

Lec 33: Synthesis of Nanoparticles (Chemical Methods)

Hello everybody! Welcome to this massive open online course on solid-fluid operations. So as we are discussing about the nanoparticles and its different characteristics and also we are talking about that what are the different methods of synthesis of nanoparticles. In the previous lecture we are discussing about that what is the physical method by which you can synthesize that nanoparticles. We have given some examples of that synthesis of nanoparticles by physical methods like ball milling process, even chemical vapor deposition and also other techniques those are available. And in this lecture we will try to learn something more about that synthesis of nanoparticles. Here we will try to understand how that nanoparticles can be synthesized by chemical methods.

As we have discussed that there are two methods, one is called physical and another is chemical method. Physical method is called the top-down method where bulk material is physically broken down to make smaller molecules whereas chemical method this is basically based on that nucleating of that atomic sized materials into that desired nano sized particles. And in chemical methods it depends on metal what type of actually materials to be generated based on which that chemical methods should be executed. And also we have discussed something about that what are the common methods for physical and chemical methods that are available and in industry also they are following those methods to produce that nanoparticles.

Though nowadays different investigators they are finding different way of that producing nanoparticles from different sources not only that material to material nanoparticles sometimes that nanoparticles are being produced from the natural sources also by physical as well as chemical methods. So here we will try to understand that chemical method of synthesis of some nanoparticles with some example and this chemical method is also will be called as that weight based approach of that nanoparticle synthesis. And what are the different weight based methods for synthesis of nanoparticles that you will see some names are given in the slides those are polyol method, microemulsion method, sol-gel method, thermal decomposition, hydrothermal, even sonochemical reactions you will see that electrochemical synthesis, photochemical synthesis as well as metal vapour synthesis. And these weight based techniques provide the simplest approach to produce that small and dispersed particles and these methods are often classified on the basis of either the source of energy or size selection. And let us have some idea of that polyol method by which that nanoparticle can be synthesized.

This polyol method basically uses non aqueous liquid like polyol example ethylene glycol, polyethylene glycol or diethylene glycol like this that will be used as a solvent and reducing agent. And from where that materials to be synthesized that metal, some metal oxide nanoparticles, even synthesis of bimetallic alloys and core shell nanoparticles are widely synthesized by this polyol method. And this method involves the reduction of a precursor such as metal salt from which that you can get that nanoparticles by ethylene glycol at a elevated temperature in the presence of polyol like polyvinyl pyrrolidone or it is said as the

PVP. So based on this presence of this solvent of polyvinyl pyrrolidone then there will be a reduction of that precursor in presence of the solvent at some temperature. And in this case the trace amounts of additives sometimes to be added which may affect on the synthetic pathways as well as on the morphologies of both nuclei and products of nanoparticles which would be easier to then synthesize these nanoparticles there.

Let us have an example of that synthesis of silver nanoparticle by this polyol method. So in this case you will see that ethylene glycol to be used as a solvent in this case this ethylene glycol around 5 milliliter typically first to be heated in an oil bath at 148 degree Celsius for 4 hours to remove that trace amounts of water from that ethylene glycol. Then a syringe pump will be used to regulate that simultaneous injection by that syringe pump of around 3 milliliter typically ethylene glycol solutions into the hot you know ethylene glycol that is made earlier at 148 degree Celsius at a rate of 45 milliliter per hour. And then one of the solutions of course that should contain 0.94 molar silver nitrate there that you have to add and the other one should contain the 0.

375 molar of polyvinyl pyrrolidone and in this case that this you have to add along with those solvent some amount of salt like 0.22 millimolar of sodium chloride. Then you have to stir those solutions by magnetic stirrer. So in this case magnetic stirring can be applied throughout the entire synthesis and the typical synthesis executes through a number of color changes. You will see that during that synthesis there will be a some change of color of that solution before the color become stable at approximately 46 hours then you can assess that what actually whether this nanoparticle synthesis direction is going properly or not.

If it is not happened then you have to change that proportion of that or concentration of that solvent there. Now to minimize that temperature perturbations during that sampling after getting that color change the glass pipette to be held just above the solution and preheated for 30 second before that immersion. And in this case the samples to be washed with acetone and then with water to remove most of the ethylene glycol and PVP solution. And during this washing you will see that the suspension that is to be centrifuged at 16000 rpm for 10 minute or 1 hour but depending on that whether this acetone or water can be used or not. Now to make sure that most of the silver particles taken from that reaction are recovered.

So whenever that silver particles nanoparticles to be produced that will be taken out after that reaction okay at least after 1 hour you can say. And also before that you have to continuously centrifuge there and also then finally that the sample is to be dispersed in water for further characterization by different characterizing equipment there or sophisticated instruments are there for characterizing for their surface area even strength even other material characteristics to know. Also what is the composition actually after that making that composition this nanoparticles and also you can assess it what will be the thermal conductivity electrical conductivity all those properties you can measure. And also how that mass will be changed with respect to time and also with respect to temperature

how it will be changing that is by T_g also you can assess that. So this is one of the important process of that synthesis of nanoparticles by this chemical method.

So you can easily make that silver nanoparticle by this polyol method. So in this case only that solvent you need one is the ethylene glycol another is you know that PVP also some amount of salt is required and also your experimental arrangement or facility should be made in such a way that there will be a serine sperm there will be what is that magnetic stirrer and also you can say that the temperature arrangement where that you can maintain up to a certain degree of Celsius and for that you need some thermocouple even with controlling system. And also this step by step that you have to follow this method to synthesize that nanoparticles of silver it is given in the slides. So based on this step by step methods you can easily synthesize that nanoparticle. Then another method of that synthesis of nanoparticle by chemical approach it is called microemulsion method.

In this case you will see that some surfactant molecules will be used to form some monolayer at the interface between oil and water. That you have to use some oil you have to use some water then oil and water is actually immiscible. So in that case microemulsion to be produced that will be thermodynamically stable and also isotropic and in that case this microemulsion whenever these two immiscible co-occurring water and oil phases are to be mixed by stirring or by mechanical agitation there you will see that formation of fine droplet and also water droplet will be there in presence of surfactant. So here surely that we have to produce that microemulsion which is stable in presence of that surfactant just by mechanical provision. And this surfactant molecules to form that monolayer at the interface between that oil and water with the hydrophilic head group and also you can say that hydrophobic tails group of the surfactant molecules in that aqueous phase and in the oil phase respectively.

And the properties of that nanoparticles prepared by the microemulsion method depend on the type and structure of the surfactant. What type of surfactant or what is the structure of that surfactant whether it will be cationic or anionic and or also whether it will be that hydrophilic tail or hydrophobic tail will be more dominant to act on that emulsion or not. And also how that monolayer it will be formed at the interface between oil and water like this. So it depends on that type of the surfactant and also the structure of that surfactant and here based on those surfactant and the microemulsion production and also monolayer product generation in that surface of that or you can say the interface of that oil and water. So let us have an example for that microemulsion method for synthesis of magnetic nanoparticles.

Here you will see you will get two different kinds of magnetic nanoparticles by this method. Some nanoparticles may be of that coated some may be uncoated way you can say that. So you can make coated nanoparticles and uncoated nanoparticles. Let us have this systematic way of that production of or synthesis of magnetic nanoparticles by this microemulsion method. So in this case first you have to produce that stable microemulsion

of some that immiscible phases.

So in this case you will see that microemulsion of cyclohexane and aqueous phase and water okay cyclohexane that is organic solvent and also aqueous phase these are immiscible phases in presence of surfactant that surfactant here is the Breese 97. This Breese 97 this is one type of surfactant this is basically polyoxyethylene n-olioether this is a one type of surfactant you can say. So this stable micro stubble micro emulsion of that cyclohexane and water in presence of this Breese 97 can be formed okay by using different organic bases as precipitant agent like cyclohexyl amine and oleolamine. And we will see that the aqueous phase to be made at 1 molar in iron 3, 0.5 molar in iron 2 and 0.

1 molar in hydrochloric acid to avoid that ferrous oxidation which is formed there. So in this case that you have to get that precipitant agent or from that different organic bases as a precipitant agent that you have to use that agent as cyclohexyl amine and oleolamine compound. And in that case for each synthesis that 250 ml of a microemulsion that will contain a volume ratio around 90 x 7 x 3 you can say of cyclohexane is to Breese 97 and aqueous phase there. So within this ratio that you have to follow that this two immiscible phases and with that surfactant there. And they are typically 250 ml of that microemulsion can be produced that containing a volume ratio of this cyclohexane Breese and aqueous phase.

So then what you have to do after production of that this microemulsion by that aqueous and organic immiscible solvent in presence of surfactant then it will be stirred and then passed with nitrogen at room temperature during 10 minutes there. After that samples to be placed in a thermostatic bath at 50 degree Celsius with magnetic stirring. Then the injection of that base for precipitating the particles to be then carried out by waiting at least for 5 minutes after the microemulsion when it is formed. And the formation of that microemulsion at 50 degree Celsius can easily be recognized by the change from a light scattering emulsion to a non scattering single transparent phases. So here this is the characteristics of that microemulsion which you can get for its identity at this 50 degree Celsius.

Then after that now you have to select whether you have to synthesize that coated nanoparticles or not. If you are not actually wishing to make that coated nanoparticles then it can be regarded as the category 1 that is uncoated particles to be produced. For that what is the step to be followed. So for that category 1 that means uncoated particles can be synthesized by injecting 4 ml of that cyclohexyl amine that will be diluted in 10 ml of cyclohexane and with that cyclohexyl amine at 50 degree Celsius. After that the microemulsion will be changed to black color and the formation of some large aggregates can be observed there.

And this will indicate the formation of that magnetic particles and their aggregation. Then after waiting around 15 minutes the product can be cooled to room temperature and to be

washed with a large amount of then acetone. And then the precipitate whatever it will be there at this room temperature it will be washed 3 times with 0.5 percent tetra methyl ammonium hydroxide to remove that surfactants which were actually earlier mixed there to form this microemulsion from that particle surface. And then you can follow after that washing of that acetone to flocculate that particles there after washing you will get that flocculate of the particles there.

And after that that particles will be dried at 65 degree Celsius at least for 24 hours. So at this particles it will be regarded as that uncoated nanoparticles of that. And then second category it will be that coated nanoparticles. So in this case what we have to do that some coating materials to be used there. So what are the coating materials to be used for that? So generally oleolemin or oleic acid that can be used for that coating material and in that case the particles can be synthesized by injecting 13.

8 ml of oleolemin which will be diluted in 10 ml of cyclohexane at 50 degree Celsius. So in this case the microemulsion also it will be changes to black without particle aggregation here whereas earlier it would be the black color will be formed just with particle aggregation. Here there will be no aggregation of that particle. After waiting of that again 15 minutes 150 ml of that synthesis product to be separated.

And then a mixture of 2.40 gram of oleic acid and 3.24 gram of oleolemin diluted in cyclohexane to be added to this part and to be steered for 30 minutes at around 50 degree Celsius. After that the particles which will be obtained in both parts of the synthesis then to be flocculated with the tunnel and separated and re-dispersed into two times dispersed two times in some other solvent like heptane. And then the final stage you can write that materials that is particles which is formed here under vacuum at around 30 degree Celsius for their further characterization. So since this is the final stage how can you get this this nanoparticles of that.

So interesting is that you need some solvent you need some that surfactant first of all you have to make some emulsion and then whether from that emulsion you are making that coated materials or uncoated nanomaterials or not that you have to decide if you are making that uncoated materials in that case you have to inject 4 ml of cyclohexyl amine diluted in 10 ml of cyclohexane at 50 degree Celsius. Whereas in case of coated materials in that case oleilamin or oleic acid it will be you know added for that coating and it can be again then synthesized by injecting of 13.8 ml of oleilamin diluted in 10 ml of cyclohexane at 50 degree Celsius. And the remaining step you will see that almost same in that case you will see some change of color it can be observed with some aggregation even without aggregation also there. So in that case you will see that final stage of that particle formation that of course will be dried at 65 degree Celsius at least for 24 hours.

And in the case of category 2 coated particles in that case you have to dry that particles under vacuum at 30 degree Celsius. So after production of that material production that is

nanoparticle size then you have to characterize it by different instruments like you have to characterize it by same, same means microscopic images for that specific surface area detection even other properties to find it out. So then we understood here that what is the microemulsion method based on which you can synthesize nanoparticles. Another method let us discuss here is called Sol-gel method. This is also one of the important method based on which you can easily get that nanoparticles.

So in this case you will see that you have to follow some proper way for that preparation of nanostructure materials. So basically metal oxides are being synthesized by this Sol-gel method and this method is based on the hydroxylation and condensation of molecular precursors in solution is being done and this actually precursors solution initiating a sol of nanometric particles there by hydroxylation and condensation. Personal condensation also being done with inorganic polymerization that may lead to a three-dimensional metal oxide network that is denominated as wet gel here and also extra heat treatments are needed to obtain that final crystalline state of that nanostructure because these reactions are performed at a room temperature and also the Sol-gel process includes hydrolysis and condensation of metal alkoxides. In this case metal alkoxides basically good precursors due to their endurance in the phase of hydrolysis that is the hydrolysis step replaces an alkoxide with a hydroxide group from water and free alcohol which is generated and factors that need to be considered in this Sol-gel method are like what are the type of solvent that you are using what temperature that you are maintaining and also what type of precursor that you are taking there will be some catalyst for that reaction what catalyst you are selecting even at a certain pH that you have to maintain that reaction some additives and also you have to use and also some mechanical agitation is required for this method of Sol-gel to produce that nanoparticles. Now let us have an example here also to produce titanium dioxide powders okay in this case it is your sol-gel method in this case TiO₂ nano powders can be synthesized by that Sol-gel method using your titanium butoxide as a titanium source so it is titanium oxide powders to be produced now titanium here it is not titanium this is titanium oxide to be produced here in this case three different alcohols can be used like ethanol propanol albutanol diethanol amine also you can use as a stabilizing agent to prevent precipitation during that preparation of that sols hydrochloric acid as a catalyst and deionized water can be used to prepare the sols and sols can be prepared in a beaker with continuous magnetic stirring then diethanol amine to be mixed with the titanium butoxide under magnetic stirring for 30 minute at room temperature after which alcohol to be added to the titanium DEA solution that means diethanol amine and titanium solution mixture.

Stirring to be continued for another than 30 minutes and then composition of that titanium butoxide even diethanol amine and that alcohol ratio to be maintained as 2 is to 1 is to 8 by volume and then finally that previously prepared that Sol-gel solution consisting of alcohol and water to be slowly added drop wise and stirred for another 30 minutes that will give you that homogeneous solution. After that that sols with that addition of hydrochloric acid to be prepared but in the last step a solution containing alcohol

appropriate amounts of water and 0.15 milliliter of hydrochloric acid to be added in this case increasing that amount of alcohol that will enable the preparation of a solution with a small concentration of acid that will prevent precipitation during the drop wise addition. Also if you are going to determine the influence of that presence of diethanol amine in the system then that sols can be prepared without the addition of a some flocculent is resisting agent is called deep flocculent and all of the sols then can be aged at room temperature for 24 hour for the hydrolysis process and then subsequently the prepared samples can be treated by heating at the rate of 50 degree Celsius for hour until the target temperature of 500 degree Celsius is reached and then you have to maintain heat at the target temperature for 90 minute. And after that you will see that that titanium oxide will be formed as a powder and you will see that after that it will be crushed for further fineness in a mortar.

So, this is called sol-gel method. So, what is the basic things is that you have to produce that sols in presence of sub solvent here with that precursor like alcohols, ethanol or butanol those are solvents along with that precursor of that titanium 4 butoxide which is coming from that titanium source and then you have to make that sols in a beaker with some continuous sharing based on that proportion of that compound along with that deionized water, water in presence of some catalyst even acid for maintaining pH that. So, in this way you can produce that sols and then some solvent that diethyl amine to be mixed with that butoxide under magnetic stirring for 30 minutes at room temperature and after which that alcohol to be added to the mixture of titanium and diethyl amine solution. In this case then I will see that some homogeneous solution will be formed after that as per step given here you will get finally that titanium oxide powder okay and it will be crossed again in the mortar and to get that final form of that nanoparticle. Another method we will discuss here is called thermal decomposition. Here also you will see that nanoparticles with a high level of mono dispersity and size control can be achieved by high temperature decomposition of some organometallic precursors or carbonyls that is by using organic solvents and also in presence of surfactants.

Generally by this thermal decomposition metal oxide nanoparticles are produced by this method. So, in this case you will see that some organometallic precursors to be required. Carbonyls maybe you can use as a precursor and also along with that organic solvents and surfactants will be required. So, what are that organic metallic precursors to be used like here it is given in the slide it is represented as that M_n plus $AcAc_n$ here M means you will see that some metal like iron manganese cobalt nickel chromium and n is the some coefficient that is 2 or 3 that number balanced and also $AcAc$ is basically that acetyl acetone net has denoted by that $AcAc$ and then you will see that another group it will be called that M_x , Cap_x that means here metal Caffeuron complexes to be used there as a precursor. In this case, Cap means here normal nitroso-phenyl hydroxyl amine here.

There other precursor maybe that carbonyls like ferric carbon net to be used or $FeCO_5$ to be used and organic solvents and surfactants such as fatty acids, oleic acid and hexadecile amine can be used. So, in this case, there will be some ratios to be followed. In this case, the

ratios of that starting reagents including organometallic compounds, surfactant and solvent are the decisive actually parameters for the control of size and also morphology of that magnetic nanoparticles and in this case the reaction temperature, reaction time are the crucial for the precise control of size and morphology of that nanoparticles. Let us have an example for this synthesis of nanocrystals of metal oxides like iron oxide, manganese oxide or copper oxide. Those oxide you can produce by this method here.

So, for that the step-by-step method is given here. Initially that you have to prepare the metal caffaron precursor as base materials on the precipitation of metal ions from aqueous solution at a specific pH with caffaron and the ammonium salt of here it is given normal nitroso phenyl hydroxyl amine. After that you have to dry it as a powder for powder of that metal caffaron nets and then you will see that it will decompose at temperature of 180 to 30 or 205 degrees Celsius for decomposing a compound like that here, FECO-P3, MNCO-P2 and then CUP2 respectively when heated in a some DTA or TGA apparatus under nitrogen. So, this is the second step then decomposition products then will be resulted as a why iron oxide and manganese oxide and copper metal. Next what you have to do to remove that oxygen and water in the complexes 7 gram of typically that amine is to be heated to 100 degrees Celsius for 1 to 1.

5 hour and then you have to do it repeatedly by evacuating at a certain pressure and then you have to evacuate it to 20 millitour and then passed with some you can inert gas like argon. And then that solution of 0.3 molar of that FECO-P3 that that decomposition compound in octyl amine to be treated to the same way at 60 degrees Celsius. And then there will be a reaction to be initiated and that reaction which is to be initiated by that rapid injection of that 4 ml of iron cup P3 solution and that will be done into a tri-octyl amine at 300 degrees Celsius under vigorous stirring and an atmospheric pressure. After that when that reaction to be allowed or initiated at that 300 degrees Celsius by stirring you will see that there will be a change of color of that solution from colorless dark brown.

And that evaluation of gas will indicate the decomposition of that metal caffaron complexes and then you will see that after the solution is heated for 30 minute at 200 around 220 or 25 degrees Celsius the reaction will be stopped and the solution can be allowed to cool. And then what you have to do at room temperature after cooling the flux you have to transfer it to a flask that flask will contain nanocrystals of that iron oxide in both dark brown clear liquid super netted and precipitate that is obtained in that after that reaction. After that you have to add some amount of organic solvents around 1 to 2 ml such as that toluene you can use even chloroform also you can use to this precipitate which will give you that clear deep brown dispersions of iron oxide in nanocrystals and then you have to cool it to again that room temperature for a weeks or you can keep it for weeks at room temperature and then form that iron oxide nanocrystals will be becoming stable at that room temperature for after one week and after that you have to add some volume of excess methanol maybe three times of that volume of that whatever solution you are giving in that nanocrystals form and then the iron oxide that nanocrystals then you will see that with the addition of

that methanol it will give you the precipitation as a brown powder and then operating of that methanol to that super netted of that reaction that will give you that brown precipitate which can also be redispersed and then reprecipitate by that suitable solvent and then what you have to do similar procedures can be used in that synthesis of manganese oxide and copper oxide in nanocrystals in that case the powder XRD can be performed for analysis of nanocrystals nature of that samples its morphology and other characteristics and in that case you can get that particles with average sizes down to 4 nanometer in this case by this method of synthesis and also if lower that temperature and lowering that feed precursor concentration you can get this even below of this nano 4 nanometer particles there so you can get up to 4 nanometer if you are just lowering that feed temperature and then lowering the feed precursor concentration but you can try further just reducing that feed temperature and then precursor concentration maybe there you can get even less a size of that nanoparticles so this is the basic way of by which you can buy by thermal decomposition you can say you can get that nano crystals of different oxide material so here we then understand here what is that method of thermal decomposition sol-gel method even micro emulsion procedure to produce that nano particles there sometimes that one step also method can be followed to synthesize that some nano particles by direct thermal decomposition method in this case tenorite one example it's given that to produce tenorite and nanoparticles by direct thermal decomposition method in this case some copper sulfate for hydrate complex or sodium carbonate and distilled and deionized water can be used to make copper oxide nanoparticles in this case as per information given in the slide here you will see that some complex of that brosenite to be prepared by addition of 0.5 molar of sodium carbonate solution to a 0.5 molar of copper sulfate solution at a rate of 4 ml per minute that will be done drop wise for one hour with vigorous stirring at around 1000 rpm at 55 degrees Celsius and in that in that case you will see that there will be a precipitation formation that will be color will be green and then it will be filtered and then to be rinsed three times with warm deionized deionized water and then it can be dried at 70 degrees Celsius for several hours and then a small fraction of that produced precursor to be used for analyze and then rest to be calcined in air in a muffled furnace at 750 degrees Celsius for two hour and you will see that the crystalline structure of the precursor and copper oxide nanoparticles can be formed at this temperature of this 750 degrees Celsius after that calcination of two hours and that nanoparticles after that it will be characterized by different characterization techniques generally x-ray diffraction being done at a certain wavelength to know that different components of that nano crystals of that copper oxide and also that a structure in morphology also you will see that thermal behavior for that precursor what is to be used actually is studied through that thermogram metric analysis which can be performed under an ambient airflow and also you have to remember that that morphology and average particle size are to be analyzed after formation of this nanoparticles and that will be analyzed by some microscopic image system that is same team there are so many other microscopic image analysis tools are there you can assess it.

So we learned here that some chemical method by which you can synthesize nanoparticles of this specific examples also given here and you can follow other different

methods which are here given in the slides also that there are other several methods but we cannot discuss here all those methods here only specific two three methods were discussed briefly for further study you can follow some reference books to more about this nanoparticle synthesis either by physical or chemical method. So as an undergraduate you know course I actually should limit this up to this brief introduction on this nanoparticle characteristics even what is the definition of nanoparticles what is the basic feature of that nanoparticles and the few methods of that synthesis of that nanoparticles by physical and chemical methods. So I think you understood this at least that some brief introduction and also you have learned something about that nanoparticles what is that how it is defined what is the characteristic methods and how it can be synthesized though here it is not discussed that how to characterize those nanoparticles after formation you can follow other course for characterization method that will be helpful for you. And then in the next successive lecture we will try to understand something more about that you know solid-fluid system where we will be discussing about some adsorption characteristics there. So in that module of that adsorption characteristics we will try to learn what is the basic principles of that adsorption what is the application of adsorption and also how to analyze that adsorption characteristics by isotherms also what is the adsorption kinetics that we will be discussing in the successive lectures.

So thank you for your kind attention have a nice day. Thank you.