your each layer thickness is less than 100 nanometers, which you have to call a 3 D nanomaterials. So, you have to call a 2 D nanomaterial, not 3 D, correct. So, as you see there are different ways of understanding these nanostructures materials, correct.

But I if I go back here. So, finally, there summarizes everything; now I have clarified these aspects. So, if 0 D, 1 D, 2 D, 3 D depending on how many dimensions are not in nanometric domain in 0 D all are, in 1 D one of them, and 2 D two of them, 3 D three

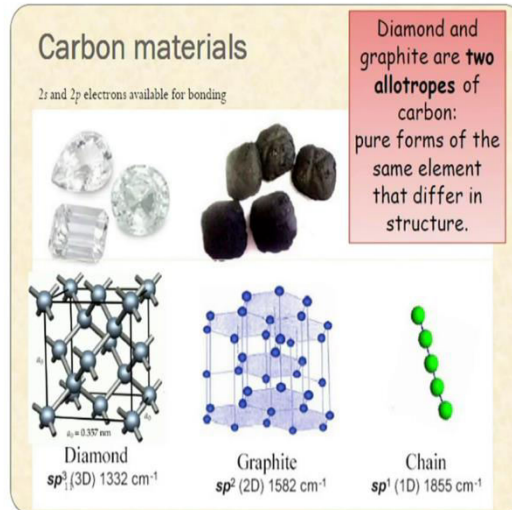
of them are not in nanometric domain that you should remember, but in 3 D materials you can create different ways, ok.

You can have nano crystalline grain as a thin layer on the substrate, you can have micro crystalline grain as a thin layer on the substrate, you can also have much bigger grains or laminate like structures, all of them will lead to 3 D nanomaterials. So, this classification is very important, which you need to really understand.

And I suggest that you read the book, because whatever I am speaking, it may not be completely understandable to you; although I am trying to give you examples to explain, I will come back to it again, but it may not be distinctly clear to all of you.

If you are not understanding very clearly, please get back to the book by Michael Ashby and others and read it; once you read it you will understand, it is not difficult at all. So, in the last couple of you know things which I will discuss is these aspects.

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You know as we have talking about carbon mess non materials, we will discuss more about it in our understanding.

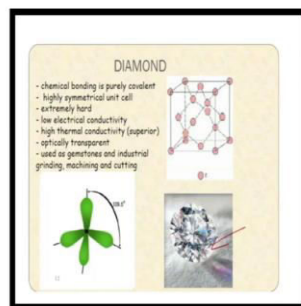
And many a times I will bring examples. So, for me it is better I give an introduction to it. Carbon is the very interesting elements in the periodic table; because it can exist in various forms, it can exist in diamonds, colorful, beautiful, not colorful, beautiful

diamonds, sparkling diamonds right all of you know that, this is something which every woman likes.

You can also have black color graphite or even you know it is present in your pencil, right. You can also have one dimensional also right; we do not know that right yeah, we will discuss about that. So, you know that these are the two important allotropes of carbon; diamond which is  $sp^3$  hybridized ok, this number stands for the wave number in the Raman spectroscopy, graphite is a layer structure  $sp^2$  hybridized, ok.

Now, there are other allotropes, but these are the two naturally available important allotropes.

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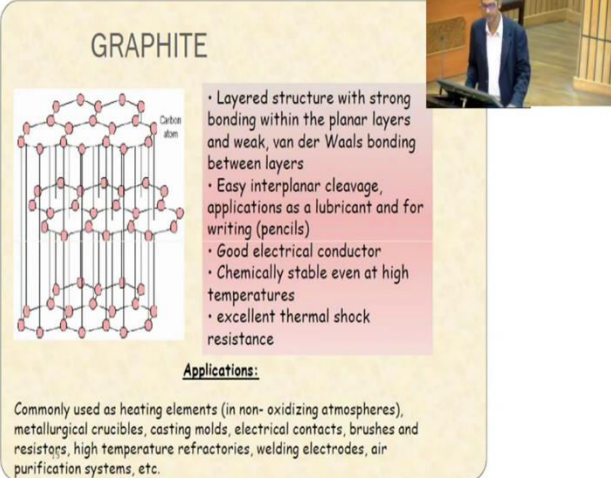


Diamond as you know is a diamond cubic structure, chemically bonded purely covalent bonded, extremely hard, very low electrical conductivity; this is very high thermal conductivity, optically transparent that is why we like it, like to wear it in your as a garment.

Used in gemstones, industrial grinding, black diamonds in use machining and cutting, but everyone likes this one, it gives a sparkling color, ok. Everyone likes to have it in their you know rings and I mean you know as a garment, all of you like to have right, but mostly girls or women actually.



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### GRAPHITE

- Layered structure with strong bonding within the planar layers and weak, van der Waals bonding between layers
- Easy interplanar cleavage, applications as a lubricant and for writing (pencils)
- Good electrical conductor
- Chemically stable even at high temperatures
- excellent thermal shock resistance

**Applications:**

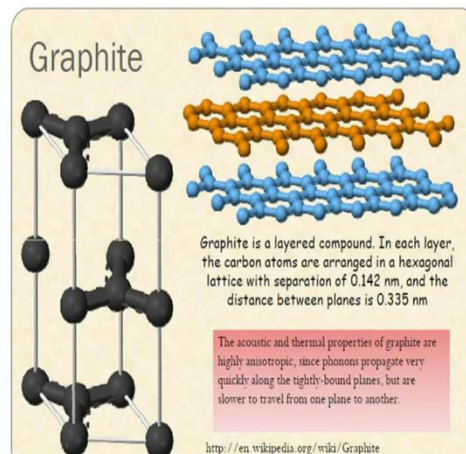
Commonly used as heating elements (in non-oxidizing atmospheres), metallurgical crucibles, casting molds, electrical contacts, brushes and resistors, high temperature refractories, welding electrodes, air purification systems, etc.

Graphite on the other hand it is layer structure, right. What is it? It has hexagonal layers and on top of each other and this hexagon; in the hexagon layer carbon atoms are bonded covalently, between the layers carbon atoms are bound by Van der Waals, right. So, easy to break, easy to cleavage, it is a very good electrical conductivity compared to diamonds, diamonds do not have; why, because diamond do not have any free electrons, all are  $sp^3$  hybridized, all electrons are used up in the bonding.

Graphite because of these Van der Waals bonds, lot of free electrons are there, it is chemically stable, very stable you know till high temperature; you can even use it thousand degrees, excellent thermal shock resistance.

It is used as heating elements, it is used in casting molds, electrical contacts, brushes, resistor many many many many many things; it is one of the most widely used materials. But what is it has to do with nanomaterials, still you are thinking about it right; you know how why sir is discussing about it, why it is important for us to understand.

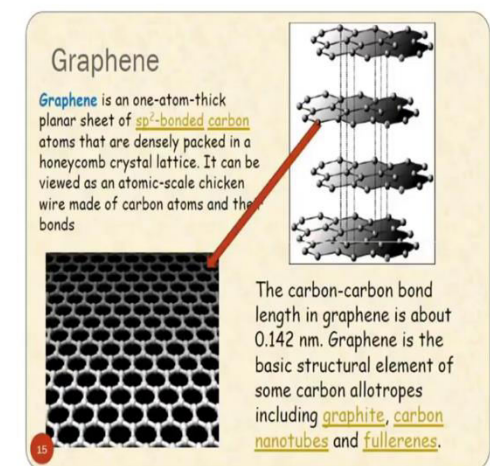
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Well, this is because of this, graphite has these layers. Now, it only takes you know one of the most thinkers in the world ok, to discover a new material and that is what happened in 2004 or sometime like that.

I do not remember exactly, if you cut off each of these layers, what you create is single layer of graphite and that is known as a graphene, right. And you know graphene is big, this you know materials which have been lot of research has been done, it is one of the nanomaterials.

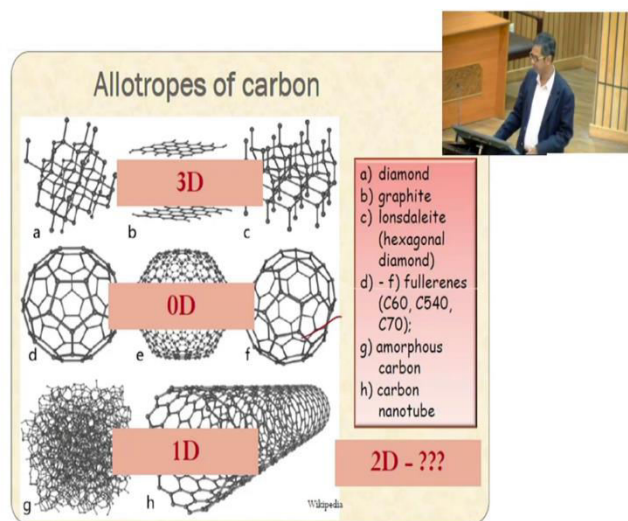
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What do you do? You can cut off one of these right, you can do many ways now; you can use this the real discoveries done using by Novoselov and Geim in UK when they use cross tape to remove each layer.

And if you do that, you create a single layer of carbon. So, you can understand it is a single layer of carbon, no van der Waal bonds; see your properties will get changed drastically.

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Or if I take single layer and then kind of you know wrap it around the layer, you create what is known as nanotube, that is what it is.

You take a single layer of carbon and thus put in a tubular form like join it. So, diamond, graphite, fullerenes all you know fullerenes 60 atom buckle balls; it can be 60, 70 or you can have nano tubes or graphene. See in one element, you can create all different kind of nano structures; like fullerenes is 3 D nanomaterials, sorry 0 D nanomaterials, all its dimensions are nanometric domain, right.

On the other hand graphite or diamonds, they are 3 D ok, none of the dimensions are nanometric; but you can have something embedded inside it, you can have nanotube inside embedded in a graphite or a nanotube embedded in diamond, then it is called 3 D. You can have 0 D fullerenes, they are nanometric to all the dimensional nanometric.

You can have 1 D that is a nanotube. Is, there any 2 D nano materials? 1 D is also you know your 1 D is also your graphene; graphene has one thickness is nanometric domain and other two dimensions are not a nanometric domain. Is it 2 D? I am not sure about it, ok. So, as you understand whatever I discussed today in the last part of the lecture is that, carbon is one of the most important and beautiful elements in the periodic table.

It can give a different kind of structures, mostly nanostructures; easily available or naturally available carbon materials are basically two electrons diamond and graphene graphite. Now, using graphite you can create different kind nanostructures; you can create 3 D as a graphite, you can create 1 D as a, what is called tubes or you can create 0 D as a fullerene, correct.

So, that is about the carbon nanotubes and the dimensions or and the different kinds of dimensions. So, please do read the books to understand it, we will come back to it. With this I complete lecture number 3, we will get back to you for the lecture number 4.

Thank you.