Nano structured Materials-Synthesis, Properties, Self Assembly and Applications

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Module - 1
Lecture - 1
Introduction to Nanotechnology

We are going to start this course on nano structured materials synthesis, properties, self-assembly and applications. The course has four modules, and today we will be doing module one and the first lecture of module one, which is the introduction to nanotechnology. And I am from IIT Delhi, department of chemistry and I will be giving you forty lectures on this subject.

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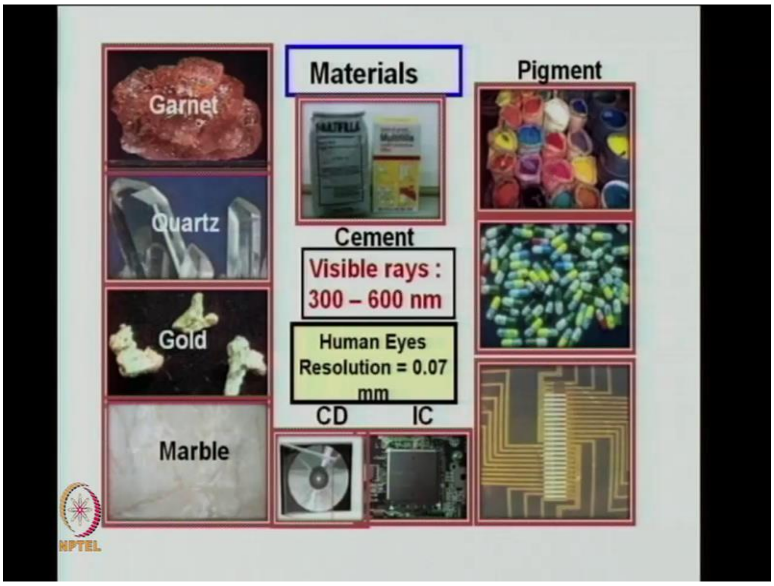

Now, before we go to nano materials, we have to know what are materials? So, there are different kinds of materials, which you can observe around you in your daily life. Some of the materials are natural like garnet or quartz or gold or silver or marble, there are many naturally occurring elements and compounds, which you can see which occur in the earth.

And there are manmade materials for example, you have cement or a compact disc or an IC chip, which are made up of different kinds of materials. For example, silicon is the material for an IC chip and you have several interconnects made of silver, which connect, which make the connections in an IC chip. Apart from that you can see there are lot of drug molecules, which are used in pharmaceuticals or dyes and pigments, which are used in daily life. These are manmade materials and most of the materials that we can see with our naked eye. This has to have a size, which is within the dimensions of the visible rays, which is 300 to 600 nanometers; we are using visible rays to see them with our eyes. And we cannot see objects which are smaller than 0.07 millimeters with our human eyes.

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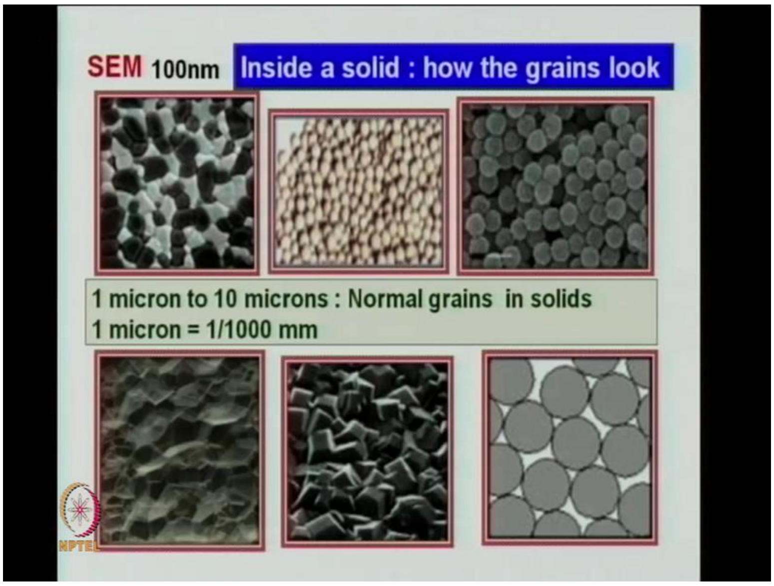

Now, if you look at these materials more carefully that is inside these materials, if we have something by which we can observe objects much smaller than 0.07 millimeters like using electrons. Then we can see that, these materials are made of particles or grains which are of the size of one to hundred to nanometers to thousand nanometers etcetera, which is like 1 micron up to 10 microns. This is the normal size of grains in any solid which we find around us.

However, as you know that our eyes cannot see these small size grains. So, we have to use what is called an SEM, which is a scanning electron micrograph through a microscope. And this scanning electron microscope uses electrons, which have a wavelength which is correspondingly smaller, much smaller than the wavelength of visible rays and hence we can see objects which are much smaller. Now, a micron is 1 by 1000 of a millimeter. So, it is much smaller than 1 millimeter.

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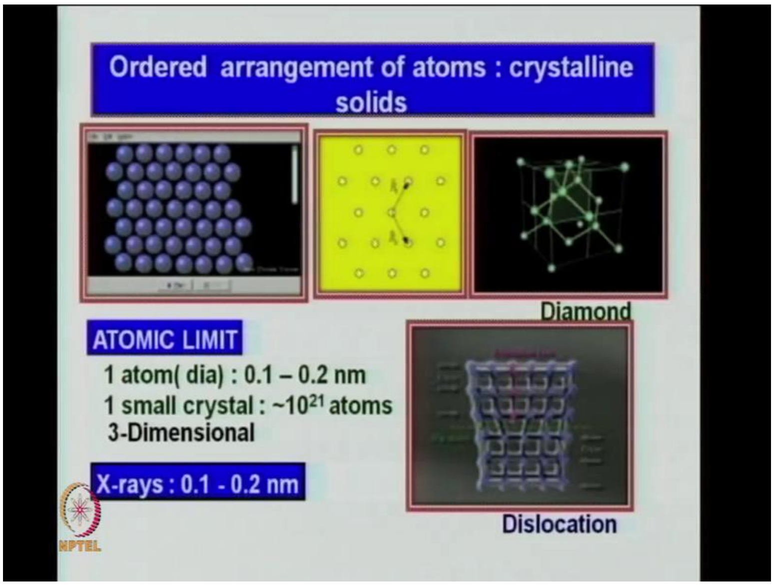

And if you want to observe still smaller objects like atoms in a solid when you have to use even smaller wavelengths, because the distances in a solid on the atomic scale is of the order of 0.1 to 0.2 nanometers. Typically in a crystal, which is of say 0.1 millimeter in dimension will have around 10 to the power 21 atoms. So, there are many many atoms in a small crystal and if you want to look at the distance between two atoms it is of the order of 0.1 to 0.2 nanometers or 1 to 2 angstroms. And for that normally we use x rays, because x rays have a wavelength which is of the order of 1 to 2 angstroms. Now, using these x rays we can observe the structures like diamond or graphite or we can observe changes in the patterns of the arrangement of atoms like a dislocation, where atoms have moved from their original positions. However these in between this atomic limit and the micron sized limit, which I discussed earlier, which is found which can be seen using a scanning electron microscope.

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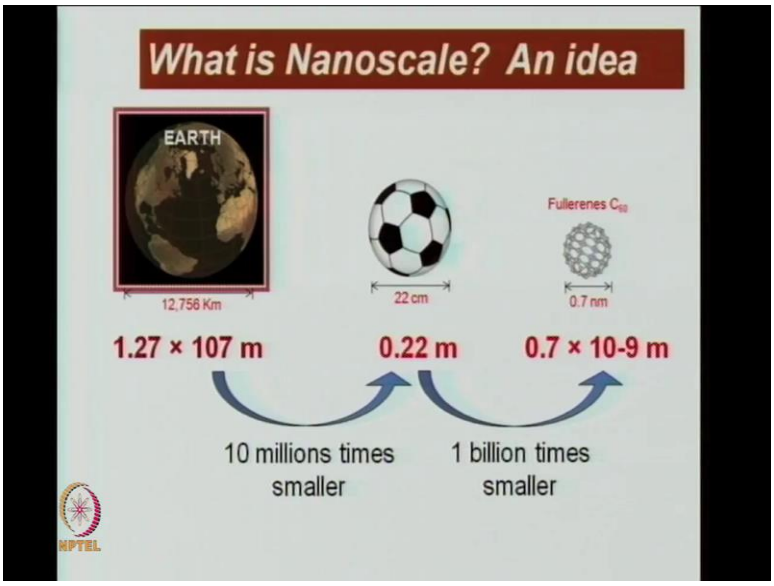

There is a regime, which is the nanoscale, which we are discussing in this course. So, what is this nanoscale. So, to give you an idea of what is this nanoscale which is of the order of one to hundred nanometers how to understand how small is a nanometer. So, to give you an idea, if you compare the size of a football or a soccer ball with the size of the earth then you see that the size of the football is around 10 million times smaller.

And now, if you compare a nanomaterial like a C 60 molecule, which is also called a fullerene. Then the C 60 molecule is nearly 1 billion times smaller than the size of a football. So, you can now imagine that how small is a nanoparticle, if you know, how small is the football with respect to the size of the earth. And the fullerene molecule which is a nanoparticle is much much smaller than the ratio of the earth size to the football as compared to the size of the football to the nanoparticle.

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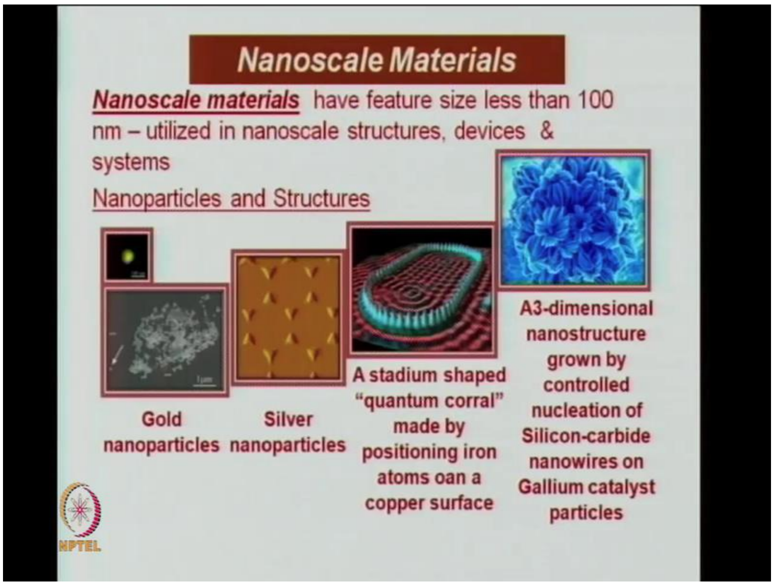

Now, nanoscale materials can be seen in many, many places. For example, you can see in gold, you can make nanoparticles, you can make silver nanoparticles, you can make nano shaped objects, like a quantum corral, which is made by having iron atoms on a copper surface as shown here. And you can see three dimensional structure of silicon carbide nanowires in the form of a flower and the size of these flowers are within few nanometers. So, you can have artificially made structures, which have dimensions closed to a nanoparticle that is in the order of 1 to 100 nanometers. So that means, these particles are very small if you have to understand nanomaterials, you have to see them using light rays, which have wavelength of the order of 1 to 10 nanometers of that order and that kind of a wavelengths you can achieve using electrons and so electron microscopy is important.

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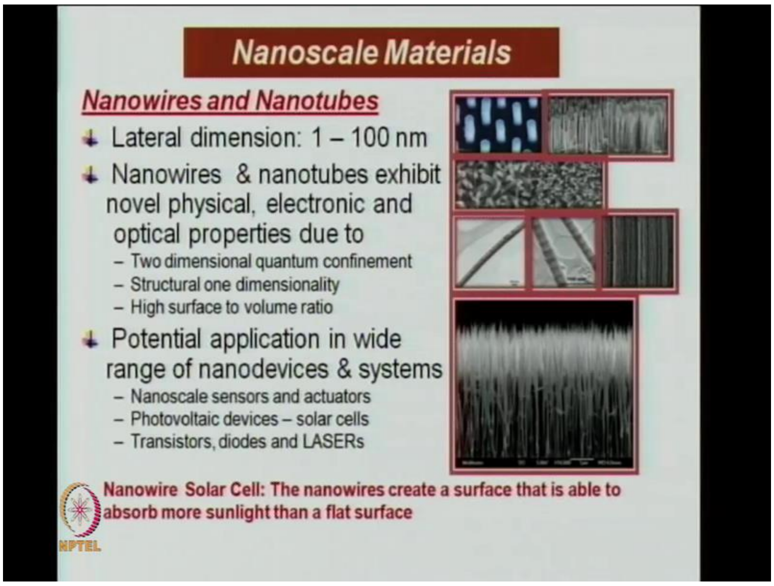

And you can see in these pictures which are electron micrographs of nanowires of carbon like carbon nanotubes, which are oriented in some fashion. And these nanowires and nanotubes have very interesting physical electronic and optical properties. So, nanomaterials which have this small dimension of few nanometers can be in one dimension and the other two dimensions can be large or it may have this small dimension of nanometer size in a two directions or even in three directions. Accordingly we call them as nanodots or nanoplates or nanowires depending on the dimension of these nanostructures. Now, if you have a two dimensional quantum confinement which is possible if you have a nanostructure like a plate with one dimension which is nanometer size.

Then you can see what is called two dimensional quantum confinements, because only in one dimension you have the effects due to the nano size. There are many many applications of these nanodevices; you can use them in sensors and actuators like motors, which are called nanomotors. You can use them in very efficient photovoltaic devices, you can use them in transistors and diodes as well as in lasers. And a lot if work has been done and is currently being done on how to increase the efficiency of a solar cell which converts the rays of the sun into electricity, which is a very important problem for the world to harvest the solar energy and convert it into useful form of energy, so that the energy problem of the world can be solved easily.

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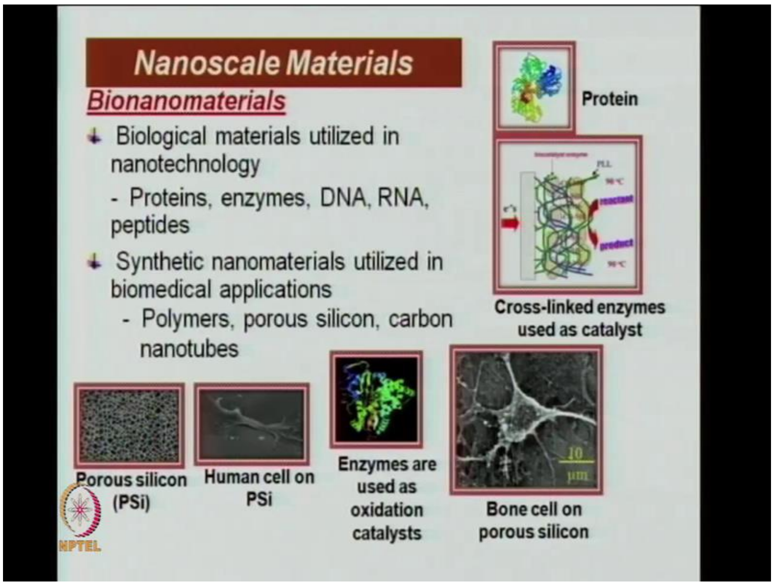

There are other nanoscale materials or nanomaterials, which have relation to biological molecules and these are also having dimensions in 1 to 100 nanometers. The examples are proteins, enzymes, DNA, RNA and of course, peptides. And there are many applications in biomedical science, which are based on the nanostructures and the utilization of the biological nanostructures in medical science.

Some of these nanostructures can be combined with other inorganic materials to form bioconjugates and they can be combined with polymers or carbon nanotubes and can be applied to several problems related to drug delivery or disease mitigation. There are here some nanostructures a porous silicon, which is biocompatible and hence can be used with biomolecules. Similarly there is an example of a human cell, which has been fixed on to porous silicon. There is an example of enzyme, which can be used as a catalyst, which are already known to be working as catalyst in the life processes.

And they can be used to have some artificial reactions carried out in a similar environment outside the living bodies. You can have a bone cell grafted on porous silicon and studies have been done how these bone cells can be made to grow on artificial surfaces.

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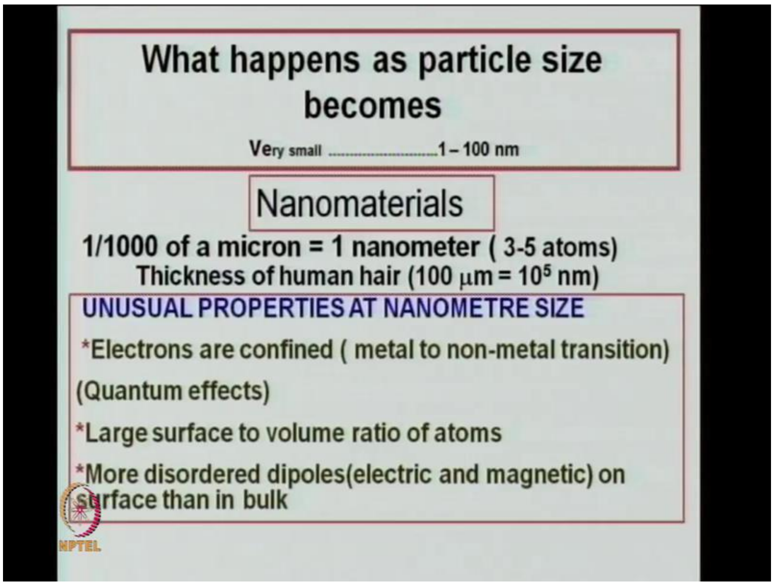

So, let us now understand, what are the properties, which change as the particle size becomes very small. So, what is very small here is with small, we mean the size of the 1 to 100 nanometers, which is not a rule, but it is a norm which is considered by all the people who work in the area of nanomaterials to consider any material, which has a size in this range to be considered as a nanomaterial.

And as defined 1 nanometer is 1 by 1000 of a micron or a micrometer and typically in 1 nanometer you may have 3 to 5 atoms. To give you another idea of this size of nanometer, if you take a human hair and measure the thickness of the human hair that is the diameter of the hair. Then the diameter of a human hair is of the order of 100 micrometers, which means one lakh nanometer, 10 to the power 5 nanometers. So, you can understand that the human hair is very large compared to the dimensions that we are talking about, which is 1 to 100 nanometers.

So, unusual properties are seen when we make a material, which is of nanometer dimensions. One of the properties is that electrons, which normally are delocalized in a metal become confined that means; they are not so free anymore. And then the property of the metal, which is due to the delocalization of electrons, is affected and the metal becomes a nonmetal. This is considered to be a quantum effect, because you change the allowed energy levels of the electrons by confining them in a region. There are other properties like the surface to volume ratio of atoms changes as you decrease the size of the particle, which means that if you have a smaller particle it will have more atoms on the surface compared to the bulk.

And hence its properties like reactivity and other things will change as the size of the particle changes. There is another property, which depends on the orientation of dipoles which may be electric dipoles or magnetic dipoles. And a particle having these dipoles will show change in the arrangement of these dipoles as you decrease the size of the particle. Form more ordered arrangement in a larger size particle, you will go to more disordered dipoles as you decrease the diameter of the particle on the surface of the particle you will have more disorder and since surface increases with size with decrease in size of the particle. Hence the disorder of the dipoles increases with decrease in size of the particles.

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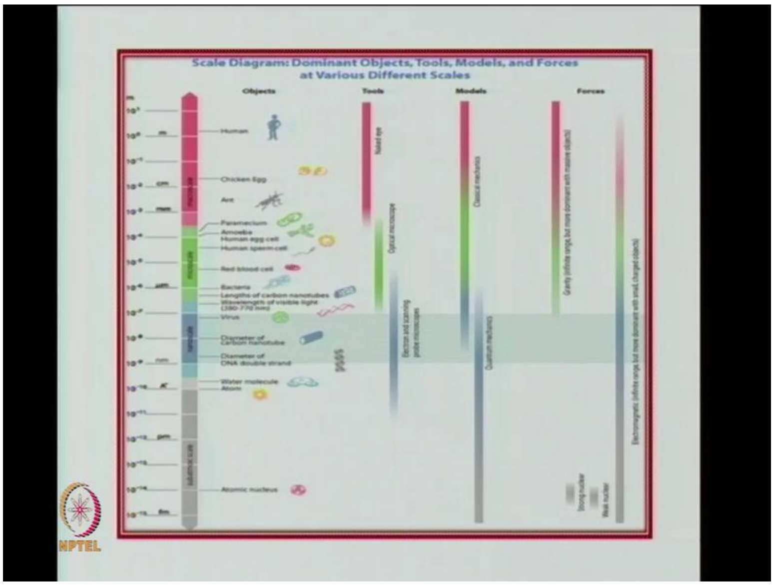

Now, if you look at a scale, where our nanoscale objects fit, then you see that, if you go from the smallest particle or smallest numbers that we can see like 10 to the power minus 15 of a meter, which is called a front meter. And you go up you see that the size of the atom is around 10 to the power minus 10 of a meter, which is 1 angstrom. And then you see a water molecule is something, which is below 1 nanometer, but more than 1 angstrom. And then if you go to a DNA double strength then the size falls into the nanometer dimension. The diameter of a DNA is around 2.5 so in 2.5 to 5 angstrom.

So, it is near to the nanometer size and the diameter of carbon nanotube is higher than it is around say 5 to 10 or 20 nanometers. So, typically these objects fall in the nano dimension of course, if you go to larger sized objects like bacteria or RBCs they are much larger they are like 200, 300 nanometers to 500 nanometers or micron size. So, we see a small region in this entire length scale, where you will have objects of the size of having the nano dimension like the DNA strand and the carbon nanotubes and the viruses. Since some of these biomolecules are falling in the nano dimension. Hence this subject of nanotechnology is equally important to chemistry, physics and biology.

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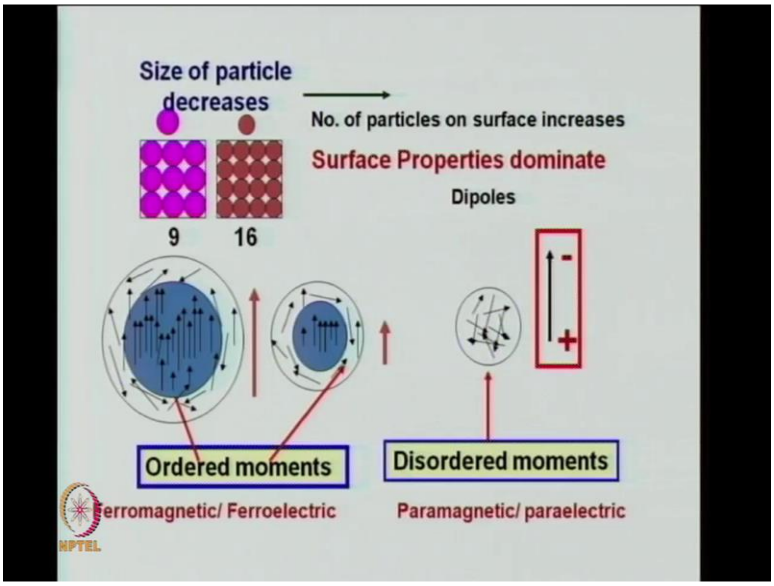

So, as I explained to you why these properties of surfaces, which dominate as the size of the particle increases and the disorder of the dipole also increases as the size of the particle decreases. So, these two properties are depicted and you can see that for the same area, if you have a smaller sized object you can, you will have more number of particles to cover the surface. And similarly, if you have a smaller size particles the bulk which has ordered moments reduces in dimension. And the number of disorder dipoles are increasing as the dimension of the particle decreases.

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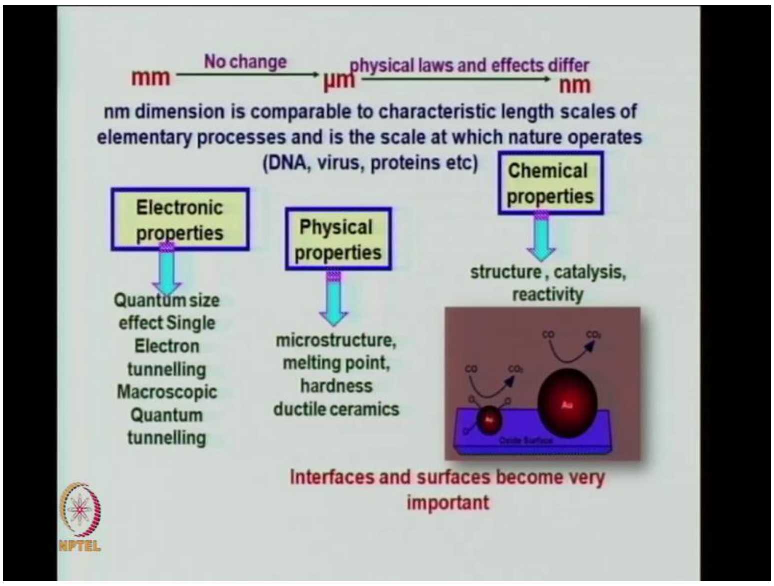

So, just to again summarize what is happening as we are going from large sized particles to small sized particles. So, if you go from a millimeter sized particle to a micron sized particle there is not much change in the laws of physics. The physical laws are more or less same; however, as you go from the micrometer size to the nanometer size you are entering the quantum region and so the laws of physics and the effects differ considerably. Apart from this many of the biological molecules fall in the nanometer length scale. And hence the size dependence of the biological properties are also important.

So, electronic properties change like you have new effects like quantum size effects they are called and examples are single electron tunneling or macroscopic quantum tunneling. These are seen whenever you confine electrons and you start seeing these quantum effects. Physical properties like melting point, hardness, etcetera we add also dependent of the size of the particles and we see them in many cases. Then chemical properties change like the structure, catalysis, reactivity there all change as you change the size of the particle. For example, a small gold particle is shown along with the large golf particle.

And you see the large gold particle cannot oxidize carbon monoxide to carbon dioxide whereas, the small particle of gold can oxidize carbon monoxide to carbon dioxide. So, interfaces and surfaces become very important, and this is of course, known for a long time in catalysis and they were not called as nanoparticles, but they were called as fine particles, but in the last 15 years we now know that these properties can be are due to the nanomaterials. And now we say that the enhanced reactivity is due to the nanoparticle nature which enhances the surfaces and hence the reactivity.

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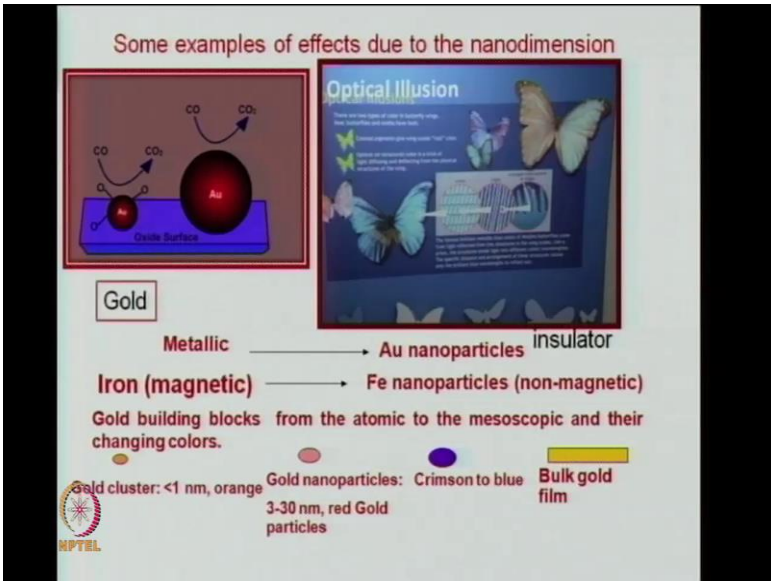

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You can also see optical effects, for example, if you look at this butterfly then it has got on its wing blue colour as well as brown colour and the colour actually changes, because there are some nanostructured in the some nanostructures on the wings of these butterflies. Now, these nanostructures interact with light in a manner such that, if you change the dimension of the nanostructures, the wavelength of light, which is scattered will change and hence you see a different colour. And this subject of interaction of light with nanostructures is today called nanophotonics, where you can organize elements, such that they differenced between two nanostructured elements is of the order of the wavelength of the light, which is interacting and minor variation in these dimension of these nanostructures will create new scattering a phenomena, and this subject is called nanophotonics. You can this case of the butterfly is a natural nanostructured feature showing nanophotonics; however, you can make artificial surfaces, which are nanostructured and there also you can observe variation in the scattered a wavelength of light depending on the distance between two nanostructured elements.

You can also see the effect the of optical properties on the dimensions by choosing a very well known element like gold which all of you know that it is yellow in colour; however, if you change that size of the particles of gold, you can have gold of different colours depending on the size of the gold particles. So, you can have blue coloured gold, orange coloured gold depending on the size of the particles and you can explain why a particular size of gold gives a particular colour. This can be very well explained today based on our knowledge of nanoscience and nanotechnology.

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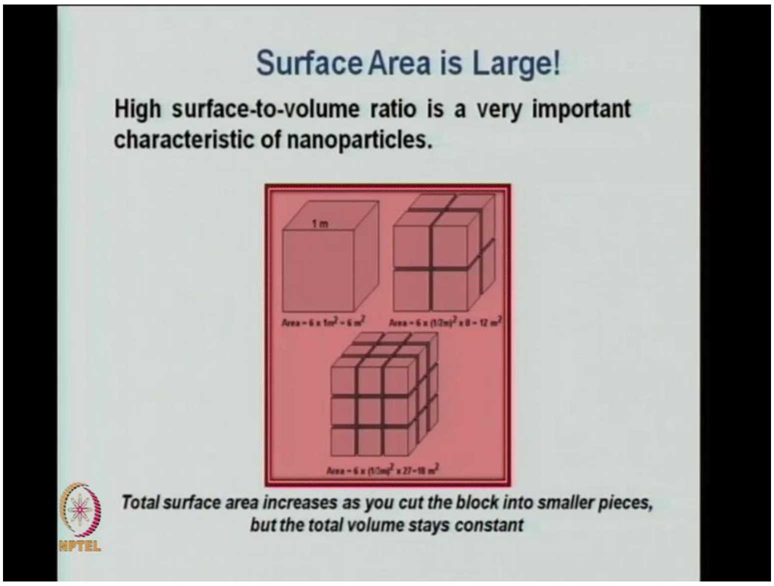

This as another example of how you can understand why surface reactivity will be large, if you take a large cube and cut it into several small cubes the surface area will increase. And hence for the given volume you have much larger surface, which is characteristic of nanoparticles. And hence enhance any property which will depend on the surface like reactivity or catalysis, etcetera.

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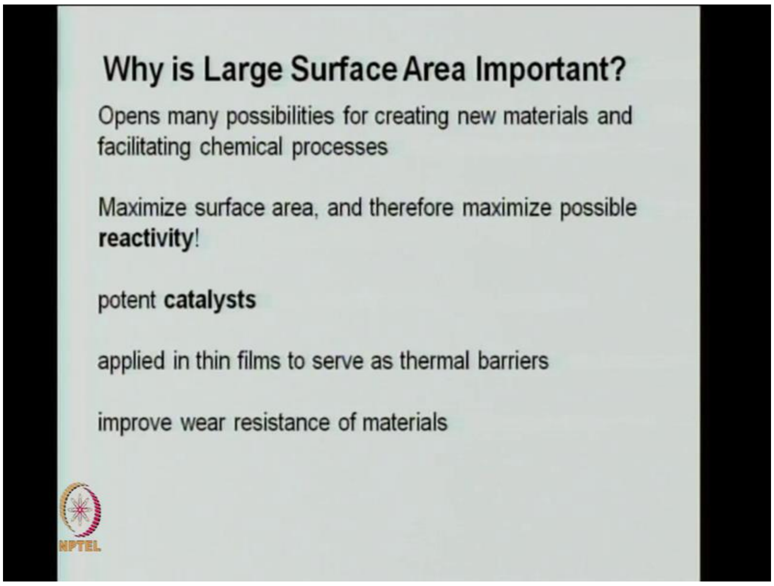

So, the surface area is a very important property for catalysts and for the increasing the reactivity and there are many other applications in thin films, where we use certain nanomaterials to act as thermal barriers to prevent something from getting too much heated or the wear resistance of materials, which are being used rapidly. And these kinds of wear resistance of materials can be enhanced by decreasing the size of the particles on the surface.

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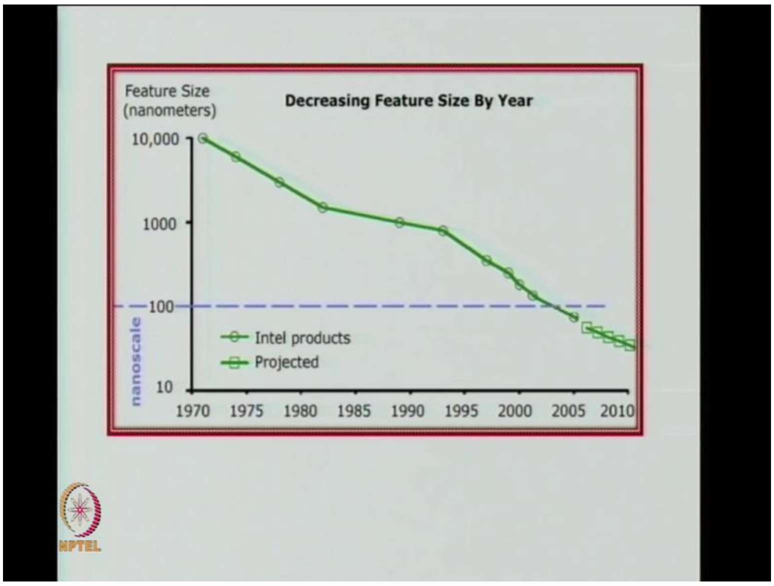

Now, in electronics these size is very important, because you want to make smaller and smaller electronic gadgets. And what we call as the feature size that is typically an electronic component, which can, you can consider an integrated chip its size is of major importance. Because the more number of chips, you can put in one square inch of area you will have larger computational properties or any feature like memory properties can be enhanced by increasing the feature size and; that means, increasing the number of ICS. That means, decreasing the feature size will help you in enhancing most of the electronic properties and as you see the feature size has decreased from around 10000. And now in 1970 to it is now close to around 20 or 30 or 40 which is in the nanoscale.

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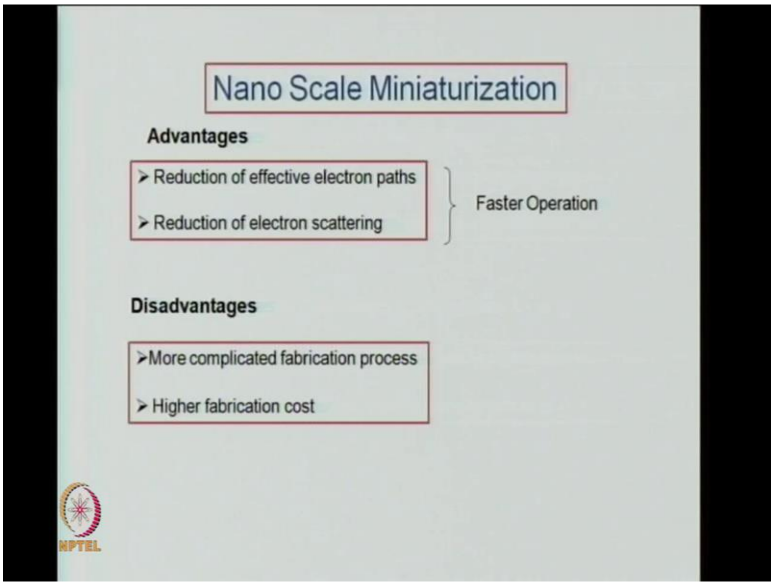

Now, this kind of miniaturization, nanoscale miniaturization has advantages, because it also reduces the length, which a electron has to travel to communicate with different circuits within the same chip. So, between different components and this also reduces electron scattering which leads to enhanced heating or resistivity. And overall you get a faster operation of the device. However, the more miniaturization you need you need to design more difficult nanostructures. And that will that normally enhances the cost of the fabrication process and you have to use much more complicated equipments to design such highly miniaturized devices. Now, to give you a brief history of a nanoscience and nanotechnology.

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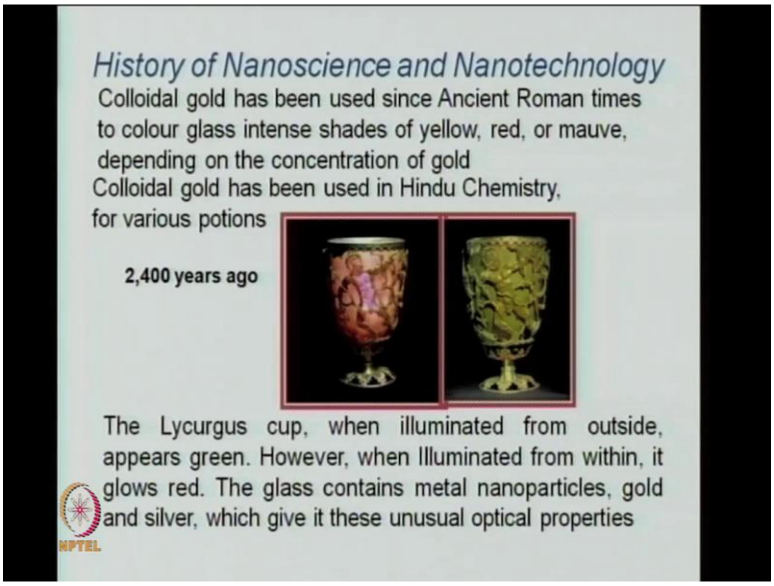

A nanoscience was known for a long time without any understanding. People have been making small particles, which today we know where actually of the size of few nanometers in ancient roman times they used to make particles of cobalt, silver, etcetera and solutions and used to mix it to form glasses, which had colour.

And this was known for nearly 2500 years back people have made such coloured classes; however, the chemistry or the exact science behind the colour in these coloured glasses was not known or not understood. Gold is one of the most frequently used colloidal solutions, which has been used in many other applications in those days. And this particular cup which you are seeing has got gold, which is a looking red when you are illuminating; that means, you have a light inside. So, you are looking at the transmitted light and that is red in colour; however, if you look at the reflected light; that means, your light source is outside the cup then it appears green in colour.

And this is currently in the London museum and it was made many many thousands of years back and it is still retaining its coloured properties. So, this unusual property of this glass is basically, because there are nanoparticles of gold embedded in the glass and that gives you the colour. The colour is different depending on whether you are observing transmitted light or reflected light.

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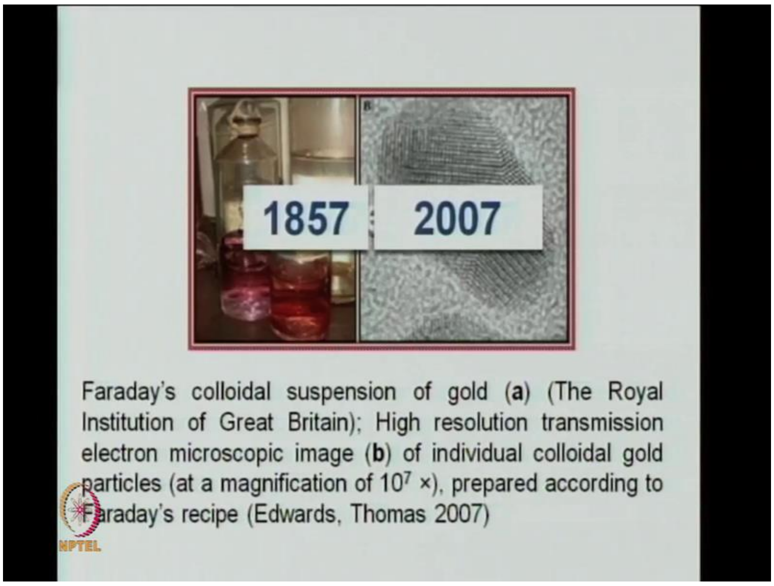

The first time scientifically nanoparticles were made in a laboratory was 1857 when Michael faraday made a gold solution. And those solutions are stable even now as you can see in these chemical bottles, these are precisely those gold solutions which were made by Michael faraday in 1857.

And if you look at these particles under microscope electron microscope then you will see the picture on the right hand side, which shows you clearly the pattern which one should observe for a gold particle. And you can be sure from these spacings between these lines that you observe that corresponds to gold and this is a transmission electron microscope picture of gold nanoparticles. From which you can see the size of the particle, and also you can prove that it is a gold particle by measuring the distances between the atoms or the lines which are fall by the atoms in real space.

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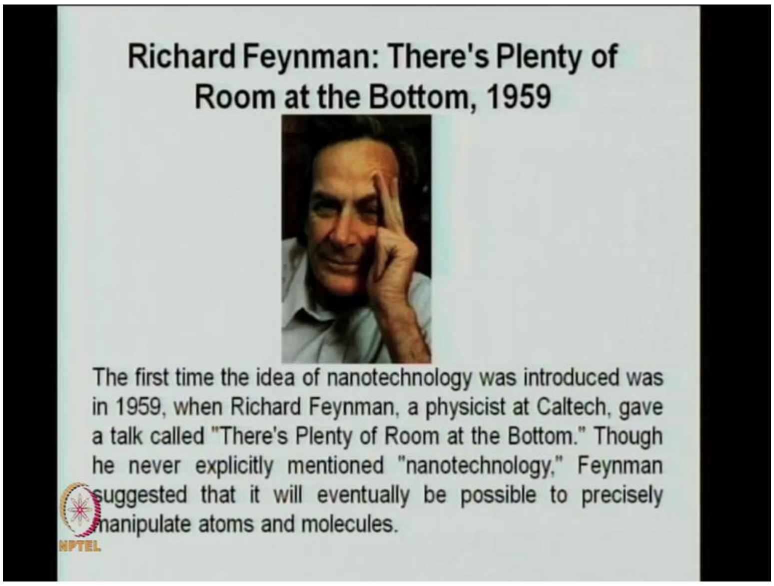

Now, the scientific thrust to nanotechnology was really given by Richard Feynman, who was a physicist and was a very important figure in the development on modern physics. And he gave a lecture in 1959, where he mentioned that lot has to be understood in the smaller dimensions. And that is when he said that there is plenty of room at the bottom and this is considered today one of the first time somebody indicated that lot of science and technology is possible in the nano dimension. However, he never mentioned the word nanoscience or nanotechnology in the lecture, but the kind of indicated that the understanding was not there on the properties or applications of particles in that smaller dimension, where we can control atoms and molecules.

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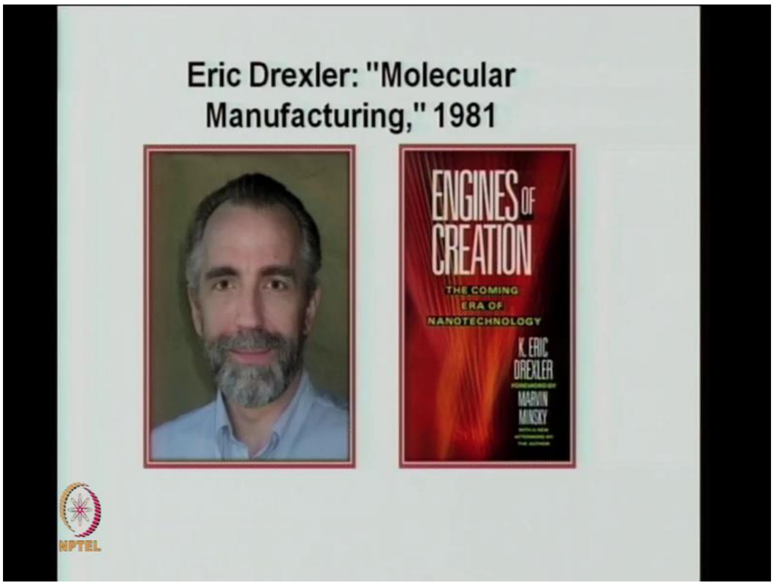

The next big thrust or actually the major thrust came after Eric Drexler who was a student at M I T wrote about molecular manufacturing in 1981. And another book called engines of creation in 1986, where he put his ideas about molecular machines nano robots and many other machinery, which could be designed based on molecules. And that was one of the major thought provoking books, which people lashed on to and made them reality within ten years. So, Eric Drexlers books though fiction gave the thrust for scientists and engineers to start thinking on really making these molecular machines.

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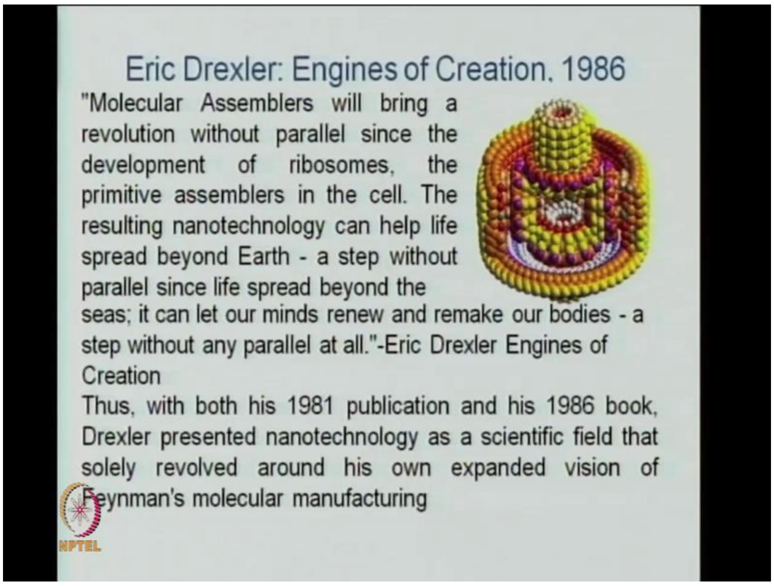

And his concept of molecular machine started from a natural molecule, which is the ribosome and which is there in our body and it is the working of the ribosome is. So, efficient and based on that Eric Drexler wrote the book engines of creation, because ribosomes help in making proteins which are very important for living beings we all the time are making proteins in our body and ribosomes are one of the key things, which stimulate the formation of proteins. And the structure of the ribosome and its action is just like a machine and that is why Eric Drexler got his idea of thinking beyond ribosome and planning or of many many new molecules, which would be doing different action based on that structure.

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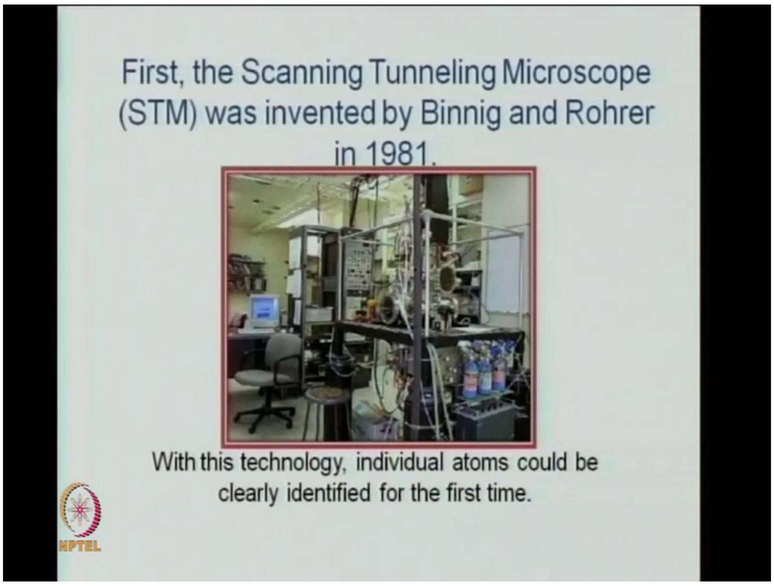

And hence, this was realized of course, later and the realization was possible, because it could be seen using some microscopes, which were then developed. One of those microscopes, the scanning tunneling microscope was invented in 1981, and we could clearly see atoms using the scanning tunneling microscope. Although even with transmission electron microscope, you can see atoms at very high resolution.

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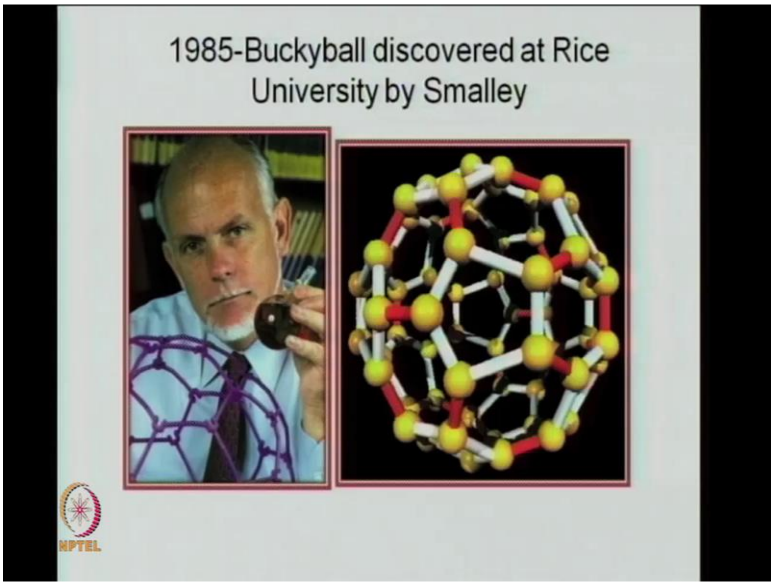

The Buckyball was discovered around this time in 1985, which is a nanoparticle, because the diameter of this. Buckyball or C 60 molecule is around 7 angstrom or few nanometers, 7 nanometers which is 70 angstroms. So, this discovery of C 60 was nearly around the time when nanotechnology was or nanomaterials was being recognized as a very important area of research.

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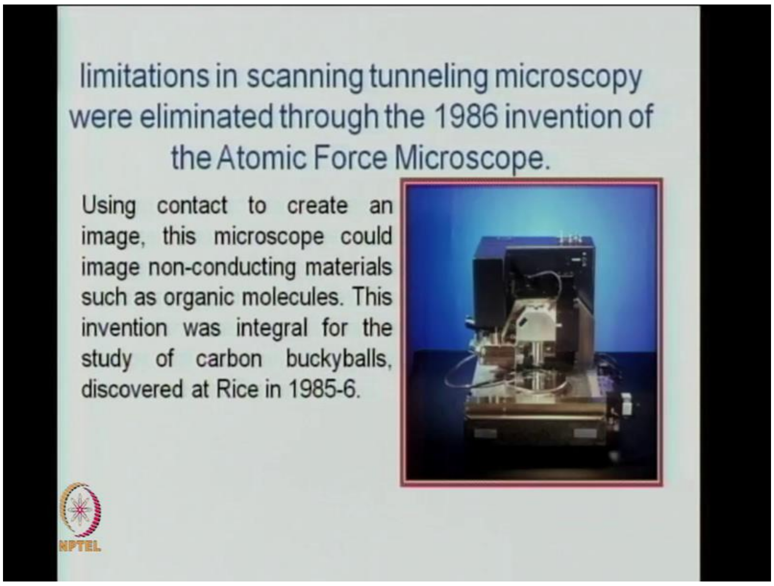

However the most important discovery probably was the discovery or invention of the atomic force microscope by the same people who invented the scanning tunneling microscope. And AFM was invented in 1986 and using this microscope any nanostructure could be seen like non conducting molecules organic molecules which could not be seen earlier using scanning tunneling microscope. So, the discovery of the atomic force microscope probably was one of the most important inventions in the development of nanoscience and nanotechnology.

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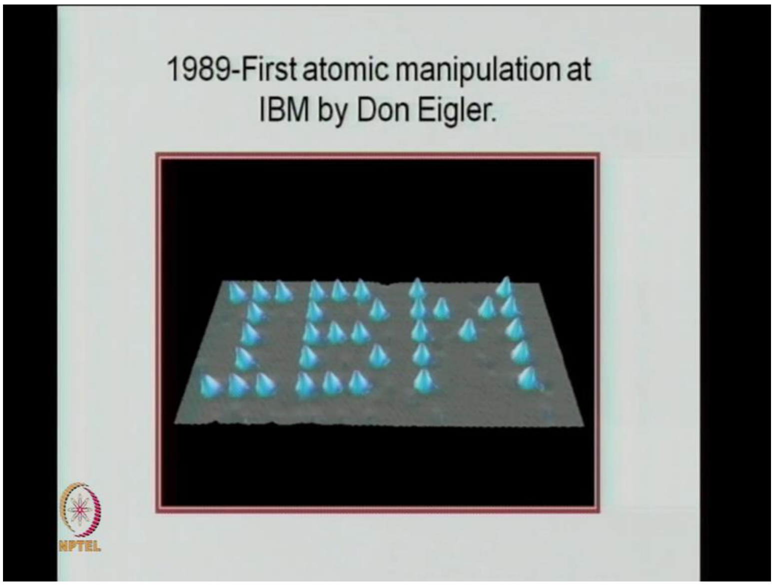

This is a picture of the first writing using atoms done by IBM, where they could manipulate atoms. And this is really what we call the ultimate of nanoengineering, where you can move atoms at your will and place them at your will. So, this I B M logo which is written here is made of xenon atoms with the blue ones you can see are actually they manipulated xenon atoms on a nickel surface. And this was first time shown in 1989 and from that day we can now say that we can write with atoms. And what happens when you can write with the atoms, when you write with atoms you can write many many thousands and millions of pages of your book in one page of your note book today.

So, a typical atom has a diameter of around two angstrom. So, that is the size of the letter you will have 2 to 5 angstroms. And so you can imagine how many letters you can write within one page of your note book, which is around say 12 centimeters by 12 centimeters. It will be a much larger then what you can write with your pen or pencil. And so there is a very very important development that you can store lot of information in very small region of space using atoms or molecules, but you have to be able to manipulate these atoms and molecules as if your writing with atoms and molecules. So, there are several other discoveries around that time in 1987, the first single electron transistor was created.

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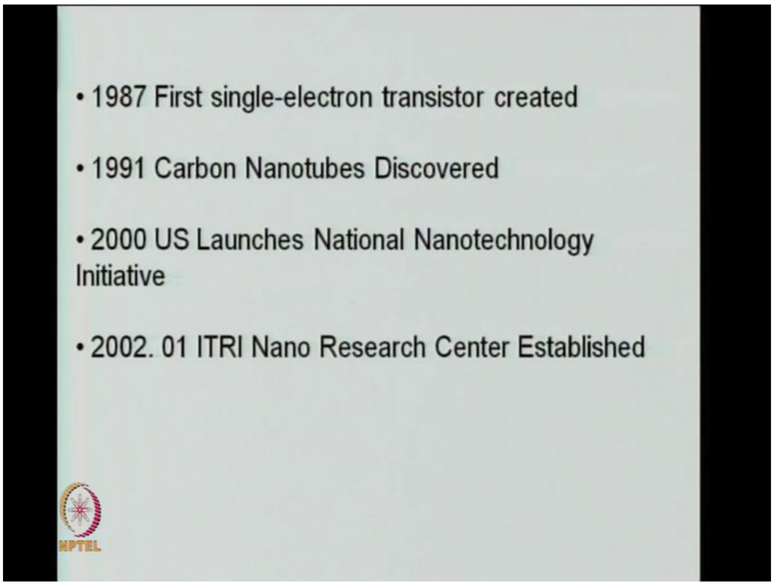

In 1991 carbon nanotubes were discovered, these are tubes made only of carbon atoms. The carbon atoms are arranged in as hexagons and pentagons and these tubes have the diameter of around 3 to 10, 15 nanometers. And these carbon nanotubes were later found to be very important for several applications. You can have semiconductor carbon nanotubes, metallic carbon nanotubes and branched carbon nanotubes. And hence the, it was predicted that they would be useful for circulatory in miniature electronic devices.

Many countries in the world around that time then launched the nanotechnology program. Unites states launched the national nanotechnology initiative in 2000 and several other nanoresearch centers in the world were established in around 2000 and 2002. Today what we have done so far is tried to give you a introduction to the subject of nanoscience and nanotechnology we tried to explain what this small size brings about in terms of properties, the variation in electronic properties, a variation in mechanical properties and variation on properties which depend on surface like catalysis and reactivity.

The points that you have to remember is first that the nano dimension is typically in the range of 1 to 100 nanometers any object or part of an object in this range has some unusual properties. However, it depends on what kind of properties one is looking at; if it is electronic properties then maybe you have to be in the region of 1 to 10 nanometers. If you are looking for mechanical properties, you may be having particles, which will create a variation in mechanical properties even at sizes like 40 nanometers, 100 nanometers etcetera. So, overall you will have different effects based on what kind of properties you are looking forward.

One of the common materials which is a nanomaterial we discussed is based on carbon the C 60 molecule and the carbon nanotube, which is one dimensional linear or it can be curved, it can make y junctions and the diameter of these carbon nanotubes of course, falls in the nanometer dimension. The length can be very long and how you observe these nanoparticles you have to use light, which has a wavelength which matches the dimensions. So, you must be using light which has wavelength of nanometers, which visible light cannot give you. So, you have to use electromagnetic radiation, which has wavelength in the order of sub nanometer, like electrons which can have wavelength in this region.

You can also use other particles; however, you have to modulate their wavelength accordingly. Typically the tools we used to study these nanoparticles, we discussed today are the electron microscopes and the scanning tunneling microscope and atomic force microscope. So, the T E M, the A F M and S T M are the pillars of study of nano particles and using these we can observe even atomic, we can have atomic resolution and see distances which are sub nanometer in size. With that I think we will close the lecture, the first lecture of this module one. And then we will start with our next lecture, next time and good luck to all of you and please go ahead and look at what you have learnt and try to understand more.

Thank you.