Nano structured Materials-Synthesis, Properties, Self Assembly and Applications
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Module - 3
Lecture - 22
Self Assembly of Nanostructures – II

Welcome back to this course on nanostructured materials, synthesis, properties, self assembly and applications. So, we are in module three and in the last lecture, which was the first lecture of module three, and today we will be doing the second lecture of self assembly of module three, which is actually the lecture number 8. So, the lecture 7, 8 and 9 of module three correspond to the lectures of self assembly in nanostructured materials.

And in the first lecture of self assembly which was lecture 7 of module three, we discussed what is self assembly, how it can be brought about, and we started with some applications. Today we will continue on the self assembly of nanostructures, which is the second lecture and the lecture number 8 of module three.

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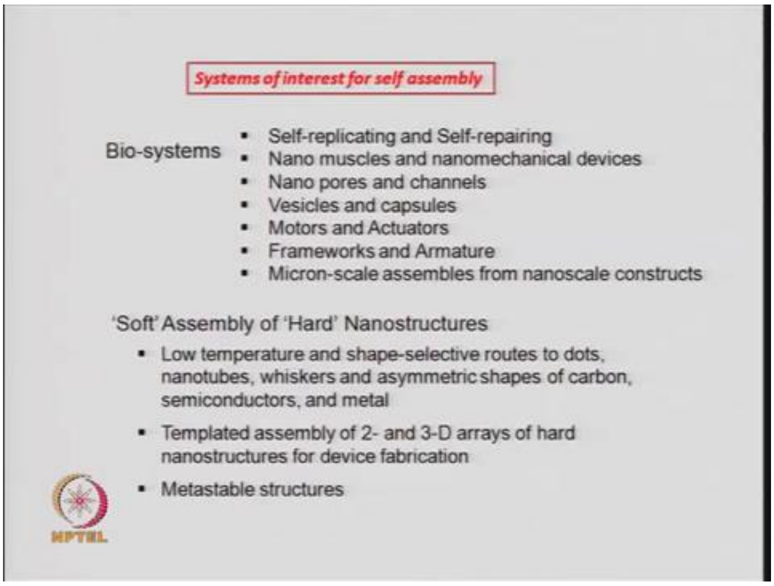

Systems of interest for self assembly

Bio-systems
- Self-replicating and Self-repairing
- Nano muscles and nanomechanical devices
- Nano pores and channels
- Vesicles and capsules
- Motors and Actuators
- Frameworks and Armature
- Micron-scale assembles from nanoscale constructs

'Soft' Assembly of 'Hard' Nanostructures
- Low temperature and shape-selective routes to dots, nanotubes, whiskers and asymmetric shapes of carbon, semiconductors, and metal
- Templated assembly of 2- and 3-D arrays of hard nanostructures for device fabrication
- Metastable structures

Now, the systems of interest for self assembly. Why are we interested in self assembly? There are lot of examples in the natural or life sciences in bio systems. For example, you have self replicating and self repairing systems. Self replicating means that they can produce objects which are similar to them, and self repairing means if some part of the molecule or a biopolymer gets affected then it can recreate that part by itself.

You have nano muscles, nano mechanical devices, where you require the concepts of self assembly. Then there are systems in biological cases where nano pores and nanochannels are involved, vesicles, capsules, motors, actuators, they all are important in bio-systems and concepts of self assembly comes in many of these cases. Further we can build micron scale assemblies from nanoscale constructs. And then you have soft assembly of hard nanostructures, the soft assembly like low temperature and shape selective routes to dots nanotubes, whiskers and asymmetric shapes of carbon based materials, they can be semiconductors and they can be metals.

So, hard nanostructures means something carbon material or cadmium sulfide, cadmium selenide, which are semiconductors. These are, we are calling them hard nanostructures, and we are calling it soft assembly, because we are using a solution route using molecules or a simple nanomaterials to make self assembled structures, which ultimately yield these hard nanostructures. So, hard nanostructures typically is something which is inorganic, mostly either a metal or a semiconductor or an insulator, it can be an oxide, a nitride, a chalcogenide, or simple carbon based material.

So, these hard nano-structures made by soft methods, soft methods mean without going using high temperatures or without using any plasma or laser for the assembly of these nanostructures, we referred them as soft assembly using low temperature or room temperature methodology using solution routes. If we can generate oxides or other metals etcetera is what we call soft assembly of hard nanostructures.

Then similarly, we can make templated assembly of 2 and 3 dimensional arrays. Instead of making particles or spheres or rods of these oxide nanostructures or metal nanostructures, which we are calling as hard nanostructures. We can make 2 dimensional or 3 dimensional array of these nanoparticles, which now we refer to as 2 and 3 D arrays of hard nanostructures using templated assembly of these molecules or molecular systems using a soft chemical approach.

And these 2 and 3 dimensional arrays of nanostructures are useful for applications, because they are used for devices and this is a methodology by which we do device fabrication on templates using a soft assembly or a self assembly process. We can also generate metastable structures using this soft assembly of hard nanostructures.

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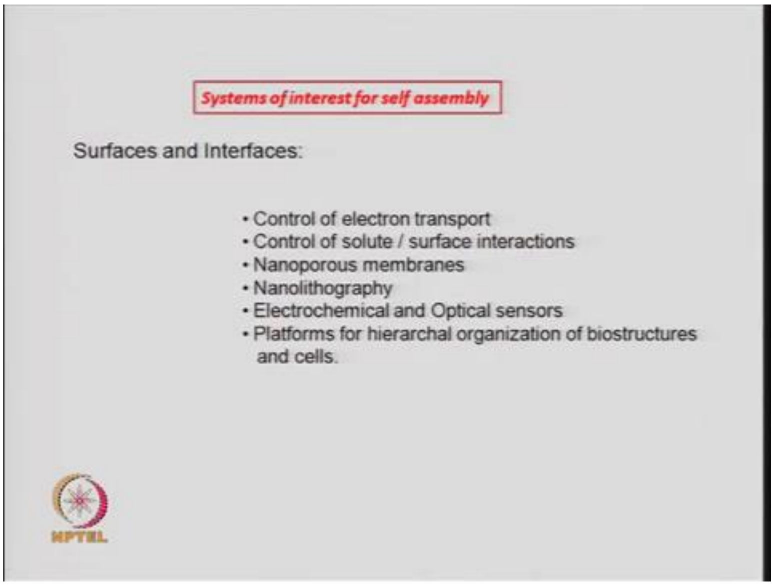

Systems of interest for self assembly

Surfaces and Interfaces:

- Control of electron transport
- Control of solute / surface interactions
- Nanoporous membranes
- Nanolithography
- Electrochemical and Optical sensors
- Platforms for hierarchal organization of biostructures and cells.

Then systems of interest for self assembly, what all systems are of interest was. For example, in surfaces and interfaces, we can control the electron transport by controlling the self assembly. Then, we can control the solute surface interactions on the surfaces. We can make nanoporous membranes with design, size and distribution of the pores, which will also then control the surface area, because if you control the size and number of these pores, will control the surface area of these membranes, which is important for several applications.

Then these systems are of importance in nanolithography where self assembly is very important. Nanolithography means, making structures in the nanodimensions based on some technique like, here we are discussing self assembly, but you can also make nanolithography using electron beams, ion beams, and lasers etcetera. Now, here we are saying that using self assembly also, we can do nanolithography which will be called soft lithography then. Then you are interested in self assembly for various electrochemical and optical sensors, and self assembly also leads to structures which are platforms for hierarchical organization of biostructures and cells. So, from the small simplest DNA and RNA etcetera, how you can get to cells and then organals and the whole system. So, self assembly is used as a platform for this kind of organization of biostructures and other cells.

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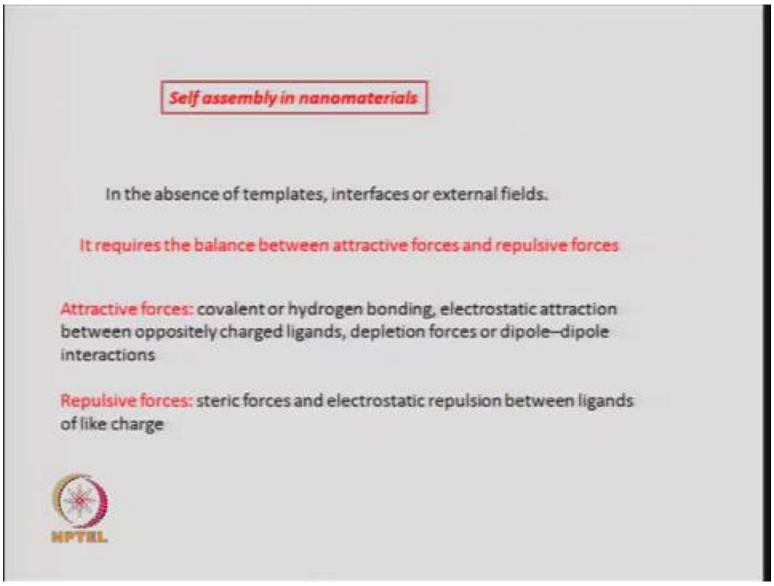

Self assembly in nanomaterials

In the absence of templates, interfaces or external fields.

It requires the balance between attractive forces and repulsive forces

Attractive forces: covalent or hydrogen bonding, electrostatic attraction between oppositely charged ligands, depletion forces or dipole–dipole interactions

Repulsive forces: steric forces and electrostatic repulsion between ligands of like charge

Now, in the absence of templates or interfaces or external fields. How do you get to have self assembly? Now, for that you need a balance between attractive forces and repulsive forces. So, if you have both attractive forces and repulsive forces in the system, and they can balance each other, then you generate a molecular self assembly, or self assembled structure, which is stabilized by this balance of forces.

Now, what are these different forces? The attractive forces can come through simple covalent bonding or hydrogen bonding or electrostatic attraction between oppositely charged ligands, and depletion forces or dipole-dipole interactions. These all one or more of these will give you the attractive forces present in a system, which is undergoing self assembly, and that self assembly will be possible if the magnitude of the attractive forces is exactly balanced by repulsive forces.

The repulsive forces are of two kinds one is the steric force, which means that if you have bulky substituents around each other, then those bulky substituents will have a steric hindrance, and that gives rise to this steric force. The other thing is if you have similar charges, so there will be electrostatic repulsion between those kinds of ligands which are present and that will give rise to repulsive forces. So, two types of repulsive forces, the steric forces and the electrostatic repulsion of like charges will balance one or more of these attractive forces. And you will get a resultant structure at a distance, which is optimized such that the attractive forces and the repulsive forces are balanced.

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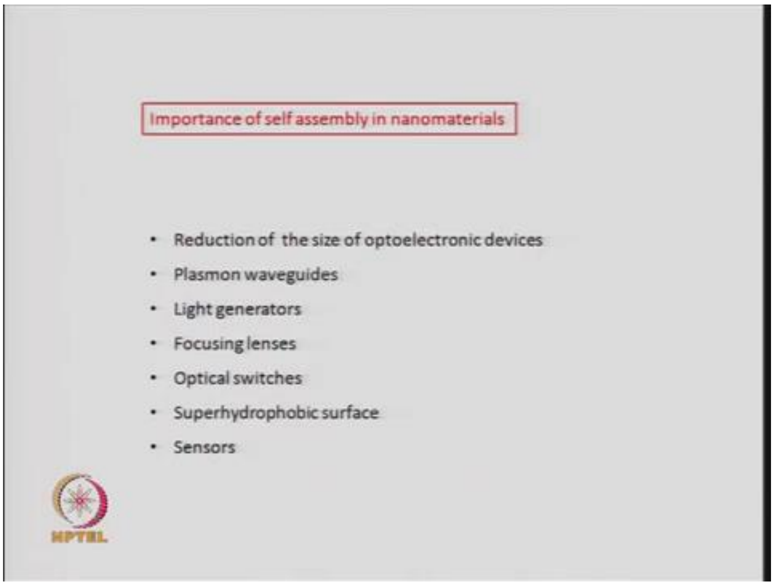

Importance of self assembly in nanomaterials

- Reduction of the size of optoelectronic devices
- Plasmon waveguides
- Light generators
- Focusing lenses
- Optical switches
- Superhydrophobic surface
- Sensors

Now, in the importance of self assembly in nanomaterials is immense. There are many-many applications for example, there is lot of use of optoelectronic devices. So, many-many everyday gadgets and devices are based on optoelectronics. Optoelectronics is a branch of science and technology, where you are combining optics or optical properties of materials with electronics.

So, you see large displays monitors like large television screens or a plasma screens, all of them have optical information and electronics involved with each other. So, there are many-many sensors which are you can make using optoelectronic devices. So, the size of optoelectronic devices is a matter of concern, because you want to make smaller and smaller cell phones, you want to smaller and smaller laptops, all of them depend on optoelectronics. And so reduction on the size of these devices involve going to nanodimensions.

So, self assembly nanomaterials is one way which people are thinking of reducing the size of optoelectronic devices. Then there are other systems like plasmonic waveguides, light generators, focusing lenses, optical switches, superhydrophobic surface. Superhydrophobic means, hydrophobic means something which dislikes aqueous solutions or water.

Superhydrophobic means a great disaffinity; that means it really has a strong repulsive interaction with water or similar solutions. And this kind of superhydrophobic surfaces are of interest, because if you coat them on surfaces, then the surfaces will be clean, you can wash them off easily with water. So, lot of applications are there of superhydrophobic windows, superhydrophobic walls, etcetera. Then there are this large field of sensors, all kinds of sensors, they can be biochemical sensors, optical sensors, pressure sensors, where you have importance of nanomaterials, and self assembly of nanomaterials becomes part of that application.

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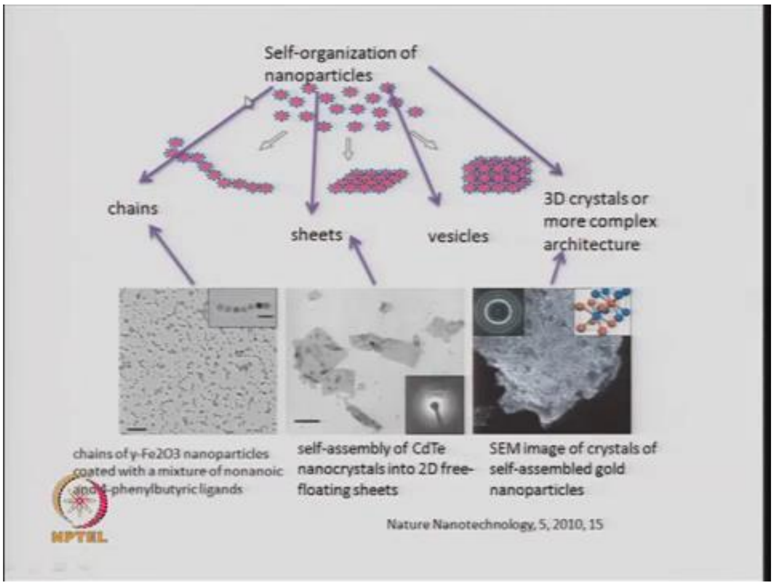

Self-organization of nanoparticles

chains

sheets

vesicles

3D crystals or more complex architecture

chains of γ-Fe2O3 nanoparticles coated with a mixture of nonanoic and 4-phenylbutyric ligands

self-assembly of CdTe nanocrystals into 2D free-floating sheets

SEM image of crystals of self-assembled gold nanoparticles

Nature Nanotechnology, 5, 2010, 15

Now coming to an example, let me show you. If you have nanoparticles, so you have a large number of nanoparticles here, and these nanoparticles can self organize or self assemble to form various kinds of structures. So, one of these structures is, if they all align in a kind of a line, it may not be exactly a straight line, but can be a curve. So, you have these particles which are disordered here, under certain conditions they can align themselves to form chains. And this is a schematic diagram, and this is a real picture taken under a transmission electron microscope, where you can see these chains and there are many chains like this. And if you look closely at one of these chains, then that will look like this. So, you will see 1, 2, 3, 4, 5, 6, 7; 7 particles are here.

So, it depends on the conditions, that you have you can have 7 particles in a chain or 10 particles or 15 particles, and here these are magnetic particles gamma iron oxide nanoparticles, which have been coated with the mixture of nonanoic and 4 phenyl butyric ligands. So, these kind of particles coated with these kind of ligands are self assembling to form chains.

This is another example, where these particles are self assembling to form a sheet, and this 2 dimensional structure, which is a schematic diagram. In reality looks like this, so these are the sheets that you get, and these sheets are observable under a transmission electron micrograph, where transmission electron microscope. And this is the micrograph where you can see these planar objects, which are nothing but sheets and these sheets are can be explain to be made up of a 2 dimensional network of these original particles.

And here in this sheet, you can see that this ordering is, there is a perfect order because you can do what we call the electron diffraction of these material. If you do the electron diffraction, you will see these lines, which you can kind of index and each of these lines are correspond to certain reflection planes of these ordered structures. So, this ordered structure is made of particles of cadmium telluride, cadmium telluride is a known semiconductor and here you have a self assembly of cadmium tellurides nanocrystals to form a 2 d sheet. This is a 3 d crystal, so a 3 dimensional crystal, where you have a more complex architecture and it is basically made up of gold nanoparticles.

So, you can have different types of organization, depending on the particles, the particles can be different kinds, can be semiconductors, can be metal particles. Also on what you cap, what you functionalize them and the conditions the ph etcetera will control the ultimate morphology or the self assembly of these particles, whether you get a chain or whether you get sheets or t3 dimensional structures as shown in this case of a gold self assembled structure.

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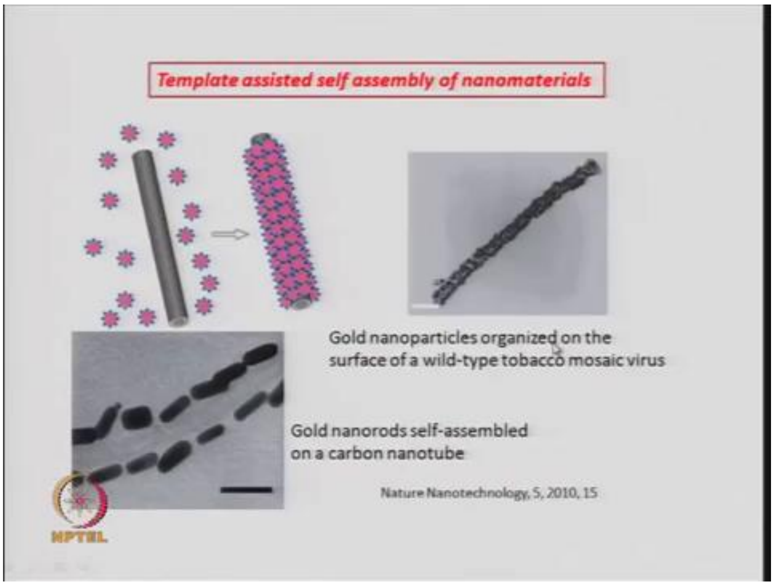

Template assisted self assembly of nanomaterials

Gold nanoparticles organized on the surface of a wild-type tobacco mosaic virus

Gold nanorods self-assembled on a carbon nanotube

Nature Nanotechnology, 5, 2010, 15

Now, you can have template assisted self assembly of nanomaterials for example, here you have a template, the template here is for example, a some kind of a tobacco mosaic virus, and you have gold particles which can be schematically shown here. It can be a carbon nanotube or any other kind of rod, so if you have a iron oxide rod, whether you can this kind of self assembly. So, these particles a form a structure on top of the rod, so then the initial rod is the template on which the self assembly is taking place.

So, this is a real picture, a transmission electron micrograph of gold nanoparticles are these small spheres, you can see on this rod, which is a virus. And this virus is a particular virus, which is called the wild type tobacco mosaic virus, and on top of the virus you have got these gold nanoparticles. So, you have self assembled the gold particles on the tobacco mosaic virus. This is another example, where you can see there is a carbon nanotube, it is light gray structure, which you can see, and you can see there is a gap at the center and that is hollow.

So, this is a carbon nanotube, which is hollow and on top of the carbon nanotube these rod shaped objects are gold nanorods. So, the gold nanorods have taken the shape of the carbon nanotube. So, this is a template assisted self assembly of gold nanorods and the template in this case is a carbon nanotube.

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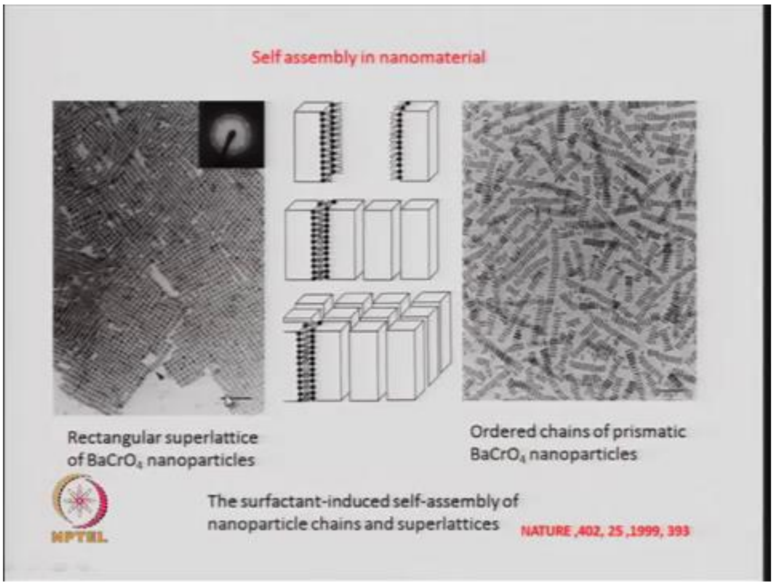

Self assembly in nanomaterial

Rectangular superlattice of $BaCrO_4$ nanoparticles

Ordered chains of prismatic $BaCrO_4$ nanoparticles

The surfactant-induced self-assembly of nanoparticle chains and superlattices

NATURE ,402, 25 ,1999, 393

This is another example where you are having a self assembly of barium chromate nanoparticles. So, you have several barium chromate nanoparticles, this is a schematic diagram, so if this is one barium chromate nanocrystal and this is another nanocrystal of the same material. The two come together in the presence of some molecules, which are shown here and these molecules are called surfactants.

And these surfactants basically act as if they have two types of charges, they have two types of properties. They have a hydrophilic head group and a hydrophobic chain. And this is typical of most soap molecules, where you have a hydrophilic head and a hydrophobic chain. Now, when you try to bring these two close together, then the hydrophobic tails interact with each other because you know like attracts like, and so both of them are hydrophobic, that means they hate being in a aqueous environment, and so both of them have the same nature, they are both hydrophobic.

So, they come together, and when they come together they bring these two crystals together and. So, it is like you are stitching these two crystals through this surfactant molecules. And then this can happen between the next two etcetera. So, in the presence of surfactant, if you synthesize barium chromate nanoparticles, you get this kind of array of particles, this is self assembled, because between two particles you have this kind of interactions, which bring the two cubes together.

Now, this kind of a rectangular super lattice can occur. In some cases depending on conditions, you may have more one dimensional organization. So, here the arrangement is along this direction only, so it is not forming a 2 d lattice, like this super lattice, where you have interaction along this axis as well as along this axis. Here you have interaction only along 1 axis. So, you get a chain of nanoparticles or nanocrystals of barium chromate, and so these are surfactant, these are examples of surfactant induced self assembly of barium chromate and nanocrystals. And depending on the surfactant, you can change them into 2 d layers or 1 dimensional chain like structures the self assembly is caused by surfactants.

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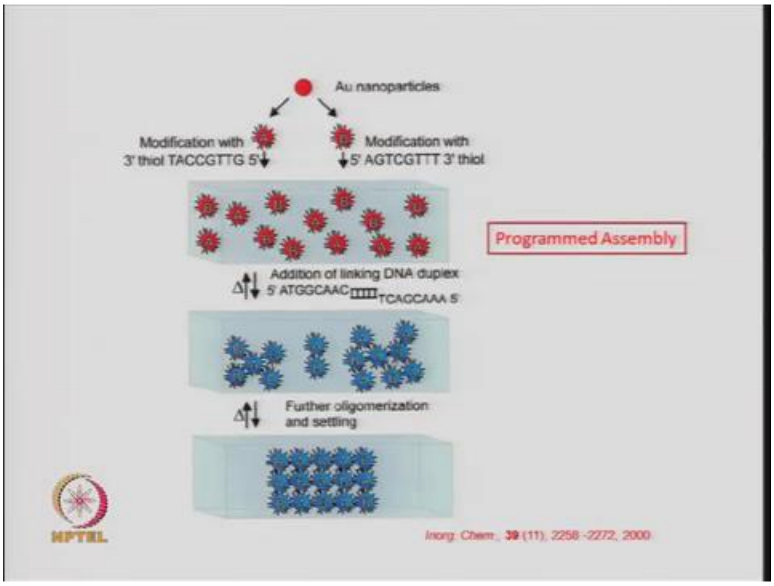

Au nanoparticles

Modification with 3' thiol TACCGTTG 5'

Modification with 5' AGTCGTTT 3' thiol

Programmed Assembly

Addition of linking DNA duplex 5' ATGGCAAC TCAGCAAA 5'

Further oligomerization and settling

Inorg. Chem., **39** (11), 2258 -2272, 2000

Now, this is another example, here you can program the assembly by doing some intricate chemistry. So, you have to design some molecules, which you want to tag onto gold nanoparticles. So, you have gold nanoparticles and you design a molecule using these kind of base pairs. So, here T stands for thiamin, A stands for adenine, and C stands for cytosine and G stands for guanine. So, you can make a chain of base pairs like this, and on this side of the thiamin, you have a thiol group attached, now this thiol group, you know thiol groups are prefer gold particles. So, wherever they will find a gold particle this thiol group will get attached to the gold particle.

So, this oligomer of bases through the thiol group gets attach to this gold particle, and so it gets modified and those are the A. The A what is written is basically gold particle modified by this oligomer of bases and it has the 5 prime free because on the 3 prime side is the thiol, and that thiol gets bound to the surface of the, of the A particle.

Similarly, you may have another gold particle, another solution of gold particles, which we call B, and which is functionalized or modified by a different sequence of base pairs. So, here was a different sequence, this is different sequence, and when this attaches to the gold particles using again the thiol group, you get a different gold particle because you have a different oligomer on the surface and this we call B.

So, when you mix A and B, both A and B have these base pairs and you know that thiamin will always attach to adenine. So, thiamin of this will attach to adenine of this, like that they two will come together right, and they will form, then you add a DNA duplex. So, you have this A particles modified by this, and you have this B particles modified functionalized by this, and you have them in solution and then you add a DNA duplex which has on one end one strand DNA. Another end another strand of DNA, and this part of the DNA will attach to the A particles, because the A has this functionality where thiamin will attach to the adenine of this, and adenine of this will attach to thiamin of this.

So, this part of this linking molecule will attach to the A particles, and this part of the linking DNA will attach to the B particles and, once they are attached this side to B and this side to A, basically A and B will come together. So, you will now have complexes of A and B, and still some functionalities will be free to bind, when those bindings occur you will have further oligomerization, and you will get a ordered structure.

So, this is called programmed assembly because you have planned exactly how this should assemble by functionalizing with a very specific chain of bases and having another particle with another specific chain of bases. When they, when you bring them together in the presence of this kind of DNA, you will have only a particular kind of arrangement, which will settle down to give you this kind of ordered structure. So, this is a programmed assembly.

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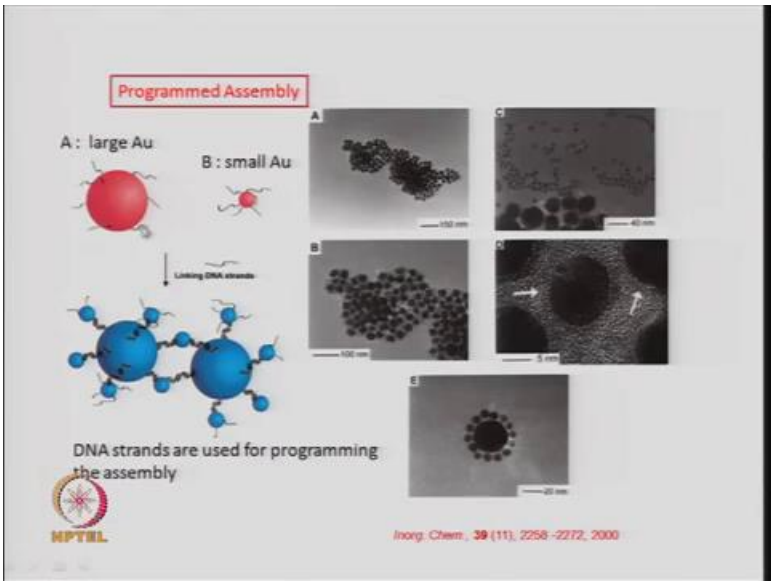
Programmed Assembly

A : large Au

B : small Au

DNA strands are used for programming the assembly

Inorg. Chem., **39** (11), 2258 -2272, 2000

Now, the same thing what we were discussing of the programmed assembly this is what happens. So, assume that your A is a large gold particle and B is a small gold particle, then the large gold particle with its functionalization and the small gold particle with its functionalization are brought together and then you have the linking DNA strand.

The linking DNA strand is basically this one, so that is the linking DNA strand and when you bring them then these two particles join together. So, the large particle and the small particle join together and then this small particle can join to another one, and then this one can join to another one, and this is the real pictures that you see. So, you can see these kind of agglomerates and you can see large particle with small particles around, and in this picture it is a TEM micrograph, where you can clearly see a large particle with small gold particles. And in between them is the linker molecule and that can be seen in between those two particles.

So, these small particles are self assembled around this large particle, and that can be seen clearly. These are several of these large particles with small particles around them and if you zoom onto one of these particles, then you see this. So, DNA strands have been used for programming, the self assembly for assembling so it may be better called programmed assembly rather than self assembly, because you have made the molecules in a manner in a particular fashion.

So you have programmed that the molecules will come together only in that fashion, and that you were successful the TEM is proof of that, that your successful in doing that. And you have those particular small particles, small gold nanoparticles around the large nanoparticle.

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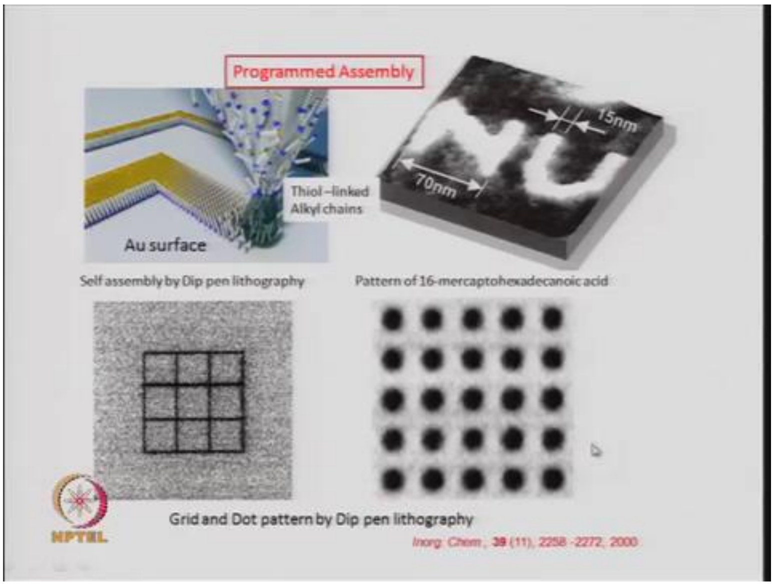

Programmed Assembly

Self assembly by Dip pen lithography

Pattern of 16-mercaptohexadecanoic acid

Grid and Dot pattern by Dip pen lithography

Inorg. Chem., 39 (11), 2258 -2272, 2000

Now, this is another example of programmed assembly, where again you are using thiol to link onto gold surfaces. So, because it is now well known that thiol can attach to gold surfaces. So, to thiol the s h group, you can link an alkyl chain now. So, these are alkyl chains, which is a schematic diagram, the alkyl chain is shown here, many alkyl chains are there and this blue dots are the thiol at the end of each alkyl chain. Now, suppose you bring them close to a gold surface through a kind of a orifice or through a hole in a tube, so this typically can be of the order of half of a micron or so 500 nanometer or even less may be 30, 40 nanometer.

So, you will have all these a chains are coming down, when they come down on the surface, since it is gold particles are there, the gold will align with the thiol, and so the thiol will be on the close to the surface. So, all the blue dots you see will be at the bottom touching the gold surface, and the alkyl chains will be pointing at upwards.

Now, if I move this, so I move my capillary or my pen which is normally, this is called dip pen lithography, you can do it using a kind of a tip which is called an AFM tip, a type of AFM tip which moves in a particular fashion, wherever it moves it brings these molecules into assembly with the gold surface and you get a pattern of molecules. So, this is acting like a pen, you are writing on the gold surface, but you do not have ink inside, you have molecules of these thiol linked alkyl chains. And the pen wherever it is moving gives you these nanostructures on the surface of gold.

So, this is a programmed assembly and that is this is a schematic diagram to help you understand, and this is a real picture, where you can see that something has been written with molecules, and this is our dimension of 70 nanometers, and this is the thickness is around 15 nanometers. So, basically this thickness is 15 nanometers, so whatever is this orifice diameter is 15 nanometers, probably close to that and that is why you can get this kind of lines.

Now, you can make many kind of patterns depending on whatever shape geometry you want, and these patterns is not only for making designs, there has to be some application based on these patterns. So, you make a particular pattern, a design because you want to make an application of this.

So, maybe you will connect this with some wires or you will connect it with some other tubes, which has its specific application, right? Now, what you have got is a particular pattern that you wanted of a particular molecule, and then you have to put this patterned surface into application into use, mostly very much useful is in the bio sensing applications where this kind of patterns are very important.

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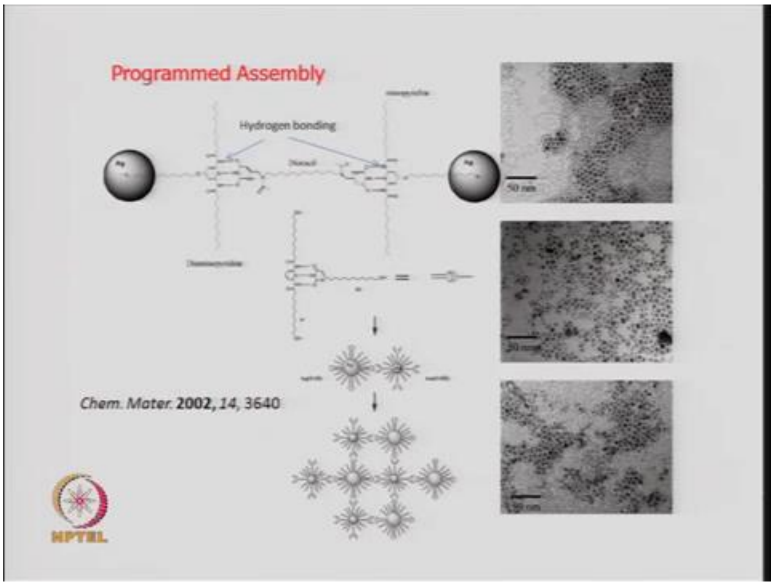

Programmed Assembly

Chem. Mater. **2002**, *14*, 3640

Now, another example of a programmed assembly is, you have again a designer molecule, you synthesize this molecule which is diamino pyridine, and this diamino pyridine is linked to the silver, here the particle is silver. Again through a thiol group and so you have this silver nanoparticle with thiol linked to this particular molecule, which is called diamino pyridine, and you have another linker molecule which is called diurasil and this diurasil has got this kind of moiety o nitrogen o.

Now, this type of moiety immediately finds this kind of nitrogen, so you have this kind of a pyridine ring here, and it forms hydrogen bonds. So, one end of this diurasil molecule immediately binds to this part of the diamino pyridine molecule. When it binds onto this side, the other side, which is free finds another molecule like that, and it binds to that molecule from the other side.

So, this is like a linker with two hands, one hand holding this silver ion, silver atom and the other hand holding this silver nanoparticle. So, both sides you have silver nanoparticles which are functionalized using thiol groups and then having this pendant molecules, which can bond through hydrogen bonding to this linker molecule which is diurasil. So, the effect is that you bring the silver particles together.

So, this kind, this can continue, you can have a molecule on this side also, you can have a molecule on this side also. And so if you look under the transmission electron micrograph, that we were there are lots of these kind of silver nanoparticles with linker molecules, you will get a large number of this kind of a silver particles self assembled, because of your choice of molecules. So, it is been programmed to assemble in a particular fashion, and you can see these assembled structures.

This is a schematic diagram of these silver particles with this kind of a hook attaching to this. So, these two molecules have been shown with these kinds of pictures schematically to make you understand, how this silver particles are coming together through these linker molecules. So, this is another case of programmed assembly.

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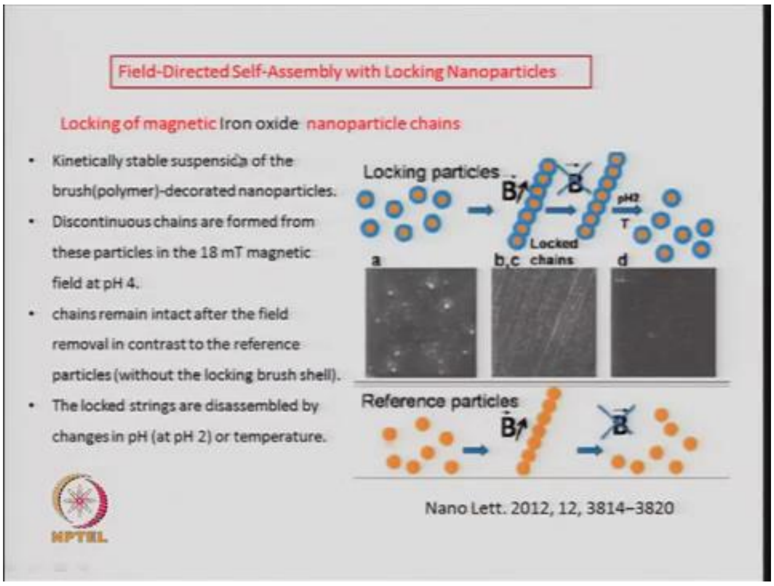

Field-Directed Self-Assembly with Locking Nanoparticles

Locking of magnetic Iron oxide nanoparticle chains

- Kinetically stable suspension of the brush(polymer)-decorated nanoparticles.
- Discontinuous chains are formed from these particles in the 18 mT magnetic field at pH 4.
- chains remain intact after the field removal in contrast to the reference particles (without the locking brush shell).
- The locked strings are disassembled by changes in pH (at pH 2) or temperature.

Nano Lett. 2012, 12, 3814–3820

Now, you can have what is called field directed self assembly. Field directed can be electric field or magnetic field or some other kind of field, but mainly electric field and magnetic field, which have reasonable kind of forces, can generate forces for this kind of self assembly. Now, you have iron oxide particles which are magnetic, and you want to assemble them into chains. Now, if you take simple iron oxide particles, so these are simple iron oxide particles and these particles if you apply a magnetic field where B is a magnetic field and you are applying the magnetic field in this direction.

So, what happens these iron oxide particles will align in the form of a chain, then if you remove the magnetic field, that means you switch off the magnetic field, that means you take away the magnet if it is a permanent magnet, or you switch off the current of the electromagnet. So, there is no magnetic field, then this chain will get disturbed and it will go back to a disordered structure.

So, from a disordered structure, you got a linear chain like structure, and then you will get again a disordered structure if you remove the magnetic field. Now, if you want to permanently have that structure, then you have to lock the particles. So, what you do? You have a polymer or on the, on top of the particles. When you have the polymer on top of the particles and you apply a field it gets aligned, when you remove the field the particles are still aligned, and then if you want to disturb this alignment you change the p h or temperature and then the particles will be disaligned.

But if you remove the field, the particles are still aligned. So, the chains remain intact after the field has been removed when you have this kind of a polymer brush on top of it, which basically interlock between themselves. So, this polymer can interact with the polymer of the other particle and form a kind of a can join together, which you cannot remove even if you remove the magnetic field, but you can disturb this if you change the p h. So, this is a field directed self assembly with locking nanoparticles.

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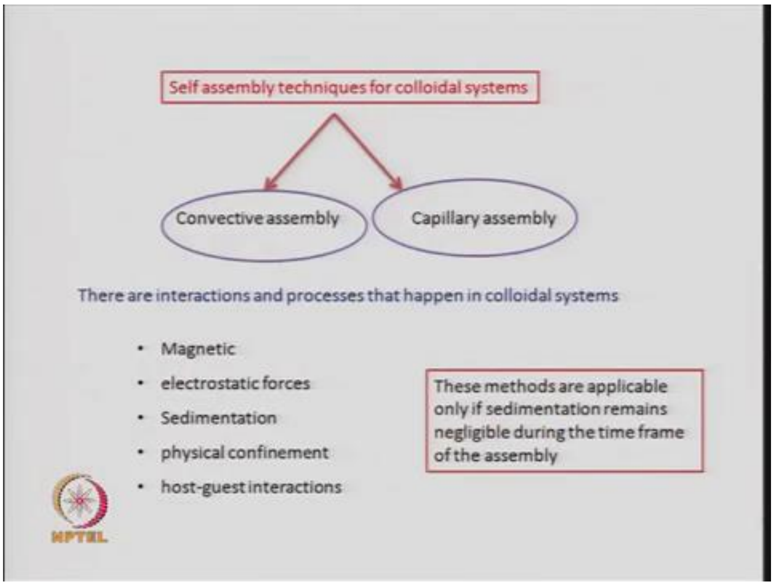

Self assembly techniques for colloidal systems

Convective assembly

Capillary assembly

There are interactions and processes that happen in colloidal systems

- Magnetic
- electrostatic forces
- Sedimentation
- physical confinement
- host-guest interactions

These methods are applicable only if sedimentation remains negligible during the time frame of the assembly

Now, you can have other kind of, what are the different techniques by which you can have self assembly in colloidal particles. Now, that is of two kinds, one is the convective assembly the other is the capillary assembly, and the interactions that happen during this convective and capillary assembly are due to several forces. And these forces are magnetic forces, electrostatic forces, sedimentation, confinement, that means your forcing the particles close together and host guest interactions. So, all these, some one or more of these forces will be involved in a colloidal system, when you bring about assembly through convective mechanisms or through capillary forces.

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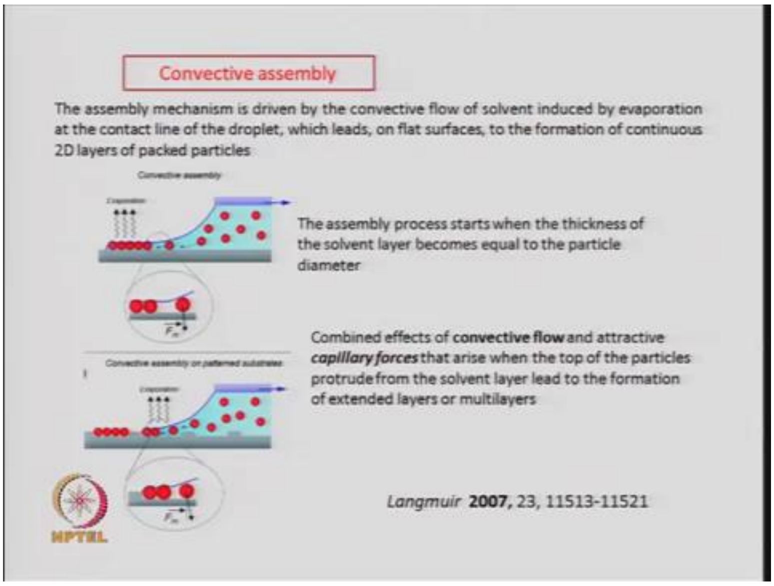

Convective assembly

The assembly mechanism is driven by the convective flow of solvent induced by evaporation at the contact line of the droplet, which leads, on flat surfaces, to the formation of continuous 2D layers of packed particles

The assembly process starts when the thickness of the solvent layer becomes equal to the particle diameter

Combined effects of **convective flow** and attractive ***capillary forces*** that arise when the top of the particles protrude from the solvent layer lead to the formation of extended layers or multilayers

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So, this is convective assembly where you have a flat surface and your particles in a solvent. Now, the solvent flow, which is called the convective flow, along with the particles is driven by the evaporation of the solvent. So, suppose you have a temperature gradient, that means wherever the liquid with the other solvent with the particles is coming here, the solvent is evaporating. When the solvent is evaporating, the particles are getting aligned on top of the surface, and since the solvent is evaporating more of the liquid or the solvent is coming in this direction.

So, the solvent process starts when the thickness of the solvent layer becomes equal to the particle diameter right, when you have more solvent, such that the thickness is more than the diameter, then the assembly is still not taking place. Only when the diameter of this particle becomes nearly equal to the solvent thickness, then the assembly occurs. Now, this is mainly being driven by convective flow and the convective flow is because solvent is evaporating, so there is a drive to come onto this side.

Now, there can also be capillary forces, which occur when the top of the particles are extending from the solvent layer, and that can lead to extended layers or multi layers. Basically capillary forces are between the valve and the liquid or between two particles when they have some liquid, then you can have capillary forces.

So, the combination of convective assembly in patterned surface, this is a, this surface is not patterned, in this case the surface is patterned. So, somewhere you see, you have some protrusion and somewhere there is a depth, so particles are sticking into these depths and that can happen due to combined effects of convective flow and attractive capillary forces because the top of the particles may protrude from the solvent layer.

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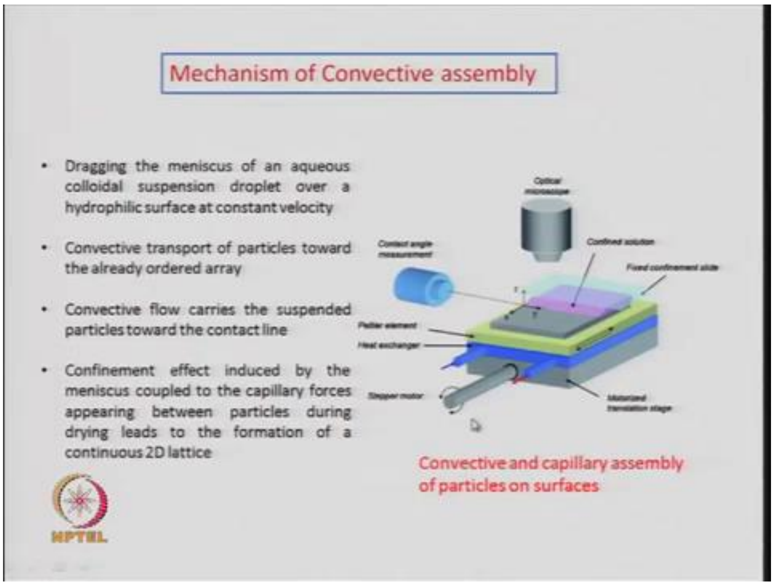

Mechanism of Convective assembly

- Dragging the meniscus of an aqueous colloidal suspension droplet over a hydrophilic surface at constant velocity
- Convective transport of particles toward the already ordered array
- Convective flow carries the suspended particles toward the contact line
- Confinement effect induced by the meniscus coupled to the capillary forces appearing between particles during drying leads to the formation of a continuous 2D lattice

Convective and capillary assembly of particles on surfaces

Now, mechanism of convective assembly is simple, that you are basically dragging a liquid layer along this plane. So, you have a surface and on the surface this film is forming, and the liquid, this is the contact line where the solution is confined and you are moving this and then that convective transport of the particles take place and it gets ordered at the line of contact. So, here already the film has formed, the particles have formed an ordered array, and on this side it is still a liquid and as it moves you can order the particles.

So, convective flow carries the suspended particles towards the contact line, and the confinement effect induced by the meniscus coupled to the capillary forces. When the particles are drying, that leads to the formation of the two dimensional lattice. So, the convective and capillary assembly of particles can be seen here and then these are basically the microscope to visualize this, and this is, if you want to measure the contact angle, you can measure the contact angle, and this is a motorized stage this is how you move the stage and this is the motor attach to it. And there are heat exchangers to vary the temperature along this surface, so you can, there is a mechanism of convective assembly.

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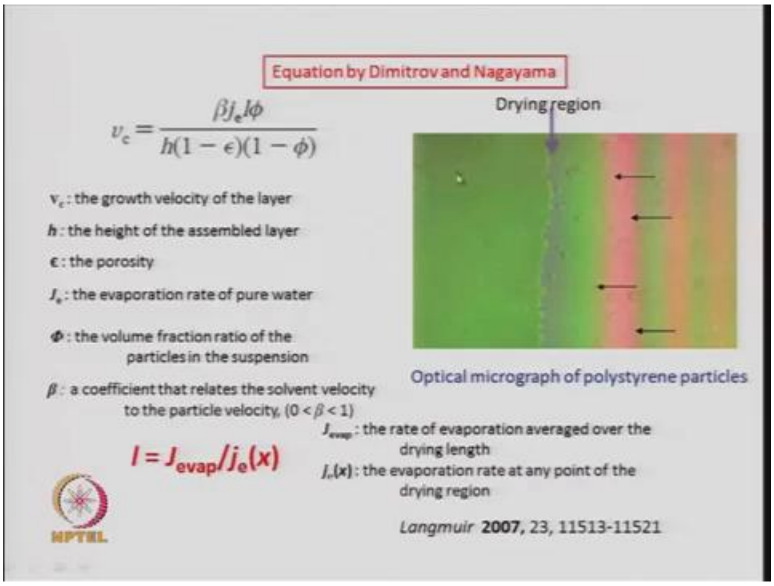

Equation by Dimitrov and Nagayama

$$v_c = \frac{\beta j_e l \phi}{h(1-\epsilon)(1-\phi)}$$

v_c : the growth velocity of the layer

h : the height of the assembled layer

ϵ : the porosity

J_e : the evaporation rate of pure water

Φ : the volume fraction ratio of the particles in the suspension

β : a coefficient that relates the solvent velocity to the particle velocity, $(0 < \beta < 1)$

$$l = J_{evap}/j_e(x)$$

J_{evap} : the rate of evaporation averaged over the drying length

$J_e(x)$: the evaporation rate at any point of the drying region

Optical micrograph of polystyrene particles

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Now, this is the real picture this was a schematic diagram of the film formation of the ordered self assembled layer, and this is a real picture and this shows that this part has dried, this is the drying region. And you can still see some particles there, and these particles will move towards this side as there are these terms which are the rate of evaporation, which is given J evap and there is the J i, that is the movement towards this interior, or towards the contact line.

So, how these factors, the growth velocity of the layer is dependent on several factors, like the rate of evaporation over the drying length. So, this is the drying length and so it is proportional to that, then it depends on porosity, it depends on volume fraction of the particles in the suspension. That means, the concentration of the particles it depends directly on that, and then there are other factors the height of the assembled layer etcetera. So, this equation gives you the growth velocity of the layer, how fast you can grow the layer on this surface. And so there are several of these terms which tell you about this growth velocity.

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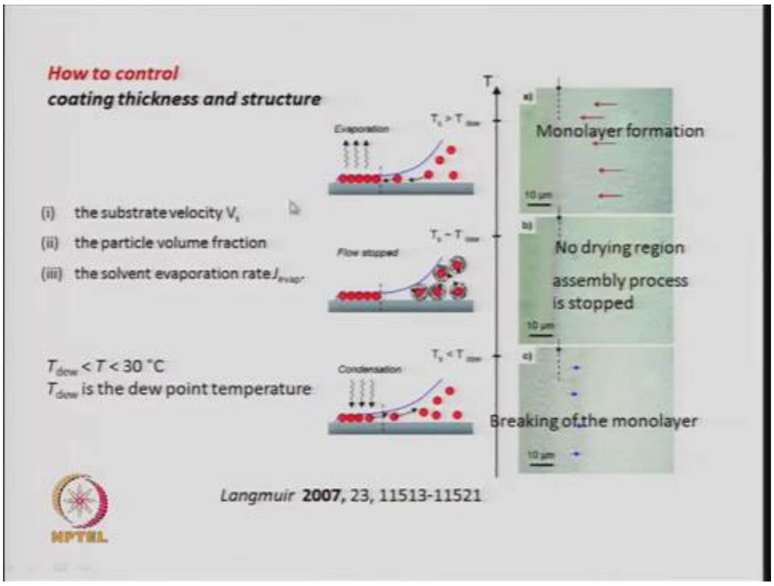

How to control
coating thickness and structure

- (i) the substrate velocity V_s
- (ii) the particle volume fraction
- (iii) the solvent evaporation rate J_{evap}

$T_{dew} < T < 30\ ^{\circ}C$
T_{dew} is the dew point temperature

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Now, if you want to control the thickness and the structure, so here you can control the substrate velocity, the particle volume fraction and the solvent evaporation rate. All these you can control by controlling the temperature. So, the temperature of the substrate, whenever it is greater than temperature of the dew point, you will not have the evaporation.

So, when the temperature of, then you will have the evaporation, whenever the substrate temperature is high, then you will have the evaporation and you will have the monolayer formation. Suppose, the substrate temperature is low than the dew point then you will have the reverse, you will have condensation and not of the solvent, you will not have evaporation.

So, in this case when you have the substrate temperature much larger than the dew point temperature, you will have evaporation and because of convective flow, the particles will align and form the self assembled structure. So, you will get monolayer formation. So, these are monolayer which is being formed, and the particles are coming rushing towards the contact line whereas, if the temperatures are same, then it stops further assembly and no further movement is there. When the temperature of the substrate is low, then you start having condensation, that means the solvent comes back and whatever layer was formed, this layer starts breaking up. And these nanoparticles start getting into solution.

So, you see whatever film was formed, now the film is again started breaking and you have particles movement in this side, towards the solvent direction. Here when the layer was forming, the particles were coming towards the layer, so the particles were coming towards the contact line from the particle rich in the solvent, it was coming towards the contact line and would eventually form layer, when the temperature of the substrate is much less than the dew point, the layer which had formed has started breaking and the nanoparticle start moving into the solvent. So, by controlling that temperature, you can control this evaporation and the condensation. And hence you can control the self assembly, you can also control using the substrate velocity, the particle volume fraction, etcetera. The particle volume fraction is basically the concentration of the particles, if you vary that also you can control the coating thickness and the structure of these monolayers.

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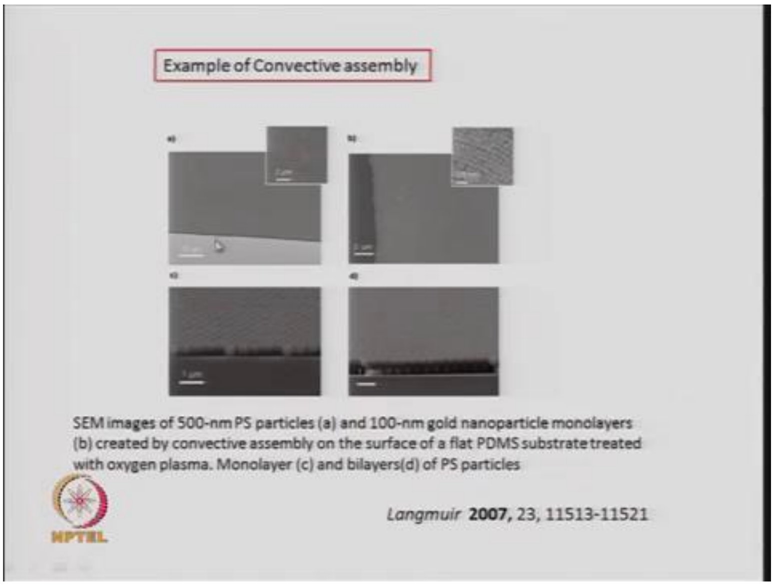

Example of Convective assembly

SEM images of 500-nm PS particles (a) and 100-nm gold nanoparticle monolayers (b) created by convective assembly on the surface of a flat PDMS substrate treated with oxygen plasma. Monolayer (c) and bilayers(d) of PS particles

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Now, this is a picture, the earlier this was a schematic diagram explaining how the monolayer formation is taking place or how the monolayer was breaking. And this is a real a picture, where with is a FESEM picture, where you can see that you have a layer and if you look closely you can see the nanoparticles arranged in the layer. This is at a much closer scale, this is some 200 nanometers scale, and this is 2 microns scale.

So, you can see it on 200 nanometer, these are approximately 100 nanometer sized gold particles, which are on a PDMS, which is poly dimethylsiloxane, a very common polymer, and on top of that you have got these gold particles which are arrange so nicely, so beautifully, it is using convective assembly.

Now, this if you take this is the top view, if you take the side view or the cross section, then you can see that this is made up of only one layer, this is the substrate on top there is only one layer of these spheres of gold particles. Whereas, on this you can see there are two layers, so you take a cross sectional picture along the side, you can see number of layers which form on this substrate of PDMS. So, this is monolayer and this is bi-layer of particles and these are of course, different particles, the particles here a basically are gold particles, whereas this c and d are of polystyrene particles made on PDMS as a substrate.

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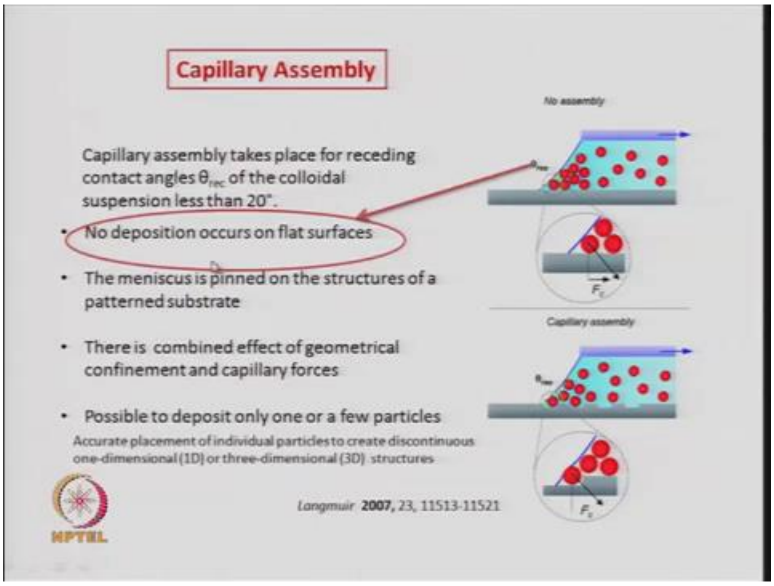

Capillary Assembly

Capillary assembly takes place for receding contact angles θ_{rec} of the colloidal suspension less than 20°.

- No deposition occurs on flat surfaces
- The meniscus is pinned on the structures of a patterned substrate
- There is combined effect of geometrical confinement and capillary forces
- Possible to deposit only one or a few particles

Accurate placement of individual particles to create discontinuous one-dimensional (1D) or three-dimensional (3D) structures

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Now, you can have capillary assembly this was previously we were discussing convective assembly, this is convective assembly, but you can also have capillary assembly. Normally in capillary assembly, you will not have deposition on flat surfaces because you need this angle which we call theta receding angle is should be less than twenty degrees for the capillary assembly to take place.

So, on a plane surface this assembly, this angle as you see is normally higher than that. Whereas if you have a patterned substrate, so this you can see is a patterned substrate, and if you zoom in to this region, you can see the step kind of thing and in this step there it is possible to deposit a particles on this stepped by capillary forces. And this kind of assembly is called capillary assembly and it is possible to deposit only few particles in this kind of process, it is not possible to deposit large number of particles using the capillary assembly, for that you have to use the convective assembly.

So, in this case you have a combined effect of the geometrical confinement because you are confining these particles within this geometry. So you have these structures that you have made, so there is a confinement effect. And as well as capillary action, the capillary forces are acting, and you are getting this assembly.

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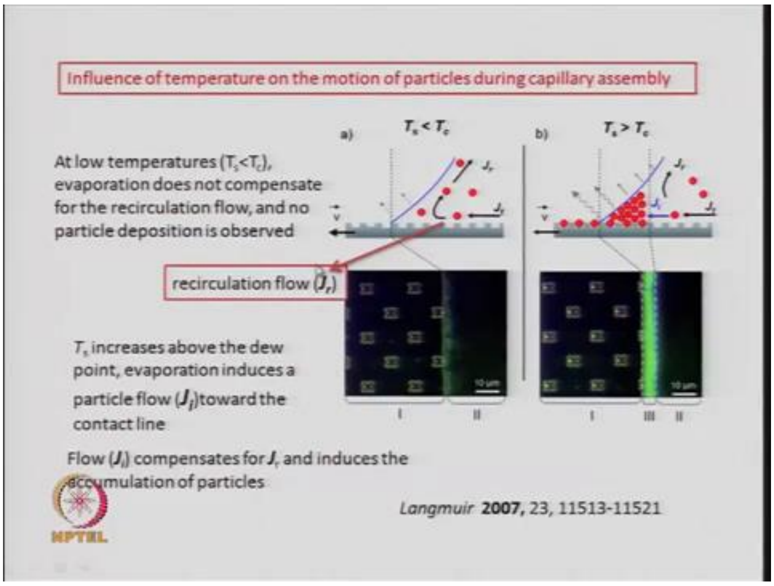

Influence of temperature on the motion of particles during capillary assembly

At low temperatures ($T_s<T_c$), evaporation does not compensate for the recirculation flow, and no particle deposition is observed

recirculation flow (J_r)

T_s increases above the dew point, evaporation induces a particle flow (J_i) toward the contact line

Flow (J_i) compensates for J_r and induces the accumulation of particles

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Now, during capillary assembly there can be an influence of the temperature and this is shown here. Suppose the substrate temperature, this is your having a substrate which has a particular geometry, it is not planer and hence it can help in capillary assembly. Now, in this case this is, when the substrate temperature is less than a particular critical temperature, then evaporation does not compensate for the recirculation flow. So, there is a flow which is given by J, so J r is the recirculation flow, and if you do not have the substrate temperature high. Suppose it is low, then the evaporation does not compensate for the recirculation flow, and you cannot have any particle deposition. However if you have, so this is a the contact line, this is the real picture, and this is a schematic diagram.

So, the since there is some evaporation, but it is not sufficient because the recirculation is pretty high and you do not have any patterning. But if the substrate temperature is high, the evaporation rate is high. And then you have this kind of a self assembly in these patterned substrate, where the particles are getting collected, and then you see this region where the at the contact region you have this self assembly of particles, and that happens when the substrate temperature is much larger than a particular critical temperature. And this large substrate temperature leads to high evaporation rate.

And when the high rate of evaporation is there, then the J i which is the rate at which the particles is flowing towards the interface, is much higher than the J r, the J r is the recirculation rate. So, the incoming rate J i compensates for the J r and hence induces the accumulation of the particles.

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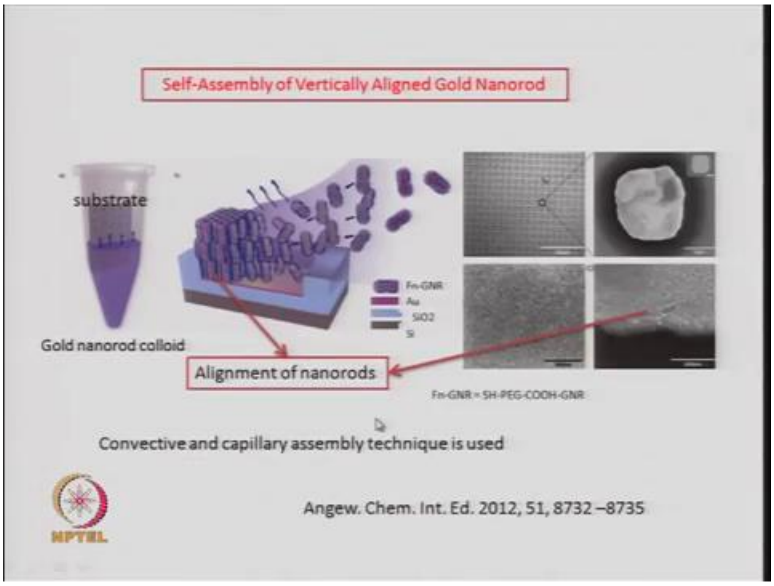

Self-Assembly of Vertically Aligned Gold Nanorod

Convective and capillary assembly technique is used

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So, this is the last slide today, and this is what we show is another example of vertical aligned gold nano rods. So, you have got gold surface and on the gold surface is of course, on top of silica surface and silicon surface. But what is important is on gold surface if you put particles which have got on the surface thiol groups, the thiol groups will attach on the gold surface and you will get a pattern like this. So, these are gold nano rods on top of which is thiol functionalized and when you drop this particles on a gold surface, they stick on top of them and so they form array. And if you look closely at this array you will get this ordered structures of this thiol functionalized gold rods on top of the gold surface.

So, here again you have self assembly of vertically aligned gold nano rod, where both convective and capillary assembly technique is used. So, there is a gold surface, and thiol capped gold nano rods are forming a pattern on top of the gold surface, this is a low resolution picture, this a high resolution picture of the gold particles capped with thiol on the gold surface. So, then you very much and we will meet in the next lecture for our final lecture on self assembly.

Thank you.