

Nano structured Materials-Synthesis, Properties, Self Assembly and Applications
Prof. Ashok K Ganguli
Department of Chemistry
Indian Institute of Technology, Delhi

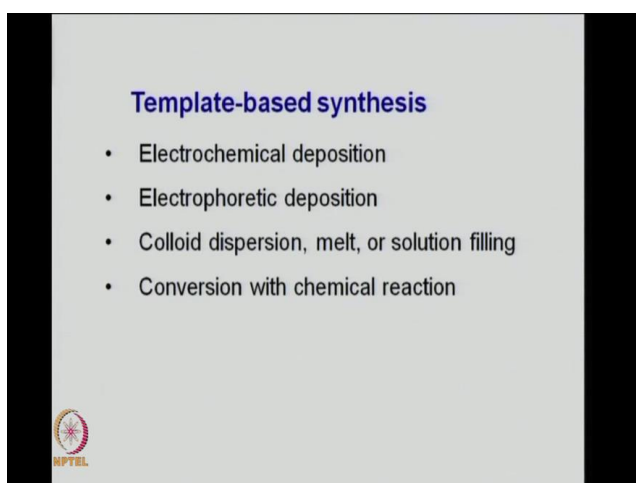
Module - 2
Lecture - 10
Template Methods – II

Welcome to this course of nanostructured materials- synthesis, properties, self assembly and applications. We are into the lecture 8 of module 2, and today we have to do the template methods - part 2. In the last lecture which was the lecture 8 of module 2, we had started the template methods of the part 1, in which we discussed various structures which can be used as templates for the synthesis of nanostructured materials. These templates could be one-dimensional, two-dimensional or three-dimensional like you can get layers; two-d layers in metal oxides which are two-dimensional or metal chalcogenides.

You can get three-dimensional nanostructures using a template like zeolites, which has large force in which you can grow nanostructured materials, and zeolite is then used as a template. Similarly, you can use surfactants as templates. So, you can design organized assemblies of surfactants and then you can synthesize nanostructured materials in them which we showed in the last lecture. We can use many other methods, like in biology or in biomineralization, there are mechanisms by which biomolecules synthesize nanomaterials.

We examined the case of iron oxide nanoparticles, being synthesized in the magneto tactic bacteria and how iron ions get inside the cell is not still clear, but the mechanism that it changes into ferric oxide within a magneto zone is now well known. These magnetotactic bacteria magnetite Fe_3O_4 which is crystallized, leads to its ability to guide itself along with the earth's magnetic field. So, these were some examples in the previous lecture on template methods, one where we looked at various templates, may be inorganic and organic or surfactant based templates for synthesizing nanomaterials. So, we continue on that and today is the second part of the template methods used for synthesizing nanostructured materials.

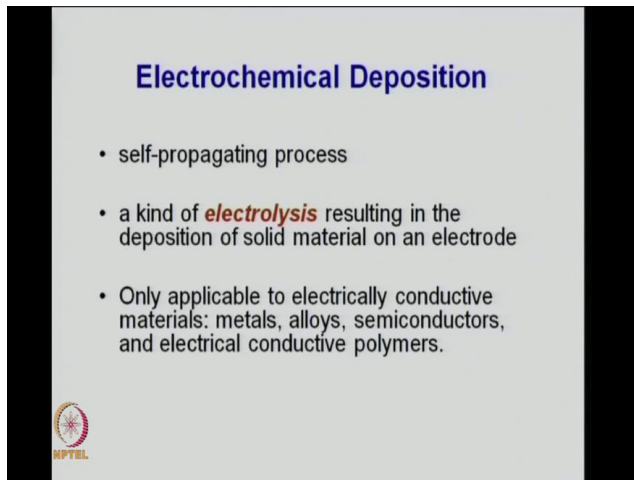
(Refer Slide Time: 03:22)



In today's lecture, we will be discussing other types of synthetic routes using templates, like the electrochemical deposition route, which is very widely used. As you are knowing from the term electrochemical, you need electrodes and you need to pass current to undergo chemical reactions and which will lead to some kind of reaction to deposit metals and that is the electrochemical deposition. You can use what is called the electrophoretic deposition which is slightly different from the electrochemical deposition, and we will discuss what exactly is this electrophoretic deposition and how it is different from electrochemical deposition. One important thing is that in electrochemical deposition you need to work with conducting specimens: that means metals, alloys, etcetera. whereas in electrophoretic deposition you can do with materials which need not be highly conducting.


Apart from electrochemical and electrophoretic deposition methods, you can also look at other methods, like the colloidal dispersion within the template or melts within a template or solutions which fill the template. This can also be through a vapour method. Here, most of the things we have mentioned are through a solution or a liquid method by which we fill the template and create nanostructures. You can also do chemical reactions within the template, and lead to nanostructured materials within the templates. So, these are the typical methods which are templates based which we will be discussing in this lecture today, which is part 2 of the templates based synthesis lectures.

(Refer Slide Time: 05:38)



Electrochemical Deposition

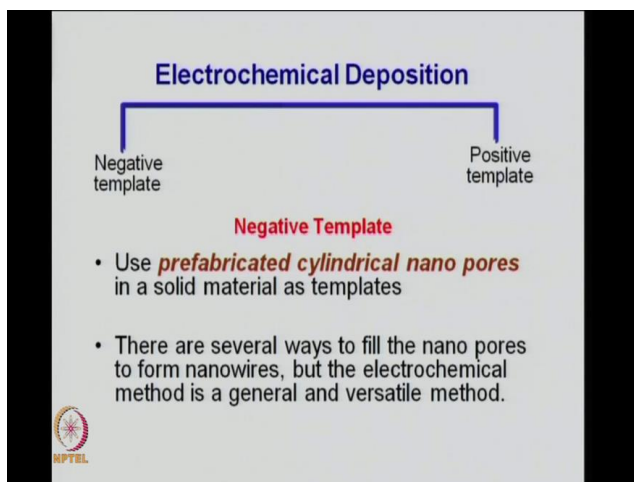
- self-propagating process
- a kind of *electrolysis* resulting in the deposition of solid material on an electrode
- Only applicable to electrically conductive materials: metals, alloys, semiconductors, and electrical conductive polymers.



Let us discuss the electrochemical deposition. All of you must be knowing that in electrochemical deposition you need to have some kind of electrodes and you need to pass current. So, it is of course, a self-propagating process. Once you start, it is a kind of electrolyses, resulting in the deposition of solid material on an electrode and as **I** mentioned earlier, it is mainly applicable to electrically conducting materials like metals, alloys or semiconductors with low band gap and electrically connecting polymers.

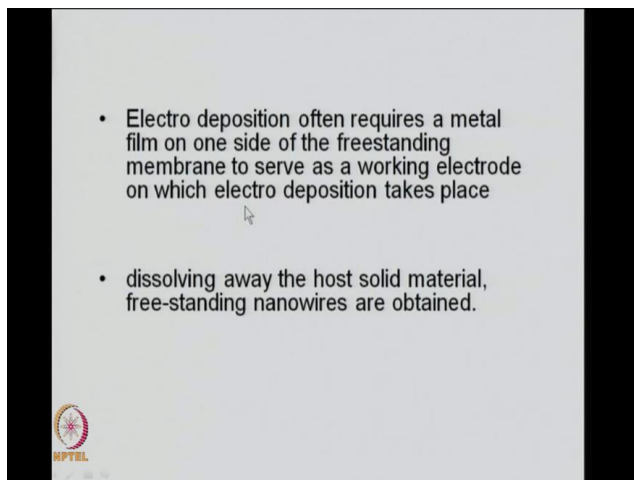
So, that is one limitation of the electrochemical a deposition method, where you can create these nanostructures using the electrochemical deposition for systems, which are conducting like metals, alloys and electrically conducting polymers, and maybe semiconductor switch have low band gap. But you cannot electrochemically deposit materials which are insulators. For example, diamond or quartz or sodium chloride or something like that. So, you need to have materials which are reasonably conducting.

(Refer Slide Time: 07:18)



Now, the electrochemical deposition can be divided into two particular methods, where in one case we call it the negative template method and in the other case we have the positive template method. So, in the negative template method, what you do is you use prefabricated cylindrical nanopores solids as template. So, you have a solid which has got pores and these pores are of the dimension which you want your nanomaterial to be, and these are cylindrical pores and then you fill this pores. There are various ways to fill these nanopores in these templates. But the electrochemical deposition technique is quite general and versatile and so that is what we discuss here. So, you have a prefabricated nanoporous template which can be material like aluminum, which is commonly used, and then you fill these nanopores using an electrochemical deposition. In this case you can use other methods also to fill the nanopores.

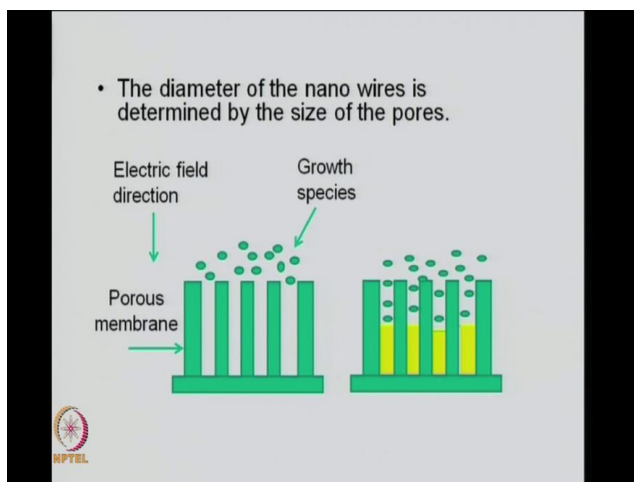
(Refer Slide Time: 08:40)



So, this electrodeposition, when you do, you may require a metal film on one side of the freestanding membrane, which will act as the working electrode and that is where the electrodeposition will take place. So, you have a membrane. The membrane is on a metal which is an electrode and this electrode acts as a working electrode, and when the electrochemical deposition occurs on this particular electrode, you dissolve away the host solid material that is the membrane or template and then you can get free standing nanowires.

Freestanding means they are not connected to the template or they are not connected to the electrode, either the working electrode or any electrode. So, you have only the nanowires which you wanted to synthesize within this template. So, if the template should be easily dissolvable and normally if you use something like aluminium you can dissolve using sodium hydroxide or something like that. Basically, your template in this case is a negative template. It has got nanopores and then we have cylindrical pores under this template where these cylinders are there. Below that you have a metal electrode, which acts as a working electrode and the metal which you deposit, deposits on this working electrode and then you have to dissolve away the host material that is the template material to get free standing nanowires.

(Refer Slide Time: 10:32)

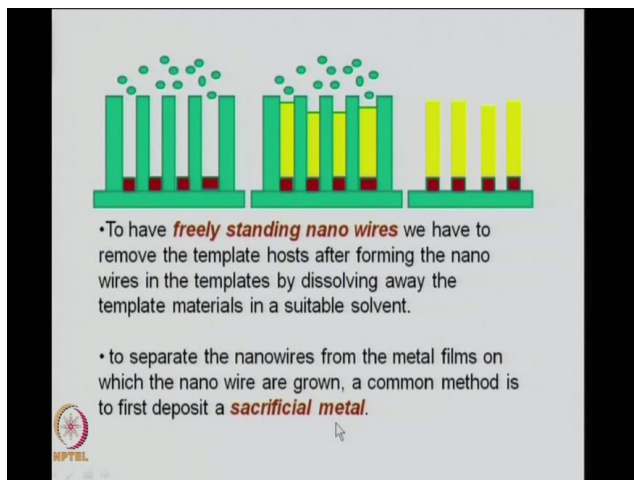


This is a clearer view of what one is doing. Here, you have the template as shown here. It can be like membranes, these are equally spaced templates and you want to grow your nanostructures within these cylindrical pores or cylindrical gaps and this diameter should be in the size of what you want. So, this should be if you want two nanometer or five nanometer wires then that should be the dimension of these cylindrical pores.

So, what you do you have this template and you have a bottom working electrode as discussed before, which is required to hold this template, and then you have your species which are in solution, which you want to grow in these nanoporous structure. So, you have these species which are present in the solution and you apply an electric field in this direction. When you apply an electric field in this direction these species will line up into these nanoporous cylinders. So, they will lineup into these nanoporous cylinders and then they will get deposited here on top of the working electrode.

This is a very simple picture of the exact process which is happening in the electro deposition of nanostructure materials using a porous template and supported by an electrode, which is the working electrode. You can control the diameter of these nanostructures that you will get by making your template appropriately. Sometimes, to get free standing nanowires, as we discussed here you will have always this electrode connected to this deposited nanostructures. So, if you want only this yellow part, that means, that is a nanowire, which is growing then you will have to remove this electrode.

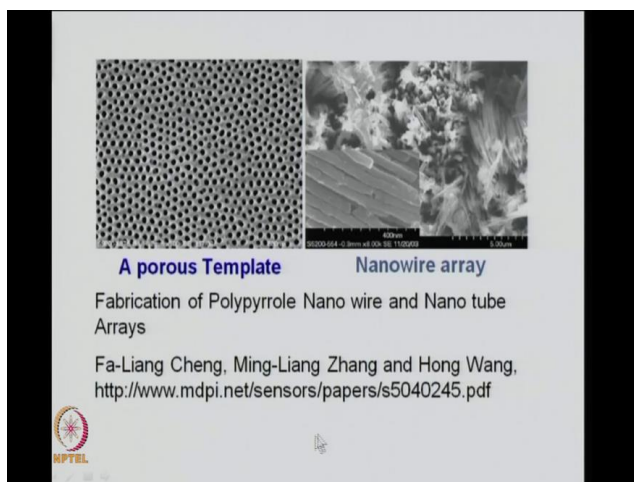
(Refer Slide Time: 13:04)



Now, the way one does this is, one has a sacrificial layer quoted on top of this electrode. So, you have your porous template. This is your porous template with the cylindrical pores, but you have a working electrode here on top of which you have a suitable sacrificial metal. On top of this then you do what you did before. So, what we did before is you apply an electric field in this direction and you have your growth species same thing you do here you apply an electric field and have these species. So, they will arrange here on top of this sacrificial layer.

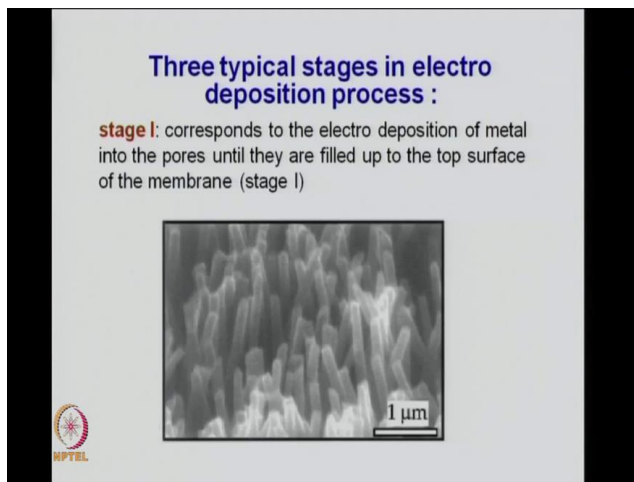
Once you remove this porous template; once this is gone, then you can remove this sacrificial layer. So, then you will be left with only these freestanding nanowires if you can remove this sacrificial layer. We have to dissolve away the template and also the sacrificial layer. To separate the nanowires from the metal film, from this electrode where the nanowires is grown, you have to first deposit this kind of a sacrificial metal.

(Refer Slide Time: 14:32)



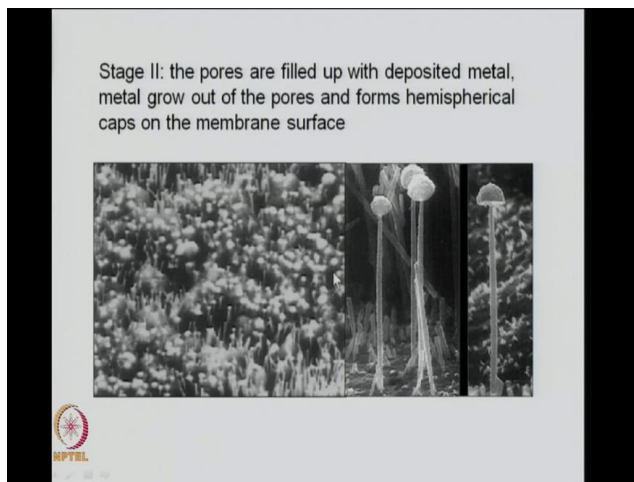
This is an example of where we have used a porous template. This is a porous template with quite homogeneous diameters of the pores and quite uniformly placed and on this porous template, in the pores you want to grow nanowires. Here, one is growing polypyrrole nanowires. It is a polymer or pyrrole and which is growing in this porous cylindrical pores, present in this template. If you take a cross section SEM or TEM after growth, then you will see that these kind of aligned nanowires are present, which are actually within the pores of these templates. After removal of the template if you take a TEM, you can see these aligned nanowires. These aligned nanowires are of the polypyrrole, which is grown within this porous network. So, this is an example of electrochemical deposition of polypyrrole nanowires within a porous template.

(Refer Slide Time: 15:51)



When this electrodeposition process takes place, it goes through three stages. The first stage corresponds to filling up of the pores using electrodeposition of the metal, till they come up till the top surface of the membrane. Say your membrane thickness from here is something like forty nanometers. So, the first stage is growth of these nanowires up till the surface of the membrane. That is the first stage. In that first stage, these wires are growing up till the surface of the templates. If you somehow remove the template at stage one, which means, up till they have come to the brim and you remove the templates then you will see pictures like this because we have only the nanowires coming up till the surface.

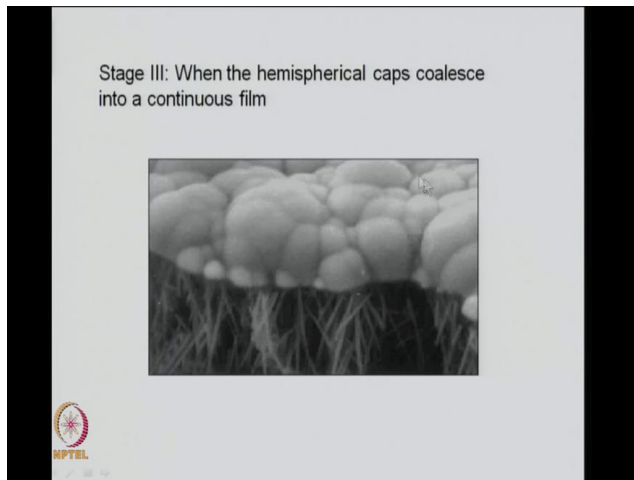
(Refer Slide Time: 17:01)



However, if you allow the growth to continue, you come to stage two then the pores are filled up with the deposited metal and they flow out of the pores. So, if you add more than this level then they will flow out of this pore and they will form flowers on top of this membrane of the template. And that is what you see in the second stage, where the membrane was up till this portion and then the electrodeposition took place out of the membrane, and you get this kind of flower like structures or hemispherical structures, which is capping the cylindrical nanowires. In this picture, if you remove the templates, you will get after stage two: that means, after the electrodeposition has continued beyond the thickness of the membrane and you have got material flowing out of the membrane on top of the membrane in the form of hemispheres.

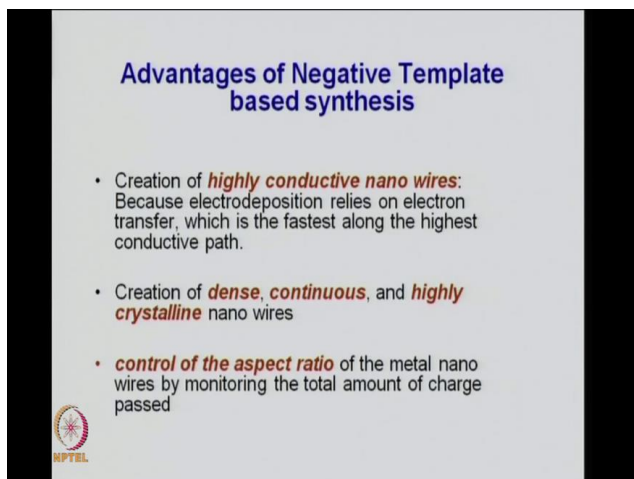
So, that is at stage two. If you continue further, then these kind of umbrellas or mushrooms, which you saw in stage two: if you allow the film to grow further without removing the templates, then the mushrooms will flow over to each other and get connected, and that is when you see this kind of coalescence of the mushrooms.

(Refer Slide Time: 17:01)



At the bottom you have these cylindrical rods which are the nanowires and on top, you have these mushrooms which have coalesced with each other to form like a blanket on top of these nanowires. So, this is at stage three when you have completely a kind of wetted the whole membrane with these flowers or mushroom like structures. So, this is negative template we have discussed, where you have a template and within the template you are making the nanowires and using electrodeposition and you can use a sacrificial template to get free standing wires.

(Refer Slide Time: 19:34)



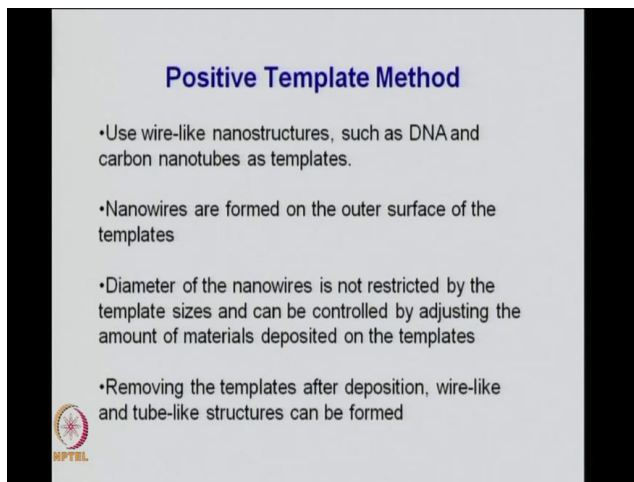
The advantages of this negative template based synthesis are that you can create highly conducting nanowires. Since electrodeposition depends on electron transfer, and electron transfer is fastest along the path which is most conducting. So, the highest conductive path is the path to which the electron will transfer and so the deposition will have along those directions. So, you will result in highly conducting nanowires. With this method of the negative template based electrodeposition synthesis you can get dense continuous and highly crystalline nanowires.

You can also control the aspect ratio of the metal nanowires. The aspect ratio is the ratio of the length divided by the breadth. Suppose, you have this nanowire or maybe better this nanowire, you find out the aspect ratio of this nanowire by calculating its length from top to bottom. If the length is say hundred nanometers and the diameter is, say two nanometers then the aspect ratio is 50; that means, 100 by 2 is 50. So, that is the aspect ratio. You can change the aspect ratio. If this is hundred nanometers and we make it as five hundred nanometers, then the aspect ratio will be five hundred divided by two, if the diameter of the rod remains the same. So, you will get an aspect ratio of ~~250~~two hundred ~~fifty~~.

You can control the numbers of aspect ratio by changing the length of the nanowires or the diameter of the nanowires. That control you have by choosing appropriate template, the diameter of the template, the diameter of the pores and the length of the pores will control the aspect ratio. Of course, how much amount of material you are adding is also important. If you have less amount of material than the length and breadth of the pores, then you will have not necessarily be guided by the aspect ratio of the pores, but will be guided by the amount of material that you are adding or into this nanoporous template. So, you can control the aspect ratio of the metal nanowires by monitoring the size of the pores and the amount of the material that you are adding, and if all those are fixed by monitoring the total amount of charge that you are passing.


This is another factor. Not only the cylindrical pores, their aspect ratio will matter. The amount of material that you are depositing matters and that depends on the amount of charge that you're passing. That will control the aspect ratio of these metal nanowires. So, in general this technique of negative template based electrodeposition allows you to make highly conducting nanowires and also allows you to make large scale nanowires with controlled aspect ratio.

(Refer Slide Time: 23:11)



Positive Template Method

- Use wire-like nanostructures, such as DNA and carbon nanotubes as templates.
- Nanowires are formed on the outer surface of the templates
- Diameter of the nanowires is not restricted by the template sizes and can be controlled by adjusting the amount of materials deposited on the templates
- Removing the templates after deposition, wire-like and tube-like structures can be formed

 NPTEL

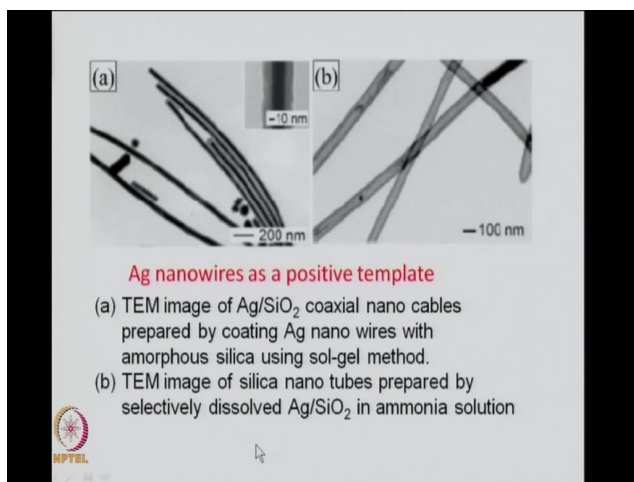
If you go to the positive template method, that is the other type of method, where you do not start with porous templates. You start with wire like nanostructures and then you make the nanostructure that you want around these nanowires. So, first you choose a nanowire which is now the template and then you grow a nanowire around it, on top of it. That will be your final material and then you remove the original wire, which was used as a template. This is called a positive template method. Here, you can use nanowires of DNA and carbon nanotubes as templates. These are commonly used as templates and the nanowires that you will form will be on the outer surface of the templates. Because, now you do not have any pores like in the negative template method. But you have a wire and you want to make nanostructures on top of those wire. So, your new nanostructures will be formed around the old nanostructures. So, they may be cylindrical if they form around them and maybe tubular in structure.

Or if they form on top of the nanowire, at the tip of the nanowire, which is being used as a template, then the new wire will form like that nanorod on nanowire. So, you can have both tubular kinds of structures as well as solid nanowire like structures by using the positive template method. The diameter of the nanowire is not restricted by the template size. This is one major difference between the negative template method and the positive template method. In the negative template method, the diameter of the nanowire that you are growing inside the template, is restricted by the diameter of the template. You cannot

make a nanowire larger than the diameter of the porous template you have chosen in the negative template method.

However, in the positive template method you can have any size of the nanowire on top of the template. So, the template diameter is not restriction to the diameter of the nanowire or nanotube that you are making. Now, removing the templates after deposition is important like in the previous case also. If you want your freestanding nanowires you have to remove the templates with suitable solutions after deposition. In this case also you have to remove the templates after deposition and then you can get your wire like or tube like nanostructures.

(Refer Slide Time: 26:01)



This is an example of a positive template method where silver nanowires have been used as a positive template. Here is a transmission electron micrograph: t e m image of silver coated with silica s I o two and nano cables we call, that means, there is a nanowire of silica, which is the template. On top of the silicon nanowire you have grown SiO₂ ~~s+i~~ ~~two~~ or silica. So, it is like a coaxial cable like the electrical cables that you see in and around you and in your house as one wire going inside and coloured polymeric wire or plastic wire outside. Similarly, here you have a silver wire inside, covered with a silica wire. This is called a coaxial nano cable and this is prepared by taking silver nanowires. On top of it you add some silica reagent which may be like tetra epoxy silane or some kind of a silane which can be hydrolyzed using the sol-gel method, and then it will

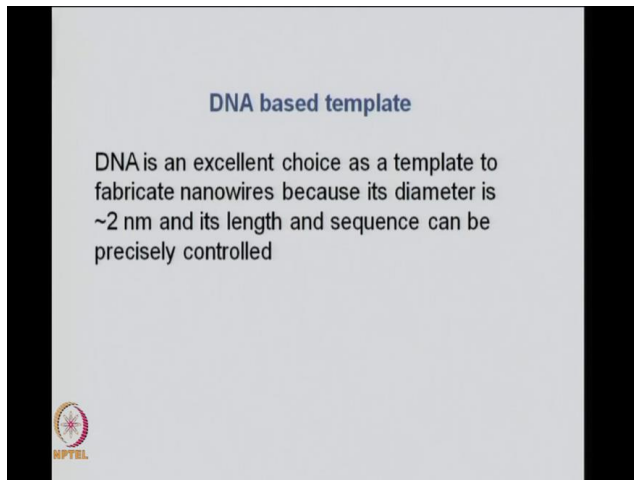
ultimately leave behind SiO₂ coated on the silica, on the silver wires. So, silica will get coated on the silver wires using this kind of sol-gel method, starting from some precursor of amorphous silica.

Amorphous is something which does not have a regular crystalline property. Amorphous is something, where silica is not having a ordered crystal lattice. Normally at low temperature synthesis you get amorphous nanostructures. If you do synthesis at higher structure at higher temperatures then you may lead to crystalline silica also. In this method, you get the amorphous silica coated on silver nanowires and as you see, the scale here is like two hundred nanometers. That means, this distance is two hundred nanometers. So, this diameter is something like fifty to seventy nanometers.

You can guess that fifty to seventy nanometers has both the silver as well as SiO₂ coated on them. Now, when you remove the silver or you dissolve the silver by adding ammonia: if you add ammonia then silver forms a silver amine complex, and that complex goes into solution. That is why silver is actually from silver metal it becomes silver ions and it goes in solution and you can wash away that is in the presence of ammonia. What is remaining is only silica. So, this tube you can see, it looks empty inside whereas, here it is very dark inside. So, all the silver which was inside this tube has been removed by leaching away the silver using ammonia. So, ammonia is being used to remove silver as a silver amine complex and you are only left behind the solid part, only SiO₂, which is the silica. It is hollow inside so it is called a silica nanotube.

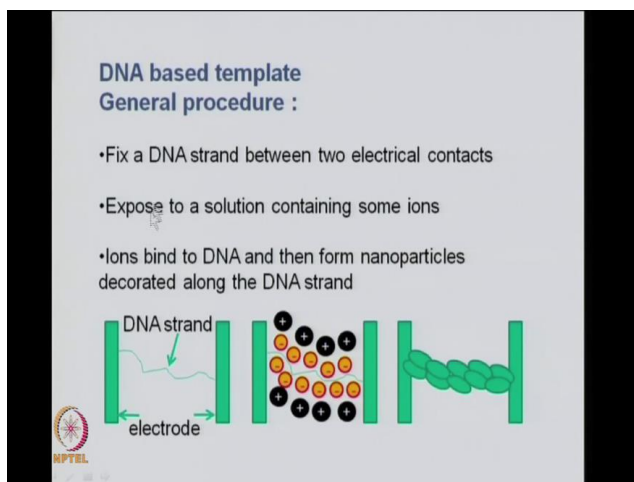
It is not a nanorod or a nanowire, but it is a nanotube. Because, it is hollow inside. If it was filled with silica then it would be called as silica nanowire or silica nanorod. The diameter of this, as we discussed, is probably around sixty or seventy nanometers. Of course, the length appears to be longer than, maybe one micron. So, length can be long and diameter is much shorter, and normally for most applications, you need very long wires which are thin for most of the applications. So, you need high aspect ratio. Large length and small diameter is what is preferred. So, high aspect ratios are preferred for most of the applications. So, this is an example of using a positive template method to obtain silica nanotubes using silver nanowires as the positive template.

(Refer Slide Time: 30:49)



You can also use a DNA as a template. DNA, as all of you must be knowing, is a deoxyribose nucleic acid. It is a kind of nucleic acid. It is also called the molecule of life. It is present in all kinds of living organisms and its structure, it has got a double helix structure. They are like two wires which are going in a helical fashion and this helix forms a very nice template for doing further synthesis and you can fabricate nanowires. This DNA helix has a diameter. If you consider this DNA as a wire, it has a diameter of around two nanometers. The length of the DNA can be very large. So, the length of the DNA can be controlled and also the sequence, that means, this DNA is made up of many kinds of nucleic acids and the arrangement: what kind of sequence it has?, can be controlled. You can then depending on the sequence, generate structures of your choice. So, the length and sequence can be controlled and hence, whatever you are going to make based on DNA templates can also be controlled to some extent.

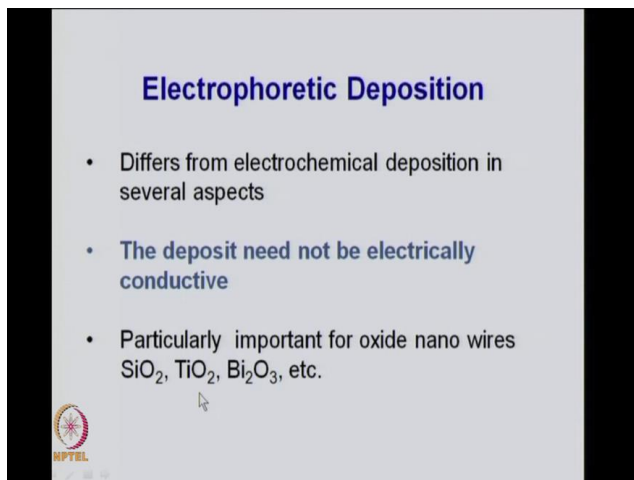
(Refer Slide Time: 32:29)



This is a general procedure where you have a DNA strand. You take a DNA strand and you connect it between two electrodes and then you bring a solution containing ions near this strand. So, you have this DNA, going to act as the template and charges these ions which are here. They arrange themselves around the DNA in a particular fashion and these are all negatively charged which are aligned here.


Then, they form nanoparticles which are decorated along the DNA strand. So, this DNA strand connected to two electrodes, can lead to synthesis of nanoparticles, which is guided by the structure of the DNA strand by using a positive template by considering DNA strand as a positive template you are growing nanoparticles around it in the presence of some electrical potential. You have electrochemical potential here and this is a positive template based electrochemical synthesis. We looked at some negative template based electrochemical synthesis to give rise to nanostructures and we also looked at some positive template based techniques to grow nanostructures. In this case, we grew silica on top of silver and here we used DNA as the template. We can grow other material depending on which ions you are choosing here you will have nanoparticles forming along the DNA strand.

(Refer Slide Time: 34:29)



Electrophoretic Deposition

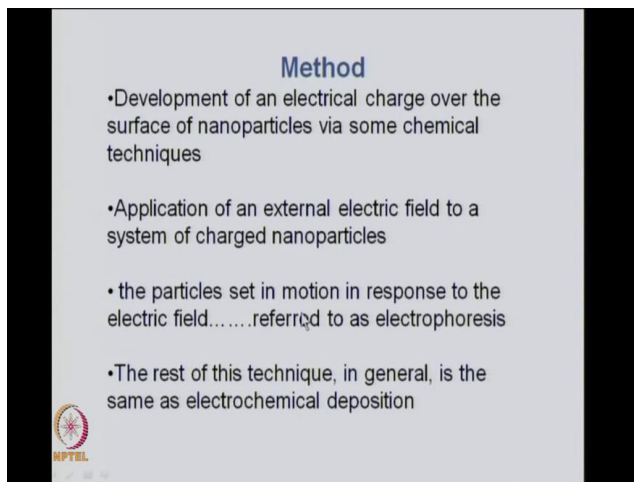
- Differs from electrochemical deposition in several aspects
- **The deposit need not be electrically conductive**
- Particularly important for oxide nano wires
SiO₂, TiO₂, Bi₂O₃, etc.

 NPTEL

So far we discussed what is a electrochemical deposition and as we said, maybe repeatedly that electrochemical deposition is normally possible when you have a material which is highly conducting. So, what happens when you have materials which are not very conducting, for example like silica, or bismuth oxide or something like that. Then it is difficult to make wires out of them using the electrochemical technique. Then we use what is called the electrophoretic deposition technique.


It has some aspects of electrochemical deposition. But, it is also different in certain aspects. The first most important point is that the deposit need not be electrically conducting in this case, which is important in the case of electrochemical deposition. Here the deposit need not be electrically conducting. Finally, what is being deposited on your template need not be electrically conducting. So, it is a very good method for variety of oxides or other insulating materials, if you want to make nanowires out of them.

(Refer Slide Time: 35:52)



Method

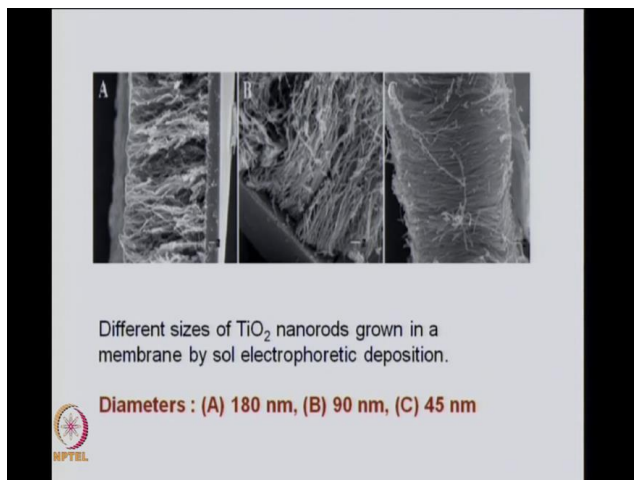
- Development of an electrical charge over the surface of nanoparticles via some chemical techniques
- Application of an external electric field to a system of charged nanoparticles
- the particles set in motion in response to the electric field.....referred to as electrophoresis
- The rest of this technique, in general, is the same as electrochemical deposition



The method is you generate a charge on the surface of the nanoparticles. The nanoparticles themselves may not be highly conducting, but you generate an electrical charge over the surface of the nanoparticles using some chemical techniques. Then you apply the electric field. So, electric field has to be applied like an electrodeposition. But here, first you generate a charge over the surface of the nanoparticles since the nanoparticles themselves do not conduct electricity, because they are not highly conducting. But, once you have this electrical charge over the surface of the nanoparticles, then when you apply an external electric field, the particles will respond. They will move with respect to the electric field, and normally we call this as electrophoresis and this effect is the electrophoretic effect.

That is why it is called an electrophoretic deposition. Because, you have some charges on top of the nanoparticles and then the applied external electric field makes this nanoparticles move, because they are having some charges generated on them. The remaining technique after this is just like the electrochemical deposition. So, you have a template and the charges make the nanoparticles move in the presence of electric field and then they settle down in the crevasses or in the gaps or in the pores of the template like in electrodeposition.

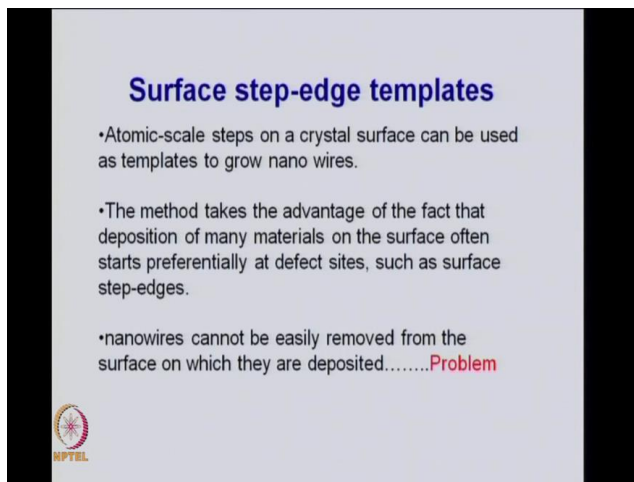
(Refer Slide Time: 37:31)



This is the electrophoretic method. This is an example of titanium dioxide nanorods which have been grown in a membrane by a sol electrophoretic deposition. So, you basically have TiO_2 particles, and you generate a charge through some methods, some chemical method, and then you apply a voltage and make electric field, and make these TiO_2 particles gravitate or move under the electric field in the nanoporous membrane. They then sit down in those pores or get deposited and depending on your template, you can get diameters of the order of one eighty nanometers; in this case ninety nanometers and much finer wires as you see of forty five nanometers, a diameter of TiO_2 which has been grown using the electrophoretic method.


Both these methods, the electrochemical deposition and the electrophoretic method depend on application of an external electric field, but there are some differences in the two methods. In one method it is easy to deposit only conducting materials, but in the other method you can deposit even non conducting materials by generating or making them charged by using some chemical methods.

(Refer Slide Time: 39:07)



Surface step-edge templates

- Atomic-scale steps on a crystal surface can be used as templates to grow nano wires.
- The method takes the advantage of the fact that deposition of many materials on the surface often starts preferentially at defect sites, such as surface step-edges.
- nanowires cannot be easily removed from the surface on which they are deposited.....**Problem**

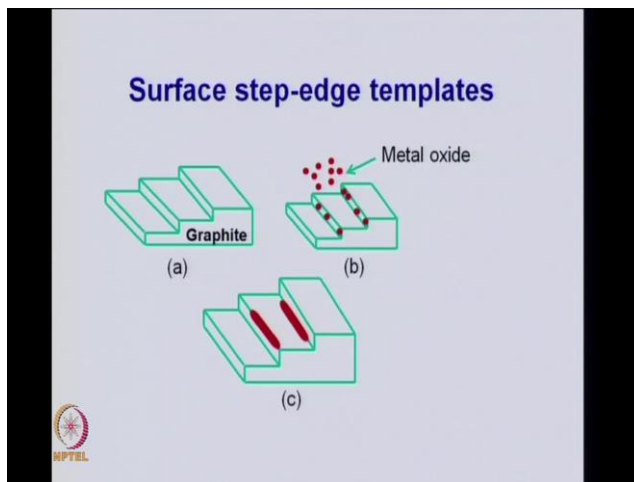


There is another method which is a slightly tricky, is what we call the surface step edge template method. Here, we know that an atomic scale; if you look at crystal surfaces there are always steps in crystal surfaces, these steps or kinks as we call them on crystal surfaces. These are the edges can be used as templates to grow nanowires. This is because, it is the tendency of any material, that it starts growing from defects sites like some corner, some edges where the crystal is not continuous.

So, this is a natural behavior and thermodynamically, it is known that most of the growth of a new material takes place on crystal surfaces, where there are edges and kinks. That is what is used in this surface step edge template method. The nanowires are growing at these edges. The only problem is that these nanowires cannot be easily removed from the surfaces on which they are deposited. So, that is a problem in this step page template method, where you are trying to use a you know well known fact that growth of new materials normally take place on some edges and kinks of surfaces.

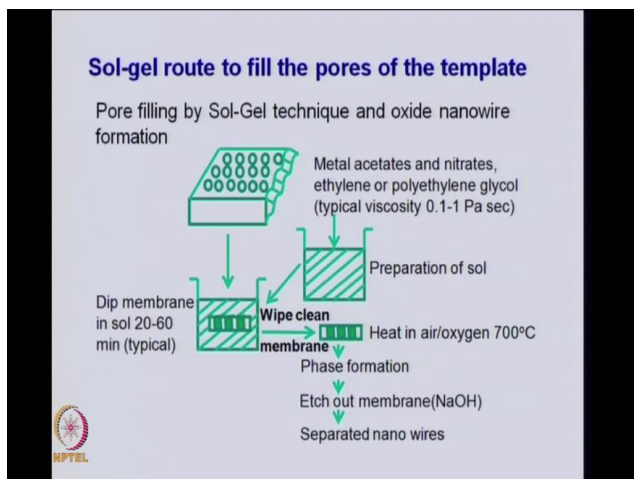
Formatted: Not Highlight

(Refer Slide Time: 40:48)



This is an example. You have a graphite surface which has got these kind of steps and then your particles, whichever nanoparticles you want to make nanowires out of them and you start depositing them. They start collecting at these edges and when they start collecting or growing at these edges, you get these nanowires. That is what is called the surface step edge template. So, these edges on the surface are acting as templates and you can get these nanowires. The only problem is these nanowires are not easy to remove. Once they form it is not easy to remove these nanowires from these edges, but if you can then this is also a good technique to grow nanowires.

(Refer Slide Time: 41:41)



Now, more commonly and a method which is probably used to a large extent is the sol-gel route to fill the pores of the template. You have a template. This is, suppose your template, which has got many pores and these pores can have diameter of the type that you want the wires to be grown in them. You can make your template accordingly choosing the diameter of the pores, and also the thickness of the template will guide how long will be your nanowires which you want to grow within this template. So, in this sol-gel route, you have the template with the nano pores and then you make a sol. A sol is typically a system of colloidal particles.

You have a particle, say some metal hydroxide or metal oxide or whatever. In general you can have metal salts like nitrates, acetates, oxalates which dissolve in ethylene or polyethylene glycol. It makes a kind of network; this polyethylene glycol and this metal form a kind of network, but this network is fluid at this time. That is called the sol. When you have this sol, is kind of a translucent clear thing if the particles are very small. So, there may be particles which are very small and not seen by the naked eye, but of course, you can use optical methods like light scattering, etc. to see the structure of the sol.

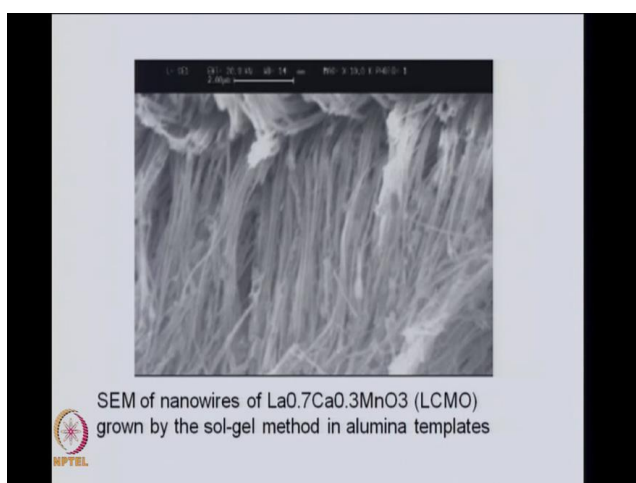
You have some very small particles in this liquid. It is like a dispersion and then you take this porous template and dip it inside this sol. You have this porous template and you dip it inside the sol. Typically, you spend some twenty minutes to one hour or two hours and then take out this template from the sol. So, this template has these pores and the sol has gone into these pores. When you take it out and wipe it, only the sol will be inside these pores. Then you heat it in air or oxygen depending on what kind of oxide you want. If you want an oxide which is rich in oxygen, then heat in oxygen. Otherwise, you can heat in air. That would depend on whether the metal oxide that you are making the metal has multiple oxidation states or not.

However, if it has only one stable oxidation state then normally, it will, you heat in air or oxygen or whatever, it always become that oxide. Typically, you heat around seven hundred or eight hundred around this temperature and you will have this sol which went in the pores, gets solidified and they are present in these pores. Then you have to take out your template. You have to etch out the membrane taking out or dissolving anything, like a solid, is also called etching out. Here, if you have a porous material in which you had these sol and the sol even here are like droplets inside, but once you heat in air at seven hundred degrees then it has become particles inside. So, you have got you particles.

They are of the shape of these original pores and then you etch out the membranes. Take out the membrane. This is the part of the membrane; this is the top view and this is the side view. This membrane will go away if you etch it in a liquid which can remove or dissolve that material. Normally, this is aluminium. Then you can etch out using sodium hydroxide and only these particles will remain. Then you can remove depending on the depth: if these are long then you get nanowires or you can get nanorods if this depth is not too much. You have to remove the template by etching out with sodium hydroxide.

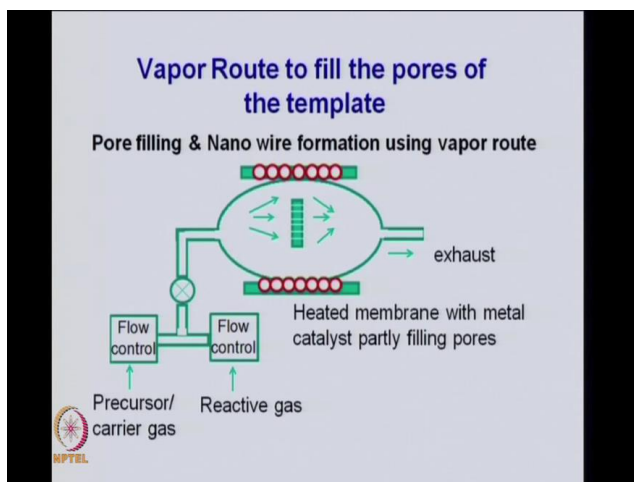
So, this is one of the most common methods and very widely used method where you use the sol-gel process. This is the sol and after you heat it, becomes a gel and then an oxide and that remains within the pores. The remaining template is etched out using sodium hydroxide. This is a very common technique of making nanowires.

(Refer Slide Time: 46:41)



This is an example where you used a sol of lanthanum calcium manganite and you used a template. Here they have used alumina templates. You can use alumina templates which are available either in the market or you can you even make them. Depending on that pore size you will get the nanowires of the material that you have chosen. Diameter of these wires will be controlled by the pores size of the alumina templates. So, this is made by sol-gel method. First you have to make a sol of this and dip it in your alumina template inside the sol solution and then dry and heat it. You get the oxide and then you remove the alumina template.

(Refer Slide Time: 47:35)



This was a sol-gel method, that is, we are going through solution or liquid method of filling the pores of the template. There you have a liquid and you have a solid, that in solid was your template. You dip it inside the liquid which is the sol. Then you get the solid nanowire or nanorod inside the pore and you etch away the template.

Instead of filling with liquid, you can also fill the pores of the template with gas or vapour. That is the vapour route to fill the pores of the template. You can do this also in several ways. We can discuss one or two. You have a chamber and this is like a furnace. This is showing the heating zone. You have a heating zone or a furnace where inside you have placed your template. This is the template or the membrane you can call it. The membrane may have some metal catalyst which will react with your vapour or decompose the vapour to form the particles that you want within these cylindrical pores present in the membrane or the template.

But here we are not passing any liquid. We will be passing a vapor. How do you pass the vapour? If you see here, there is a flow control. That means, I can have a controller with a gauge, etcetera. I can exactly monitor how much gas I can pass from here. Similarly, there is another flow controller here because I have two types of gases. I have a precursor or a carrier gas, which is normally not the gas which is going to give me the compound, which I want. It is only a gas which is inert and it helps movement of the gas and other particles. It gives pressure or movement of the particles and the reactive gas.

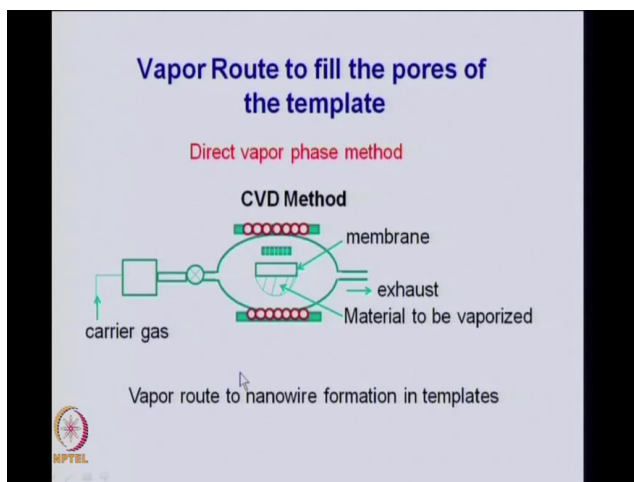
The reactive gas actually gives the particles which you want inside the pores, which will lead to the nanowire formation. So, you have two entry points. One from this side and one from this side and then they mix. They will mix here and then go together. This shows a valve. That means, \bar{I} can control the mixed flow. Once the two gases mix I can control the flow here. I can make the flow very high. So, lots of gas molecules going per unit time are very slow. I can even control the ratio of these two. Suppose, my carrier gas can be, say nitrogen or argon or helium gas, these are normally the gases which are unreactive.

So, they do not participate in the reaction, but they make the flow of the other gas more easy. The reactive gas will be the gas which you want to make the particles or these nanowires or nanorods in this case. This mixture \bar{I} can vary by controlling the flow. I can pass say, hundred molecules per second of this gas and say, five hundred molecules per second. That is you are passing lot of these reactive molecules. If I want to have less molecules coming here, then I increase my carrier gas pressure. Instead of hundred molecules per second I increase my flow to say, five thousand molecules per second.

The carrier gas molecules will be very much large in numbers compared to the reactive gas. When the mixture is going, the density of the reactive gas molecules will become much lower. Basically, I can control how many reactive gas molecules are falling on my template per unit time. If I do that and when it is falling here on the membrane, it is already being heated. So, reaction takes place and the nanowires or nanotubes form. Remaining gasses will all be taken out through an exhaust here, so the solid particles, which form at high temperature, because this is being heated.

The gas comes, this reactive gas and you have this metal catalyst and high temperature is there. That deposits nanowires of solid material inside the porous membrane or the template and remaining gases come out. So, this is a vapor route to filling the pores of the template and getting nanowires, not like the sol-gel method where we use solutions, here we are using gases, we are using a carrier gas and a reactive gas.

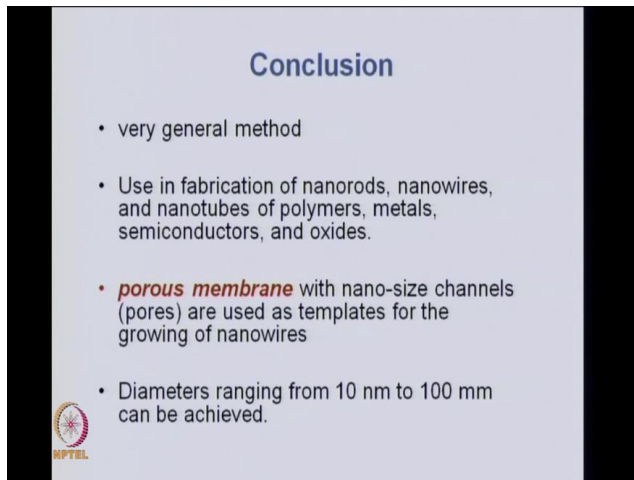
(Refer Slide Time: 53:06)



There is another method where you can use the same vapour route, but it is a simpler method. You do not have two, the carrier gas and the reactive gas; you have only carrier gas on this side. The reactive gas, instead of the material which has to be deposited being in the gaseous form; it can be in a solid form and it is kept here, suppose I want to deposit some material in my template, which is the membrane. This arrow actually should be here. So, let me correct it. This is the membrane and this is my material which is to be vaporized and you have this furnace. When you are heating the furnace then material from here will vaporize and fall on this membrane. There is a carrier gas coming from here which keeps the pressure on this side. So, nothing will go on this side.

So, whatever vapors are being produced, this is like a CVD method of the chemical vapour deposition method, where you have these materials, which is a solid or a liquid and then it is vaporized, and those vapors react with your membrane or template and form your nanowires. This carrier gas which is coming, whatever other gases are formed during this reaction, it pushes them out through the exhaust. The vapor route can be two types. You can have your reactant, as a vapor coming through this channel or you can have your reactant to be a solid and vaporized within this chamber like the CVD method. That also can make particles on these templates or membrane material which has got this columnar or cylindrical pores and that way also we can make the nanowires.


(Refer Slide Time: 55:33)



The slide is titled "Conclusion" in blue text. It contains four bullet points: a general method, use in fabricating various nanomaterials, use of porous membranes as templates, and a range of diameters from 10 nm to 100 mm. A small NPTEL logo is in the bottom left corner.

Conclusion

- very general method
- Use in fabrication of nanorods, nanowires, and nanotubes of polymers, metals, semiconductors, and oxides.
- *porous membrane* with nano-size channels (pores) are used as templates for the growing of nanowires
- Diameters ranging from 10 nm to 100 mm can be achieved.



So, the conclusion is that this method is quite general. We can use this in fabrication of nanorods, nanowires and nanotubes of polymers, metals, semiconductors and oxides. You need to have porous membranes with nano size channels as templates and you can make wide variety of diameters, ranging from ten nanometer to hundred millimeter.

-So, we conclude this lecture today and we will be continuing our course on these nanostructured materials- synthesis, assembly and applications in my next lecture.

Thank you.