Physics of Functional Materials and Devices
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Lecture – 08, Week 2
Synthesis protocols - III

Hello, let us start the final lecture on synthesis methods to obtain functional materials. In today's lecture, we will continue our discussions on a few more top-down and bottom-up approaches to obtaining functional materials. Let us start with a method which is called soft template. Template means what? It is a molecule or structure that serves as a pattern to generate another form of molecule or structure. You have seen it quite commonly and you have been using it in recent years during the making of rangolis. What do you get in today's market? You have these sieves or structures which are given to you and you place them on the floor and then you throw the powders or colored powders on top of it and press it and then you can lift the whole sieve or the template.

So, this is what we are talking about. You have a molecule or structure that serves as a pattern. So, you will make the particles that will replicate the structure of the template which is what a template is. You define a template in Microsoft Word.

This is the way the whole document will look like. So, you have defined the template that is a similar concept that is being used in the templating method. It can be a soft template and you will see that there can be hard template methods also. So, the template is a molecule or a structure that serves as a pattern to generate another molecule or structure. This soft templating refers to self-assembled arrangements of structure directing molecules like surfactants or precursors leading to the creation of particles.

So, suppose you disperse surfactants in water. Surfactants are what? They have a hydrophilic and a hydrophobic end. Hydrophilic like water molecules, hydrophobic like to be away from the water molecules, and therefore, they self-assemble. So, you have water molecules on one side and then you have the hydrophobic ends and then you have the self-assembly of the surfactants. This is what is used in the cleaning detergents.

What do they do? You have the hydrophobic ends attaching to the dust, the hydrophilic end attaching to the water molecules and then, when you have the rinsing taking place, the hydrophobic end which is attaching to the dust pulls out the dust particles from the cloth and then you remove it from the whole washing machine or the solution in which the cloth was dipped and that is what this soft template means they are self-assembled arrangements of structure directing molecules. You can have various kinds of micelles to get different morphologies of materials or nanomaterials as per say. You can use micelles, you can use inverse micelles, you can use vesicles, you can use cylindrical vesicles and you can also use bilayer laminar micelles. So, you can clearly see the shapes and sizes of the micelles and bilayer laminar micelles are very different, and therefore, if I am trying to make a material using these two different templates the nature of the particles that will form is the shape and the size of the particles which will form would also be very different because in this process we replicate the nature of the template. This is what is typically done what you do for example, let us take sodium and phosphate you take the source of iron, you can take the source of sodium then you can take another source of phosphates.

You have dispersed them in a template then what you get you get certain particles that are obtained after you calcine the reactants. What happens in this means that you are actually removing the template from the you are removing the template from the product. So, you ask the reactions to take place by following the structure which is similar to the template. Then you remove the template how can you remove the template just heat it that is calcination heat it and these templates will burn out or they will evaporate they will just leave the structures and what is left behind are the particles of the desired material in this case sodium iron phosphates. So, these are the kinds of morphologies of particles which you can easily get and in the previous lecture I ended up talking about hollow morphologies and therefore, I am talking today about this hollow morphology only.

You can also have different kinds of particles need not be hollow, but they can be layered or any other shape, but the whole concept remains the same that after the reaction you will remove the soft template. Hence, you have again advantages and disadvantages associated with this method. If you know the template and you can synthesize the template with similar structure and morphology after each batch, then you can use the same template to make the material and hence the whole process becomes reliable. You do not need to have any external precursors while the reactions are taking place. You can remove the templates easily.

You do not need to heat it to very high temperatures to remove the templates and hence you can control the pore size and the pore volume which you see in these kinds of materials and they have very high structural integrity. But because you are calcining these materials at a lower temperature otherwise suppose you have a material that you want to replicate the shape of the template and the template is removed at 200 degrees. So, the structure forms at the interface and you get a hollow ball-like structure. But you say no now I will take this material and heat it at 1000 degrees. What will happen? This structure because of the extreme excess heat will collapse and it will not have the same shape and size as that of the template.

So, you have lower thermal stability of the structural as per say. The material may remain the same. You may still have sodium iron phosphate, but you may go from a solid or hollow morphology to a different morphology if you heat these materials to very high temperatures. The molecular unit may remain the same, but the shape and the size of the particle will be quite different and hence you will see the collapse of the pores. During template removal, this will lead to an increase in particle size and reduce the pore size.

Why? Because you are heating the materials and therefore, you will bring them together and hence the size of the particles may increase. So, if you are talking about nanomaterials the third point becomes quite relevant. The next technique which is used is the hard template method. And in the hard template method which is a facile synthetic method, you can get porous materials with stable and systematic porous structures. This process involves three steps.

First, that is the fabrication of a hard template with a well-defined design. Then the coating of the precursor molecules of the targeted materials. So, what you are targeting, what material you want you must have the precursors for that. On the surface or pores of the template method. So, if you have let us say a material like A that is the template or you can have another template like B.

So, you can deposit the reactants on the surface or in the pores of the surface. So, you can have various combinations. Once the reaction is completed the incorporated hard templates are removed without affecting the properties of the product by either chemical etching or dissolution. Leaving behind the targeted materials with reverse replicas of the templates. Why reverse replicas? If you have understood the concept of template-based synthesis, you should be able to answer why am I talking about the reverse replicas of the templates.

So, you have the template, then you have precursor filling. So, you have the precursors filled inside the templates. And then you have the removal of the templates. And hopefully, you will be able to answer about the reverse replicas that I asked for in the previous slide. You will understand why I am calling them reverse replicas.

The advantages are you can see that you will have ordered and porous structures along with that you can also have highly crystalline materials. However the associated disadvantages are it involves multiple steps, it is a process where the removal of the template is quite complicated. Hence, it becomes time-consuming and the templates are mostly not cheap. So, you will have high costs coming in from the template itself and they are not going to be used in the final application. So, you are going to have the use of a material which has to be discarded.

So, the input cost becomes quite high. Then comes another technique which is called PVD which is physical vapor deposition. Very simple. What do you do? You have a material, for example, titanium dioxide. You want to have titanium dioxide coated on a substrate.

So, you want to have a material which is deposited on a substrate. So, how do I do that? It is a very simple process. You use a target excitation. So, you can use lasers and then you hit the desired material, the material or the metal or the material both it is not only metal. You hit this material with high energy.

What will you get? You will get these particles ablating. So, they will ablate. Now, once you have these small particles with the same chemical formula, but smaller sized then they will start falling from the top to the bottom. And if you have the inert gas which is there, then these particles will start falling and getting deposited on a substrate in an ordered fashion layer by layer. So, you can have a vapor depositing on a substrate and then growing, and as you cool the substrate the materials will remain on the substrate if the addition is properly ensured.

There is one technique that you should understand very nicely because as India is moving towards the aim of becoming the hub for making ICs and wants to have a major say in the semiconductor industry, the technique of lithography becomes essential. This technique is basically coming in from the word lithos and graph. Lithos means stone, graphe means you have a certain well-defined graph or shape or some pictures. So, if you are drawing well-defined structures on a piece of substrate then it is called lithography. So, what do you do? You have a substrate on which you want to grow another structure.

So, this is the final form of the structure which I want to obtain. What do I do? I will start with a substrate which is coated with that particular material. Now, you can clearly see I have to cut down this whole substrate into a small piece. I am just taking the example of a quantum dot. What should I do? I need to simply you can take I have to take a knife and cut the portions on either side so that I can get a small particle, but this size is 1 to 100 nanometers.

How do I cut it? Which knife I take? So, that is where the technique of lithography comes in. It can be optical beam lithography where you use optical wavelengths to design the pattern on a material or it can be electron beam lithography where the source of the incident radiation is electron beam or you can even use ion beam lithography. So, depending upon the source you call them as optical beam or E beam or ion beam. Let us take an example of E beam lithography. So, I have a material on which the desired structure has to be drawn.

First thing I coat it with a resist which is called as photoresist. What is a photoresist? It will change its nature when there is some radiation falling on it. A typical photoresist which is used is the polymer PMMA poly methyl methacrylate. So, I coat it. Then I use a shield to restrict the region in which the irradiation should fall.

Now, if I have the beam here also they will not be able to reach the structure because I have a shielded beam. So, the only region that gets affected is this region by the source beam. This is a photoresist. What happens? The source that is the beam in this case electron beam changes the resistance of PMMA. As the resistance and the chemical formula change then I can use a solvent to remove only this region because that solvent will not remove the remaining two parts because their chemical formula and the molecular weight has not changed because no beam could reach there.

Then what do I do? I cover that area with the mask. So, I put a mask on top of it. Once I put a mask on it then in the second step I can use a solvent that will remove PMMA. What happens? Now, I have a photoresist which has been removed, but a mask has been introduced. Hence, figure E clearly shows you have a Q-well based structure and a substrate on which this quantum well has to grow.

Now, you see this is an extra region that needs to be removed. This is removed by the process which is called etching. So, you use etching. Mostly you can use HF hydrofluoric acid for etching. Please remember hydrofluoric acid HF is one of the most dangerous acids and should not be used by untrained people under any circumstances.

It is very very dangerous and should only be used under supervised conditions and only to be used by experts, not by people who have no training to use HF. There are training processes that have to be passed before you can use HF. It is not to be used by untrained people. Then once you etch this process that means, you are cutting it, you are removing, you are etching the remaining structure. So, you have removed the structure from this time.

And finally, by removing the mask on top of it you will get what? You get the remaining structure here. So, you can clearly see you started from this place and you have reached a much smaller size structure. Sometimes the question comes why do not you use a mask directly? The use of mask is not always desirable directly because this is just one quantum structure that I talked about. But when you talk about the whole electronic board or any substrate on which these structures have to be grown they are in thousands and thousands. And there you cannot just put on a mask and then carry out the whole process you have to go step by step.

So, that you ensure that the process gives you the desired characteristics of the material. Another important top-down methods which are there and you can read about them from the references I will give are laser ablation. Here as the name suggests you use a laser to ablate the material and then you can get these materials to deposit on a substrate. Then you have thermal decompositions where the compound decomposition is due to the application of heat that can lead to the formation of two or more products and you can have these products being formed from one reactant. It is a very common technique and it has been used for many many decades now.

So, you can have for example, iron oxide formation from iron oxalate complex under heat treatment and then you will get iron oxide. You can have sputtering where the ionized gas molecules accelerate towards the target and the atoms eject from the surface of the target and then get deposited on a substrate and it is a physical process which you have. Once you go from one technique to the other, the reason why you get different properties are because of the growth mechanism by which you get the particles. If you talk about the growth mechanisms, there are mostly two types of processes which are there, the thermodynamic process and the kinetic approach. In the thermodynamic process of growth mechanism, the reactions continue till the conditions are maintained, and in the kinetic approach, the reactions continue till the reactants are present.

Once the precursors are over, then the reaction stops and in the thermodynamic approaches, it is mostly the condition that drives the reaction. So, if precursors A and B are both available, but you do not maintain the temperature or pressure, the reaction will not take place. The reaction is mostly driven by the minimization of Gibbs free energy. So, if you take ΔG_v as the Gibbs free energy per unit volume of the solid phase and you have the concentration of the solute as C, then you can write the change in Gibbs free energy as:

$$\Delta G_v = \frac{kT}{\omega} \ln(\frac{C}{C_0}).$$

And you will see the reaction is only driven in a supersaturated condition.

That means you have gone to a condition that is in a supersaturated condition defined by $\frac{C - C_0}{C_0}$. So, once you go to a state that is a supersaturated condition, then you suddenly find that there is the formation of a new particle, and if that new particle has lower Gibbs free energy, then there would be a transformation taking place and you will go from phase 1 to phase 2. So, the reaction is driven by the concept of minimization of Gibbs free energy. So, if you talk about the concept of growth, then mostly you talk about two concepts nucleation and growth. So, what happens? First, there is nucleation and then it is growth.

So, there is nucleation and then only there is growth. So, if you plot solute concentration as a function of time, there will be reactions taking place, but you will find that you will have conditions where the system can go back to the initial phase. It is only beyond a certain condition that the nucleation will occur and then only the growth will take place because the initial phase will not allow the formation of this new phase unless the thermodynamic conditions force the whole structure to go to a new phase. So, there are two terms that take place and there are they are considered and here you will find that two things are there. The surface term, the surface energy, and the volume energy. The surface energy term varies as a function of square and the volume energy term varies as a function of q.

So, you will have q and square term. Initially, the square term dominates, and beyond a certain value, the cube term dominates. So, up to a certain point, you will have the formation of the particles which will not occur because you have a lower energy. This is a convoluted curve. So, it is taking care of both surface and volume energy terms. This is the final curve that you are seeing which is the convoluted curve.

So, the total Δv_g for a particle, for example, a spherical-shaped particle is what? $\Delta\mu_v$ and $\Delta\mu_s$ that is given by $\frac{4}{3\pi r^3 \Delta G_v}$ and $4\pi R^2\gamma$. R that is the critical radius at which you will see the growth will then become equal to R^*. You can minimize the Gibbs free energy and then differentiate and equate to 0, you will get the value of $R^*$and that R^* terms out to be $-\frac{2\gamma}{\Delta G_v}$. And then the value of ΔG^* is equal to $(\frac{16\pi\gamma}{3\Delta G_v})^2$.

So, this is the critical radius. Below this radius, the nucleation will not take place and growth will not occur. Once the nucleation takes place the system goes to a new state and you get the volume increasing without the change in the surface energy and you minimize the Gibbs free energy. So, the particle growth mechanism plays a critical role in deciding the shape and size of the particles that will form and as you move from one synthesis protocol to the other you have different growth mechanisms and hence different particles. Can you list and find out the types of particle growth mechanisms that occur in the different synthesis protocols that we have discussed till now? You will be amazed to see that there are various protocols and hence you will understand that you can make new materials with new properties by just tuning the particle growth mechanisms the final materials will have different behaviors and you can now understand that synthesis protocols can define the properties of the materials as well as the growth mechanisms.

There are the synthesis protocols are mostly classified under two broad headings top down and bottom up and in today's lecture we talked about PVD soft template and hard template methods. I will give you an assignment today can you differentiate between hard and soft templates and how do you use these templates in your daily lives? You will see that you are using soft and hard templates routinely, but you do not realize it and that is why I did not define it earlier. One of the most useful techniques is lithography which is used in the field of semiconductors and would become extremely useful for India in the future and you must understand it clearly. Finally, I reiterate every technique has its advantages and associated disadvantages.

You have to choose the right technique that will give you the desired material for an application that is in the device that you aim to design and get fabricated. These are the references that can be followed to understand more about the topics that have been covered in today's lecture. I thank you for attending today's lecture and we will move on to the next topic from the next. Thank you very much.