

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

**Lecture – 06, Week 1:**  
**Synthesis protocols - I**

Greetings once again. Welcome to the second week of this course on Physics of Functional Materials and Devices. In the first week, I gave you an overview of the type of materials which we will be studying in this course. But if you talk about materials, you should first know how to fabricate or synthesize or make a material. Then only you can understand the properties of those materials, tune that properties according to the need of the end user and then finally, make a device out of it. So, let us begin in this lecture the various ways by which you can make functional materials.

About the devices, we will come bit later. Let us start to discuss about the synthesis protocols which are routinely used to fabricate different types of functional materials. We will start with two major types of sub classification of synthesis protocols namely the top down approach and bottom up approach. As you will see that there are two general approaches which are followed to obtain the type of materials which we are talking about in this course.

They are the top down approaches or bottom up approaches. As the name says top down, it involves breaking down of the bulk materials into smaller size structures or particles or materials. In a very very layman language, I will give you an example of a top down approach. If you remember how do you get a wheat flour? You start with a wheat grain, take it to a mill and in that mill as a function of milling you get the flour. So, you, but wheat as a unit remains as a wheat.

It is only the structure has changed you have gone from grain to powder form. That is the typical way of top down approaches. Bottom up, so you start with smaller size materials, you can start as low as atomic level discussions and then you can go on making a larger structure. Again a very very crude example, if you want to make a wall let us say 10 feet by 10 feet, how do you make a wall? You make a wall by putting brick over brick and then you go in the x direction, the y direction and the z direction and that is what you actually follow and you get a wall and that is the way you are talking about the bottom up approaches. You bring smaller units together to obtain a larger side structure or unit.

So, if you want to understand using a cartoon, then you can see that you have for example, if this is the substrate on top you have the structure of which you want to have a smaller size structures. So, what you can do on this substrate, the structures which are on the top

are then cut into smaller pieces. And you can clearly see that the shapes of the bulk structure and the smaller size structures are quite different. In the other way if you talk about bottom up, you start with smaller units then you bring them together and what do you get? You get a similar shape structure. In top down bulk to fragments to nanostructures or any kind of structures which you want to obtain, but the structure which you obtain in the final phase is less in size than the starting point.

In bottom up you start with atoms or any other smaller units, then you go to clusters and then you can get similar shaped structures. For this I just took an example of a nanostructure because in the previous class we had discussed about the importance of nanomaterials and nanostructures in today's world. These two techniques the bottom up and top down techniques are sub classified into various headings. For example, these are just certain examples which I have taken. For example, if you can classify them into biological methods.

These biological methods they use bacterias or fungi, algae or any other biological templates to create a superstructure or a larger size structures. You can have chemical methods such as sol gel method to make a material, co-precipitation method or you can even go a step further and you can go to force co-precipitation method, hydrothermal method, chemical vapor deposition methods, the CVD, the emulsion both mini and micro emulsion methods or you can have solid state reaction methods. Similarly, the top down methods can include mechanical milling most common, ball milling method. Lithography if you talk about nanomaterials or nanostructures then nanolithography you can have various types of lithographies e-beam, optical lithography or you can also have ion beam lithography. So, even within a sub classification you can have different types of synthesis protocols.

Why I am telling you all this I will come to that in a minute. Then again in physical methods you can have laser ablation, you can have sputtering or you can have thermal decomposition. As I said why am I giving you so many types of synthesis protocols. The reasons are very simple. If you use different type of synthesis protocols then you can expect different types of materials and if you have different types of materials what do you expect? You expect that the properties of those materials can also be different and hence if the properties are different the applications of those materials will also be different.

Therefore, it is essential to investigate the fabrication of a particular material using various techniques and then optimize the synthesis protocol which gives you a material with a desired property that you want to extract from a given material. So, that is why we are giving so much of emphasis on the synthesis techniques to obtain the materials that were discussed in the first week. Remember if you want to do good physics get the chemistry right chemistry of what? Chemistry of materials right because if you have materials then batch after batch after batch you must be able to synthesize a given material with the same

properties same behavior. Otherwise, if you use a material whose property is changing from one batch to the other then the characteristic of the device which you are fabricating or designing would change from one batch of material to the next batch of material which comes in and that is utilized to make that device. And then the user will not like to buy a device from your company why because the properties of that device will be varying from one batch to the other and that is not what a user actually wants.

Another way to classify the synthesis protocols more so in nanomaterials are based on the growth mechanisms. What do I mean by growth mechanism? Suppose I have one particle and I have the other particle they come and join together to make an agglomerate you cannot distinguish the two particles this is one way of growth mechanism. Suppose you have one particle and the other particle comes and sits next to it, but you can distinguish between the particles and then you have an ordered and self assembly of these structures and you are able to distinguish clearly there is no agglomeration as such. So, depending upon the growth mechanism which gives you the overall structure you can have various sub classifications of the synthesis protocols. Again why are we trying to investigate so many synthesis protocols because we will be able to tune both physical and chemical properties of these materials and then I have the capacity to make newer and newer devices or have different properties.

Based on the growth mechanism you have synthesis protocols such as vapor phase growth, liquid phase growth, solid phase growth and hybrid phase growth. As the name suggests you are talking about the phase which will lead to the growth of the final particle. According to the form of the product what is the nature of the product which you get by following a given synthesis route. You can have colloidal processes, you can have template assisted processes, you can have MBE, you can have molecular beam epitaxy, you can have ALD or you can even have the structures which will lead to photonic crystals the self assembly of nanoparticles so that you have a photonic crystal. Based on the confinement of the structure that means you can have confinement in 1D, you can have confinement in 2D or you can have confinement in all the three directions you can classify the synthesis protocols that means protocols which will give you quantum dot or quantum wire or quantum well like structures.

For example, one of the most common ways to synthesize 1D materials are spontaneous growth where you can have evaporation followed by condensation leading to 1D structures or you can have vapor phase which is then cool to liquid phase and then finally, you get a solid phase that is a VLS growth mechanism or you can go from a solution phase to a liquid phase then a solid phase and that will give you a SLS growth. You can have template based synthesis such as electroplating or electrophoretic depositions, you can have colloidal dispersion methods, you can have melt then that melt is then forced to solidify and then you get a solid structure or you can even have solution filling. You can have with certain kinds of chemical reactions. If you want to make fibers, then you use electrospinning and

if you want to have a well defined structures then you use lithography. Let us start with one of the most common techniques which are being used in today's world and they are quite easy.

You have learned about them in schools, maybe in the first year of your bachelor's program and you will see that they are routinely used to make fashionable structures and materials which are finding large-scale application. So, the use of these protocols would become very very evident and that is the sol-gel method. What do we do in this method? First, you make a sol. So, the formation of a sol is followed by gelation of the sol and finally, you can calcine these sol or you can heat it at a higher temperature and you will get the densification and crystallization of the material. The first step hence would become hydrolysis of precursors, the second would be condensation followed by polycondensation, the third would be gelation followed by drying, and finally, densification and crystallization at an elevated temperature.

So, mostly what would be the criteria of choosing the initial method that is the raw material which you will take so that you can have reaction between those raw material to get a product which is desired. So, you must choose materials which have a tendency to form a gel. You cannot just randomly choose any material. So, choose a material which have the tendency to form a gel. Example, alkoxides you can choose alcohol or you can start with various types of chlorides.

These have a tendency to form a gel. So, first, you will take the raw material make a solution of it, then you will initiate the process of hydrolysis, and then let the whole gel to cool down and you will get a stable gel. Now, you have a stable gel that is still warm and then it also has water. Then you what you need to do? You need to initiate the process of drying. So, you can dry either it can be evaporated drying or supercritical drying.

Finally, once you have a dried product it is still not in the structure or molecular formula unit that is desired, then you initiate the process of calcination. What is calcination? It is the temperature at which the chemical formation will take place or the temperature at which the chemical reaction will be completed to give you the desired molecular unit. For example, if you want to make a structure like  $ABO_3$ , then you have to calcine the materials at which you get a unit that is the unit cell which has  $ABO_3$  as the molecular unit. If you have  $A_1B_2O_{3-x}$ , then it is not the unit that you are desiring. So, calcination at which the material actually forms and that is where the chemical bonding is taking place, and that gives you the final product.

This is an example that I have just chosen that is sodium iron phosphate. You can try this and you will this is the protocol that is followed. I can give you this protocol because this was actually discovered by my own team and hence I can discuss it with you without any IPR issues. Sodium iron phosphate is one of the materials that is slowly becoming very

very important in a technology which is called as sodium iron batteries and supercapacitors. The battery that you use are all based on lithium till now, but slowly you will see that people are looking for batteries beyond lithium.

And, this is one of the materials which is being extensively used and is finding application in energy storage devices. You can make this material. How will you start with that? Use ferric nitrate as the initial raw material. Then you have ammonium dihydrogen phosphate. Make a solution in deionized water.

DI water means deionized water. In this drop add citric acid which acts as a fuel and the complexing agent. Then you have the ethylene glycol which drives the gel formation. Once you have all these components in the solution heat it at 60 degrees. You will find that a gel-like structure will form. In this gel-like structure, you add sodium nitrate.

So, you have the source of sodium, you have the source of iron and you have the source of phosphates. Obtain a solid mixture after drying then ensure that you have removed all the volatile components and you have obtained a solid mixture which is there then you crush it, crush it into small pieces. You can ball mill it or you can take it in a mortar person. This powder was heated to 300 degrees for 2 hours and finally, the powder was heated at 600 degrees for 6 hours so that you can obtain the desired unit which is  $\text{NaFePO}_4$ .

This is a stable molecular unit. So, if you take a scanning electron microscope you will find that these are the scanning electron microscope pictures. These are the typical particles of sodium iron phosphate which are used as electrode materials in batteries the scales which you are looking at is around 1 micrometer here and around 200 nanometers here and then you can scale and you will be able to find out the size of the particles which we are talking about. But you can clearly see that you have different particles that are coming together and scientifically what do we call them? The coming together of these smaller size particles to make a larger size cluster or an agglomerate is called agglomeration. The advantage that is felt in the synthesis protocol that I discussed just now is also extendable to the general advantages that are associated with the Sol-gel methods. Those are that they occur relatively at a lower temperature.

They can create fine powders in addition to that these cost-effective techniques can lead to reproducible protocols that will deliver high-quality materials with similar homogeneity and purity. What is the advantage? The massive advantage is that you can have similar properties from these materials batch after batch after batch. But the disadvantages are also there such as if you want to calcine a material, mix the solution, heat it, then cool it, then you have to take it into a mill, then it is a long processing time method. You can have residual hydroxyl or carbon groups. How do you dispose of them? Then you have certain issues with the disposal strategies.

You just cannot throw waste from a chemical reaction into the wash basin. There has to be a given protocol by which you can throw out the waste of these chemical reactions. Then once you have toxic organic solutions that are being used, then again their disposal strategies also become an issue. And formation of fine pores is sometimes an issue, but sometimes you want that you should have fine pores. So, this disadvantages which you read in the books out of them the limitation that is formation of fine pores can be advantageous or can be disadvantageous depending upon the use of the material which we are talking about.

Similarly, you can have the next technique which you have been studying from school days that is the precipitation techniques. What do you do? You have two or more compounds that are precipitated simultaneously in a solvent. So, you ask two different precursors to come together and then precipitate out at a given pH at a given temperature so that they form a new chemical unit. The nucleation process helps to form a large number of small particles. Nucleation means you have to have a site on which a particle will start to form and then grow.

This process where the formation of a particle of a given material which is desired starts is called nucleation that is and the process is called nucleation process that is what you mean by nucleation. Once you have nucleation then the particles will start to form in different parts of the solution and Ostwald ripening process leads to aggregation. What is Ostwald ripening process? The smaller particles will then become bigger and the bigger particles will grow at the expense of these smaller particles because once there is a bigger particle it will also capture the smaller particle in its vicinity and it will become even bigger and that is what it is said that the ripening process would be basically at the expense of the smaller size particle. And the time you will give to the particles to grow will decide its final size shape and morphology and that will then decide the application of those materials. So, you will start with an anion solution and a cation solution why? Please remember we discussed that a material has to be charge neutral therefore, you will if you have an anion then you will also have a cation and then they have to form a material that is charge neutral.

So, you will take two solution then you will have nucleation and growth and this precipitate which will form will have to be collected washed. So, that you do not have any solution which are there from the initial phase of the reactions they are washed out you only get the material which you desire. So, after filtration you will wash it and finally, to ensure densification and completion of the chemical reaction you will perform the process of calcination. Sometimes in the field of ceramic the process of ensuring the completion of chemical reaction and formation of a chemical unit is called calcination and the process of densification is called as sintering where you densify the material is called sintering. So, if you are talking in terms of ceramic you will also go to a step further and then you will follow after calcination the process of sintering.

Then you can have co-precipitation methods such as solvotherm or biopneumatic approaches. Here again, you can change the pH of the solution and you will have different reactions taking place. Viscosity, surface tension, temperature, concentration, and the stirring speed at which you are mixing two solutions will affect the properties of the material. So, you will have a precipitating agent in a solution where you have the source of cation and a source of anion you will have a precipitating agent which will drive the formation of a precipitate. Once this precipitate once formed you will have in the form of hydroxide, dry it, calcine it and mostly you will end up if you have a hydroxide you will end up with an oxide solution.

This is a typical example that is used to make nickel oxide via the co-precipitation method. You can clearly see that the structures that you obtain or the particles that you obtain of are very different to what I discussed earlier. So, if you have different types of morphologies, different type of materials obviously you will have different types of materials being formed. If you want to make such nickel oxide you can start with a nitrate solution which has a source of nickelate, then you can use sodium hydroxide in Di water, you can use a surfactant CTAB for example, and you will in this solution add the solution one which is dropwise, centrifuge it the precipitate which you get, dry it and the particles which will obtain would be the ones which are shown here. So, you can clearly see a very easy protocol to make nickel oxide.

You can make another set of materials that are being used in catalysis, in sensors, in batteries, in solar cells, in optical devices the Zeolitic Imidazolate framework type structures which are known as ZIF 67 depending upon the concentration of Imidazole and you can make these structures also using this technique. Again you can see here you have cube-like structures or polyhedral morphologies and you will have different kinds of materials. These kinds of techniques are highly efficient, you can have a wide range of analytes that can be collected and mostly there is no solid waste that you have to encounter. But you have to use of toxic liquid waste which is a byproduct and then you need to eliminate and dispose of them using well-defined disposal strategies. I repeat once again the toxic liquid waste must not be thrown directly through the sink drain otherwise it will go and get mixed with your groundwater and that will contaminate the water in and around the laboratories and that should not be allowed.

You have to readjust the pH value once you go from one type of initial raw material to the other and then the whole process has to be optimized once again. Possible contamination and loss in all handling steps. If at any point of the synthesis protocols you do not follow the steps carefully and ensure that there are no contaminants entering the precipitate, you may get an altogether different material than what is desired. This brings us to the end of the first lecture on synthesis protocols. I have discussed with you the classification of synthesis protocols.

I have discussed with you the two most common ways to obtain materials that are being used as functional materials. These are the rules by which you can have high-yield synthesis protocols which means you can make large amounts of materials per batch. In addition, you can have materials with similar properties batch after batch. So, that is why we have started our discussion on Sol-gel and co-precipitation methods. These follow the set protocol that is classified under which of the headings top down or bottom up.

I believe you can answer now it is bottom-up. So, you have these techniques which fall under the heading of bottom-up, and the advantages of the top-down and bottom-up approaches to obtain a material were also highlighted today. In addition, you may have different synthesis protocols, but there is no single technique that can cater to the needs of all the devices and all the physical and chemical properties required in a material what do I mean by this that if you need different materials with various kinds of properties you may have to try and fabricate these materials using various techniques and then choose the technique which is giving you the properties which are desired for a given application. To prepare for today's lecture these are the references that were followed you can go and refer to them. In the next lecture, I will talk to you about a few more synthesis protocols that are routinely used to fabricate functional materials which are then utilized to make smart devices. Thank you very much.