

Nanotechnology Science and Applications
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Lecture - 01
Introduction

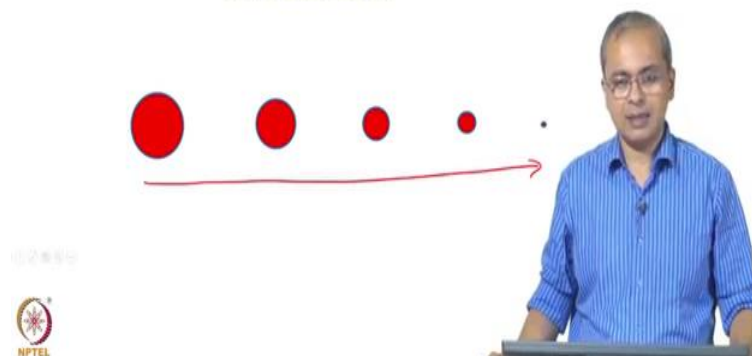
Hello, welcome to this course on Nanotechnology Science and Applications. So, this is the introductory class. This course is should be accessible to anybody with an engineering background or a science background, and I expect to take you from very preliminary ideas of what nanotechnology and its associated sciences, through a series of examples of where it is used.

So, that is how this course will be designed and in this class; its which is an introductory class, I will lay the framework of some of the ideas that are necessary for us to understand nanoscience and technology and if you are just interested in just getting a quick overview of nanoscience and nanotechnology, then probably this introductory class will provide you with that kind of quick overview.

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Nanotechnology: Science and Applications

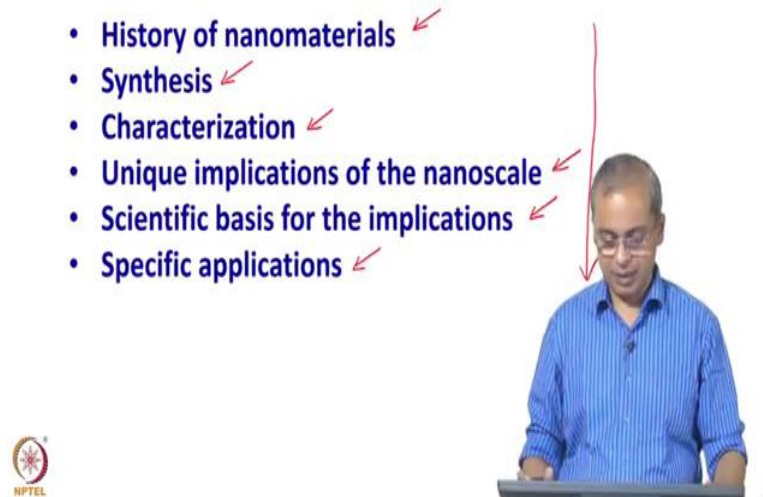
Introduction



So, if you can actually see here I have drawn a cartoon of something going down in size or a sketch of something going down in size and that is at some level that is

fundamentally the idea between nanoscience and nanotechnology, but there is more to it, we will see as we progress through this class and this course.


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The slide contains a list of six topics in blue text, each with a red arrow pointing to it from the right. The topics are:

- History of nanomaterials
- Synthesis
- Characterization
- Unique implications of the nanoscale
- Scientific basis for the implications
- Specific applications

To the right of the list is a video inset showing a man in a blue shirt speaking at a podium. A vertical red line is drawn over the video inset, extending from the top of the list down to the bottom of the video frame.



So, that is start for the class and in this course as such, we and I over and above this introductory class that I am going to have here, we are going to look at the history of nanomaterials because it is a nice to get a sense of how old it is and how long it is being there because it is being in popular discussion much more significantly. Let us say in the last 20 years and today if you see if you take anybody working with materials in any technical institute anywhere in the world, there is very high probability that some of the work that they do is associated with nanotechnology.

So, today it seems like the thing to do I mean, almost everybody seems to be involved in it, but if you go back let us say 40 years ago, you might not have heard of this term that much in the literature and so, it's it all seems to have come together the last 20 years or so. But still, there is it has an interesting history So, we will look at that briefly.

Through the course, once you talk of materials, we have to look at the synthesis process. So, that will always be an aspect associated with all are descriptions in this course, we will look at different materials and also what kind of application that might come for, but particularly in that context we will look at the synthesis process. And there is a wide range of synthesis processes that are possible and we need to understand what is going

on. In today's introductory class, we will talk about some general aspects associated with a synthesis of nanomaterials and certain approaches that are normally used for the synthesis of nanomaterials.

But as we go to progressively later classes, we will look at for a particular material and a particular application, what is that synthesis process that is used. More specifically sometimes a process that has been used for a variety of different materials may get modified for the sake of nanomaterials or there may be some particular variation of it, which may be used for nanomaterials. we will look at that.

Something very similar is also true for characterization; if you are characterization broadly means looking at a material much more closely from different perspectives to understand, it is let us say its structure or its composition and so on its microstructure, crystal structure lot of different details of how that material has been put together and understating that is called its characterization and again if you have been involved with materials at any level maybe you are a material scientist or a mechanical engineer or a biologist or so on. You already been familiar with a range of characterization techniques and you are already even using those characterization techniques probably.

So, once again with respect to nanomaterials, there is sometimes a variation of the techniques that are used or the data that you get from the technique looks different for the nanomaterial than it would do for a conventional material. And therefore, for us it is interesting to understand why is the data looking different and what additional information you can get off the nanomaterial by looking at this data that now looks different. So, that is the idea here about the characterization of nanomaterials.

We will look at the unique implications of the nanoscale. This is actually very critical because at the end of the day that is the reason why people are interested in nanomaterials. Because there are certain unique implications of the nanoscale, which create certain unique features and that is what makes the whole field of nanoscience and nanotechnology interesting and something that key known getting and understanding of key known finding ways to utilize it for our applications and so on; so, that we will see.

In addition to just looking at what is the implication here, we will also like to understand the scientific basis for the implication. So, what is the science behind the implication?

Where is it coming from? What is it at something that is happening at the atomic level, some other level that something is happening now for nanomaterial that leads to its behaviour being unique creating some unique circumstances with respect to that material what is the scientific basis for it? Why is it the same feature appearing for conventional materials? Why is it appearing only for nanoscale materials? So, understanding that is particularly of great utility to us. So, we will look at the scientific basis for that implication.

And of course, we will look at specific applications. At the end of the day, we want to use these materials. It is perfectly fine for us to understand interesting science and there is a great utility in just that knowing the science behind something interesting that is happening in material. But from an engineering perspective, we are also interested in applications the general public is also interested in applications and so on. So, we will look at specific applications.

Now, I must point out that even though I have put this all up in some kind of a linear scale here one after the other. In reality certain topics I might deal with separately. So, for example, the history we may deal with it deal with the historical aspects of them separately, but many of the other aspects the synthesis, the characterization, implications of the nanoscale, the scientific basis for that implication and also specific applications this may come as a package.

So, we will actually look at a particular material see how it is going to be used for something interesting also nanomaterial and in the context of that material we will look at its synthesis, we will look at its characterization what is it that is interesting about that material in the nanoscale, what is the scientific basis for that interesting feature for that particular material, the nanoscale and also its application.

So, we may package it differently as we go class to class, but this is the general idea. So, we will try to put all this information out and then towards the end, we will try to do a summary when we finish this course, a summary of what all we have learnt together in this course and how these things have been related to each other. So, this is what we will do in this course as an overall activity.

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Learning Objectives

- 1) Define nanomaterials ↙
- 2) Explain why nanomaterials are of interest ↙
- 3) Indicate different types of nanomaterials ↙
- 4) Describe the different options available for synthesis of nanomaterials ↙
- 5) Mention challenges associated with work in the area of nanomaterials ↙



More specific to this class which is the introductory class, our learning objectives are as follows; we will first try to define what is a nanomaterial. So, nanomaterials again is a term that gets used quite extensively today in popular literature, if you read newspapers, if you read magazines and so on you will see some mention of this. You may also see it in journals and so on where you are doing much more in-depth analysis of and systematic analysis of some research. So, then you will also come across this term nanomaterials nanotechnology and so on. So, let us try to see if there is some kind of a definition that we can use for nanomaterials; so that we will see.

We will try to explain why nanomaterials are of interest. So, that is another aspect that we shall focus on. We will also look at different types of nanomaterials. Interestingly again based on where we came across this term or in what context we came across this term, we may think of a certain type of material or a certain range of materials as the nanomaterials.

So, it is of interest to spend few moments at least, to see what are the different types of nanomaterials that are out there so, that it gives you some sense of perspective that this is the range. And therefore, if I am reading a paper journal paper on some particular type of nanomaterial within this range this is where I am and also that there are these other things that are not being dealt with this particular paper. So, to give you that sense is

where we will try to get a sense of the different types of nanomaterials that we might encounter.

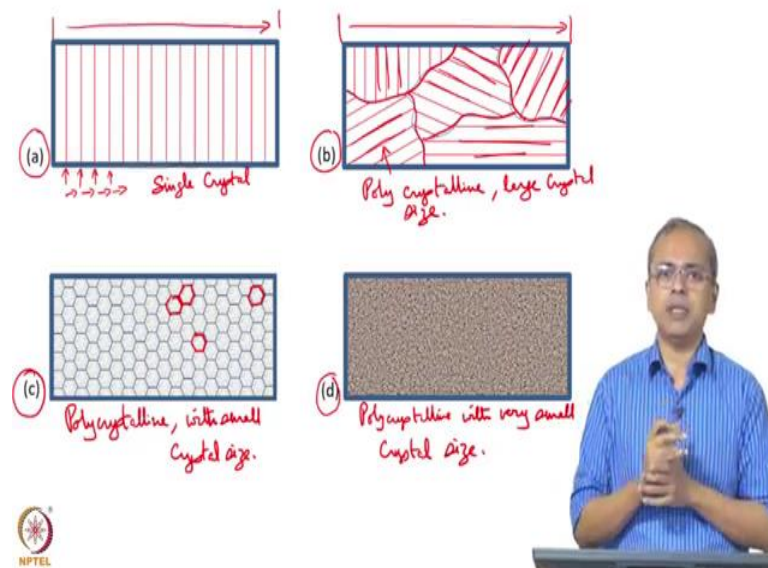
We will also look in a from a broader sense, as I said later in this course, we will look at synthesis from for a every specific material that we are looking at we will consider its synthesis process and implications of the synthesis process and so on. But broadly for nanomaterials, the general types of synthesis processes that are available can get classified into few different varieties. So, this broad classification is something that we will look at in this particular class.

So, in that, we will look at the different options available for synthesis of nanomaterials. So, if you are in a lab, chances are you use any technique you use for synthesizing nanomaterial, we will fall broadly within these classifications that I will show you and each type has certain positives and negatives and challenges associated with it. And therefore, knowing what you are, where you are in the synthesis arena, really helps you focus your effort on certain aspects and it also tells you upfront. these are some limitation. So, you are prepared mentally ahead of time, that when you get done with your synthesis you are going to have some issues of certain nature. So, we can accordingly deal with it.

And finally, we will look, we will mention challenges associated. So, this is important challenges associated with work in the area of nanomaterials; and this is in the important to know because as researches many of us are working with nanomaterials. So, we need to know what are those challenges and how significant those challenges are, how alert we need to be to those challenges and perhaps the fact, now we have to keep thinking the back of our mind we have to keep thinking of ways to mitigate these challenges, that is as a researcher.

In addition, if to the extent that nanotechnology becomes a very successful filed and it is in that, hided in that direction. You will find increasingly you are going to find products that are out there which the public will be handling which will be consisting of nanomaterial. So, what are the challenges there? What are the concerns there? What are the safety issues involved there and so on? So, these are something that we need to pay some attention to. So, in this class, we will also look at the challenges associated with working in the area of nanomaterials.

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So, let us begin with a material in general. So, and in the in that context, let us try to understand what is said that we are referring to as a nanomaterial. So, normally you may go and have let us just say, you have a brick in your hand. So, brick physically has some shape it has a length, it has a width and it has a height. So, length width and height it has. So, it is a solid objective you can hold in your hand.

So, now you have a range of possibilities; even though you have a solid objective in your hand, I can give you essentially, I mean something that is shaped like a brick. I can give you three or four different samples which outwardly look the same, but internally or dramatically different. So, I have just shown you on this slide various options that you could have. So, the first option that is out here is a situation where these are let us say these are crystallographic planes. Let us say these are crystallographic planes which means on these planes the atoms are in perfect order. So, whatever is the interatomic spacing, they hold that interatomic spacing in that plane and in this direction, they have the known interatomic spacing aligned in this direction.

So, you have the series of planes in perfect each plane is also having atoms in perfect order and then those planes are arranged in perfect order. Importantly in this sample which is marked a, you have the planes in perfect order from this end to this end. This entire stretch of this sample you have planes in perfect order this is refer to as a single crystal.

So, this is a single crystal and both in the laboratory as well as commercially, you can buy single crystals, single crystals which are of significant size something that you can actually hold in your hand comfortably. You can hold that single crystal in your hand, you can look at it through the light I mean with light shining through it or light falling on it and then you can do experiments with it. So, you can get single crystals in a microscopic scale.

So, please remember; you are having a sample in your hand which you can hold in your hand, anatomically from one end of the sample to the other end of the sample atoms are in perfect order in throughout the entire length of the sample entire height of the sample entire width of the sample it is in perfect order. So, that is a single crystal.

We next come to another sample here which is mark b. You can see here these are all like grain boundaries here, which means within this grain within each grain the atomic planes are in perfect order. So, within the grain, you can see all these planes are in perfect order.

So, it is like you have taken the sample and sort of broken it into like, in this case, let us say 4 pieces and done some little rearrangement and then assembled it back. Of course, this you let us say you take four samples of a each of which has a different orientation and then you break it up along similar geometries and then put it back together so, that each is individually a part of the original sample, but within it the orientation of the same planes that you see in a are now oriented this way. Here the same planes are oriented vertically here the planes are oriented this inclination, here they are almost horizontal and so on.

So clearly, you can see if you go from this end to this end perfect order is not maintained. So, you see changes in order distinct changes in order not cartel changes in order distinct changes in order which we go from this end to the other end. So, this is a sample that is polycrystalline with larger crystal size. So, it is polycrystalline with large crystal size and so, that is another option that you have.

Sample c here is an example where it is also polycrystalline, but with small crystal size. So, you can see here several crystals I have drawn here, I am just highlighting a few. So, we will just assume I mean this is just I know sketch. So, it does not have to be exactly

like this, I mean this is just representation of what you can expect in the material, I am just saying that in this case it so, happens what I am showing you are all uniformly sized grains. These are each individually called a grain each of them and all of them come together to form this sample c.

Please note between a b and c, these overall sizes of the sample is the same. So, the physically what you hold in your hand; if this were a sample that you could hold in your hand physically, these three samples are all of the same sizes. They are also of the same composition. You are using the same atoms to make these samples they are also having the same crystal structure. So, whatever is the atomic arrangement within this sample that atomic geometry between the atoms is maintained the crystal structure is maintained; there is no difference between these three only differences is the crystal size.

So, the first one consists of a one large single crystal, the second one consists of 4 or 5 in this case 5 large crystals put together which forms the same external dimension. The third one which is c has several small crystals which all come together and form this sample.

We can consider another option d where you which is also polycrystalline, but the crystal size is extremely small and we are almost not able to make it out, but let us say we are using an optical microscope, we are not able to make it out using an optical microscope. So, let us say this is polycrystalline with very small crystal size. So, if you have polycrystalline with very small crystal size, then you sort of see what sampled might look like; you can imagine that you are hidden in that direction.

So, it is in this manner with keeping the overall sample dimensions the same, you can move from a large crystal size to smaller and smaller and smaller crystal sizes and at some point, we say that this is a nanocrystalline sample it means the crystals here are in a nanocrystalline size range. So, we will see what that size range is, it is basically an indication of the fact that the size range of the crystals has become extremely small it is gone into the nanoscale. So, that is the idea and that is how when you do that you are approaching a nanocrystalline material. There is certain more detail aspects to it, but broadly this is the direction in which we are heading.

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Nanomaterial : Particle having one or more dimensions less than 100 nm

The 'Nano' effect

Many properties that you encounter in materials, show size dependence



So, a nanomaterial is one where the particles that are present in the material have one or more dimensions less than 100 nanometers. This is like a broad definition. So, a broad definition if you are want to have it has one or more dimensions. So, you can think of materials as always have 3 dimensions, but if it does not mean that all three dimensions have to be less than 100 nanometers if one or more dimensions happen to be less than 100 nanometers chances are you are working with something that you can call as a nanomaterial.

So, that is the sort of this starting point at which we start thinking of in term of nanomaterial, there is still some more detail here that you need to think off and that is the idea of the nano effect. I call it the nano effect just for so, that we can focus on this idea, and the and that convey something. The reason I point that out is that it is not sufficient if one or more dimensions less than 100 nanometers. So, like I said that is just starting point for the definitions, it says that if you are in that range chances are you are working with something that is a nanomaterial.

But for us to actually call it a nanomaterial, in any meaningful sense you can still you can incise that it is less than 100 nanometers, I will call it a nanomaterial. You can do that, but if you want to meaningfully call it a nanomaterial, you should see you should be dealing with a situation where not only is the size less than about 100 nanometers, but

you are also seeing some change in property, some change in one or more properties that is related to the fact that it is now less than 100 nanometers that it is in that size range.

And more specifically many properties already have a size dependence. So, many properties that you see; so, many properties already show you some dependents on sizes, but the thing is when you are coming from this microscopic single-crystal to smaller and smaller and smaller crystals, there will be a trend there will be a certain trend in the way the property changes. So, or it may be a weak trend, it may be reasonable trend etcetera as the particle size changes, you will see certain change in the property.

What is interesting about this effect that I am calling the nano effect is that at certain size range the impact of size on the property is dramatically significant is dramatically exaggerated. Suddenly you see very significant change in the value of the property because you have now come into a certain size range and only when you only when that happens you are actually seeing the nano effect. If you are not seeing that there is no great interest in having small crystal size. The interest comes only because when you get to the small crystal size suddenly the properties dramatically different.

So, whereas, initially that material could only be used for a certain range of applications because its property was in a certain range of values, because you have now come to the nanoscale suddenly its property has new set of values then the same material can now be used for newer applications, that is the interesting thing.

That since you came to the nanoscale the same material is now showing you completely different properties and because of that you can take the same material and put it for completely new applications. This combination where a size change leads to a dramatic change in properties and therefore, I enable you to use it for new applications. This concept which seems to happen in the nanoscale, which seems to happen in these 100 nanometers for less scaled is the whole idea between which is the whole idea behind this topic of nanomaterials nanoscience and nanotechnology. So, that is the nano effect.

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What is a Nanomaterial?

How tall are you? $\rightarrow 1.5 \text{ m} \rightarrow 1.5 \text{ Billion nm tall !!}$



Human hair $\sim 50 \mu\text{m} \rightarrow 50 \times 10^{-6} \text{ m}$

Pores in skin $\sim 50 \mu\text{m} \rightarrow 50 \times 10^{-6} \text{ m}$

Wavelength of visible light $\sim 10^{-7} \text{ m} \rightarrow \text{Less than dimension of hair}$

One nanometer is $(10^{-9} \text{ m}) \rightarrow 2^8 = 2 \times 10^{10} \Rightarrow 1 \text{ nm} \approx 5 \text{ atoms}$

Nanomaterials typically 1 nm to 100 nm in dimension
5 atoms to 500 atoms



So, what is a nanomaterial? Let us see something more about what is a nanomaterial. So, let us start with something we can relate to. So, let us ask ourselves how tall are we. So, what is a typical height? So, let us say I mean most of us are more than 1.5 meters tall. So, let me just put our value 1.5 meters, we will always like any population you will have some distribution of people who are taller and some people who are shorter and so, on and of course, based on your age group it might change. So, let me just put some number down 1.5 meters. So, 1.5 meters is how tall we are so, that something we can associate with.

So, it starts from there and then we will associate with other things. On our body, we have hair and that hair is if you look at the dimensions of that hair that is about 50 microns. So, this is 50×10^{-6} . So, 50×10^{-6} is how thin are human hair is. Along similar lines, the pores in our skin is also of the same nature. So, we have about again something like 50×10^{-6} meters and that is why with those dimensions being somewhat similar the hair is able to stay in our skin. So, that is the pore of our skin. So, this is again 10^{-6} meters.

If you look at the wavelength of visible light, this is 10^{-7} meters so less than dimension of hair. So, the wavelength of light is less than the dimension of hair. So, hair is 50×10^{-6} . So, that is actually 5×10^{-5} this is 10^{-7} meters. So, almost two orders of magnitude less than the dimension of our hair.

So, that is light that is what we are able to see. So, if you are able to see your hair. So, whatever hair you see on your hand if you look at that dimension if you go 100th the dimension that 100th width of the hair then you are in the dimension of the light the wavelength of visible light. So, you can see somewhere there our eye is limited. So, we are able to see individual hair strands of hair, but you cannot see individual waves of light. So, that is the wavelength of light is like that and that is how it is.

A nanometer is 10^{-9} meters and hence the word nano 10^{-9} meters. Incidentally, if you look at the interatomic spacing in most materials if you look at interatomic spacing, that is of the order of 2 angstroms. Interatomic spacing; that means, which is equal 2×10^{-10} meters therefore if you look at 1 nanometer that is roughly. So, this implies 1 nanometer has approximately 5 atoms. So, 1 nanometer has 5 atoms. So, that is the thing. So, that is how we can relate the size scale. So, 5 atoms if you take and you are into the nanometer range. So, that is how we are.

So, we are coming down on this scale. So, if you see here nanomaterials, as we said, are typically between anywhere between 1 nanometer and 100 nanometers in dimension. So, 1 nanometer to 100-time nanometer in any one dimension may be more than one dimension. So, you are looking at anywhere from 5 atoms to 500 atoms. So, typically if you say nanoparticle chances are it has somewhere between 5 atoms and 500 atoms that is. So, there is a little bit of fuzziness in this definition, we are mostly used too much sharper definitions in science, but there is a little fuzziness in this. As we progress along the course, you will understand the need for this fuzziness, even later in this class I will bring that out as to why we have this fuzziness in this definition, we do not have a hard cutoff saying that exactly a 252 nanometers is what we are going to use does not work that way we have a range. So, we will think about it.

So, having put is down together let us revisit this question. Today everything is a nanomaterial world; we talk of nanomaterials a lot. So, it would not be surprising if you ask somebody how tall they are and they say they are 1.5 billion nanometers tall. So, you can see how suddenly if you want to be in the nanoworld this is how you will have to talk. So, that is just for giving you a sense of perspective, but this is sort of some of the data that is of interest.

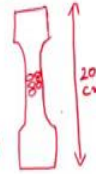
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Why Nanomaterials?

Various macroscopically measured properties are based on phenomena that occur at an altogether different size range.

Manipulating materials at or near this characteristic size range often results in new control on material properties

Interesting nanostructures with unique properties



Why do we care about nanomaterials? So, why should we be interested in nanomaterials? Well, what happens is basically this? This is this what we are going to discuss at this movement is really this nano effect and what is this nano effect let us get a better sense of it. The idea here is this, various macroscopically measured properties.

So, various macroscopically measured properties what are these properties? Let us say electrical conductivity, let us say magnetic properties some let us say mechanical strength. So, these are all properties that we measure so, many materials that tell us where we can use that material. So, if you want to use something for bridge, you expect certain level of properties, you look for a material that has those properties, you use it. If you want to use something for the landing gear of a plane again there is some expectation of some properties, you look for that material which has those properties you will put it to use.

So, there are properties and we measure those properties; what is important is that various macroscopically measured properties are based on phenomena that occur at an altogether different size range. So, you are measuring; you are having a sample in your hand let us say you are doing a mechanical strength measurement, tensile test you are doing then you will take a dog bone sized sample. So, some sample that looks like that dog bone sized dog bone-shaped sample, which you will take and this is what you will use for your mechanical test.

So, this sample could be I do not know let us say this is 20 centimeters. This could be 20 centimeters tall sample and using this sample you get stress-strain curve from which you pick out lot of properties of the material mechanical properties. But what is important is that the mechanical property is coming from phenomena that are occurring at much smaller scale. So, if the some small inside the grain in terms of how the planes of atoms are moving, how they slip with respect to each other that is where that phenomenon is occurring.

So, it is occurring in the planes of atoms range that is where it is happening. It is not happening at the sample size is simply consolidating all that information and showing it you in a manner in which you can record, but it is coming from a phenomenon and that is occurring well inside the sample at a much more microscopic scale.

So, it is so that is the first thing we should understand. The first thing we should understand is many properties that we measure it could be mechanical property, it could be optical property, it could be magnetic property etcetera. In many cases, we are measuring that property for using a sample that is reasonably large which we are able to hold in our hand, which we are able to mount on a measuring instrument.

But the phenomenon that is occurring inside that is a sample which is resulting in that property is actually occurring at a much smaller size scale. So, it is occurring at a much smaller size scale due to something maybe that an electronic level, something at an atomic level, something at the level of planes of atoms etcetera each phenomenon each property is based on some phenomenon occurring at someone of these levels. So, that is the first point that we need to keep in mind.

Now, if you manipulate the material at or near this size range if you manipulate the material at or near this size range from which that phenomenon is happening. So, if the phenomenon is happening it an electronic level, you should get down to size ranges closer to the electronic level. If it is happening at the atomic level, you should get down to sizes which are close to the atomic level. Tens of atoms cause that phenomenon, then you should get down to that size range of tens of atoms.

If you do that then you end up having a totally new control on the material property. So, what do we mean by this? Let us say mechanical property has some range. So, some

tensile strength has some certain range of values. Now since that it is happening at the range it is happening due to a phenomenon that involves planes of atoms, if you start creating a sample where the crystal size is getting close to the range of a few let us say few planes of atoms, then suddenly you get new control on the mechanical property and the mechanical property looks dramatically different.

So, therefore, if it just happens that way that many of those properties, we start rearranging the material at the size scale from which that property is coming, then you are sort of rearranging that phenomenon itself. You are rearranging that phenomenon and that leads to dramatically different property coming from the material which has exactly the same chemical composition and many times the same crystal structure.

And therefore, manipulating materials at or this at or near this characteristic size range often results in new control on the material properties which is why the nanomaterial becomes interesting because now with the exact same material in olden days this control was not there. In olden days, if you came up with a new application let us say, you could use the material up to 800° C and at which point some phenomenon is not working as well. So, typically you could not use it higher than that in temperature even though let us say it's melting point was only 1500° C.

Now, by manipulating so, in the in olden days what would happen is, let us say you came up with a new application where the application had to operate at 1100° C. So, an 1100 ° C this material that you currently have we will not function. So, it because its property is not that good and 1100° C; it was good at 800° C. So, what is the approach people did in the olden days? So, they would abandon this material they would search for a new material new composition for which they will try to understand if they can make it operate at 1100° C with all the properties that are required for 1100° C.

They will do a search around through the periodic table search for various combinations of elements and so, on use some scientific process and then arrive at this new material. What is the problem? The problem is that you now I have to have new synthesis process for this new material, you have to have new appliances new industrial set up for it, you will have new environmental concerns for it the costing may be high because you are looking at some more exotic material. So, many problems associated with repeatedly try to come up with some totally new material to address a new requirement.

If you deal with nanomaterials because you are able to change the property or control the material property and change it dramatically by simply going to the nanoscale, you can actually use the possibility opens up that even at 1100° C, you can use the same material that was previously usable only up to 800° C. The huge advantages that all your industrial processes are significantly unaffected your whole procurement processes are unaffected. So, many things are unaffected even compatibility issues are not there, often when you put dissimilar materials together there are compatibility issues in terms of a coefficient of thermal expansion reactions between those materials and so on.

All those things can be avoided because you now have the same material giving you a new property and that is why this is of interest, we are also able to come up with new interesting nanostructures, and just because the structure itself is different we get a unique set of properties. So, all these things come together with the fact that you can get new properties you can get new structures and with the new structures we get even more new properties. So, this whole combination is why nanomaterial sort of interest and that is why so, much of research is now moved into the direction of nanomaterials

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Types of Nanomaterials

Natural nanomaterials: Existing in nature,
Example: smoke, volcanic dust, bacteria

Incidental nanomaterials: Unintended by product of human activity: Diesel exhaust, coal combustion, welding fumes

Engineered nanomaterials: Intentionally created; Nanotubes, fullerenes



So, what are the different types of nanomaterials that we are likely to encounter? Interestingly again as I said due to popular reading, due to what we read in journals and magazines and so on. We may think of certain things when we somebody says

nanomaterial, but there is more to it and that is why we would like to discuss this in a more systematic manner.

First of all, you may or may not be aware there are nanomaterials that be that are basically natural nanomaterials. That means, in nature, we already have these nanomaterials what are such materials? For example, we have smoke, you could have volcanic dust, you could have bacteria. So, these are all things that are already materials which are in the nanoscale and have many aspects associated with them that we could call we could reasonably say that it is a nanomaterial and, but these are of natural processes.

We could also have incidental nanomaterials. So, what is incidental nanomaterials? In fact, for the longest time in technical activity, much of the nanomaterial that was there was incidental nanomaterial. People did not even know that they had synthesized nanomaterials it just so, happened that in the normal synthesis process nanomaterials had been synthesized. They were unaware that they had the synthesized nanomaterials and so, this is unintended by result of human activity unintended result of human activity. And for example, things like exhaust from diesel coal combustion, welding fumes these all contain fine particles which are in the nanoscale and as a result, we have created nanomaterials without formally aiming to create them without formally synthesizing them.

Later when once people realize that this was happening and then realize that there was something interesting, they manipulated their synthesis process may be using ideas from these are unintended methods of creating nanomaterials to formally intentionally create the nanomaterial. So, that is a thing that they have done and that brings us to the third type of nanomaterial that you could deal with which is the engineered nanomaterial.

This is exactly what I mean by saying now we are deliberately creating the nanomaterial; we are not accidentally or incidentally creating it; we are deliberately creating it we are deliberately setting our synthesis technique parameters such that the nanomaterial is produced in significant quantities.

So, this is intentionally created and their many examples these are just two that possibly immediately stick in our mind one is the nanotube. So, carbon nanotubes is one example

and of course, fullerenes which are also sort of related to this carbon nanostructure. So, these are two that you might have heard of a lot in the popular literature. So, there are various variations of this and so, on, but these are engineered. So, people have deliberately aim for these materials and created these materials.

So, you can have natural nanomaterials, you can have incidental nanomaterials which we are not really aim for, but accidentally present and you could also have engineered nanomaterials where you deliberately having understood what was going on, you deliberately go and see the nanomaterial that you wish to synthesized in larger quantities.

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Age of Nanomaterials?

Bulk
Particles
Nano particles
Clusters
Atoms

↓

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In many ways, I think today is the age of nanomaterials in olden days we had like the bronze age, the iron age so on. If you really look at where the technology is gone, where human interest is, where the scientific interest is, where technological companies are pushing towards; it is all in the area of nanomaterials.

So, you could sort of say that today we are dealing with an age of nanomaterials, it is very likely that some of the products you use today already contain nanomaterials in them it is highly likely that as you go forward more and products that you use will contain nanomaterials in them.

Again, as we discussed earlier in the class, this does not mean that the composition of the material. This does not necessarily mean that the composition of the material has

changed maybe it is the same composition as the material you were using 5 years ago, except that the and neither might the size might also might not have changed. You may still have let us say it may even be a knife you use for cooking purposes; it is the knife still looks the same it may still be made of the same material. But internally if you look at the knife in the microscope, you will find that the older knife which was say 10, 20 years ago had a different structure, the knife that you currently use may have a different structure and enabling it to last much longer, enabling it to do much better cutting off whatever it is that you are trying to cut.

So, this is sort of the age of nanomaterials, it is almost impossible these days for you to see you can go to the website of almost any university and look at people who were working in material science and engineering. It is almost impossible for you to come across a researcher, who is doing nothing in the area of nanomaterials. Almost everybody is doing something in the area of nanomaterials or nanotechnology. That is the extent to which it is now prevalent all around the world and therefore; it is not a major exaggeration to say that we are sort of in the age of nanomaterials.

So, if you see here again similar to some of the discussion, we just had we have bulk materials starting on to the large scale, we have particles which again you just break something into smaller pieces your particles that you can hold. If you go into even smaller scale as I said if you go into the nano several nanometer size range, then if the particles are in that size range then you will be dealing with nanoparticles. If you go into even smaller somewhere in this area we have something called a cluster, which we are not spending much time on it is a certain unique combination which we and I will briefly touch upon in this class, but we will not spend too much time on it and then of course, if you go all the way down you have atoms.

So, you can sort of see how we are going down in the size scale, and dealing with different constituents of materials I mean same material, but smaller chunks of the material which take you to lower and lower size scales and therefore, you are moving closer and closer to the atom and so, that is the general tendency.

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Clusters :

Collection of atoms that are between individual atoms or molecules and bulk materials; 3 to 3×10^7 atoms

Magic number of atoms enables closed shell formation and stable geometries

Au 55



So, as I said we will not spend much time on clusters in this class, but it is just interesting to know what it is because it again talks of something small, but generally nanomaterials is a little broader is much broader than just the cluster. Cluster it turns out that in certain systems collections of atoms that are somewhere between individual atoms or molecules and bulk materials.

So, somewhere in the middle and therefore, you are talking of anywhere from 3 to 30 million atoms you are looking at some collection. You find that in some materials certain collections of atoms are preferred by that material, because it gives it some energy minimization something that is convenient for it to stay that way and therefore, you can actually get some unique properties from it.

So, in fact, they one give this word magic number. So, for example, with respect to gold one of the combinations is 55 atoms with 55 atoms it seems to form a structure, where it holds together the surface area is sort of minimized if you add an atom the surface to volume ratio goes up, if you remove an atoms also surface to volume ratio goes ups. So, you are putting generating more surface. So, somewhere at 55, it seems to have a sort of a local minimum. So, to speak of its energy and therefore, it prefers that 55 combinations. And therefore, that is a sort of as it is because it seems to be a sort of a random number that you have pulled out of somewhere, it is not really random, but since

it seems to be a somewhat arbitrary number. So, to speak, they give it they have given it the name a magic number and it is, therefore, some of these atoms.

It enables them to create some kind of a stable formation based on some geometry that is stable. So, this is a cluster, it has certain unique properties and therefore, gets used for certain applications. I said nanomaterials is much wider than this. So, we will not in our course we will not spend much time on clusters, this is much more very specific combination and needs to be really looked at differently. It comes about in a somewhat different way and possibly not as prevalent as the nanomaterial general scope of nanomaterials.

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Synthesis

Top -> Down

- Suitable for bulk industrial production
- Crystal imperfections ←
- Surface imperfections ←
- Mechanical Grinding ← Ball Mill

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So, if you look at synthesis. So, in the next 2 or 3 slides, you will look at synthesis again from a broader perspective. We are not going down to any specific synthesis technique, but in general, for nanomaterials there is a broad possibility with respect to synthesis.

The first is this idea of a top-down approach. I just showed you in our earlier slide we had a large crystal sample having a large crystal size and then, you get progressively break it down and then you can put those broken down pieces into the same overall shape and therefore, your overall sample shape does not look different, but it is consisting of many broken smaller crystals, which are held together very closely and actually they form boundaries which hold then stable together.

So, this idea of starting with something large and breaking it down to create particles which are in the nanoscale, which can again be put together to sort of show you this large overall shape this is called the top-down approach for making nanomaterials.

The good thing about it is that it is extremely conveniently suited for bulk industrial production. So, if you go to any industry, they already have machines which are doing something similar already, they are already cutting something down, they are breaking it, they are breaking into pieces, then welding it together. So, all industrial processes are already set up for larger-scale materials which they can handle easily.

So, if you want to make nanomaterials and you want to make it such that the industry readily accepts it, readily incorporates it into their processes it helps to have a top-down approach to create that nanomaterial. So, that the industry existing machinery in that industry or some relatively minor modification of that existing machinery, will enable them to take this technology that you are trying to give them and put it for production. So, therefore, a top-down approach which breaks a large-scale large crystal size material into a nanomaterial and progressively were set down to a nanomaterial is suited for from that perspective.

Problems are the following we invariably have crystal imperfections because you are hammering it down breaking it down let us say you may start with the hammer and break it down then you may put it in some other machine which keeps grinding it and breaking it further and further and further. So, you will introduce imperfections which may not necessarily be convenient or useful from the perspective of the property that it is trying to demonstrate or the property that you think we will get high light it when you go into the nanoscale.

So, imperfections will add an additional variable into the system which may be good may not be good. So, you have to deal with it. So, therefore, crystal imperfections are something that you have to worry about and a top-down approach tends to do that.

Surface imperfections also come because of again this same process. So, if you wanted a certain shape to that particle it may not have that shape it may have some different shape because of the surface imperfection. You may also end up introducing impurities because you are breaking something down you are using a hammer. So, some hammer or a ball

mill or something you are using to break it down. So, some atoms from that material may also end up in this material which you are working with and therefore, you may introduce impurities and that is not necessarily something that you are interested in it.

An example of this process mechanical grinding which is simply using, for example, using a ball mill where you have a series of hard balls which are like tungsten balls inside the cylinder and the and the cylinder rotates, we will see this technique in greater detail later. But those balls keep on beating the material that you have that you want broken down which is also loaded into that cylinder. So, mechanical grinding is a way in which you can go about it.

So, this is the top-down approach. So, this is the way it is a certain aspect associated with it.

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Bottom -> Up → Starting at or near the atomic size scale

- Nature uses this technique
- Useful for nanostructures
- More homogeneous Chemical Composition
- Chemical Precipitation

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Also related to the synthesis is the exact opposite approach which is the bottom-up approach. So, this essentially means from the way the word is defined; this is sort of starting from the atomic scale at or near the atomic scale atomic size scale. So, you start with one or two atoms and then from there you build up the nanoparticle. So, that is how you build it up the nice thing is nature uses this technique. So, if you look at nature generally, of course, nature also you have where entire. So, if you take pebbles they are being over and on by nature.

But generally, anything else in nature, if you see a plant growing you see even life coming together human life or animal life everything it starts small and then grow speak. So, that is a general growth process. So, nature typically does that, everything it starts with some very tiny template and then builds more and more of that template and slowly, you see this mega-structure that is come about.

So, nature uses this technique. So, you can mimic certain processes from nature if you are trying to do this bottom-up approach it is very useful for nano creating a nanostructure. So, creating like carbon nanomaterials or some interesting nanostructure, it helps to sort of start from separate atoms and put it together under some control conditions so, that structure builds.

So, therefore, whereas, if you start from big and break it down very small number of particles by shear statistics may have the structure because you are just randomly breaking everything down you do not have that level of control. Whereas, if you start from the atomic scale and grow it up you have much better control.



Again because you are starting from the atomic scale and you are controlling the atoms that are present there, usually it is much more homogenous with respect to chemical composition and usually you also have much better purity you are not going to have extraneous things being push into the material because you are avoiding extraneous contact. You are controlling the contact that the material has with whatever is around.

So, a good example is chemical precipitation you precipitate out some constituent from solution, you could also have some condensation process some wafer is formed and then it condenses on some substrate and you create it. In all these cases, you are creating sort of a separate atom and then they come together to create the structure that you want this is the bottom-up approach.

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Synthesis goals

- Identical size – mono sized ←
- Identical shape or morphology ←
- Identical composition ←
- Individually dispersed – mono dispersed ←



In both top-down approach as well as bottom-up approach what are the goals that we have from the perspective of nanomaterials? Nanomaterial functioning nanotechnology and so on what are the goals that we have? The first thing is that there is a significant interest in having all the particles to be of identical size. Specifically, because the property that you are seeing from the nanomaterial or nanotechnology perspective nanoscience's perspective is a very size-dependent property.

So, if you had the size of the particles to be all of 10 nanometers, you will see some property. If all the particles were actually of 15 nanometers, you will see a different value for that property that is the whole interesting part of the nanomaterial and nanoscience field.

So, therefore, if you have a sample where you have a mix of 10 nanometers and 15 nanometers, you are neither seeing the 10-nanometer property fully nor seeing the 15-nanometer property fully. Maybe for some applications that is ok, but often the more you are trying to do some extremely interesting application which happens only at a particular value of that property, you want the size range also to be of uniform size so, that you see only that value of property. So, identical size is very important many times. So, this is called mono sizing of the product.

Identical shape or morphology: so, let us say you wanted to be circular, let us say you wanted to be flat pieces, flat flex etcetera you want all of the sample to have that shape only then again that particular value of the property stands out for you to measure for you to utilize. So, identical shape or morphology.

An identical composition as I said impurities are always an issue. So, particularly if you go down to the atomic scale, if you have only if you are sitting with a sample that has only 100 atoms even if you introduce 5 atoms, you have a 5% impurity. So, your purity is down to 95%. Many times, we buy commercially we are buying powder particles from various sources which is 99.99% pure three nines purity, five-nines purity you are getting samples.

Given the situation, if you actually have a sample which is in the nanometer scale, but you are actually having only 95% purity that is not very helpful. So, therefore, composition is very important and the composition should be identical across all property. So, that is something that is very important

Individually dispersed mono dispersed which means the particles are not touching each other because if they touch each other, they may grow. See we should remember that extremely small particles are also extremely reactive particles they will react with air they will react with each other. They will grow because the surface area is large the surface energy is large it helps for particles to agglomerate and become larger particles with less relatively less surface area. So, they will tend to do that therefore, having monodispersed particles where there is some space between them so, that they cannot touch each other and grow is actually very useful.

So, these are all goals that we have mono size, identical morphology, identical composition and mono dispersion. So, any technique whether it is top-down or bottom-up etcetera, we are always accessing to see that these parameters these four parameters are being met or at least get a sense of how well these four parameters have been met. So, this is what you have accomplished, this is what you have not accomplished and so, if you are trying to improve your synthesis technique you will try to accomplish those remaining aspects. So, this is the synthesis course.

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Challenge!

Safety. We rely on our skin to be a protective barrier

Nanoparticles that slip through our skin can enter the blood stream and interact with our immune system



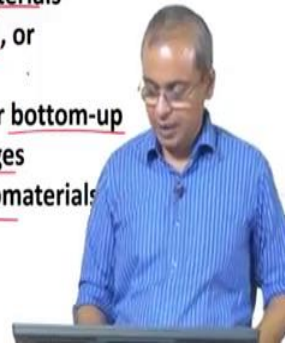
What is the challenge? A major challenge is a safety; particularly we rely on our skin to be a protective barrier we rely on our skin to be a protective barrier. As we saw earlier in the class the pores in the skin are only 50 microns in size there only 50 microns from the perspective of our larger-scale world that we leaving. But with respect to nanomaterials which are 3 orders of magnitude less in size, you can actually put 1000 nanoparticles into the pore of your skin. If an assuming some similar values we can put 1000 nanoparticles into every single pore in your skin.

Therefore, if you are working in a lab that has nanoparticles or you are using a technology that consists of nanoparticles, there is a chance that you can have those particles enter your skin. So, there is a big safety issue. So, nanoparticles are slip through our skin can enter the bloodstream and interact with our immune system. So, you need to be careful about this both as a researcher as well as a utilizer of nanoscience and nanotechnology. So, that is a major challenge.

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Summary

- 1) Nanomaterials have dimensions 1 to 100 nm ←
- 2) Nanomaterials are of interest since they enable properties otherwise not seen in the materials
- 3) Nanomaterials can be natural, incidental, or engineered
- 4) Synthesis techniques can be top-down or bottom-up
- 5) Uniformity as well as safety are challenges associated with work in the area of nanomaterials



So, in summary, we have in this class, we have looked at what are nanomaterials, in particular, we said nanomaterials have dimensions in the 1 to 100 nanometers. So, that is one major definition nanomaterials have dimensions 1 to 100 nanometers, and they are particularly of interest because they enable us to see properties and utilized properties otherwise not seen in the material this is very important. Only because they are showing us properties that are otherwise not seen in the material when they are in the microscopic scale or macroscopic scale that is the primary reason why nanomaterials out of interest.

Nanomaterials can be natural they can be incidental or they can be engineered. So, all options are available; you can select, you can deliberately select some naturally occurring nanomaterial and use it, isolate it and use it you can use some incidental material much to your advantage or you can deliberately engineer it.

The synthesis techniques can be top-down or bottom-up, each has certain limitations associated with it and so, for example, bottom-up as I said is something that is going atom by atom. So, many industries may not be readily set up for it whereas, top-down they may be more readily set up, but in any case, they have some advantages and some disadvantages. So, we have to recognize that and utilize these techniques within the scope of those advantages and disadvantages.

Uniformity of the nanomaterial in terms of size, in terms of dispersion, in terms of morphology composition is a challenge as well as safety this is another major challenge that we need to be aware of and focused on when we work in the area of nanomaterials.

So, that are summary for the class, this is our overall introduction for the area of nanomaterials science and technology and through the rest of the course, we will belt on these.

Thank you.