

Experimental Nanobiotechnology

Prof. P. Gopinath

Department of Biosciences and Bioengineering,

Indian Institute of Technology Roorkee

Lecture 01: Synthesis of Nanomaterials Using Ball Milling

Hello everyone, I welcome you all to this course on experimental nanobiotechnology. I am Gopinath, a professor in the Department of Biosciences and Bioengineering and also a joint faculty in the Centre for Nanotechnology. The title of today's lecture is 'Synthesis of Nanomaterials Using Ball Milling.' In today's lecture, we are going to learn what ball milling is, what the principle of ball milling is, and what the various types of ball milling are. We will also learn about ball milling process parameters.

At the end of the lecture, through practical demonstration, we will learn this ball milling technique in more detail. Before I talk about what ball milling is, let me briefly explain what a nanoparticle is. A nanoparticle is any material that has at least one of its dimensions in the range of 1 to 100 nanometers. The word 'nano' is a Greek word that means 'small.' Most of you know that a nanometer is one billionth of a meter, which is 10^{-9} meters.

Let us see the classification of nanoscale dimensions. Zero dimension means materials having all dimensions (x, y, z) within the nanoscale, that is, less than 100 nanometers. Examples are quantum dots and nanodots. One-dimensional material means it has two dimensions at the nanoscale, and the remaining one dimension is larger than 100 nanometers. Examples are nanotubes and nanowires.

Two-dimensional material means it has only one dimension at nanoscale, and the remaining two dimensions are larger than 100 nanometers. Examples are nanofilms and nanocoatings. 3D materials are not nanomaterials because none of their dimensions are at nanoscale. It means all three dimensions are larger than 100 nanometers. Examples are bulk powder and diamond.

So, how do we make this nanomaterial? There are two approaches. One is the top-down approach. The other one is the bottom-up approach. The top-down approach is like building something by starting with a larger component and carving away material, like a sculpture.

A simple example for understanding this concept is making a statue from a rock. From a very large size, you are making the nanostructure. So, that is the top-down approach. For example, from the bulk, you are making the nanomaterial, so this is called the top-down approach—from a very large size, you are reducing it to nano size. The next approach is the bottom-up approach, which is like building something by assembling smaller components, atom by atom.

A simple example for understanding this concept is using a brick and constructing a building. Most of you know the amino acids are the building blocks for the proteins. If you see the size of each amino acid, these are in the range of Angstrom. These amino acids combine and form the nanoscale protein. Most of you know the DNA is made up of nucleotides, that is A, T, and GC.

The size of each nucleotide is in the range of Angstrom. These nucleotides combine and form the nanoscale DNA. So from a very small size, you are reaching the nanoscale. That is called a bottom-up approach. Whenever we talk about nanomaterials, when the size goes down, the surface area to volume ratio will be higher.

Let me explain how this surface area to volume ratio increases when the particle size decreases. Let us see a simple example. Take a 2 mm box and cut this same 2 mm box into small pieces of 1 mm size. This is like your bulk material, and this is like your nanomaterial. Apply the surface area formula, then you can calculate and see that the surface area is greater for your nanomaterial.

But the volume will be the same. And when you calculate the surface area to volume ratio, the surface area to volume ratio will be higher for the nanomaterial. That is why whenever the particle size decreases, the surface area to volume ratio will be higher for the nanomaterial. So, these nanoparticles can be prepared by various methods like physical, chemical, and biological methods. So, today we are going to learn how to make nanoparticles by the physical method.

And these physical methods involve breaking down larger materials into nanoparticles. It can be through mechanical force or it can be through an energy-based process. Some of the common examples are mentioned here, and you can see this. That is the mechanical

method. The ball milling technique is there. Today, we are going to learn this ball milling technique.

There are several other techniques: energy-based physical vapor deposition, laser ablation, ion sputtering, and arc discharges. And in today's lecture, we are going to learn the ball milling technique in more detail. This ball milling is also known as mechanical milling, pebble milling, or tumbling milling. And this ball milling technique is a top-down process because, from a very large size, we are going to make nano-sized material. And this is your bulk material.

And here we are going to use these balls. That is why it is called ball milling. So, you will be using these balls and breaking the bulk material into nano-sized material. This ball milling is a cost-effective technique and it is an eco-friendly green technology. Because we are not going to use any toxic chemicals for preparing these nano materials, and at the same time, it will not consume much energy.

So, that is the advantage of this technique. So, what is ball milling? Ball milling is one of the most powerful techniques for reducing the particle size to the nanoscale. And here, what happens is the particles which you want to break—the powder—will be trapped between the two colliding balls. And when the particles are trapped, it keeps on milling and reduces the powder's particle size to nanoscale.

And what is the principle of this ball milling? The principle of ball milling is mainly based on attrition and impact. So, what is attrition? Attrition is where the balls rub against one another. So, the balls will be rubbing against each other.

And then it makes the powder to reduce the size to smaller size and impact. So what is impact? So when the ball milling is rotating, what happens is, so these balls will be taken to the top due to the centrifugal force and it will fall down along with the powder and it breaks the powder and that leads to reduction in the particle size. So that is the impact.

So the principle of ball milling is mainly based on impact and attrition. So attrition means the balls are rubbing against one another and the material being ground and the impact is the balls are taken through the centrifugal force to the top and it will fall down and it will break the powder and reduce the particle size. So what are the various types of ball milling? So broadly we can have it like three types that is horizontal ball milling, vertical ball milling and planetary ball milling.

So, in the horizontal ball milling, it is a continuous process and it is mainly suitable for larger quantities and it can be also used as a kind of batch process also. And in the vertical ball milling, it generates less heat and it is mainly useful for wet grinding. For example, if you are using some solvent, you can use it, the vertical ball milling is one of the important technique. And the third one is the planetary ball mill. It offers a high energy milling through the complex orbital and rotational motion.

which i'll explain detail in the my subsequent slides so let us see what is horizontal ball mill so horizontal ball mill is a cylindrical grinding equipment and again as i explained earlier the ball milling principle is based on impact and attrition and when the mill is revolving the grinding media that is the balls the grinding media is balls so that will be lifted by centrifugal force and

and cast it down to impact and grind the material so it is lifted to the top by the centrifugal force and the balls will fall down and break your powder into nano size material that will reduce the particle size and this horizontal ball milling mainly useful for continuous processing so we can add the feed material in one side and we can collect the final product in the other side so in this picture you can clearly understand so you can Feed the material here and we can collect the final finished product by using these adjustable discharge slots and the dust will be collected from the top.

So the next type of ball milling is vertical ball mill. The primary principle behind this vertical ball mill is centrifugal force generated by the rotating drum. As the drum spins, what happens to the grinding media, that is the balls, so that will be lifted against the drum's inner wall. And this creates a cascading effect and the balls fall back onto the material and that leads to the material will be broken into small size and that leads to the reduction in the particle size.

So you can see here, the balls will be lifted to the top, and they will fall back and grind the material. So the advantage of this vertical ball mill is that we can also use liquid media or solvents. So when you use a solvent, it will also be useful for wet grinding. So that is the advantage of this vertical ball milling. And the next technique we are going to learn is the planetary ball mill.

So this ball mill consists of one or more grinding bowls. You can see here there are multiple grinding bowls that rotate around a central axis. While simultaneously revolving on their own axis, this base will rotate in this direction, and the balls will rotate in the opposite direction. So you might have also played this cup-and-saucer ride during your childhood;

it is similar to that. So you can see here, the base is revolving in this direction, and each cup is also revolving on its own axis.

So the planetary ball mill principle is similar to that. So the grinding balls move with combined rotational and orbital motion. This creates a high centrifugal force, which results in intense impact between the grinding balls and the material. So that leads to the reduction in particle size. So in this slide, you can clearly understand.

So, the rotating spindle is rotating in this direction, and the central main disc will be rotating in this direction. You can see this will be rotating in this direction, and this grinding bowl is rotating in the counter direction, so this bowl will be rotating in this direction. From this slide, we can understand the rotation of the grinding bowl in this direction and the supporting disc in the other direction. So, what happens due to these centrifugal forces is that the balls, along with the powder material, will be lifted and taken to the other side. And it will repeatedly hit the vial content, which leads to the reduction in particle size.

So, next, we are going to learn about the various ball milling parameters and how these parameters will affect the final product's size. Under these ball milling parameters, we are going to learn about the container material, milling medium, rotational speed, BPR ratio, milling duration, as well as the vial filling volume. So, let me explain each one in detail. So, the first parameter in the ball milling technique is the container material. So, the container material is a very important parameter.

So, we have to select the right container based on our material. Only then can we get the final product in a smaller size. For example, if you are using high-purity natural agate, which is chemically resistant, this will be very useful for materials where you want to use acids and solvents. In this case, we can go for the high-purity natural agate material. And if you want to work on the non-stick properties of the material or reduce contamination, the ideal choice is a Teflon container.

And we can also use the stainless steel container. It depends on the final application. If it is for metallurgy and electronics applications, we can go for grade 304, and if it is for food and pharmaceutical applications, we can go for grades 316 and 316L. And the next important parameter is the ball milling medium, which is the ball. So, the milling medium is the ball, and we have to select the right balls for the correct material. Only then can we achieve particle size reduction without any contamination.

For example, we have metallic grinding media, which are metallic balls mainly used by most industries. These metallic grinding balls are useful for breaking hard surface materials, such as hard materials. So, they can easily break hard materials. In some cases, we have to use non-metallic grinding media. For example, if you are working on a polymer or a biological material and want to avoid contamination,

in this case, we can use non-metallic grinding media. So, how do we select the correct milling media, that is, the correct balls for our ball milling technique? That is very important. So, the first point is density. The milling media, that is, the milling balls with greater density, will produce finer particles.

So we have to make sure that the gravity of the medium should be greater than the milling material. And the next one is the particle size. So the size of the media impacts the milling efficiency. So the media is, you know, it is balls. So if you are using the big size balls, which can reduce the particle size faster. And if you are using these small size balls, so which can achieve the finer and uniform results.

So when you are using the big size balls, it can reduce the particle size in a faster rate. And this smaller size balls will be helpful for making the fine size particle. And third one is hardness. So if you are using these harder media, that is the harder balls, So what happens is it can significantly improve the milling.

It can efficiently mill the material and it can reduce the contamination. And fourth one is the composition. So selecting the right ball, for example, metallic balls or the non-metallic balls, you have to select the right ball. So with respect to the particular material, then only you can get the best results without any contamination of the material. So the final one is the cost. If you are using these high cost media, higher cost balls, what happens is you get a better grinding performance.

But the problem is it will lead to an increase in the final cost of the product. The next important parameter is the rotational speed. And here, with the increased rotation speed, what happens is it will produce a greater transmission of energy to the powder and milling media. And the speed of the ball is expressed as the percentage of critical speed. And critical speed is the speed at which the centrifugal force is high enough that all balls stick to the mill wall during the rotation of the mill.

So the critical speed means at a particular speed, all the balls will stick to the mill wall. But under this condition, your grinding efficiency will be lower. So for that, we have to reduce

the critical speed. So that is called your normal operating speed, which is about 75 percent of your critical speed. And how can we calculate the critical rotational speed?

So by using this formula, we can calculate the critical rotational speed.

$$n_c = \frac{1}{2\pi} \sqrt{\frac{g}{R - r}}$$

Where,

- **R** denotes the radius of the cylinder, which is the milling container.
- **r** denotes the radius of the milling media (balls).
- **G** denotes the gravitational force.

So if you are using this high speed, as I mentioned earlier, at high speeds, the balls will be held against the milling container wall due to the high centrifugal force and revolve with the mill.

So in this case, the grinding efficiency will be lower. And in the case of low speed, Attrition action will be greater. That means the balls will rub against each other. The attrition action will be greater.

And at the optimum speed, we will have both attrition and impact. So the balls will be taken by the centrifugal force, fall back, and break the material. So that is the advantage of this rotational speed. We have to use the optimum speed to achieve smaller particle sizes. So the next important parameter is the BPR ratio.

BPR is the ball-to-powder ratio. So, this is one of the important parameters because the powder transformation rate is mainly determined by the BPR ratio. Generally, we keep a higher ratio between the milling ball and the coarse powder, usually 15:1. For example, if you are using 5 grams of powder, you have to use 75 grams of milling balls. So, that is a 15:1 ratio.

If you are using that ratio, then you can get the smaller-sized particle. So, the next important parameter is the vial filling volume, ensuring the milling balls gain sufficient energy for impactful collisions. So, the vial is typically filled one-half or one-third of its capacity so that it will have empty space, allowing the balls to move freely and generate stronger impacts, enhancing the attrition process. So that's why you must always keep this headspace at least one-third.

It should be kept empty so that the balls can move freely and create more impact as well as attrition. So, the last parameter is the milling duration. So, the total time the material is subjected to milling. So, it depends on the material size. It can range from a few hours to a few days and also depends on your material type, such as the material hardness. So, it can also range from a few hours to a few days.

So, over time, the particle size will decrease, and as the size decreases, the surface area-to-volume ratio will be higher and what is the mechanism behind this ball milling? How does it turn coarse powder into nano-sized powder? The first stage is the squeezing stage, where overlapping of the powder particles occurs and the next stage is the welding stage, where the particles join together through welding amongst each other.

And the third stage is the fracturing stage due to the impact as well as the compression. The powder will be flattened, and the crack will be initiated due to the repeated impact by the balls. And once the crack is initiated, it is due to the repeated hitting of the balls on the material. So it will have different kinds of fragments, and the particles will be broken into very small pieces. And finally, what you get is the nano-sized fine powder. That is the dynamic balance stage. I hope you understood the principle and theory of these ball milling techniques.

Now, let us move to the lab and see the practical demonstration to understand the technique in more detail. In this demonstration, we are going to synthesize nano powder through the ball milling method. For that, we require our bulk material, which is Tragacanth gum. Here, you can see the size of the bulk material. Next, we require 5 mm balls, 2 mm balls, a tungsten carbide jar, a spatula,

a sieve for separating the powder and balls, a glass Petri dish, a mixer grinder, and tissue paper. First, we are going to grind the bulk material into a coarse powder using a mixer grinder. Now, we are going to weigh 5 grams of this coarse powder using a weighing balance. We have weighed two sets of powder.

Next step is to weigh the balls. For that we have 5 mm balls. You can see the size and 2 mm balls. You can see the size. Here we are going to weigh 37.5 grams of zirconium oxide balls using a weighing balance. We have weighed two sets each of 2 mm balls and 5 mm balls. Next in a tungsten carbide jar, we will add coarse powder, 2 mm balls,

and 5 mm balls close the jar properly and tighten the screw to secure it Here we have prepared two jars with the same composition which will be balanced while performing the process in the ball milling setup. This is the ball milling machine by which we are going to convert the coarse powder into the nano powder. So first turn on the machine. The door will open and then we will place the jar inside the machine. Lift the handles. Place the jar inside.

Push the button and press the jar into the space then close the handles. Select jar number 2 and then repeat the same process. Then close the door. Now let us set the settings. We will set the speed at 400 rpm. run time will be 10 minutes for each cycle and 15 minutes pass for each cycle. We are setting a total of 75 cycles. This reverse option changes the rotation of the jaws from anti-clockwise to clockwise and vice versa for efficient milling.

After setting the parameters, press Start to begin the process. When the process is completed, open the door, and now we can remove the jars one by one. Pressing the button lifts the jar up so that we can pull it out. Repeat the process for jar 2. And then turn off the machine.

Now we will open the jar and take out the materials by unscrewing the cap first, and then taking off the lid. Strain the material through a sieve to separate the balls from the nano powder. You can see that the balls are separated from the powder. So, in this demonstration, we have successfully converted a bulk material first into a coarse powder by using a mixer grinder and then into a fine powder through the ball milling method.

In this image, you can observe that the coarse powder of Tragacanth gum, when added to water, forms a hydrogel despite not dissolving. In contrast, the ball-milled powder dissolves completely, indicating that the dissolution properties of Tragacanth gum improve as the particle size decreases. At the same time, the hydrogel-forming property of the material decreases. The scanning ultramicroscopic images of both the coarse powder and ball-milled particles, taken at the same magnification, clearly show the size reduction of ball-milled Tragacanth gum. When further magnified, the nano-sized particles of Tragacanth gum become visible.

In the transmission electron microscopic image of the ball-milled nanosized particles, the size of the particles is observed to be 35.54 nanometers. So, as a summary of this lecture, we have learned how to synthesize nanoparticles using ball milling. We also learned what the principle of ball milling is, what the various types of ball milling are, and what the role of various process parameters in ball milling is. Through a practical demonstration, we also learned the ball milling technique in more detail. Thank you for your kind attention. I will see you all in another interesting lecture.