Physics of Renewable Energy Systems Professor Amreesh Chandra Department of Physics Indian Institute of Technology, Kharagpur Lecture 40 Nanotechnology and Nanomaterials for Energy Applications

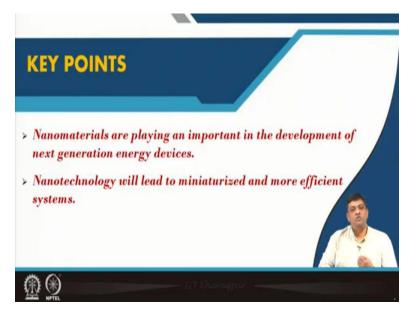
Hello, welcome to the first lecture of this new week; we are into the tenth week of the course. And let us today actually discuss about a topic, which is very relevant to the kind of discussions we have had till now; and this deals with the use of the nanomaterials and nanotechnology in the field of energy. The area of nanomaterials and nanotechnology is a vast area and you will find large number of online courses which are dealing with these two topics. For this course we will focus only on some of these topics, which are relevant to our course; and in the next four lectures we will be focusing on the use of nanomaterials and nanotechnology in the field of energy.

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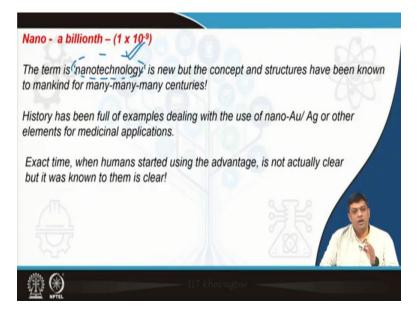
You will be able to see today as to how we define nanomaterials. You will see today that there are various types by which you can classify the materials; but broadly there is one definition that is used to define a nanomaterial. Why should a property change when you go from bulk or micron level to nano scale; that concept will also be covered today. And based on these two concepts, we will be also giving you the various ways in which people classify nanomaterials.

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So, you will realize that nanomaterials are playing an important role in the development of next generation energy devices, the devices which we have already discussed. And the large number of applications, which may have been mentioned; but not discussed in details. As we move towards future, where we are looking for miniaturization of devices; but these miniaturized devices or systems are expected to be more powerful, and with higher performance. And these two will become a reality that is miniaturized systems with higher performance will become a reality, when nanotechnology is brought into the whole concept. And then we use the concepts of nanotechnology to develop next generation, and more efficient systems.

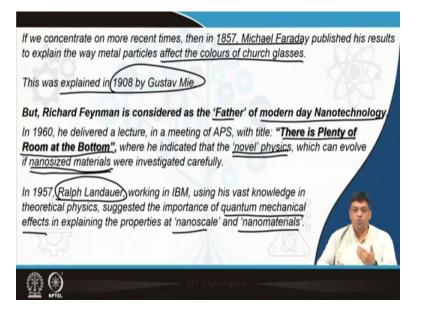
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The word nano means a billionth, so this is 1 into 10 raised to the power of 9 meters, if you say in terms of meter scale. The term nanotechnology is relatively new term; it became more prevalent and more used over the last three decades or so. But, the concepts of nanomaterials and nano devices were known to mankind for many many many centuries. If you look into our books there the use of utensils based on silver, or use of motor pestle made up of gold, have always been mentioned. Because nano size gold particles can be excellent carriers for medicines, nano size particles of silver have various properties like antibacterial; it is good for digestion.

And it therefore becomes very useful if you make utensils made of silver. And if you look around in India, that is one of the reasons that when a newborn baby; when he or she is given the food for the first time; people say give them using spoons made up of silver. Because slowly science was integrated with our daily lives; and that has been going on for centuries and centuries onwards. So, although we have been using the concept, if you look into the published literature, or exact books, or time when humans started using the advantage of nanomaterials and nanotechnology; that exact time may not be possible to pinpoint or give a number to it. But, the concepts were known this is clear to us.

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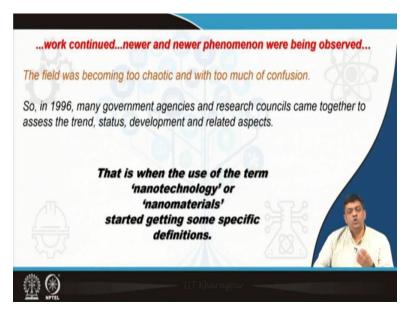
In the previous modules also, we have been focusing on a time period of around 200 years plus minus. So, let us discuss the evolution or the development of this field of nanotechnology or nanomaterials, in this time period itself. If you concentrate in this time that you will, then you will find that in 1857, Michael Faraday published a result; where he attempted to describe the use of metal nano particles, which could lead to the affect of colours in the church glasses. So, he proposed and tried to explain, but this was explained in 1908 by Gustav Mie. But, it is Professor Richard Feynman who is considered as the Father of the modern-day nanotechnology.

In 1959, 1960 he was proposing this idea. And in 1960 he delivered a lecture in the meeting of American physical society, with the title There is Plenty of Room at the Bottom. And here he actually meant that as you go to very small size; then there is lot of physics, or lot of new information which is hidden there. He indicated that the lot of novel physics can emerge, if you carefully analyze and investigate the nano sized particles; so, there is plenty of room at the bottom. This is famous lecture by Professor Feynman, and therefore he is considered as the Father of modern-day nanotechnology.

Around the same time Ralph Landauer, who was working in IBM, and he was an exceptional theoretical physicist. He using the concepts of quantum mechanical effects said that to explain the physics and properties at nano scale that is when you go to low dimensions then quantum mechanics will play a critical role; and one of the most useful application of the concept of

particle in a box problem is actually the field of nanotechnology. Particle in a box means what? Particle is confined and cannot go outside the box. And then how do the energy levels change and how can the particle move from one energy level to the other? Same is the concept of nanotechnology or nanomaterials.

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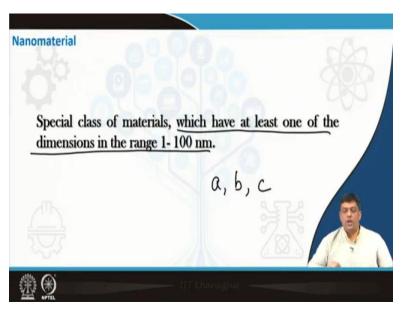


What do we mean that nanotechnology and nanomaterials have to have the coming together of experimentalists and theoretical scientists, who would be working together; and then only the field will progress further. And if you look around from 1950s onwards, lot of work was being done; and as you came around 1980s, you would see there were discoveries of GMR the Giant Magneto Resistance, CMR the Colossal Magneto Resistance. Then there was discovery of various other kind of nano particles that can have very different optical properties, or even semiconductor nano particles were discovered.

Now, what happened? People started calling all type of materials as nanomaterials; so, something like thousand nanometer that is 1 micrometer. 1 micrometer particle was also being called as thousand nanometers; and 10 nanometers was also 10 nanometers. In between you so you found people using the term nanometer more and more; but if you looked at these systems, you saw that there were actually in a different scale. You had micron size, then you had maybe you had two nanometer, only after significant reduction in the size. So, there was lot of confusion and the published literature in this field became too chaotic.

Hence around 1990s, people started asking that there should be consistency in results; and the way we refer to this word nano in the field of technology or materials. So, in 1996 many government agencies and research councils mostly led by the agencies in US, and other countries. They all came together to look into the aspects the trend and how to ensure that the word had some specific meaning. And when you were comparing the materials, then you could do it in a more realistic manner.

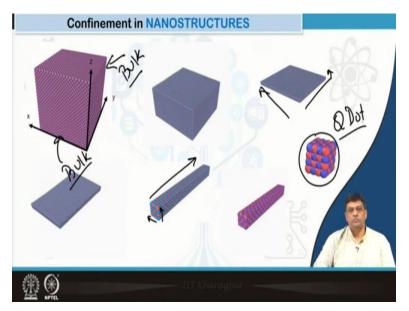
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And that is where the definition of nanomaterial came. It was then decided that nanomaterials would be those, which have at least one of their dimensions in the range of 1 to 100 nanometer. That means if you have a, b and c as the lattice parameters, or if you say the dimensions in terms of particle; then the particles would be such that a would either be in the range of 100 to 1 nanometer range. b would either be in 1 to 100 nanometer range, or c would be in 1 to 100 nanometers range. Both a and b could be in 1 to 100-meter nanometer range; or all three could be in the range written here.

But at least one of the dimensions of the particles would have to be in this range, if you are talking about nanomaterial; and that is where the definition and the concept of nanomaterial which is now well accepted was defined.

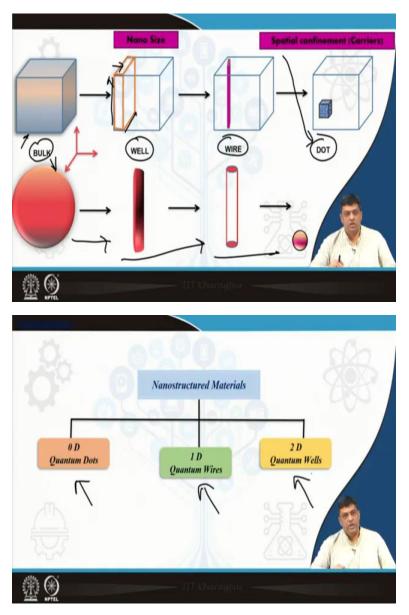
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So, we have seen this if you start from bulk material. If you let us say reduce from the z direction; then you have a particle which looks like a plane; but the c-axis is very very small. So, the height in the c-axis is quite limited. Then if you cut this plane further, from the direction of x which is given here in the slide; then you get a much smaller size particle. And you can clearly see that what you obtain is you have in the z direction, which is quite small; the x-direction is also quite restricted; but, the y-direction remains quite large. Now, if I start cutting the particles such that I am also reducing the diamonds; I will just repeat.

If I now cut the particle from the y side also; then what will happen that I will reduce the size in all the three dimensions. And what you will get is a much smaller particles compared to the starting point. So, you can see from the number of atoms which are now present in comparison to the bulk; and this is quantum dot.

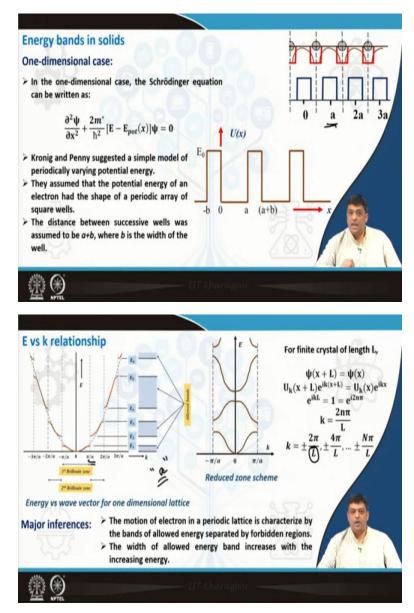
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If you look into the two examples. Let us say we start from bulk either spherical particle or let say cubic type particles. Then, if you have a structure where you have confinement in one direction which has been reduced; then you have particle which can move in freely in two directions; here in these two directions. But the third axis is not possible, then you are calling it as a quantum well typed structure. The second is the quantum wire structure. And if you see the spatial confinement is such that the particle or the free charge or the electron, is forced to remain confined in all the three directions; then it is a dot structure same thing can be seen.

If you take this spherical type bulk particle, so you had quantum well, quantum wire, and quantum dot structures; confinement in one direction, confinement in two direction and confinement in all the three directions. So, you had 0 D or quantum dots, 1 D quantum wires, 2 D quantum wells structures.

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What have we seen earlier? We have seen in module two and three, that energy band gaps in semiconductors are linked with the parameter a. And we have also seen that the energy band gap is directly linked with the parameter a. Now, if I ask you a question at this point that please change the value of a; that is the size of the box which you are considering. The potential box

which you are considering, it can be a particle or it can be a potential rounded atom. So, or you can consider the whole particle as such; so, it is basically the area which you are defining. Now, if you change the length scale of this, then what is happening?

Obviously, the answer would be very simple and straight forward as you change the value of a or L, if you are talking about the whole particle; and then you are talking about the restricted motion near the atoms defined by a. So, if I change the value of a or if I change the value of L; the nature of band gap will change; and therefore, the properties of semiconductors will also change appreciably. So, what was happened? Just by changing the size, you have got a new semiconductor. The semiconductor may have the same molecular unit, the same molecular formula; but just by changing the value of L or a, what have you got? A new semiconductor, which has a different band gap. So, that is the reason why people started working in this kind of systems even more; because the use of semiconductor is evident everywhere.

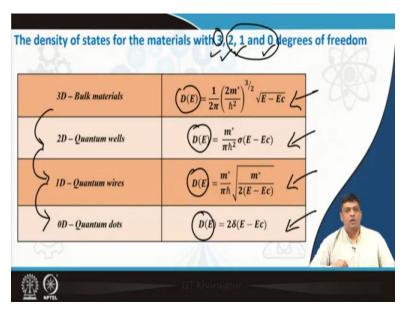
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Density of st	tates	n Ch
Let $D(E)$ d	lenote the density of states as a f	function of energy.
D(E)dE range: (E,	the number of states per unit E+dE).	volume in the energy
	number of electrons in the band in $\int D(E)dE$.	
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What else have we seen? Density of state also plays an important role. What is density of state? Density of state D(E) denotes the states per unit volume in the energy range E and E plus dE; so, you have the density of states. What will the number of electrons in a band? This is given by integration D(E) over the whole entire energy band.

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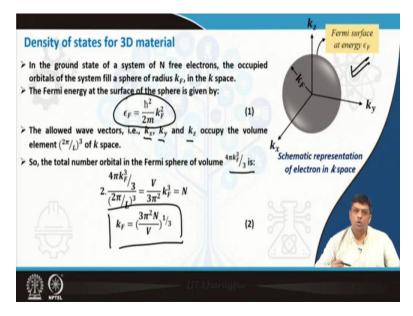


And for 3, 2, 1 or 0, so from bulk to confined structures you can see that the density of states goes on changing. You can clearly see that the formulas are different; I will just explain these formulas in next two or three slides. But to come to this discussion at this point, you can clearly see that the values are very different. And if the values are different, if you have the number of

states available for the electrons or the charges in a unit volume; then what will happen immediately you can say your electrical, the electronic or the semiconducting properties would be changing.

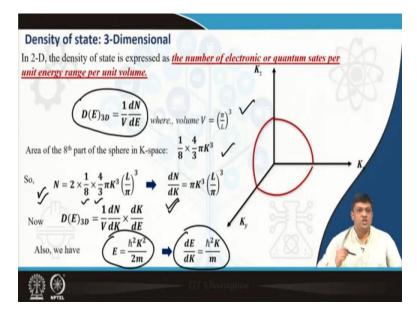
So, just by going from three-dimensional bulk structure to various kind of confined structures, you can modulate the density of states. And that has a very serious repercussion on the properties which you maybe measuring or you are expecting from a material.

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So, how do you calculate density of states? In the ground state of a system of N free electrons, what do you get? You have the Fermi levels. And then you have the Fermi surface at an energy of epsilon F; we are considering the K space. The Fermi energy is written as epsilon F is equal to h cut square by 2m into K_F square; where K_F is the radius of this sphere.

Now, the allowed wave vectors that is the K_x , the K_y , and the K_z occupy the volume element 2 pi by L whole cube of the K space. So, the total number of orbital's in the Fermi sphere of volume 4 pi K_F cube by 3, is given by K_F is equal to 3 pi square N by V, raised to the power of 1 by 3. So, now you have the relationship between the dimension of the sphere and the total number of orbitals. (Refer Slide Time: 23:31)



In the 3-dimensional case that is the bulk structures, how will you obtain? You will get D(E) in 3-dimensional is equal to 1 by V dN by dE. Now, the volume is pi by L cube, the area of the eighth part of the sphere in K-space is 1 by 8, 4 by 3 pi K cube. So, n is equal to so you can occupy how many states? 2 into 1 by 8, into 4 by 3 pi K cube, L by pi cube. Therefore, dN by dK is equal to pi K cube L by pi whole cube. And if you rearrange, you will straight away get dE by dK is equal to h cut square K by m; because E equal to h cut square K square by 2m. So, this is what you have seen earlier also.

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Bulk material **Density of state: 3-Dimensional Bulk** Using all the equations, we get: N(E) $D(E)_{3D} = \frac{1}{L^3} \times \pi K^2 \left(\frac{L}{\pi}\right)^3 \times \frac{m}{\hbar^2 K} = \frac{mK}{\pi^2 \hbar^2}$ E $D(E)_{3D} = \frac{m}{\pi^2 \hbar^2} \frac{\sqrt{2mE}}{\hbar} = \frac{\sqrt{2m^{3/2}}}{\pi^2 \hbar^2} E^{\frac{1}{2}}$ $D(E)_{3D} \propto$ D(E)E

Using this equation and if you are plotting these equations, you can clearly see that for bulk material the changes of N and the corresponding density of states, is proportional to the under root of E.

Quantum wire Density of states for 1D material $1 \, dN$ 1 dN dK D(E)L dE D(E dE LdK N(E) ζ 2KLdN 2L N dK π E $\hbar^2 K$ dE dK m where, $K = \frac{h}{\sqrt{2mE}}$ 21 m ħ D(E)D(E) $\overline{\hbar^2}\sqrt{2mE}$ $m^{\frac{1}{2}}E^{-\frac{1}{2}}$ D(E)E $D(E) \propto E$

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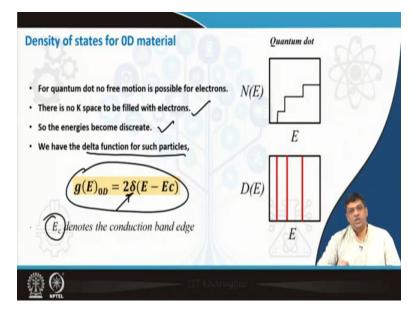
Similarly, you can calculate the variation in 1-D structures; and you will get that is the density of state is varying as 1 by under root E.

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Density of states for 2D material	layered material
In 2-D, the density of state is expressed as <u>the number of</u> electronic or quantum sates per unit energy range per unit	
area. N(E	
$D(E)_{2D} = \frac{1}{A} \frac{dN}{dE} \qquad \text{where., area } A = \left(\frac{\pi}{L}\right)^2$	
Area of the 4 th part of the circle in K-space: $\frac{\pi K^2}{4}$	
So, $N = 2 \times \frac{\pi K^2}{4} \left(\frac{L}{\pi}\right)^2 \implies \frac{dN}{dK} = \frac{L^2 K}{\pi}^4$	Е
Now, $D(E)_{2D} = \frac{1}{A} \frac{dN}{dK} \times \frac{dK}{dE}$ Factor 2 is because of the up and down spin.	
$E = \frac{\hbar^2 K^2}{2m} \implies \frac{dE}{dK} = \frac{\hbar^2 K}{m}$	
$D(E)_{2D} = \frac{1}{L^2} \times \frac{L^2 K}{\pi} \times \frac{m}{h^2 K} = \frac{m}{\pi h^2} = \frac{4\pi m}{h^2} \Box D(E)_{2D} \propto L$	E
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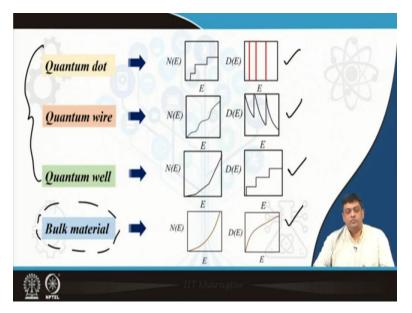
In comparison to 2-D structures you perform the similar calculations; and you will find that the density of states is in as e raised to the power of 0.

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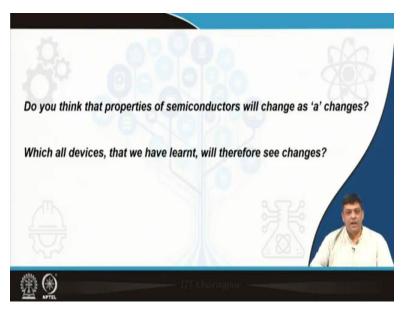
And finally, if you look into these 0D structures, there is no K space to be filled by the electrons. So, the energies become discrete and if that happens you have a delta function for such particles. And what you get? You get the function which is including delta function, where E_c denotes the conduction band edge.

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So, if you compare the number of electrons and the density of states for electrons in the three structures, where confinement effects are there with the bulk structure; where you consider that the electrons are free to move all the three directions. Then you can clearly see that the nature of density of states are changing; and if that is changing, then many properties will change. And that is why you have so much of interest in nanomaterials.

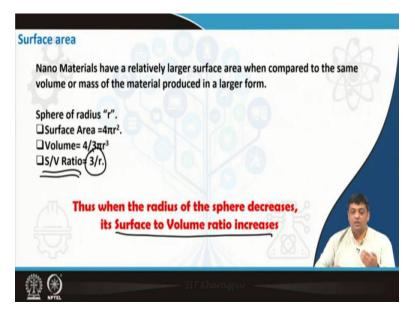
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If I ask you a question at this point, we have given you enough hints that you change the size of the particles. The band gaps will change, the conductivity will change; you will have very different electrical properties. Then, which all devices that we have learnt till now you think will have a different property, if you use different type of nanomaterials? Can you think some of them and list them? Let us say I am giving you some hint; maybe solar cell or did you use some kind of semiconductors or composites, while you are making any kind of turbine blades. Or, you are using some kind of semiconductors in solar panels or solar heaters.

So, I am giving you hint just try to list them. And you will see that when we were indicating that during those modules, that materials will define the new development and the trend in this kind of field. Because, if you have new materials, you can make new systems and devices.

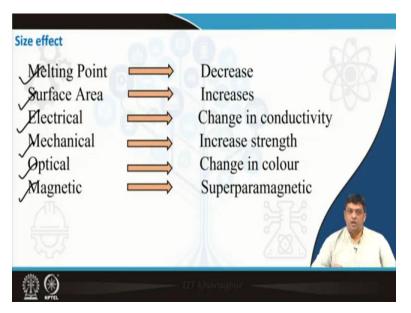
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Another way of which we have seen earlier that the surface to volume ratio; let us say we start comparing just the sphere, then the surface to volume ratio is equal to 3 by r. So, if you change the radius, then the surface to volume ratio increases. And if the surface area is accessible to the system for any kind of catalytic activity or redox activity; then, which devices do you think will have a very different performance, and this is what we have discussed in last three weeks. What do you think will happen to the behavior of lithium ion batteries if you use nanomaterials? If you use metal oxides in super capacitors, then what will happen to these systems, if you use different types of nanomaterials?

We have also talked to you about fuel cells. And there we have explained the use of catalysts, which are essential for developing fuel cells; be it conventional or the ones which were we talked about microbial fuel cells; and so, we had talked about catalysts. So, if you reduce the size of these catalytic nano particles, or particles to a nanometer range, then what will happen to them? Can you anticipate and think? And if you have systems or particles which have higher surface to volume ratio; then that device performance is bound to change.

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And because of this size effect, you will see changes in the melting point, the surface area, the electrical, mechanical, optical and magnetic properties. And the discussion on each one of these topics requires dedicated lectures or modules, which you may refer to in the NPTEL course; where the instructors are dealing with nano science, or physics of nanomaterials. And you will see how in detail these aspects can be explained or investigated; more detailed discussion is beyond the scope of this course.

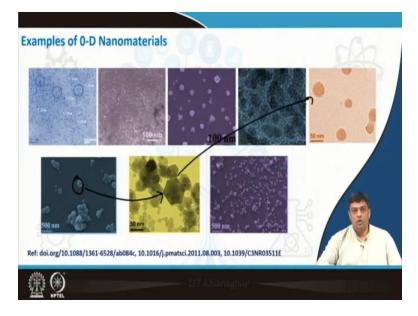
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There are various kind of structures which you can see, if you start from spherical structures; then you can go on reducing the size. If you can see rod type structures or you can have tubular morphologies or any other morphologies which you think. And if you control the synthesis protocols, you can actually obtain very different kind of morphologies. And it is important to note again that use of proper synthesis protocol is essential to obtain the desired nano particle. And then only you will get all the advantages that have been discussed till now.

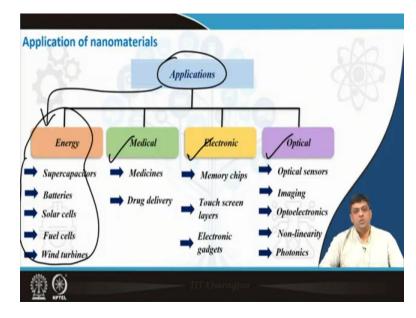
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So, for example, you can have morphologies which are very different, even at zero dimensions. So, you can get particles which have very small size, but you can see the structures are very different to each other. You can have very different kind of structures even in 1-D. You can clearly see the tubular morphologies here; but these are different kinds of morphologies. What is the effect you have different surface to volume ratio? And, as you have different surface to volume ratio, you have different kind of accessibility to pores and the porous network in these materials are different.

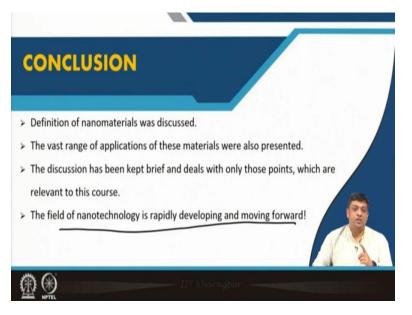
So, different catalytic redox activity, semiconducting properties or resistive properties would be obtained from these materials. Similarly, you can see you can go from layered structures to open structures or porous networks, in 2-D dimensional structures.



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And it must be clear by now that use of nanomaterials in the field of energy is driving the development of energy storage devices, energy generation devices, and also integrated energy systems; where you have inbuilt capacity to generate, as well as store energy. But, the range of application for these materials is enormous; and I have just managed to list a few out of them in this slide. But if you look around the use of nanomaterials can be just listed in slides after slides after slides. But, just to give you a few, I have listed some of the applications here; and the use of nanomaterials in the field of energy must be clear to you now.

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So, in today's lecture, we have given you the definition of nanomaterials, the way it is defined, and why we are using these nanomaterials in energy systems. The field of nanotechnology and nanomaterials is rapidly developing and moving forward. And as this field moves forward, it will have a direct impact on the area of energy devices; and you will see development of new and novel systems, because of the development of nanomaterials. And also, because nanotechnology will lead to miniaturization, you will see size reduction in energy generation or energy storage devices; and that will become even more useful to us in times to come.

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These are the two major books from where we have taken the reference and the data. And in the next lecture onward, I will be talking to you about the synthesis of these nanomaterials. So, that if you are interested to make these nanomaterials, and then use these nanomaterials in energy devices or systems which we have discussed in this course; then you will be able to understand and choose the kind of technique which will be useful. And then you would be getting the desired nanomaterial. Thank you very much.