**Physics of Functional Materials and Devices**
**Prof. Amressh Chandra**
**Department of Physics**
**Indian Institute of Technology Kharagpur**

**Lecture – 07, Week 2**
**Synthesis protocols - II**

Welcome to the second lecture of this second week. In this lecture, we will continue with the details of synthesis protocols that are routinely used to fabricate the functional materials which we have been discussing till now. In today's lecture, we will continue with our discussion on top-down approaches and bottom-up approaches. We will also take some examples to explain to you the usefulness of various techniques and I will also give you some examples which you can carry out in your research laboratory or you can go to any laboratory in your department or schools where you can carry out these simple reactions and you will get a novel material. We started in the previous lecture by classifying the synthesis techniques into two broad subheadings. The first was bottom-up and the second was top-down.

We also explained the way these two are different from each other. Let us today start with a very simple technique that is commonly used and that is solid state synthesis protocol. As the name suggests, this process consists of heating two non-volatile solids and the initial raw materials are also in the solid phase and then they react to give you the required product. Basically, this solid-state technique consists of two primary steps.

Step number 1, this step consists of weighing the desired quantities of the precursors. So, suppose you want to make barium titanate which is $BaTiO_3$ as a material. Now, what you have, you start with barium carbonate as one of the raw materials and titanium dioxide as the other material. You have to mix them, but their molar ratios must be correct so that you get a stoichiometrically correct material that is $BaTiO_3$. So, you have to weigh the materials according to the molar ratios required in the reactions.

Once you have powders, you then grind them together in an agate motor vessel, then you heat them in a ceramic crucible using a heating unit which you call a furnace and the typical temperature range you are talking about to obtain single phase materials using solid-state synthesis protocols are between 800° to 1400° C. This is what the typical range is, but it is not a fixed temperature. I repeat it is not a fixed range, it can be slightly higher or it can be slightly lower than the temperature range which I have just mentioned. But please remember you are looking to get a temperature range in which you will get the single phase of the materials. This is absolutely essential.

So, what do you do? You actually start with a precursor, then you weigh the second precursor and you mix them in a motor vessel. So, if you look into this video, you can see

that this is a typical agate motor vessel and two compounds starting raw materials in the solid state are actually being mixed. But if you see the way the motor vessel is being rotated is just not in one direction, it is in figure 8. So, you are drawing the figure of 8 in the motor vessel while you are mixing the powders. And, why do you do it? It is very critical to understand that if you just take two powders and move them in one direction, then it will not lead to homogeneous mixing.

You can have regions where precursor A is dominating and you can have a region of precursor B which is in higher concentration. But what do you want? Homogeneous distribution of precursor A and precursor B, so that when the chemical reaction takes place, you have the required reactants near each other to give you the desired product. So, figure 8 actually cancels any preferred orientation or motion of the particles and ensures what? Homogeneous mixing of powders, so that when they are taken into a furnace, then you have the reactants which are homogeneously mixed and you get the desired reactions taking place. So, this is critical and this information is many times not mentioned in the books. Now, this was the example where we had taken a solid state simple gate motor mixing and then taken it to high temperature and the reaction took place.

There is an additional step that was introduced and that led to the process of the ball milling method to get the desired products. So, what you would do in a ball milling process? In this process you would grind the materials that are larger sized into extremely fine powders or much smaller size particles in comparison to the starting particles. And then you will ensure that the size of the particles is much smaller and they are also uniformly or homogeneously distributed in the whole mixture. So, you would increase the homogeneity and reduce the size of the reacting particles, and therefore, when you take this powder into a furnace, then the reactions between smaller size particles become even more uniform and you get homogeneously grown particles and the single phase formation is expected in this ball milling method. And the homogeneity or purity of phase in the ball milling method is going to be higher than what you see in a solid state mixing.

Why? Because there you are using just the pressure which you are giving by hand and then you may actually end up getting tired and you will not be driving the figure of 8 in the motor vessel and inhomogeneities get introduced in the mixtures. And when you have the reaction taking place you do not get the pure single-phase material. So, what is there in a ball milling? You have these balls that are called milling balls. So, you take a jar, you drop these milling balls and you mill it. So, they are made to revolve, it can be both horizontally or vertically depending upon which axis you are talking about.

And as the rotation takes place the balls fall from different directions, and they hit the wall of the jars. And now if you see two balls what happens? When one of the balls is coming from one direction, the other is coming from the other direction and there is a powder in the middle it gets crushed, it gets crushed and then you have the larger size particles being

reduced to smaller sized. In addition, when the balls hit the walls of the jar there is also some powders which are there and then they get crushed here also. The rotation is such that for some period there will be clockwise rotation and then you will have anti-clockwise rotation. Why? Again you need to cancel any preferred directional movement of powder.

So, if the powders are moving in one direction then you need to then move it in the anti-clockwise direction so that the mixing is homogeneous. Now, if I ask you one simple question, you have one solid particle then you have another solid particle, you mix it and then you drop a ball on top of it. So, what will happen? And then you rotate. What will happen? These solid particles if I take a jar will then get deposited at the bottom and the balls would be moving at the top. So, you will have solid powders at the bottom and the balls are only moving at the top which will lead to mixing or it will lead to in homogeneity.

Obviously, it is not going to lead to mixing it is some kind of mixing, but only at the surface. Therefore, what you need to do in addition to this you need to add a mixing media. That mixing media is what is mostly an organic solvent, but in this, you choose an organic solvent that does not react with the raw materials or precursors that you are taking in the ball mill. Otherwise, there will be some reactions organic reactions taking place and then you will get secondary phases that are forming. So, mostly acetone is used as the mixing media or methanol is used as the mixing media.

So, now, you have a slurry you do not have solid powders, but you have a slurry and now when you are moving the balls you are moving in a slurry and therefore, this liquid-like phase can accommodate balls within it and then you can rotate it more easily. And that is why you have seen when you are making dough for idli or dosa then when there is a mill moving you drop some water in it. So, you have uniform mixing and the dough is actually getting the proper shape, and the dough is then later on used. That is why you have this additional component which is there. And as a function of time, you can see that you will go on getting a much smaller size particle.

Between the two balls, you will get laminar flow and because you have a laminar flow why because there is a distance up to which these balls will be able to reach and then there is a powder. You cannot transfer the complete energy of the balls to the particle and there is a limit to it. So, the balls will come and then there is a particle, but then you will have a laminar flow which means, similar size particles and they are between the balls. As a function of time with continuous mixing and grinding you can have homogeneity levels which are much higher than what you get in the solid state technique. And nowadays to get materials which are easy to fabricate you can produce them in bulk the technique of ball milling is extremely useful.

Till few decades back the technique of ball milling was only considered as a top-down approach. That means, you have a material you put in a ball mill and it will reduce the size,

but now this can also be used in bottom-up approaches where you take precursor 1, then you take precursor 2 and then you can react in a ball mill that is called solid-state synthesis and you will get the desired product. So, this is a very unique technique that can have the characteristics of both top-down and bottom-up. This is an example of actually a bottom-up technique, but using a ball milling method. You have a material like sodium titanate.

Other materials are used from sensors to batteries to capacitors to optical capacitors to optical sensors and solar cells. So, this is a kind of material that is being used in many places, and making this material is so easy that you would find why can we not make it routinely and then take it to industrial application. You just need to take sodium carbonate reacted with titanium dioxide and first mix it in a motor vessel so that at least you have a certain degree of homogeneous mixing then you take it in a ball mill this is a typical Resh ball mill in my research team and then you ball it for 4 hours. So, ball milling you have a run time then a stop time then a run time in this typical planetary ball mill. First, you will run let us say for 15 minutes then stop for 5 minutes then another 15 minutes it will be in the anti-clockwise direction if the previous cycle was the clockwise direction.

Then it will be run for an effective 4 hours. So, it is the 4 hours of running time of the ball mill not the run plus stop time it is the running time that is given. Then you dry the powders and what you get is particles which are having the chemical formula of sodium titanate and their typical shapes are given in this SEM micrograph. So, you can clearly see you have a microbar type morphology and the shapes in the particles have shapes of microbar in size which is typically in the range of 400 to 500 nanometers in length and the dimensions at the top are somewhere around 100 nanometers to 200 nanometers. Because of the simplicity ball milling is finding application in a large number of industries.

It is used for mixing, blending, dispersing, amorphization of materials, and mechanical alloying. It is easy that is essential to understand it is an easy protocol. It is cost effective it is very reliable if you have the same raw materials if you maintain the same temperatures then you can get similar materials batch after batch after batch. The reproducible results are high because you can control the energy and speed at which your ball milling would be rotating. You can apply it in wet and dry conditions.

So, it is easy and you can make a wide range of materials from polymer type to oxide type materials. There are certain disadvantages. The primary disadvantage which is associated with the ball milling process is the possibility of contamination. Now, you will say why contamination and this is true for most of the techniques which we will discuss. You must understand that there is a possibility of contaminating your material.

Why? Now, if you take a jar typical jar that is taken when you are mixing hard materials is made up of zirconia. Zirconia is not a cheap material. If you take a 100 milliliter or 100

ml jar of zirconia in today's market it may cost you somewhere around 2 lakhs to 3 lakhs. This varies I am taking a rough estimate it can be slightly less or it can be slightly more.

So, it is quite expensive. If you want to go to a slightly cheaper material that also is a submarine grade stainless steel. Why? Because if you take a soft material-based jar then when these balls are going to hit the jars the jars will deform and they will break. So, you need to have a jar that is made up of very hard material that does not have any deformation or degradation during the reaction. Otherwise, the material from the jar surface will start eroding and coming into your material. So, you need to have a jar of very very hard materials and therefore, the cost of the jar is very high.

Now, suppose one day you want to make barium titanate. The next day you want to make sodium titanate. Will you buy a new jar? No, you will not buy a new jar. What will you do? You need to ensure that the jar is properly cleaned, and dried, and then only it is used. Otherwise, the reactants from the previous cycle reaction which was carried out in that jar will contaminate the next round.

Therefore, cleaning the jars becomes a very very careful and essential step in the ball-weighing process. Cannot be ignored this one-hour process it is not an easy process you have to clean it in a way that you have to clean it with water then DI water then you have to clean it with very dilute acid then dry it and sometimes you have to pass dry air. So, as to ensure that there is no water in it from the previous cycle which can be on adsorbed on the surfaces. Then only you can use it in the next cycle and that is why the possibility of contamination is there sometimes if you do not follow this step you may end up getting impure materials in the next cycle. No matter what you do there would be a limit to the size you can get using these ball mills and therefore, you can have a limit to the shape and size which can be obtained using the ball milling technique.

Obviously, this is a technique that has the limitation that it needs lot of time. The typical time to make an oxide material is 12 to 24 hours with the laboratory-scale planetary ball mill. If you go to an industrial scale then that process can be brought down because the energies you can transfer us are much higher, but then the cost of those ball mills are also much higher. But at the laboratory scale you are looking at a synthesis time of 12 to 24 hours this is just the milling time. Then there is a drying time, then there is a collection time, then you have to if there are any agglomerates then you have to use the motor vessel once again to break the agglomerates which may form during the drying process.

So, the reaction time can sometimes be quite long. Then comes the next technique which is called hydrothermal synthesis. As the name suggests you are having a reaction where it is high temperature and high pressure is both used and you are using it in a liquid phase reaction. So, hydrothermal. In this process, the concentration of precursors is taken to be low so that you can perform the reactions.

So, what do you do? Generally, what is the process? You take reactant A, then you take reactant B, mix it together, and heat it and then you say the reaction is going to take place. But in hydrothermal you do an additional step you also increase the pressure. So, you can also form materials by increasing pressure you can see all around that you can take one material, then you can take another material and then bring them together with high pressure and then you can have a third material being formed. So, we use the advantages of both high temperature and high pressure in the hydrothermal synthesis protocol. Generally, it is carried out in a stainless steel autoclave and at high pressure.

So, this is the stainless steel chamber that we are talking about. What do you do? You take the reactants or reagents, then you have solvents example water in them. The inner lining is of Teflon so when you react is taking place and after the materials form you need to take the crucible out and collect the powders. Then you have the stainless steel lid from the top and then you tight it with a screw and you also have the safety mechanisms coming in because if there is very high pressure it gets built up. Why high pressure? Please remember when you are heating this chamber when you are heating this chamber, the solvents are also getting evaporated, then you have the possibility of volatile compounds coming out of it, the reactions leading to the release of exothermic energy, then you will have high pressure inside the chamber and this pressure is not going out.

So, it is just like a pressure cooker and if the pressure is increasing tremendously because of some factor that the temp for example, the temperature could not be controlled, then you must have a safety mechanism which releases the pressure otherwise this whole chamber will explode. The temperature gradient is always maintained at two ends of the reaction vessel. So, you have a uniform temperature at both ends so that you can have the desired temperature gradient. It is a gradient. So, from one end to the other, you have a gradient, but at the ends, you maintain the temperature.

I have already discussed why we need to have nutrients supplied with solvents like water so that you have a reaction uniform mixing of the solutions and then you have a homogeneous distribution of the reactant species. At the hot end, the nutrients dissolve and deposit on the seed crystal at the hotter end. So, you break the nutrient and then you react it with the seed crystal, and as the temperature is increased this reaction takes place and the crystal grows and then you can have the growth of the material. This is a typical example that you can try for making carbon and carbon you believe is a very simple material. It is one of the most useful materials which you have around.

You have talked about let us say coal and coke, and you have talked about activated carbons, but there are various types of carbons that are there and are being used right from your toothpaste to aero planes. You have different types of carbons being used. For example, let us take an example of how to make a carbon microsphere. So, you just take

dextrose, take dextrose. Then you throw it in an autoclave of a hydrothermal method and heat it at 160° C for 6 hours.

This will drive the polymerization and condensation process once the system cools down you have the nuclei. Then what will happen is you let it cool down and then slowly these nuclei will agglomerate and then they will start forming larger-sized nuclei. Then you give more time for these particles to form and slowly you will be depending upon the time which you are giving you will go to much larger size particles. Once you calcine and then remove the solvents you dry these particles the solvents will go out and you will be left with the carbon microspheres. Similarly, by playing with the temperature one here it was 180° C here it is 160° C and the time let us say initially in the first case it was 6 hours now you are 10 hours you can go from one shape to the other and you can go to nanosphere.

So, from larger size spheres to smaller size spheres. You can also make materials that we have discussed earlier using this technique that as hydrothermal sodium titanate. Here what do you take you to take titanium dioxide and sodium hydroxide in deionized water and heat it this material at 180° C for 24 hours you will have the contributions coming in from both high pressure and high temperature after drying and washing the powder which you have obtained you will get single phase materials of sodium titanate and the shapes would be very different. So, you are using another technique which is very simple, but please remember do not try this in any uncertified jars because of high pressure it can have very serious consequences. So, these reactions must only be performed in certified jars that can sustain high pressure and high temperatures which are seen in a hydrothermal process.

Although simple it should be carried out very carefully. Another material that can be synthesized which you can see is $V_2O_5$ and has a large number of applications. Can you find the number of applications for this material? You will be amazed to see the range of applications this material has just go and try to find out. In addition to that look at the picture of the form particles they are very different. Earlier you were getting rod like particles or flake-like particles, but now you are getting nano-sheet-like particles you are getting sheet-like structures you can clearly see here if they are sheet-like particles their lengths are much bigger, but if you see their dimensions are very very small. So, by playing with the temperature time and the starting reactants you can tune the morphology that is the shape and size of the particles using the hydrothermal method.

Again it is a simple process you can fix the temperature if you have the known amount of solvent and the precursors then everything is constant and it can be reproduced batch after batch. So, you can have a high yield with good morphology same crystalline phases and crystal structures and you can have high homogeneity, but because of the nature of autoclaves that should be used it becomes expensive. If not performed carefully it can lead to safety issues and then you can have uncontrolled growth if you do not monitor the reaction times and every reaction is taking place inside a closed jar. So, you cannot observe

the reaction processes it should not be the jar should not be opened when the reaction is going on. Then comes a very nice method which is the mini emulsion method of making materials.

Here you have emulsions. So, you take emulsion in which particles are dispersed and then you have reactions taking place at the interface of the oil and water phase. So, you have two phases, you have two phases one phase is called the oil the other is the water phase and then there is a boundary that is forming. Then the reaction takes place at the boundary and you can change the shape of the particles by changing the nature of the interface that forms and you can start going to many novel structures which in this case you can see are hollow particles. Till now you have seen solid particles, but now the world is moving towards the utilization of novel structures which are hollow in shape. What do I mean? They have a cavity in the middle and they have a much higher surface area therefore, their properties mostly chemical properties are much more higher than the solid particles.

This process gives you the way to have hierarchical structures. One of them which I discussed is the hollow structure and you can also have very high vapor pressure near the melting points. These advantages are they are thermodynamically unstable if you do not have a stable emulsion forming then you will always end up getting inhomogeneous materials and you cannot use those kinds of materials. So, it can only be used if the emulsion is stable. Because of the nature of the reactors the nano reactors which are forming and they are being utilized you have these processes which are low yield processes. Then you have to wash and clean the solvents which adds an additional step in the whole process, this process itself is a lengthy process and therefore, it becomes a disadvantageous process or step in this mini emulsion technique.

Finally, in today's lecture, we have a discussion on chemical vapor deposition. So, we have talked about solid-solid reactions, we have talked about liquid-liquid reactions and now can we have vapor-solid reactions. So, this is an example of a vapor-solid type reaction where you start with vapor and you end up getting solids. It is a bottom-up method that can be used to obtain small-size materials. Mostly it was being used initially for thin film deposits on substrates, but now you can have the growth of certain nanostructures be carbon nanotubes or it can be the growth of any other nanotubular structures or wire-type structures on a substrate.

Mostly metal-organic compounds are generally used as precursors and surface topography of the substrate is one of the factors that play a critical role. You will understand this thing in the next slide, but this is the basis of the CVD process the chemical vapor deposition that is chemical reactions taking place in the vapor form of the precursors. The reactions take place in the range of 600 to 1100° C and the gas flow decides the nature of reactions that will take place and the kind of materials that will form. This is a typical CVD chamber or process.

So, as I said the technique is an example of vapor vapor-solid reaction. It is a thermochemical reaction. So, you have temperature and chemical reaction and you are taking advantage of both. So, you what you have? You have a reaction chamber let us say this is a reaction chamber. You have this source of precursor chambers. So, precursor A, precursor B, and then they are moving into the reaction chamber.

Now, how do you push these precursors into the furnace? You have the carrier gas. So, you have the precursor A and precursor B and then there is a carrier gas it can be argon or any kind of inert gas. So, it does not react with the precursor and then it pushes the precursors into the furnace. You heat it and then when you heat it you break the precursors and then you break them into small particles.

So, you have the carrier gas carrying the reactants. Then you have a cold finger which is at a lower temperature. So, these high particles move from the high temperature side and then they get deposited on the cold finger and the reactions take place in between in the furnace then they come and get deposited on the cold finger and finally, they then drop down the powder collector funnel. This whole chamber before you start has to have a vacuum. So, if you remove any kind of air in it that means you want to remove water content, you want to remove oxygen, you want to remove nitrogen and then you remove air from it and this is not a single step. First you go and go to the step of vacuum then you purge it with dry air, then you remove the whole air, then you purge it again, then you remove the whole air.

Why? Because after repeated purging and removal what you do? You ensure the condition that there is no water adsorbed on the surfaces of the chamber because water can really change the way reactions will take place between the precursors. So, you have vapors coming in reacting and then getting deposited and simply getting collected. As I said this is a technique which occurs between 600 to 1100° C, but what happens this is growth on a substrate. So, cold finger is acting like a substrate and now suppose you want to use this process in which you want to grow certain kinds of films or any kind of wires or any kind of electronic structures which are coated with another materials. If you heat the electronic structures or let us say your IC or the silicon bread board in this furnace and take it to very high temperatures let us say 600° C, then they will melt and you will not have any deposition taking place.

So, depending upon the range of temperatures you can have various sub classifications of chemical vapor deposition. So, for electronic circuits or depositing materials on electronic substrates which are used in the devices you use a technique which is called plasma enhanced chemical vapor deposition PE CVD. And there you have plasma being generated which drives the reaction, but the overall temperatures are much lower and the reaction can take place between 120° to 150° C hence the substrate that is an electronic board is not damaged. So, you can also have various types of CVD methods.

The advantages are it can coat the complex topographical substrate. So, the whole substrate can be coated at one go and uniformly it can be coated. It is useful to fabricate thin films and you can go up to nanometer range. It is cost effective once you have bought the whole instrument the apparatus is there with you, then it becomes cost effective and it is quite versatile because you can use different types of precursors you can take different kinds of carrier gas and then you can play with temperature you can play with pressure and you can get different kind of morphologies. But this involve chemical reaction.

So, it is not applicable for all types of materials. In some cases the difficulty arises of controlling the thickness of the deposited films in addition to what I said of high temperature use the toxic precursors may lead to certain problems in the first phase of the whole process. So, in today's lecture you have seen that there are many more techniques which are being utilized to define and tune the properties of final materials. We have discussed techniques like CVD, hydrothermal, solid state reaction and ball milling technique to obtain materials. Ball milling was mostly considered as a top-down process, but it can also be called as a bottom-up process of making materials.

And please remember every technique has associated advantages and disadvantages. No technique till now has been found to have only advantages and no disadvantages associated with it. These are the references which you can follow to obtain more information about the topics which were covered today. And in the next lecture we will continue with the synthesis protocols and discuss a few more of them. Thank you very much.