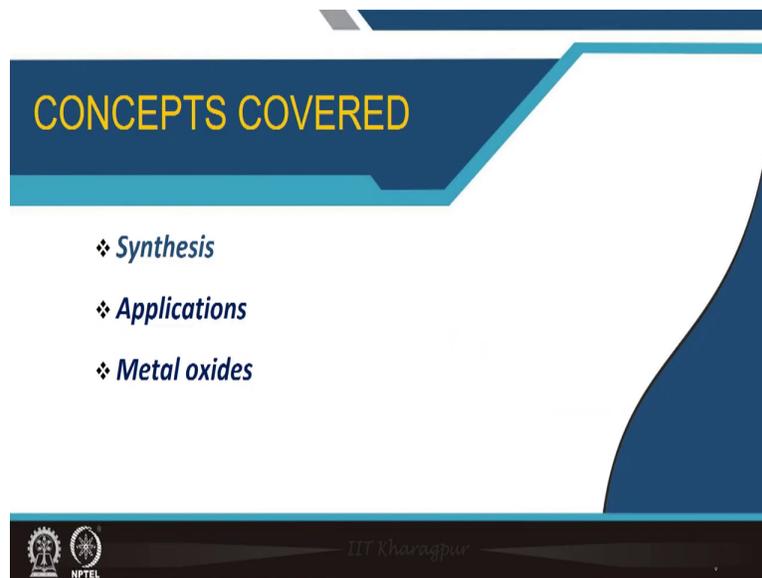


Physics of Renewable Energy Systems
Professor Amreesh Chandra
Department of Physics
Indian Institute of Technology, Kharagpur
Lecture 42
Carbon-and Metal-Oxide Based Nanomaterials

Hello, welcome again to this course on Physics of Renewable Energy Systems. And in this week, we are dedicating our attention on the way we can obtain the kind of materials which have been discussed in this course and how do they differ from each other and why is it important to have nano size materials for most of the devices that have been discussed till now.

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In today's class, we will go to the next step from where we had talked earlier. In the previous class, I gave you an overview of the kind of synthesis protocols which are there, what are the advantages and disadvantages associated with them, but we have not specifically discussed about each one of them or at least few of them, which are going to be useful for us in this course.

So, it was more like an introduction and overview lecture on the synthesis protocol. In today's class will talk to you more in detail about the synthesis protocols which are used to obtain carbon structures. And subsequently, I will also spend the latter half of this lecture on the protocols which are used to synthesize metal oxides.

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KEY POINTS

- Methods to synthesize various carbon-based materials
- Various morphologies of metal oxides

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The slide features a dark blue header with the title 'KEY POINTS' in yellow. Below the header, two bullet points are listed in blue. A video inset in the bottom right corner shows a male speaker in a white shirt. The footer contains the IIT Kharagpur and NPTEL logos.

So, using these techniques, you can obtain various types of carbon-based materials, which we had proposed as the materials for devices such as lithium ion batteries, fuel cells, super capacitors supercapacitors, the turbine blades or few others. You can also use these techniques to obtain metal oxides semiconductors, which we had proposed right from module two or three onwards in solar based devices.

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Favorable properties of Carbon-based materials:

- Large specific surface area ($>1000 \text{ m}^2$) ✓
- Large pore volume ($>0.5 \text{ cm}^3/\text{g}$)
- Chemical and thermal stability
- High processibility for various specific applications
- Abundance
- Biocompatible
- Low cost

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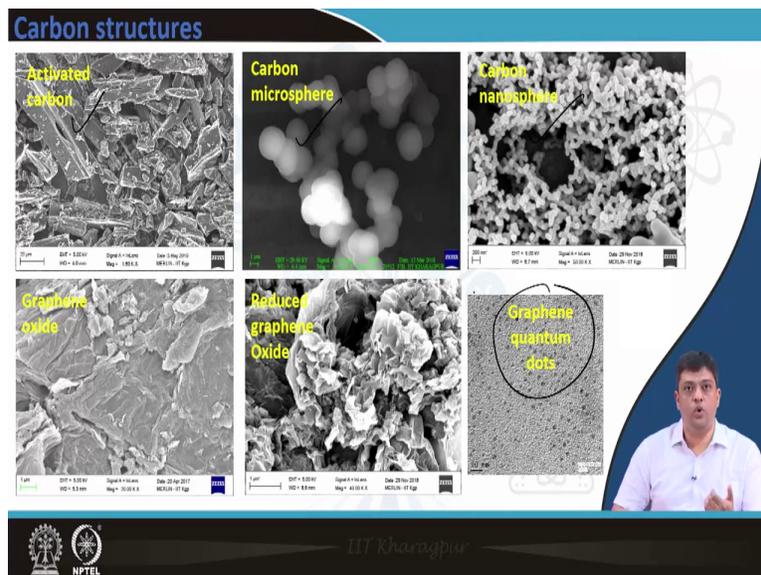
The slide has a blue header with the title 'Favorable properties of Carbon-based materials:'. A yellow box contains a list of seven properties. The first property includes a checkmark. The background features faint icons of gears, a hard hat, a tree, and a beaker. A video inset in the bottom right corner shows the same speaker. The footer contains the IIT Kharagpur and NPTEL logos.

So, let us start with our discussion on carbon-based materials. If you have understood what we have proposed or indicated till now on carbon based materials, we have mostly utilize the properties of carbon based materials which are that these materials can have very high specific surface area, their pore structure can be tuned in a way that you can go from very large pore volumes to very small pore volumes as we are using carbon structures then you can have these structures which are chemically and thermally stable.

Also, by tuning the synthesis temperatures or synthesis protocol, you will see that you can obtain different types of carbon it is not only that you will use graphite, but you can have very different kinds of carbons with application in very different kind of devices. Carbon the usefulness is it is abundant, biocompatible and is also mostly associated with low cost synthesis protocols.

Hence, carbon is extensively used and the usability is just not limited to pencil. The usability of carbon structures varies from a pencil to an aircraft, to a Formula One car, to your automobiles, to your mobile phones, to even any other structures where you are using as high strength coatings. So, the usability of carbon-based structures is in a wide spectrum.

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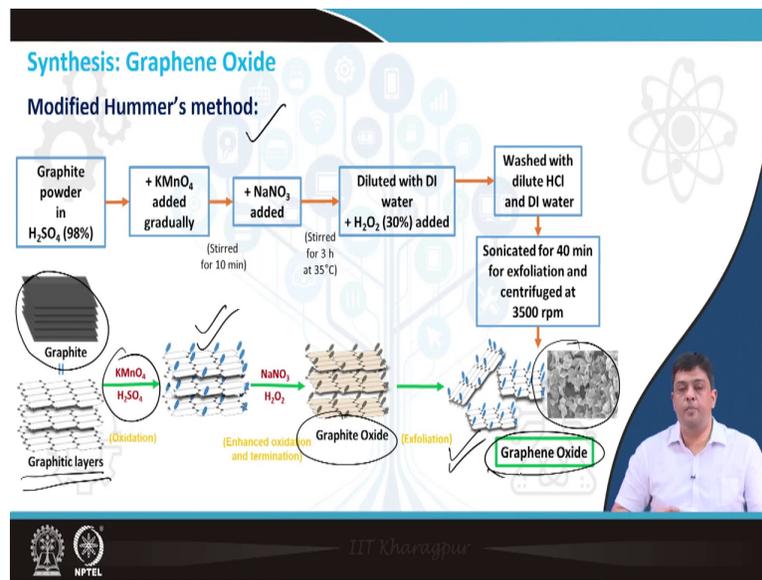


We have talked till now about what type of structures, so if you go back and see the slide in the time when we were talking about either the anode in lithium ion batteries or the EDLC type super capacitors, this is the common structures which we have seen. You can get activated

carbon, you can get carbon micro spheres, you can get carbon nano spheres or you can even go to very small size carbon quantum dot structures.

And you can clearly see that the morphology of these carbon structures are very different from each other and hence, the properties would be different this we have seen from the earlier slides onward.

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So, let us discuss the synthesis of graphene oxide, a material which is very fashionable today and you will hear this material and it is used in various kinds of devices. So, it can be synthesized using a simple modified Hummer's method. What do we do, you take graphite powder in H_2SO_4 . So, concentrated H_2SO_4 .

Then you add potassium permanganate gradually, then sodium nitrate you add it, stir it, stir means on a magnetic stirrer, you put the vessel in which you are having the solution then you have a magnetic ball or any kind of a bead which is the bottom and that as this stirrer rotates this magnetic bead also rotates and that sets this rotational motion in the solution.

So, you are stirring using a magnetic stirrer, then dilute this solution using DI water and hydrogen peroxide. Once you have obtained this precipitate wash it with dilute HCl and DI water, deionized water. What you need to do, now you have got some kind of an agglomerated

structure. So, you then ultrasonic it and when you pass energy you will exfoliate. So, what you will do when you are giving energy the layers will come out. So, exfoliation. So, you are ripping it apart. So, that is exfoliation.

And then you take these solutions in the centrifuge, centrifuge at very high RPMs and what you will obtain is the layered structures of graphene oxide. So, this is what if you look into the structure from a scanning electron microscope, this is what it looks like. But if you go and look at it much smaller level that, is you go to 20 nanometres or lower using transmission electron microscope then you will see some kind of a layered structure in it.

And from there you can even go to graphitic layers. This is what you have. Now, if you want to move from the whole picture once again then what have we done, we have taken the graphite, KMnO_4 and H_2SO_4 you get the structure which is agglomerated, you get graphic oxide and then you exfoliate passing through sonicated then you get the layered structures and that is the graphene oxide structure. So, this is the modified Hummers method which you can use.

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Synthesis: Reduced Graphene Oxide

Reduction of GO by Sodium borohydride (NaBH_4):

GO (0.6 gm) suspension in 200 ml DI water → Ultrasonicated for 3 h + 2 gm NaBH_4 added → Heated in an oil bath at 100°C for 24 h → rGO was precipitated by centrifugation or filtration → washed with acetone, DI water, and ethanol → Dried in oven at 100°C for 12 h

Graphene Oxide + NaBH_4 → Reduced Graphene Oxide + $(\text{NaBO}_2 + \text{H}_2)$

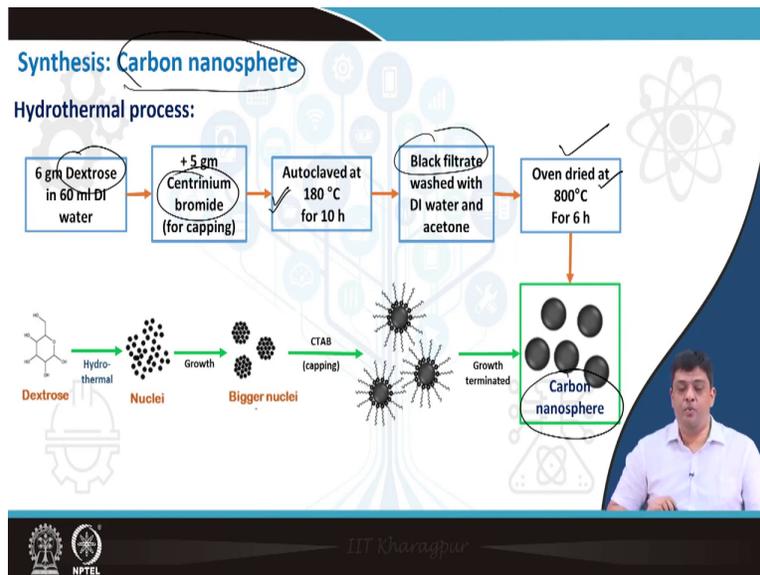
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Similarly, you can get reduced graphene oxide and here what you are doing is primarily you are reducing GO by sodium borohydride and what you get is reduced graphene oxide. So, you take

graphene oxide, then you reduce with the reducing agent sodium borohydride, and then you will get the reduced graphene oxide.

So, it is a very simple process, there is nothing hidden here. And if you have any access to a lab, chemistry lab nearby, you can actually follow the protocols given in this slide and you will get the materials which have been indicated to you. So, it is a very simple process and the kind of materials you get, they have a large range of applications. So, you can make it yourself.

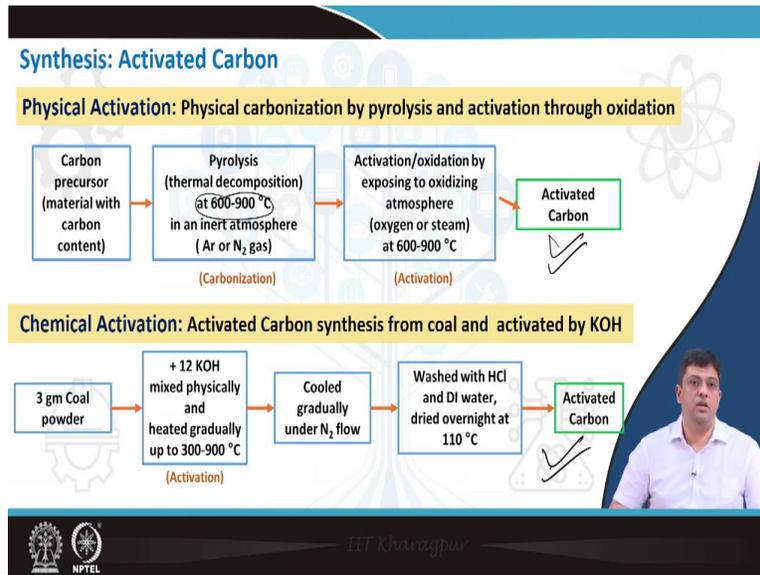
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Similarly, to what I mentioned in the previous class, you can have a hydrothermal process-based growth of carbon nanosphere. So, you what you do in hydrothermal, you have a vessel the autoclave, where pressure can increase as well as temperature can increase. So, you will take let us say dextrose, then you will have the capping agent, the role of capping agent is what it prevents the agglomeration of nanoparticles.

So, you take dextrose, cap it, and then in an autoclave you can heat at for 140 hours, what you will get is a black filtrate which can be washed and then dried and the structure which you will get is the nanospheres. Why washing, because then you are removing the capping agents also that is why you have to wash the structures. Very simple processes are there.

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The next kind of materials which you hear are the activated carbon structures the activation process is basically of two types either you can activate the surface that means, you can have very high surface area materials either by physical activation or chemical activation. So, in physical activation you have the physical carbonization by pyrolysis and then subsequently you activate using the process of oxidation.

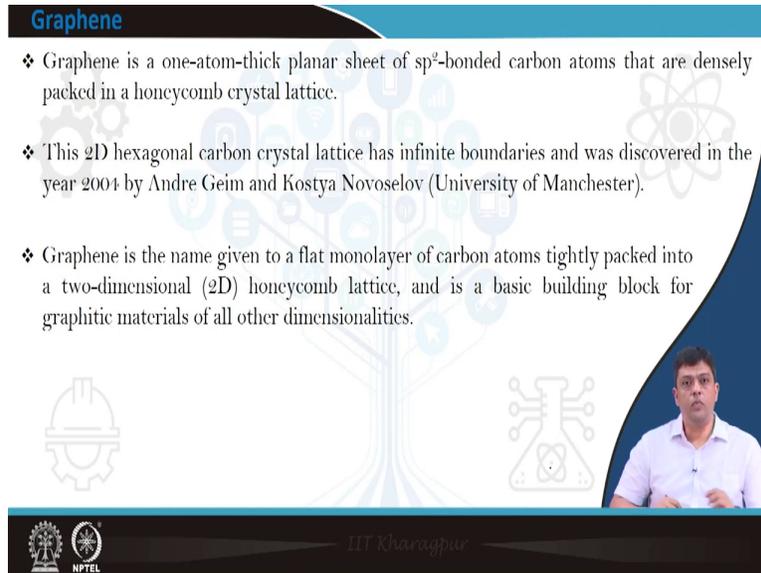
So, what you do, you take the carbon precursors and then they are made to undergo the process of pyrolysis at different temperature range and this is the whole process is carried out in an, in an inert atmosphere. Then, what will you do, you need to activate that means you have to increase the high surface area condition in these materials.

So, you can activate by exposing to oxidizing atmosphere that can be a stream of air or oxygen at similar temperatures or slightly higher temperature than the pyrolysis temperature and what you get is the activated carbon. In comparison to physical activation, you have the chemical activation, where you activate the carbon from coal and then activate the whole carbon structure using KOH.

So, you can take coal then mix it with KOH, cool under the nitrogen flow, wash this material, remove the unreacted metal or any absorb metal metallic impurities on top of these carbon structures and then slowly let them cool down a bit and then heated again So, that you can

remove the volatile components and what you will get is an activated carbon structure. So, using physical activation or chemical activation processes you can get the activated carbons.

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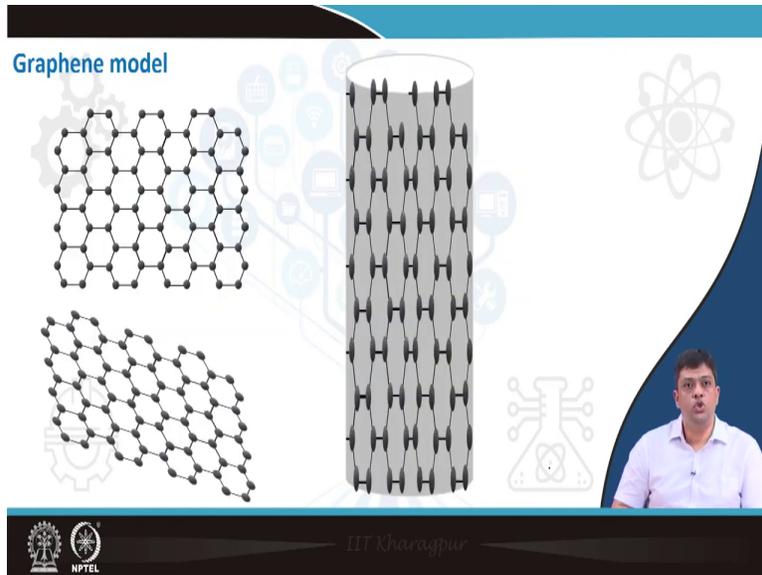
Graphene

- ❖ Graphene is a one-atom-thick planar sheet of sp^2 -bonded carbon atoms that are densely packed in a honeycomb crystal lattice.
- ❖ This 2D hexagonal carbon crystal lattice has infinite boundaries and was discovered in the year 2004 by Andre Geim and Kostya Novoselov (University of Manchester).
- ❖ Graphene is the name given to a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, and is a basic building block for graphitic materials of all other dimensionalities.

The slide features a blue header with the title 'Graphene'. The background is white with faint icons of a hard hat, a tree, and a flask. A video inset in the bottom right shows a presenter in a white shirt. The footer contains the IIT Kharagpur logo and the NPTEL logo.

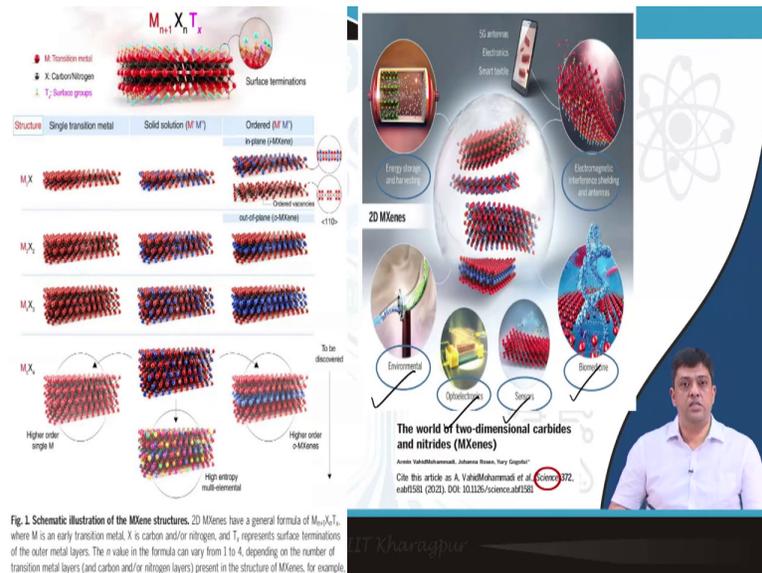
The next structure which is becoming extremely useful or is talked about because this is one of the fastest discoveries which have been given Nobel Prize is the graphene structure, which was discovered in 2004 in University of Manchester So, it is a 2d structure and it is a layered structure.

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So, what you see is a 2d structure. So, you have a two dimensional structures. So, layer structure of carbon. So, this is the graphene structure.

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From the discovery of graphene, there has been an advent of large number of two dimensional structures which are called MXenes. And here what you have the transition metal made it is called M transition metal it is arranged in a layered structure separated by the carbon or carbon

nitrogen networks and the termination atom on the either side of the end layers is the X termination atom.

So, and they have large number of applications ranging from environmental, optoelectronics, sensors, energy and law a lot of work is going on, but we will not discuss too much about this because we have not used these materials still in the devices which were discussed, but they are being extensively used and maybe in coming years you will see many devices which use these kinds of materials as an intrinsic component.

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Advantages and disadvantages of 2D structures

- ✓ High surface area
- ✓ Large no. of surface active sites
- ✓ Superior electron mobility and transfer
- ✓ Excellent photo catalyst support
- Retain control of surface interface
- Difficulties in large scale fabrication and reproducibility
- Difficulties in the synthesis of defect free 2D material

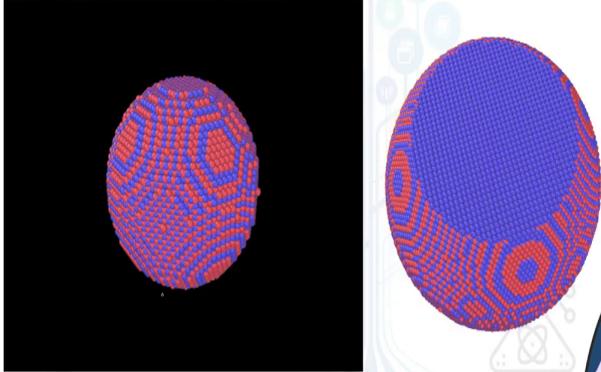
The slide features a blue and white color scheme with a background of faint icons related to technology and science. A small video inset in the bottom right corner shows a man in a white shirt speaking. The bottom of the slide contains logos for IIT Kharagpur and NPTEL.

Now, once you have layered structures they give you high surface area, large number of surface active sites the electron mobility and transfer mechanism is quite superior to other structures and they can also have catalytic properties.

The problem comes is that it is difficult to retain the control over the surface interface it is difficult to reproduce and then even the processes are low enough processes and the cost of synthesis protocols continue to be quite high compared to the normal three dimensional current structures and controlling defects in these structures still remains a challenge. So, there is a lot of work being done in these materials. And as the knowledge increases, you will see these kinds of materials becoming more and more prevalent in the devices which we have discussed.

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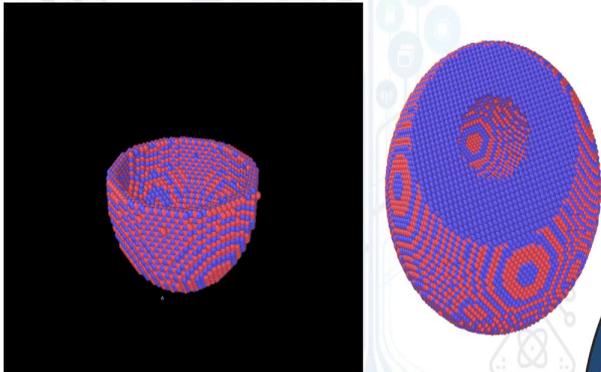
Let us see the **HOLLOW NANOSTRUCTURES** once again but with different point of view...



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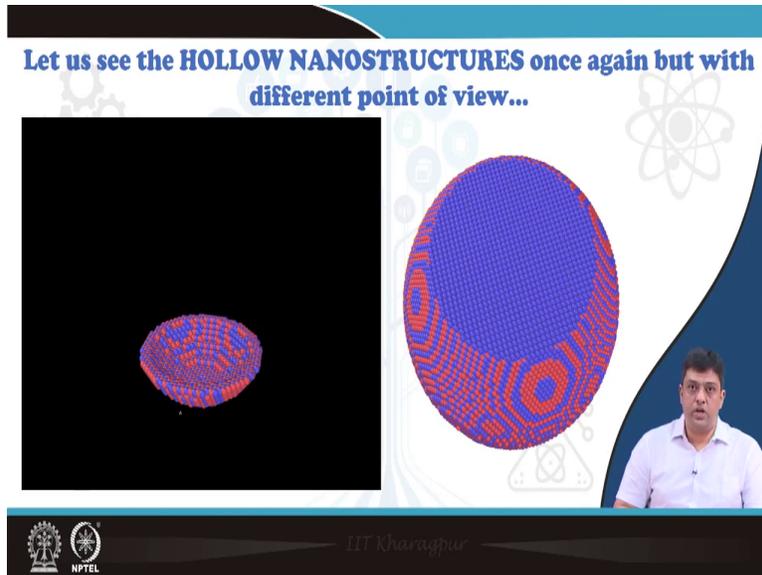


Let us see the **HOLLOW NANOSTRUCTURES** once again but with different point of view...



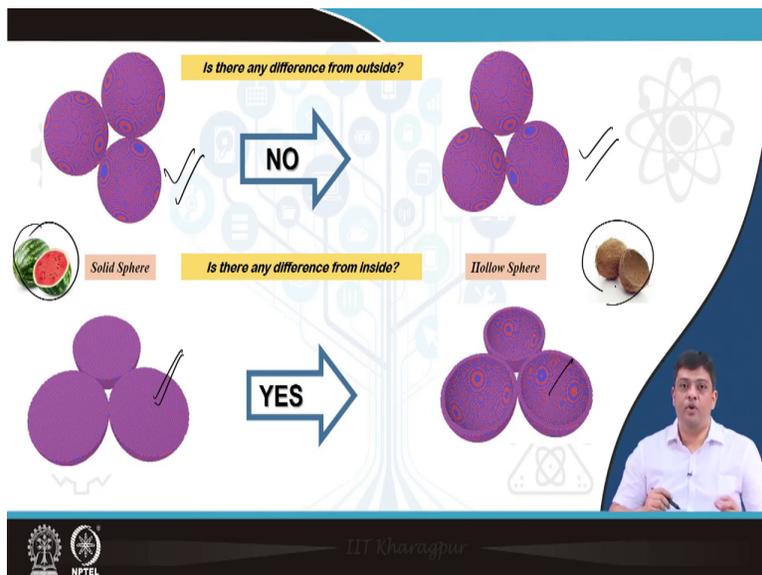
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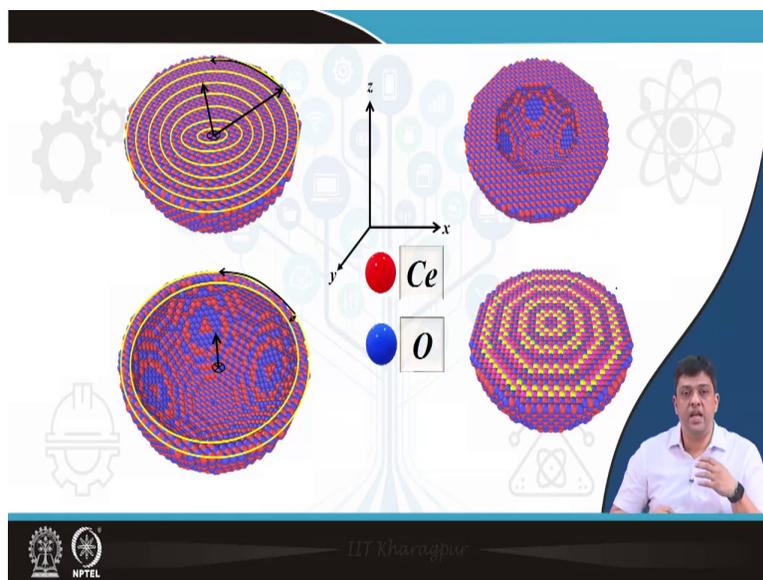
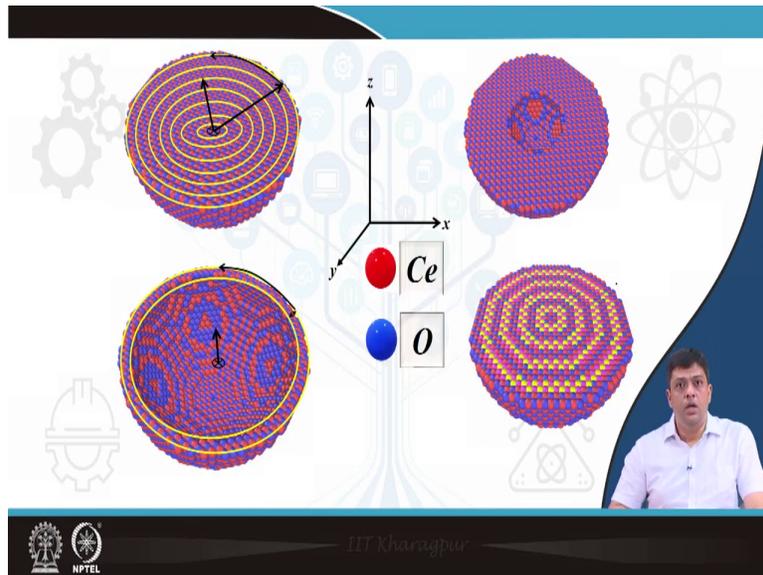
Now, we have discussed in earlier modules, the hollow structures which are not ideally the two-dimensional structures, they are the structures which from the outside look very similar.

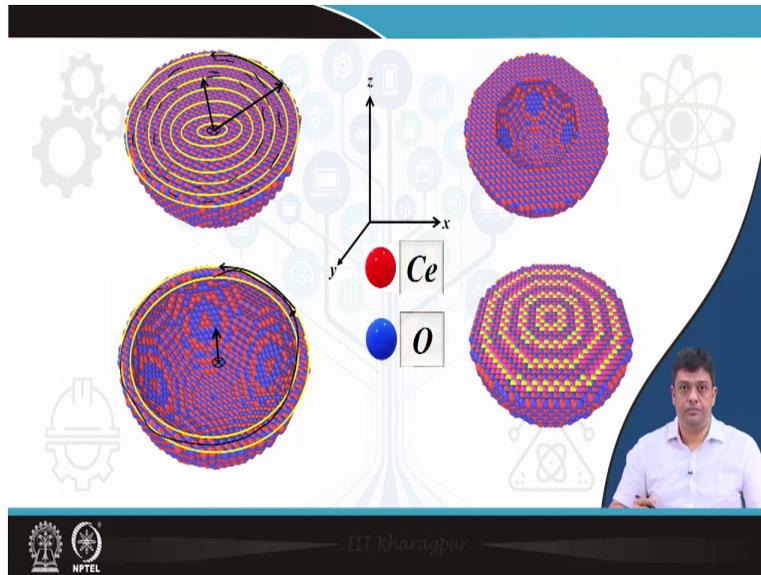
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So, if you see a solid sphere then it looks very similar to a hollow sphere. But if you look closely then from inside one of them is completely filled like the watermelon, but the other is empty like an empty coconut shell. So, from outside it is difficult to distinguish, but from inside they are very different.

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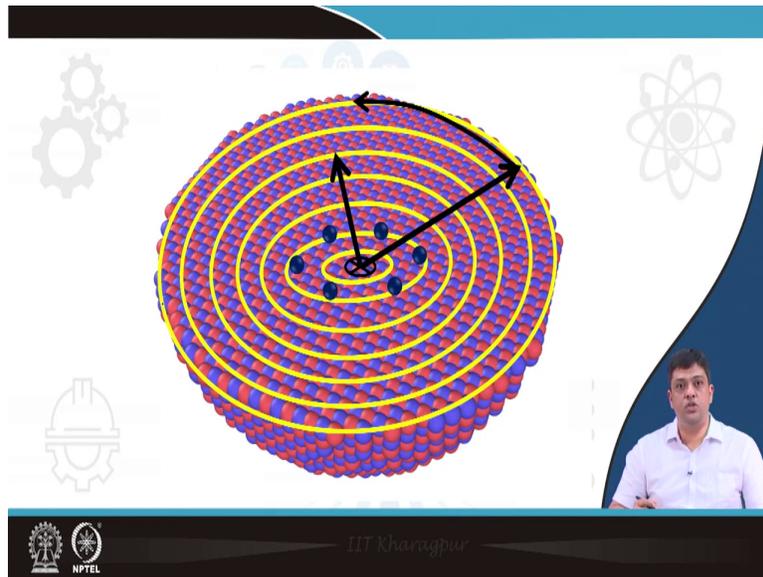


It has been recently seen and you will be able to understand the importance of these materials. What is it, that if you take the solid structures then you have available paths for the electrons to move throughout these particles, but when you go to hollow structures, then they can only move around the boundary.

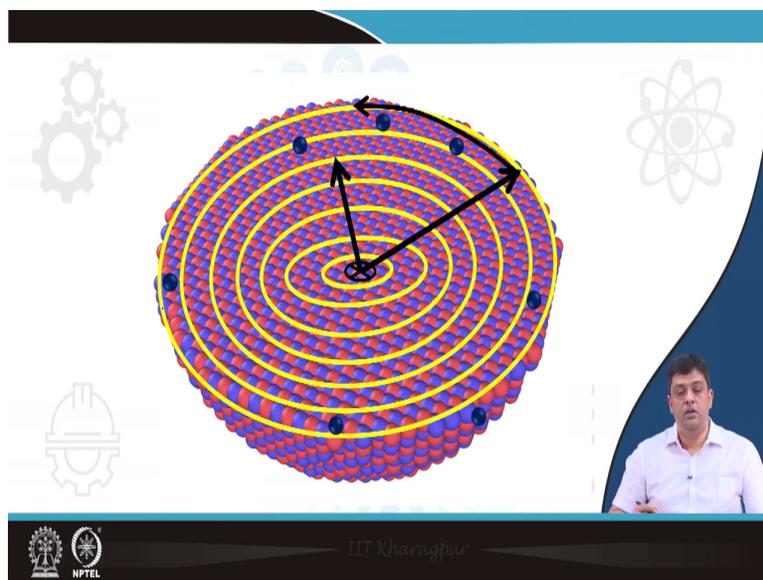
The moment I say that they can only move along the boundary because then you have a gap in the middle then you are only routing at the boundaries at the periphery that means you have induced confinement and the moment I have induced confinement that means, I am moving towards the advantage of nano structures.

So, even if these structures are much bigger, but then you are inducing confinement both in x and y direction and maybe one other direction is free. So, you are confining maybe in spherical terms you are confining in r and theta whereas, phi is the free path.

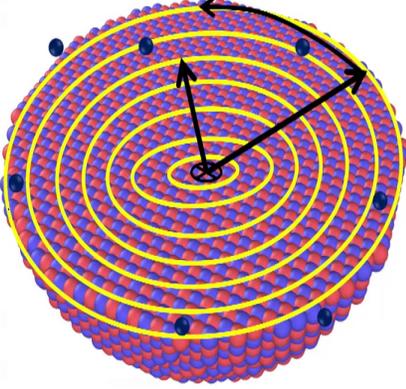
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The slide features a Bohr model of an atom with a central nucleus of blue and red spheres. It has four concentric yellow shells. The outermost shell is completely filled with blue and red spheres. Two black arrows originate from the nucleus: one points to the outermost shell, and the other points to the inner shell immediately inside it. The background includes faint icons of gears, a hard hat, and an atom. A small video inset in the bottom right shows a man in a white shirt. The bottom of the slide has a black bar with the IIT Kharagpur and NPTEL logos and the text "IIT Kharagpur".

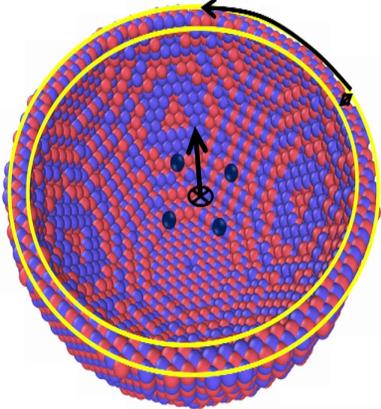


The slide features a Bohr model of an atom with a central nucleus of blue and red spheres. It has four concentric yellow shells. The outermost shell is partially filled with blue and red spheres. Two black arrows originate from the nucleus: one points to the outermost shell, and the other points to the inner shell immediately inside it. The background includes faint icons of gears, a hard hat, and an atom. A small video inset in the bottom right shows a man in a white shirt. The bottom of the slide has a black bar with the IIT Kharagpur and NPTEL logos and the text "IIT Kharagpur".



The diagram shows a spherical crystal lattice composed of red and blue atoms. Concentric yellow shells are drawn around the center. A central atom is marked with a circle containing a cross. Two black arrows originate from this central atom: one points radially outward, and the other points tangentially along the surface of the outermost shell. The background features faint icons of gears, an atom, and a hard hat.

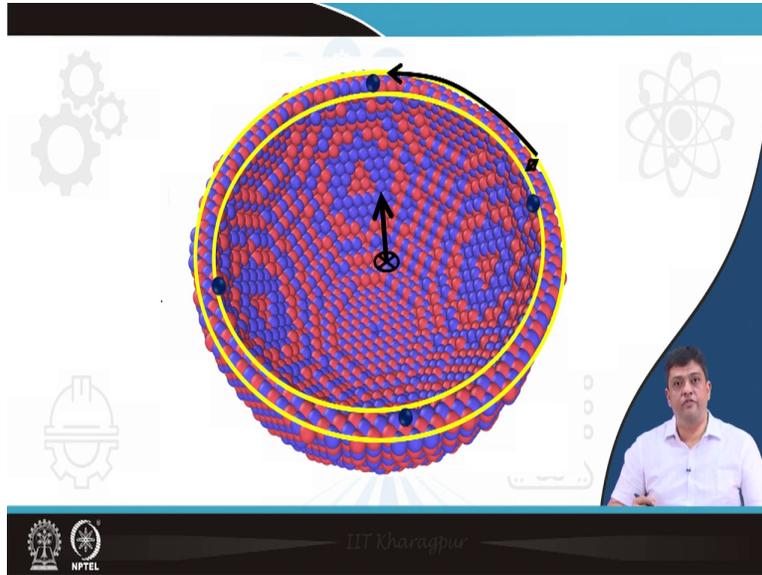
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The diagram shows a spherical crystal lattice composed of red and blue atoms. Two concentric yellow shells are drawn around the center. A central atom is marked with a circle containing a cross. Two black arrows originate from this central atom: one points radially outward, and the other points tangentially along the surface of the outermost shell. The background features faint icons of gears, an atom, and a hard hat.

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So, what happens in solid structures you can see that you can have electron motion all around. But when you are seeing the hollow structures, they have to move only in the periphery.

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6 nm sphere
Lets count atom number!

Solid sphere: 33401	Hollow sphere: 8896
Ce atom: 11133	Ce atom: 2965

Calculate the number of nanospheres in 1 gm of CeO₂

Solid sphere: $\frac{N_A}{1914908}$

Hollow sphere: $\frac{N_A}{509996}$

Consider the thickness of the hollow sphere is such that all the atoms present are equal to the no of atoms participating from the solid sphere in any application.

Ratio of Ce atom!!!

Solid sphere: Hollow sphere = **1:4**

And hence, what happens that the ratio of atoms in hollow spheres is quite small that means you have hollow spheres which are constructed using a much lower number of atoms in comparison to solid structures and you can have the solid sphere and hollow sphere ratio as 1 is to 4 So, you can have much lighter materials, but with higher surface area and this is what is typically the property of two dimensional structures.

So, even if you look at the structures which can be much bigger, you will see that these kinds of structures can simulate 2d structures. And therefore, these kinds of metal oxides are becoming extremely important.

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pseudo - 2 D nanostructures
and
deliver the expected advantages over solid structures?

The slide features a central text block with two images of nanostructures: a circular one with a central void and a rectangular one with a central void. The background includes a gear icon, a molecular structure icon, and a person in a white shirt. At the bottom, there are logos for IIT Kharagpur and NPTEL.

SYNTHESIS PROTOCOLS – MORE THAN ONE...Each have their advantages and disadvantages

The slide illustrates three synthesis protocols: Hydrothermal, Carbonnanosphere, and Mini-emulsion. The Hydrothermal section shows a reaction between Dextrose and Hydrothermal conditions (180°C, 10h) leading to Nuclei, which then grow into Bigger nuclei, and finally into Carbonnanosphere after Capping with CTAB. The Carbonnanosphere section shows Growth Terminated. The Mini-emulsion section shows a process involving Toluene with surfactant, Ultra-sonication, and $\text{Ce}(\text{NO}_3)_3$ leading to Precipitated Particles, which are then Washed and Dried. A Soft template section shows Spherical template formation, Calcination, and Soft template. The background includes a gear icon, a molecular structure icon, and a person in a white shirt. At the bottom, there are logos for IIT Kharagpur and NPTEL, and a citation: Chandra et al. Frontiers of materials (2019), Nanotechnology (2020).

There are other metal oxides which are becoming quite important. And we will discuss about them in a minute, but you will see to obtain hollow structures there are various kinds of synthesis protocols that we have already discussed, you can use hydrothermal you can use many emulsion, you can use soft template methods, the sacrificial template methods or the hard template methods

and you will get various kinds of systems where you can clearly see the formation of hollow cavity.

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Transition metals and their valance states

Periodic table of the elements

Alkali metals		Halogens	
Alkaline-earth metals		Noble gases	
Transition metals		Rare earth elements (P1, 36, 67-71) and lanthanoid elements (57-71 ions)	
Other metals		Other nonmetals	
Actinoid elements			

Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC). © Encyclopaedia Britannica, Inc.

Major properties of transition metals

- 38 elements in groups 3 through 12 of the periodic table
- Both ductile and malleable
- Conduct electricity and heat
- Possess unfilled electron level
- More than one oxidation state
- Ex- Fe, Co, Ni, Zn, Sc, Ag, Au, Pt etc





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And then they have significant advantage. And the advantage has been more so, in transition metal oxide. So, you will see from earlier models that we have always been talking about the use of metal oxides in lithium ion batteries, the super capacitors the fuel cells and you have used large number of oxides based on these transient metals. What happens these metals can exist in various valance states.

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Classification of MOs:

Depending on number of metal elements present in the MOs they are of three types:

Unary MOs:

- ❖ Presence of single metal.
- ❖ Ex: ZrO_2 , TiO_2 , NiO , CuO , etc.

Binary MOs:

- ❖ Presence of two metal elements.
- ❖ Ex: Ni_xMo_yO , Ni_xCo_yO , etc.

Ternary MOs:

- ❖ Presence of three metal element.
- ❖ Ex: Zn-Ni-Co oxide ($ZnCO$), $Ni_xCo_yCu_zO$.



So, either you can use unary metal oxides, the binary metal oxides or ternary metal oxides depending upon the number of metal lands you are having in a oxide.

(Refer Slide Time: 22:25)

Properties of MOs:

- ❖ Oxide material can present ionic or mixed ionic/electronic conductivity. 
- ❖ Properties of MOs covers the entire range of metal (RuO_2) to semiconductor ($YMnO_3$) and insulators ($BaTiO_3$).
- ❖ High optical conductivity.
- ❖ High mechanical stress, hardness, super plasticity.
- ❖ They show diverse ferroic properties like ferromagnetism (CrO_2), Anti-Ferromagnetism (NiO , $LaCrO_3$), Ferroelectricity ($BaTiO_3$), Ferro elasticity ($KNbO_3$).
- ❖ Good thermal and chemical stability.
- ❖ Ternary MOs shows high theoretical specific capacitance.
- ❖ In transition metal oxide, vacant d-shell gives them unique characters like reactive electronic transition, high dielectric constant, Ferromagnetic, Ferrimagnetic state.



These kind of oxides have the capacity to deliver ionic, electronic or mixed ionic electronic conductivity. So, you can take the advantages of all kinds of conductivity, you can use them for optical properties, you can use them for semiconducting properties, you can use them for ferroelectric properties, you can use them for federal elastic, ferromagnetic you can use it for

GMR, CMR properties, you can use them as anode material or cathode material in energy storage devices you can use them as catalysts. So, there are large number of properties associated these metal oxides.

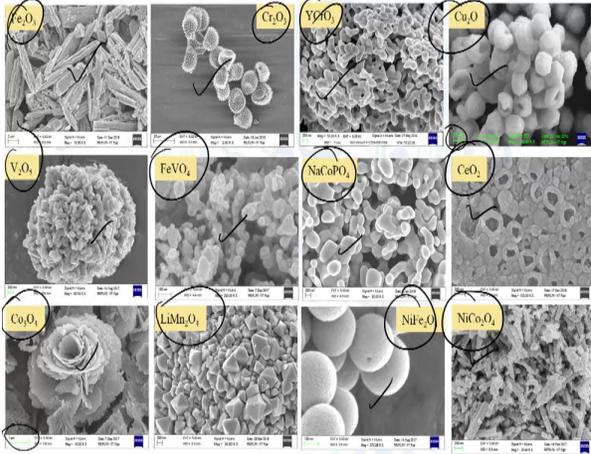
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Various Morphological structures for nano metal oxide

- ❖ Nanotubes : Co_3O_4
- ❖ Nanoribbons : SnO_2
- ❖ Hollow Nano shells : Amorphous ZrO_2
- ❖ Nano wires : ZnO
- ❖ Nano belts : PbO_2
- ❖ Nano Particles : $\text{TiO}_2, \text{CeO}_2$



Different morphologies



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So, let us look into some of them. You can clearly see that the morphologies can be very different in different types of oxides which are mentioned in the slide. So, you can go from various kinds of morphologies. Now, what is morphology, the size and the shape of the particle that will define the specific surface area. This will define the chemical properties, this will define the reactivity,

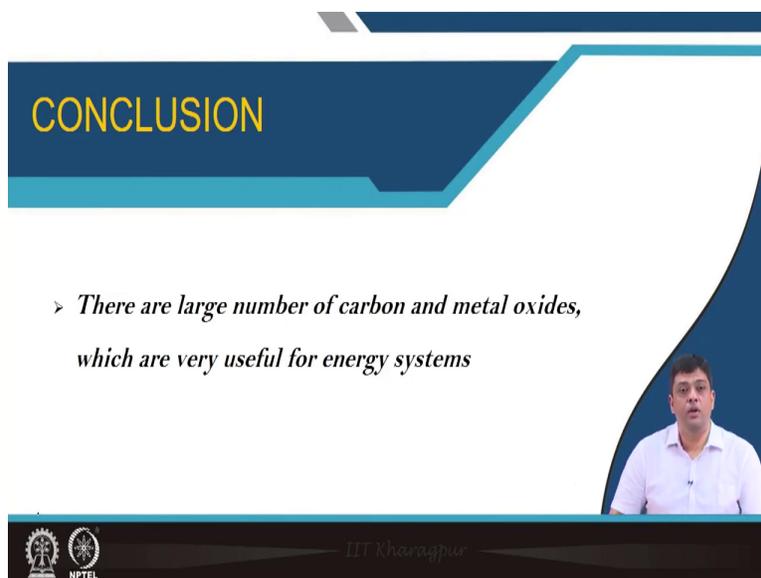
it will define the redox activity, it will define the semiconducting properties because it will lead to variation in the bandgap, that is correct.

So, you are changing a and as you change a you are going to change the bandgap in these kinds of semiconductors if you choose semiconductors around this, you will have different kind of optical properties. So, it is clear you can have different kinds of materials, you can synthesize different kinds of materials and you will get different kind of morphologies. And these are at very small scales, so this is like picture taken at 200 nanometres level.

So, few 100 nanometre level, so this is like 1 micrometre. So, this is the scale you are looking at. So, the whole picture is maybe around 6 micrometres by 6 micrometres. So, this is a picture from the outside all the particles may actually all them may look like the powder, which is white in colour, but when you see them at the nano or the micron level, then the reality comes out that they are shapes and sizes are very different.

And hence their properties would be different. Their properties can be electrical properties, optical properties, electrochemical properties, magnetic properties or any other property which is related to the surface of the particle, the shape or the size of the particle or even the balance state of the particle or the bandgap in these particles.

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CONCLUSION

➤ *There are large number of carbon and metal oxides, which are very useful for energy systems*

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The slide features a dark blue header with the word 'CONCLUSION' in yellow. Below the header, there is a white area with a blue border on the right side. A small video inset of a man in a white shirt is visible in the bottom right corner. At the bottom of the slide, there are logos for IIIT Kharagpur and NPTEL.

So, it must be clear that there are large number of carbon and metal oxides which are very useful energy systems. It is very, very simple to actually synthesize these materials. So, if you got scared at any point during any of the modules earlier as to how you can make the materials which can then use in a device then I hope that this lecture and the previous lecture has given you the confidence that you can easily make these materials, you can make new materials, you can make materials as per as your defined required characteristics and then you can make new energy storage or energy generation or integrated energy generation storage system.

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These are the major references from which you can get more idea about the topic. And in the next class, we will talk about nano catalysts, where you will see that the catalysts which we discussed during the module on fuel cells can also be made quite easily and then you will be able to convince everyone that yes, you can make materials which can be used in lithium ion battery, or you can use them in super capacitors or you can use them in fuel cell. Thank you very much.