

Lec 32: Synthesis of Nanoparticles (Physical Methods)

Hello everybody. Welcome to this massive open online course on solid-fluid operations. So as we are talking about that nanoparticle systems and also how that nanoparticles are defined and what are the applications of nanoparticles, what are the basic features of nanoparticles, how that nanoparticles can be synthesized. So in the previous lecture we have discussed all those things. So in this lecture we will try to understand the brief about of synthesis of nanoparticles by physical methods. As we have discussed that there are two basic methods by which you can synthesis, you can make these nanoparticles.

One is called that top-down method or it is called that physical method. Another is bottom-up method which is called chemical method. In the case of top-down method, basically it is a physical way by which that particles you can break into a finer one and then you can break further to make these nanoparticles. And this is actually the method by which you need not to have chemical reactions there.

So in that case you can synthesis that nanoparticles just by mechanical action. So that mechanical action earlier we have discussed that size reduction method. There are different types of mechanical devices based on which you can reduce the size of the particles. One of them is called milling. So you can use that milling process to reduce the size of the particles from its conventional size to its micro and also to nano size.

And millings are, there are different types of millings there which I think we have discussed earlier. Some will be ball mill is there. So ball mill can be used to reduce the size of that particle from very fine to that nano size. Also other methods are available, it is called chemical vapour deposition. Also laser ablation method, even spark ablation method.

These are physical methods. It is also named as dry production method. Another method or it is called that APPROS also, it is called bottom up. Where you will see that some atomic sized materials that will be converted into the eventual nanoparticles by just nucleation of that atomic structure or atomic sized materials. And it depends on that material which is being generated and also it is called that wet production method.

So there will be certain chemical reactions and also you will see that change of that materials just in presence of other chemicals and it will give you that nano size particles just by different changes of phases. Some common methods like this Tarkiewicz method, even citrate reduction method, gas phase synthesis, also block copolymer synthesis method, even sometimes it is happened like microbial synthesis method. So these are two different approaches or method you can say or technique you can say by which you can synthesize these nanoparticles. And as a physical method you can say that we are converting that materials just by mechanical action from its fine size to that nano size. And for that there will be different techniques for getting this mechanically of this size reduction.

That may be some will be mechanical, higher ball milling, mechano-chemical method,

severe plastic deformation method, cryo milling method. And some will be you will see that gas phase synthesis, in that case inert gas condensation, aerosol spray pyrolysis, combustion flame synthesis, plasma spray or thermal spray method, chemical vapor deposition, chemical vapor condensation, evaporation techniques, atmospheric pressure electric discharge method. So these are called gas phase synthesis method and others methods also sometimes it is seen or nowadays being done for this nanoparticle synthesis like cryo milling or cryo milling cryo milling process, laser pyrolysis process, reactive plasma, arc evaporation method, microwave plasma process like epitaxial growth, rapid quenching solidification method, ion beam sputtering method, self-propagating high temperature synthesis, even hydrogen reduction method. So these are actually broadly classified different physical methods by which you can synthesize these nanoparticles. So among those methods we will not discuss here all the methods but you can follow some standard textbook that will be actually given here in this lecture that takes two issues to be followed.

And as per that textbook referred that you can go through that but some of the techniques one or two techniques that we will discuss here in this lecture which will be very useful for you. In this case let us discuss that ball milling method by which you can synthesize that nanoparticles. So in this case reactant powder generally taken or then it will be introduced typically in a sealed vial as shown in this picture with hardened steel coated balls. In this case the milling is performed by shaking and violent agitation as shown in the picture it is as an animation it is shown that how that powder of that around 50 micrometer particle is added in the vial where there is some solid steel ball is there and whenever that vial will be rotating there will be a formation of violent agitation and this vial will be filled with sometimes gas that will be inert gas that will enhance that agitation inside the vial. And also the powder then after violent agitation it will be splitted and exposed highly reactive surfaces between those powder and steel ball and the severe plastic deformation happens during this violent agitation which result to nanometer scale structure of the powder.

So this is the basic way by which you can convert this micrometer size of particles to the nanosized particles. Also this production of nanoparticles by using this ball milling sometimes involve a significant amount of solvent like water solvent other solvent like normal butyl acetate, acetone, ethyl acetate etc. during particle size reduction. And in this case why this solvent to be added this addition of the solvent inside the mill can moderate the mechanical shock and minimize the amorphization of the material like if you are converting that graphite nanoparticles then in that case that is required some solvent to be added and also reagent. Every mill has been used to synthesize metal sometimes they are like lead, zinc, cadmium, copper like this nanoparticles.

In this case nanocrystalline particle on a large scale of that lead, zinc, cadmium or copper this type of as an example at room temperature can be produced. Also in this case you will see that this technique is used for the synthesis of alloys even nanocomposites. You will see that some other intermetallic materials like titanium, aluminum alloys to get its

nanoparticles even iron carbon alloy nanoparticles even lead nanoparticles, zinc nanoparticles, magnesium, titanium even carbon nanocomposites that can be synthesized by this ball milling process. So by when you will see that solvent to be used for this nanoparticle synthesis in that case it will be called as wet process of ball milling that is wet ball milling process. Also sometimes in cryogenic temperature that means cryotemperature means very low temperature by this cryogenic liquid medium in a ball mill this nanoparticles can be synthesized and in that case it will be called as cryomilling.

Now let us have an example of this production of nanoparticle from eggshell by wet ball milling. Here you will see that if we use some eggshell membrane then we can have some nanoparticle from this eggshell membrane. So the eggshell membrane is to be first separated. Here step by step method is given the eggshell is to be washed with distilled water then dried in a drying oven at around 70 degrees Celsius for 3 hours. And then it will be pulverized in a grinder.

Now the crude eggshell powder is then boiled at 0.03 mole per liter of hydrochloric acid for 10 minutes and then subsequently the mixture is to be cooled down and it is to be placed in distilled water and also then it is to be stirred for 15 minutes and then it will be allowed to stand for 30 minutes to remove the floating eggshell membrane there. And subsequently that eggshell powder is to be dried at 70 degrees Celsius for 3 hours. After suction of filtration, suction filtration that is why filtration that you have to suck it and collected for analysis after it is sheathed through 75 micrometer mesh. Here shown in the picture where you can do this process.

Let us discuss in more details here step by step the schematic representation of this overall experimental procedure is given here. If you take eggshell after that you have to clean it with distilled water and then you have to separate that eggshell membrane. After that you have to dry it around 70 degrees Celsius then you have to crush it to make it more finer one and then you have to add some hydrochloric acid around your concentration 0.03 mole per liter. For 10 minutes you have to boil it after that you have to stir it with deionized water for 15 minutes and then standing for 30 minutes.

Then you have to filter it after filtering you have to pass it through 75 mesh sieve and then you have to allow it through that wet ball milling process where 75 milliliter per 100 milliliter of ethanol can be used as a solvent there and then at a certain process parameter that you have to do this operation of this milling and then after milling you will get that nano size particles and after that you have to characterize it. Means characterization here you can identify what will be the size of that nano particles even what would be the strength of what will be the surface area per gram of that nano particles. These are the characteristics that you can even also you can have what would be the you know what are the moisture contents is there any amorphous or other type of materials there is formed then you can characterize it by different equipment. Also you have to measure that zeta potential even other particle size distribution there by different equipment. Also what are

the chemical compounds are there you can also identify by that XRF or FTIR method there.

So these are the characterization techniques by which you can then characterize. So basic objective is to here to synthesize the nano particle by this wet milling method. In this case we have taken eggshell from which you can synthesize that nano particle. Now typical operational parameters for this operation milling time can be typically 2 to 14 hours. Operational speed will be 300 to 500 rpm.

Ball to powder ratio that can be allowed here 4 is to 1 to 8 is to 1. Solid to liquid ratio within a range of 1 is to 2 to 1 is to 6 and filling ratio 10 to 40 percent. In this case the ground nano eggshell powder suspension is taken out of the milling jar after grinding according to the prescribed operational parameters. So in this way you can synthesize nano particles. Then another technique is called gas phase synthesis.

There are also different techniques available by which you can get these nano particles. First category is that to fabricate nano particles the first category consists of solid precursor used in like inert gas condensation, laser ablation, spark discharge. These are the methods these are called first category. In this case some solid precursor to be used there. Another category is called method where you will see the liquid and vapor precursor will be required in conjunction with that combustion flame synthesis spray and laser pyrolysis and also flame pyrolysis it is called.

Also you will see that plasma processing even evaporation techniques also used to synthesize that nano particles. So basically these two categories of this gas phase synthesis method by which you can get that nano particles. Now what is that inert gas condensation? Let us discuss here that one or two techniques of this inert gas condensation here or that gas phase synthesis. So there let us have this general production on this inert gas condensation. In this case this method generally used to synthesize metallic compound and oxide nano particles like manganese nano particle, nickel nano particles, iron and iron oxide nano particles and size control gold or palladium nano particles like this.

And the evaporation is done by thermal evaporation techniques, laser evaporation techniques, sputtering electric arc discharge and plasma heating method. The first step involves the evaporation of the material and the second is the rapid condensation of the evaporate material to favor the particle size and morphology. So inert gas condensation you will see that some evaporation techniques will be required to evaporate that molecules and after that it will be depositing on a hot plate like that and then it will be condensate to deposit on that. So here this is the techniques. So the first step is basically that you have to evaporate the material and second is to rapid condensation will be done of that evaporate material to favor that particle size and morphology.

This is the main techniques here. And in that case the inert gas is condensed in a condensation devices whose pressure is evacuated to fall down up to 2 into 10 to the

power minus 6 torque using a diffusion pump. After evacuation is done, inert gases like helium, xenon and argon are leaked into that chamber with lower pressure of about 0.524 atmosphere with the subsequent first heating of chamber at constant temperature and inert gas pressure. So at this point the particles with ultrafine sizes that are formed in the inert gas phase are collected in a surface that is cooled by water. So let us have an example for that how to synthesize a nanoparticle by this inert gas condensation.

So in this case we will see that we can synthesize some nanoparticles by this inert gas condensation here. In this case you will see that experimental arrangement here as shown in the picture and in this section you will see that nitrogen cylinder, resistance heating tube, furnace and vacuum pump are required for this experimental facilities and you will see that the furnace included three heating chambers with total length of 1.2 meter. This is typically, each chamber deployed a thermocouple to detect that heating temperature and the vacuum pump consists of a mechanical pump and an oil diffusion pump. A water cooling jacket is to be designed in such way that at the end of that quartz tube to realize complete condensation of the metal vapour.

And crucible also can be placed in the heating chamber which can be heated up to around 1300 Kelvin by resistance furnace. So this is the experimental facility by which you can do it. Now let us do that synthesis of that nanoparticles by this inert gas condensation. In this case we can prepare the zinc nanoparticles from that spent zinc manganese battery waste. So in this case the zinc cathodes from the battery loaded with a corundum crucible to be placed in the heating chamber initially.

And then a 200 mesh stainless steel net to be covered on the crucible to avoid that spreading of residues. And then the system is to be first evacuated to 1 Pascal when the furnace will be cooled down then nitrogen gas that is of different pressure like 100, 1000s, even 10,000 Pascal can be can be flowed into that chamber. And after that the furnace to be heated to the preset temperature with the heating rate of 10 Kelvin per minute. And then when furnace will be cooled down the phase of that prepared products to be characterized by a different characterization system like x-ray diffraction ACM machine like this for instrument. So this is the basic techniques of that nanoparticle synthesis by inert gas condensation okay.

And then another method it is called the combustion flame synthesis. This is also physical method by which you can convert this conventional size particles to the nanosize particles. In this case you will see that some example to production of carbon black, silica, titania these are the materials of nano size to be produced or can be produced. And the combustion heat can here activate a number of reactions such as oxidation, hydrolysis, pyrolysis and reduction which can manipulated based on precursor used and the flame environment there. So this is basically in a flame you will see that nanoparticles to be synthesized just by its some pyrolysis, hydrolysis and reduction reaction.

So this method basically widely this method widely used to synthesize small oxide particles from redox oxides. And in this case you will see that whatever flame will be produced that flame heat will be used to initiate nucleation of both aerosol and non-aerosol precursor. Sometimes this aerosol and non-aerosol precursors to be used. So initially that flame heat will be used to initiate that nucleation of both that aerosol and non-aerosol precursor. And that precursor will consist of redox mixers like that.

And the reducing agent like fuel is an organic compound such as urea, citric acid or polyphenyl alcohol like this. And the oxidizing agent also to be used which will be a metal salt such as nitrate. And after ignition you will see that using an external source the precursor mixer that will burn via an exothermic redox reaction to form the product. And the presence of large volume of gas formed after the combustion induces disintegration of the large particles into nanoparticles here. So here basically that after combustion of that particles and during that combustion there in presence of that reducing agent, oxidizing agent, this precursor in presence of that flame heat will be converted into a nanoparticles.

Here also one example is shown here for conversion or you can say that synthesize of titanium nanoparticles by this combustion flame techniques. In this case there will be a some methane flame premixed methane flame it is called by which you can convert this titania particles into its nano sized particle. So in this case titania nanoparticles can be synthesized in the premixed flame by using titanium, tetraisopropoxide material or chemicals as a titania precursor. So here this is called TTIP. So this TTIP will be used as a precursor for this synthesis of titania nanoparticle.

This TTIP as a liquid it will be placed in a flask here as shown in the picture which is to be connected with that gas carrying lines here as shown in the picture. Then the TTIP vapor is to be carried by that bubbling air through the liquid as shown in the figure. And the premixed flame burner composed of two parts it will be the bottom portion is in a divergent shape to decrease that flow velocity and it is filled with small steel balls to encourage the mixing of methane and air. So in presence of methane and air that TTIP to be mixed initially. After that the upper portion is a stainless steel tube with a diameter of 12 millimeter near the exit port of the burner here.

And you will see that several layers of the steel wires screen are also to be installed to ensure the uniformity of gas flow. So here you will see that methane and air that will be mixed with that TTIP precursor which will be set to mix with that TTIP in presence of nitrogen atmosphere and after that by check bulb that will be allowed to pass through that premixed burner. In this premixed burner whenever that flame will be produced that premixed gases are to be then prepared by the air with the methane and hydrogen which are to be blended in a mixing chamber filled with small glass balls that we have discussed. And then before entering that burner the combustible mixture is to be further mixed with that TTIP vapor that is carried here. It is carried by an air stream in the other mixing chamber which is also to be filled with glass balls.

Then the synthesized titanium nanoparticles in the post flame region are to be then collected via deposition on a stainless steel plate which is inserted into the flame zone at different heights above the burner exit port here. And in this case you will see there will be three consecutive ways this flame this nanoparticles can be produced here. So that will be this first of all these precursor nucleation first of all you will see that here and then nucleated this particles will be converted into nanoparticles after its growth. So here this is the method by which you can simply get this this nanoparticles of this titanium nanoparticles based on this methane. Another method it is called chemical vapor deposition method.

In this case the chemical vapor deposition method basically a chemical reaction will be there though it is coming as under physical operation. The substrate in this case will be used which is to be exposed to those precursor that decomposes on it and form the desired deposit. The vaporized precursor as actually then inserted into a CVD reactor that is chemical vapor deposition reactor and adsorbed onto a substance being placed at high temperature and then the molecules that get adsorbed react with other molecules or decomposed to form that crystals. The homogeneous nucleation occurs in gas phase and heterogeneous nucleation happens in a substrate and the reaction can be controlled to produce nanoparticles of size ranging from 10 to 100 nanometer. The three steps in CVD method are reactants that will be transported first on the growth surface by boundary layer and then chemical reactions will be allowed to occur on the growth surface and after chemical reactions there will be some byproducts which will be produced by the gas phase reaction and that has to be removed from the surface.

So these are three steps to be followed for this chemical vapor deposition technique by which you can get that nanoparticles. Let us have an example for this also to synthesize molybdenum and tungsten disulfide nanoparticles by aerosol-assisted chemical vapor deposition. So this can be carried out in a vertical tubular quartz reactor with an inner diameter of about 23 millimeter. And ammonium thiomyelidene here and ammonium thiotungsten here this chemical formula is given here can be used as precursors and from that precursors you will see some aerosol will be formed and that aerosol of their solutions in dimethyl formamide can be generated using a piezoelectric nebulization which will be operated at a frequency of 2.

4 megahertz typically. And then the reactor will be equipped with three resistive heaters. The first heater will be used to evaporate that solvent from aerosol particles and the second heater is used to heat that thiosols in the pyrolysis zone and the third heater maintains a temperature of about 300 degrees Celsius in the deposition zone to avoid condensation of the solvent there. Let us have this schematic diagram of this whole process here. You will see that the piezoelectric nebulizer here it will be produced and due to this piezoelectric nebulizer by action of that you will see that precursor solution will produce that vapor and vapor particles will be flowing out and there will be a zone where it will be you know that

fluidized or you can say that pyrolyzed here at a certain temperature and after that it will be going through that and it will also pass through another heat exchanger to maintain a certain temperature here and after that it will be allowed to deposit on that steel plate where it will be adsorbed here and it is also a hot plate there. So in this hot plate you will see that the particles will be deposited at a substrate and then that substrate will be taken out which will be as nanoparticles.

So in this case the experiments on that deposition of nanoparticles of that mixed solution is carried out at temperature at around 700 degrees Celsius and 900 degrees Celsius. That aerosol particles are transferred to the reactor by helium carrier gas that is supplied to the reactor at flow rate of about 0.3 liter per minute. The concentration of the precursor in the solution can be used as 0.

0.05 mole or molar. The values of that concentration ratio of that precursors in the solution can be taken as 0 to 1 typically. Then the synthesized particles to be collected on the substrate here quartz placed in the reactor on the graduated substrate holder using an electrostatic filter. So basically we are having this method, brief method by which you can synthesize. So in this case very interesting that what are the precursors to be used that you have to remember and also that aerosol of their solutions in that chemicals that solutions like in dimethyl formamide that can be generated using a piezoelectric nebulizer that will be operated with a certain frequency. And then that reactor you have to heat it in three consecutive sections to get that temperature at around 700 to 900 degrees Celsius and after that it will be taken or deposited in a steel hot plate systems as a substrate and which will be collected as a nanoparticle.

Here this aerosol assisted chemical vapor deposition is used to prepare that nanoparticles and is mostly used for thin film deposition on solid substrates, sheet particles or simply material supports. Also this aerosol assisted chemical vapor deposition involves the use of a starting precursor solutions followed by its atomization. Using a carrier gas aerosols are formed from the precursor solution and afterward nanoparticles are obtained either by homogeneous reaction as free powder that is flowing vaporization or via heterogeneous reaction on a heated substrate. So here this is the you know schematic of different foods by which you can get that nanoparticles by this aerosol assisted chemical vapor deposition. So in this case you can directly get that from that precursor after atomization and carrying by this carrier gas and then aerosol droplets to be transported to that heating zone and after that evaporation of that solvent and that will be transported to the to a chamber and then after heterogeneous reaction by absorption on that heated plate it will be deposited that will be getting as a heated substrate and that also can be taken as a nanoparticle here.

Or you can get it after heating and supplying that some reactive gases and vaporization through that vaporization you can get it that vaporization then vapor it will be then nucleated by a homogeneous reaction and then after again homogeneous reaction you can get that powder products and that as a substrate on the hot plate. So in this way you can

emphasize that nanoparticles not only this particular nanoparticles to be produced but you can get other different metals nanoparticles like rubidium, platinum, even tungsten nanoparticles they are by this method. So in this lecture what we have discussed that what are the physical methods by which you can get that nanoparticles or you can synthesize that kind of particles out of which you can get some mechanical method that is a very useful method and also widely used method where that there will be no chemical reaction whereas some other methods by chemical reaction like chemical vapor deposition in presence of that gas phase and there you can get that nanoparticles but all those techniques actually depends on that what type of materials to be converted into its nanosize that also important criteria and also other operating parameters to be considered and also some optimization condition to be followed to synthesize this. So as an undergraduate you only just know this methodology not in detail but you not have that facility to do that experiment on it on it I think in future those who have that interest on higher studies they may learn more about this nanoparticle synthesis and then can you can do research on this also there are several techniques also nowadays coming for synthesis of nanoparticles either by physical or chemical method. So please go through this brief of this nanoparticle synthesis by physical method one or two examples are given here those will be helpful and you please go through again systematically even reference also given here from which that it is taken and please go through this once again in details and you try to understand and have a idea to synthesize that nanoparticles in physical methods.

In the next lecture we will try to again discuss briefly about that synthesis of nanoparticles by chemical methods there also we will try to give some examples of that you know synthesis of nanoparticles by chemical methods. So thank you for your attention and have a nice day. Thank you.