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UNIT – I

NANO SCIENCE AND TECHNOLOGY

1.1 BACKGROUND TO NANO TECHNOLOGY

The history of nanotechnology traces the development of the concepts and experimental work falling under the broad category of nanotechnology. Although nanotechnology is a relatively recent development in scientific research, the development of its central concepts happened over a longer period of time.

The emergence of nanotechnology in the 1980s was caused by the convergence of experimental advances such as the invention of the scanning tunneling microscope in 1981 and the discovery of fullerenes in 1985, with the elucidation and popularization of a conceptual framework for the goals of nanotechnology beginning with the 1986 publication of the book Engines of Creation.

The field was subject to growing public awareness and controversy in the early 2000s, with prominent debates about both its potential implications as well as the feasibility of the applications envisioned by advocates of molecular nanotechnology, and with governments moving to promote and fund research into nanotechnology.

The early 2000s also saw the beginnings of commercial applications of nanotechnology, although these were limited to bulk applications of nanomaterials rather than the transformative applications envisioned by the field.

1.2 SCIENTIFIC REVOLUTIONS:

A few million years ago we worked out that rocks could be used to break things that were impossible to break with bare hands. The rock was our first tool. Once certain types of rocks became specialised, they were manufactured by craftsmen and different types of rock became useful for different purposes. The use of these tools increased the food supply and allowed the new specialists not to spend their time hunting.

One valuable tool was fire. Around 5000 to 6000 years ago, some one put a rock containing copper ore on a campfire. The copper melt ed out and was collected. Now people had access to new metallurgical materials and the boundaries of technology expanded. Humankind could make new substances that were not visibly present in nature. Soon alloys — in which two types of metal are smelted together, such as bronze were discovered. Then iron was made from iron ore, and from iron, steel.

Millennia passed, and all of industry until the 18th century was powered by the energy of human or animal muscles, or by natural energy sources like river water and the wind. However the discovery of steam power may well have been as big as the discovery of copper. Now there was an alternative source of energy. Trains and railways followed and then petroleum, cars, jet planes and spacecraft were produced

Let us ponder for a moment. What led to the discovery of steam power? Were more scientists researching better horse -drawn vehicles or were they simply interested in the potential of steam as an energy source? Those who provided the money would probably have been more interested in the first proposition. We need to remember this when determining where we should spend our research dollars. The theme of steam power will be used again in the last chapter of this book .

Two different types of discovery followed. These were mass production and computers. Mass production was a very important step for humankind because it made the rate of supply faster than the rate an individual human could deliver. It was the product of the discovery and use of electricity. Computers, made useful by micro transistors, delivered mass production in mathematical transformation. Before this, any computation or information processing required the human brain and could only proceed at the speed a human could work.

DNA is short for deoxyribonucleic acid. It carries genetic information in living organisms called genes. RNA, or ribonucleic acid, puts this information to work in cells in various ways. A type of RNA called messenger RNA is very important. RNA and DNA are dealt with in Chapter 6. Genetic engineering, the ability to elucidate and modify the nature of genes in DNA, is a major revolution that is happening now.

It is the first time we have had control over our own evolution and that of animals and plants rather than having to rely on breeding. It will increase longevity in a different way. Rather than reducing the chances of accident or disease it has the power to change us as a species. However, if the masses of long -lived people are unproductive, some would argue that we might be better rid of them.

Let us ponder again for a moment. During revolutions, wealth is made by pioneers. Knowledge of the old science is not important. Think of the sales opportunities for the people who had the first arrow heads, think of horses and carts, candles and electric lights, transistors and valves, and pharmaceutical medicines. Think of Ford, Gates, Nobel and those two rich cave people, Mrs Fire and Mr Wheel. A lot of people are already making plenty of money out of genetic engineering and gene therapy. So what else is coming?

The answer is nanotechnology. What is nanotechnology, and why will it make a lot of money? Why is it more important than all previous scientific advances? Nanotechnology is an anticipated manufacturing technology that allows thorough, inexpensive control of the structure of matter by working with atoms. It will allow many things to be manufactured at low cost and with no pollution. It will lead to the production of nanomachines, which are sometimes also called nanodevices. It is therefore an advance as important as the discovery of the first tool. However, rather than shape what nature offers, we can do it ourselves. Unlike metallurgy, natural substances are not used as the starting materials, but atoms — the ingredients of the universe.

Has this all started? Indeed it has. The concept of nanotechnology is attributed to Nobel laureate Richard Feynman in a lecture that he gave in 1959 and which was published in 1960: ‗The principles of physics, as far as I can see, do not speak against the possibility of manoeuvring things atom by atom.

If Feynman was the philosopher, then Drexler was the prophet. Feynman's definition was expanded by Drexler in a most stimulating and lateral thinking way in his book, Engines of Creation, the Coming Age of Nanotechnology. This is essential reading.

'Nanotechnology is the principle of atom manipulation atom by atom, through control of the structure of matter at the molecular level.

The origin of the term ‗nano‘ comes from the Greek word for dwarf, but in scientific jargon, nano means 10^{-9}, so a nanometre is 10^{-9} metres, (that is, the size of ten or so atoms). Technology means the building of useful things from scientific principles. Thus nanotechnology means building useful things at the 10^{-9} level. So how is this different from chemistry?

Nanotechnology is not synonymous with chemistry, since it is more specific and concerned with observing atoms and molecules and manipulating them through visual observation at the nano scale level. However, it may eventually encompass all of chemistry and a large part of physics and molecular biology. Feynman's and Drexler's definitions now define the field of molecular nanotechnology, which is sometimes also called molecular manufacturing. The latter is a poor description, since it is synonymous with synthetic chemistry.

The discovery of nanotechnology in the broadest sense has immediate implications, since we can design a whole new range of machines from nanoscale objects, but not necessarily by breaking up matter into individual atoms. Rather, it may be done using bits of crystal or bits of biological material.

The scientific rewards for building nanomachines atom-by-atom should be greater than the shaping from top down approach, as researchers will achieve an ultimate level of control in assembling matter one atom at a time.

Drexler has described the assembler as a device having a nanorobot under computer control. An assembler is a nanomachine, but a very special one that can both build nanomachines and reproduce itself in the same process. It will be capable of holding and positioning reactive atoms and molecules in order to control the precise location at which chemical reactions take place. This general approach should allow the construction of large atomically precise objects by a sequence of precisely controlled chemical reactions, building objects molecule by molecule. If designed to do so, assemblers will be able to build copies of themselves — that is, to replicate.

By working in large teams, assemblers will be able to build objects cheaply. By ensuring that each atom is properly placed, they will manufacture products of high quality and reliability. Left over molecules would be disassembled and then re-used, thereby making the manufacturing process extremely clean. In an analogous fashion to a production line, an assembler will build an arbitrary molecular structure following a sequence of instructions. It will provide three-dimensional positional and full orientation control over the molecular component being added to a growing complex molecular structure. In addition, the assembler will be able to form any one of several different kinds of chemical bonds.

Are viruses nanomachines? Yes, but not man-made, and that really leads to a significant point. What will happen when biotechnology and nanotechnology combine? What will happen when we combine assemblers and genetic engineering? The answer is clear: the combination of assemblers, molecular computers and genetic engineering means new life forms. Not just the sorts of life forms created by modifying genes, such as genetically engineered crops, but life forms based on things other than DNA with their own intelligence.

Philosophers may argue that structures that form these life assemblers may believe they are a kind of god. Perhaps this is the fate of Homo sapiens: just as we evolved from lower life forms and contributed to their demise, so we will produce life forms which make a choice about us, and indeed about everything. However, some would say that it would be naive to believe someone else had not got there first somewhere else in the universe.

1.3 TYPES OF NANO TECHNOLOGY AND NANO MECHINES:

What then, is a nanomachine? As discussed above, forty thousand years ago cave men and women used pieces of flint as tools to fashion materials into new objects such as pots and pans, which could be used as tools for boiling water. The definition of tool and machine then becomes blurred. Individual tools were used together for new functions.

For example, a knife and a stick can be bound together with rope to form a spear. The two tools form a killing machine, which in turn is a tool. Such technology has been refined and further refined so that now we can break down objects and join bits of them together to form extremely complex machines. A silicon chip and some copper wire form a microcircuit that can be used with other components to form a computer. These are micromachines.

Life consists of a whole collection of machines. For example, apart from ribosomes, in each human there are huge numbers of copies of machines that convert carbohydrates to carbon dioxide and use the energy generated to perform life functions. This is not a lot different from a coal-fired power station, which does the same with coal rather than carbohydrates, except it is a lot bigger! Although it is smaller, the living machine is much more sophisticated because it has the capacity to reproduce itself. This is a mechanism of maintenance. A power station cannot do that.

There is no reason why we cannot use parts of living organisms as machines in much the same way as we use engineered machines such as power stations. Any substance in a living organism can be extracted and its chemical reactions can be used as a machine. Reactions that generate heat can be used as a source of energy.

Bits of life forms, such as membranes, which involve the combination of a number of chemical materials, can be used as machines to detect very small amounts of substances. However, there are many macroscopic examples that use collections of thousands of different nanomachines. For example, when light shines on a human eye, brain waves are generated. Thus, a living organism converts light energy to electrical energy as a brain response. A vat of eye tissue connected to the national electrical grid is not out of the question! Biological tissue can be grown in culture. These machines could be self-reproducing and therefore almost maintenance free.

Humankind has not been constrained by nature, and has built machines that nature never bothered to evolve at the macroscale, such as the wheel and axle, although increasingly we are finding at the nanolevel that these objects are used by nature.

Humans have built these machines from macroscopic materials; first from wood and then from materials extracted from rocks, such as copper, then steel and then plastics.

As technology has developed, many machines and objects have been miniaturised. Machines that were a metre in size have been reduced to a hundredth the size (a centimetre) and even smaller. Table 1.2 lists the prefixes used to describe the size of things. Many machines in use today, such as those that use microelectronics, operate at the micro level. In fact, blood capillaries are a similar size to an integrated circuit component. There is no reason why we can't build machines one size smaller — at the nano level. Because this is the size of atoms, atoms or groups of atoms — molecules — must be used.

Indeed, wheel-shaped molecules exist and so do molecules that are spherical, geared and sprocket shaped. These shapes are the components for humankind's mechanical machines, but in nanotechnology they are used at the atomic rather than at the engineering workshop scale. It is also possible to build complicated molecular machines involving lots of molecules, such as railway lines of nanometre dimensions with stations and trains that can be stopped and started.

Molecules that can be used as electronic devices such as switches and transistors are most important Chemists have worked with molecules (which are nanostructures) for one hundred and fifty years. In the past, chemists, unlike nanotechnologists, have used conjecture to understand what is going on, since they have not been able to see atoms. The atomic theory, which says that matter is made up of 109 different types of atoms, is just that — a theory — but one that works. Now we know it is not a theory, because we can actually see atoms through the transmission electron microscope (TEM).

1.4 ATOMIC STRUCTURE:

The seeds of the atomic theory go back at least to the time of the ancient Greeks. They developed the concept of elements as basic substances from which all forms of matter can be built. It was believed that when four major elements; earth, fire, air and water, were combined in correct proportions, they could produce all of the other substances. The idea that the elements are the building blocks of matter is consistent with our present day knowledge, but the difference is that we know there are different elements that make up all the matter on Earth. This includes some that do not exist naturally but which have been made in the laboratory.

What are elements? An element consists of only one type of atom. The ancient Greeks believed that matter could be divided endlessly, but this hypothesis was not based on the results of scientific experiments. It was only in 1807, when an English schoolteacher, John Dalton (1766-1844) revived the concept of atoms and proposed an atomic theory on facts and experimental evidence. The essence of the theory is expressed by the following postulates:

(1) Elements are composed of indivisible particles called atoms.

(2) All atoms of a given element are identical (now known to be incorrect); the atoms of different elements are different in some fundamental way(s).

(3) Chemical compounds are formed when atoms combine with each other. A given compound always has the same relative number and types of atoms.

(4) Chemical reactions involve reshuffling of atoms from one set of combinations to another. The atoms themselves are not changed in a chemical reaction.

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Dalton's atomic theory was a milestone in the development of chemistry. The major premises of his theory are still valid today. However, some of the statements were modified to accommodate new observations that have been made since his time. Dalton considered the atom to be indivisible, but this statement must be clarified. 'Indivisible' means that atoms cannot be broken down further without changing the chemical nature of the element. For example, when a car bon atom is broken down into smaller particles (known as subatomic particles), it loses its chemical properties.

We have all heard of atoms in connection with atomic bombs, and in terms such as 'splitting the atom'. The atomic bomb and the nuclear reactor both depend on self - sustaining nuclear fission chain reactions that release a tremendous amount of energy. In nuclear fission, a heavy nucleus splits into several much lighter particles, and many of these particles in turn may also be unstable. The energy released can be used for constructive or destructive purposes. German scientists Otto Hahn and Fritz Strassmann reported the first instance of a nuclear fission reaction in 1939. Subsequently, the first atomic bomb was used in warfare in 1945 at two Japanese cities, Hiroshima and Nagasaki.

There are three major fundamental subatomic particles: electrons, protons and neutrons. The protons and neutrons are collectively known as nucleons. In addition to these, there are a host of other subatomic particles — among them the positron, the meson, and the neutrino — but a discussion of these is beyond the scope of this book.

Electrons are tiny, very light particles that have a negative charge (-). Protons are much larger and heavier than electrons and have a positive charge (+). Neutrons are large and heavy like protons but have no charge. Since t he total charge on atoms is neutral, they must have equal numbers of electrons and protons. Contrary to Dalton's original hypothesis, not all atoms of the same element have the same mass. These different forms are known as isotopes. Any mass differences that exist between the isotopes are due to the different number of neutrons in each atom. For example, carbon - 12 and carbon-13 both have six protons (atomic number = 6) but the number of neutrons in each is 6 and 7 respectively.

1.5MOLECULES AND PHASES:

Phases are states that we define by their properties, such as liquids, gases and solids. Molecules are collections of atoms bound to each other that exist in these phases. Thus the oxygen that we breathe is a molecule made up of two oxygen atoms combined, and written as 0 2. Likewise water, H_20, is the combination of two hydrogen atoms and one oxygen atom. Molecules are formed by atoms in one of two ways. One way is by sharing electrons.

This type of combination is called a covalent bond. Secondly, molecules can be formed by transferring electrons between each other.

They are represented by superscripts + and -. This is called an ionic bond. When an electron is transferred between two atoms, they are said to be ionised. An example is sodium chloride, NaCl, in which the sodium atom is positive, Na^{+}; and the chlorine atom is negative, CI". A positive ion is called a cation and a negative ion is called an anion. When there is a covalent bond, as in chlorine, C_{12}, the bond is written as a straight line Cl-Cl. The line represents the two shared electrons.

In covalent solids, the molecules are discrete and can be differentiated from each other. In ionic solids such as sodium chloride the atoms are arranged in a regular pattern in space called a lattice, such as in Figure 1.2, and there is not a single discrete molecule. There are a large number of different types of lattices depending on how the atoms pack together. This depends not only on charge but also on atomic size. Once an atom is charged its size differs considerably from that in a free atom.

A different type of bonding exists in metals. This is depicted in Figure 1.3. In metals all the electrons are shared by all the atoms at one time. Thus metals easily conduct electricity because an extra electron can be added or removed without removing it from a single discrete atom. Metallic bonding will not be discussed further here, however the ability of different material s to conduct electricity or not is important since it affects how we see atoms.

There are some other types of bonding which are important in nanotechnology. Molecules and atoms can also be drawn together by relatively weak forces collectively called van der Waals forces or interactions. These types of force are named after Johannes van der Waals who studied them in gases. There are three types of these forces: London forces (Figure 1.4a), which are sometimes called dispersive forces; dipole-dipole forces (Figure 1.4b); and hydrogen bonding. We will deal with each of these briefly.

In an atom, the electrons tend to Svash' around the nucleus like a wave, and more electrons can be found at any point of time in a given space. This creates charge differences in space (depicted as an oval, Figure 1.4a, left side). This charge separation is known as a dipole moment. In London forces, the charge is present in a particular direction only for the instant in time that the electrons are in that particular place. London forces exist between all atoms and molecules.

They can affect the charge of other molecules or atoms not otherwise instantaneously charged (depicted as a rounder oval, Figure 1.4a, right side). The electrons in the second atom are attracted to the part of the atom that is more positively charged. In nanotechnology, London forces can be used to pick up and move atoms.

Some molecules do not share their electrons equally in bonds. One nucleus can be greedier than the other. When the electrons are not shared equally there is a small charge difference across the bond. This is also a dipole but a more permanent one. When two molecules with dipoles approach each other they may interact, because the positive charge on one molecule may interact with the negative charge on the other molecule. This interaction is called a dipole-dipole interaction.

The third type of van der Waals force is called hydrogen bonding. It occurs in water and in a number of other compounds containing hydro gen, such as selenium hydride, H_2Se, ethanol and DNA. A hydrogen bond forms when a hydrogen atom lies between two atoms whose electrons are not involved in bonding, such as oxygen, fluorine or nitrogen. The hydrogen is attracted to these electrons and the original bond is weakened. The hydrogen in water is pulled from one water molecule and partly bonds with another. In turn, the hydrogen atoms in this second water molecule are hydrogen bonded to other water molecules.

As noted above, molecules as compounds and atoms as elements come in phases. There are three simple phases; gases, solids and liquids, but mixtures of phases also exist. They will be discussed in Chapter 3. Nanotechnology is largely concerned with solid phases because the molecules or atoms do not move around so much and are hence easier to see. In solid phases, the molecules can be arranged in a regular order. They are said to be crystalline.

In this case they are said to be amorphous and the solids are described as non - crystalline. The types of bonds mentioned above are important in these phases. When the bonds between molecules are strong, as in ionic bonding, solids are formed even at relatively high temperatures. When only London forces are present, solids can be formed only at very low temperatures. When the temperature rises, these intermolecular forces are broken. The weakest bonds are broken first. Without hydrogen bonding water would be a gas at room temperature.

Other variations in structure can exist. In a crystalline solid there is a three dimensional lattice and the molecules are all oriented in the same way. However, the same kind of orientation can also exist in some liquids. These are called liquid crystals. The molecules are organised to form a lattice but there is still enough motion t hat the structure is fluid. Other liquids can exist in which the molecules are oriented but they move so much in one direction that there is no lattice.

Electrons behave differently in different states. In the gaseous state, atoms and molecules are isolated and hence each molecule or atom has individual electronic properties. The electrons can move around on a molecule or atom in different energy states but they do not transfer between atoms unless they are activated in some way. When atoms come together in a solid, however, the situation is different. It turns out that only two electrons may occupy a given energy state at one time, so there are lots of energy states corresponding to each pair of electrons. Each of the energy states is so close that they overlap. This means that electrons occupy energy bands rather than discrete atomic energy states.

1.**6MOLECULAR AND ATOMIC SIZE:**

We have discussed at some length that nanotechnology involves working with materials around 10^{-9} metres in size, about the size of a few atoms. However the size of an atom is not a simple issue, since atoms are mainly space. The nucleus has been described as a football in the middle of a football stadium, where the stadium represents the space in which the electron moves.

Moreover, electrons behave often either more like a wave or more like a particle, so it is not possible to say that an atom is defined by the space in which an electron orbits because it does not orbit. In short, there is the issue of the duality of matter. That is not all. The size of an atom, whatever that really is, changes considerably when it loses an electron (ionizes). Not only is the region of space that the lost electron occupied not part of the atom but the atom shrinks further because the remaining electrons are held closer to the nucleus. The nucleus now has a greater pull on the surrounding electrons because of the charge imbalance.

Despite all these factors we need to have an idea of how big things are if we are to undertake molecular nanotechnology. The relative sizes of various atoms are shown in Figure 1.6. However, as noted above, the sizes of atoms differ considerably in different environments and in different bonding arrangements. Some definitions are needed. The distances between atoms and ions have been determined very accurately, so it is useful to use these as a measure.

Atomic radius is defined as half the distance between the nuclei of identical neighboring atoms. The value of atomic radii depends on the type of chemical bond in which the atoms are involved (metallic, ionic, or covalent). When the neighboring atoms are not alike, as in sodium chloride, part of the observed distance between atoms is assigned to one type of atom and the rest to the other type.

The radius of the sodium atoms bonded together in sodium metal is larger than the radius of sodium in the compound sodium chloride. In sodium chloride, each sodium atom has lost an electron to become a sodium ion (charged atom) of unit positive charge. On the other hand, each chlorine atom has gained one electron to become a chloride ion of unit negative charge. The ionic radius of chloride is nearly twice as great as the radius of a neutral chlorine atom.

This is how the metallic radius and the ionic radius of atoms are described. The bonds between the pair of chlorine atoms in a chlorine molecule and between the carbon atoms in diamond are examples of covalent bonds. In these and similar cases, the atomic radius is designated as a covalent radius. Similarly we can have the van der Waals radius, which is the radius in which van der Waals forces are operative. Van der Waals radii are important in nanotechnology.

1.7 SURFACE AND DIMENSIONAL SPACE:

Another very important element of the universe is space. If the universe had no dimensions it would not exist. If it were one dimensional it would be a line or a dot of infinitely small thinness. If two dimensional, all objects would be flat like a square and also of infinitely small thinness. In three dimensions there are objects that can be observed; a sphere, a box, a human. Of course it is also possible to have four dimensions.

The best way to imagine this is by understanding how three-dimensional objects are represented in two dimensions on paper. We draw them in perspective as a cube. Thus a box is easily represented by additional lines to depict the third dimension. In a molecule of methane, one of the bonds appears to be in front of the plane of the paper and the other one appears to be behind it. To draw a four-dimensional object in three dimensions we need to construct a three-dimensional structure but include perspective. This is possible but it produces some strange shapes. It may one day become a new art form!

Imagine if you were a two dimensional object living in a two dimensional world but in reality there were three dimensions. It would be possible to disappear without breaking the laws of physics by moving into the third dimension. These concepts are important in nanotechnology because as objects get smaller, their dimensions become smaller and smaller. What are the dimensions of a row of atoms 1000 km long and 0.05 nm wide and high? Is that object one-dimensional? It is not, but it certainly approaches one dimension: that is, it tends to one-dimensional.

Nanotechnology is often concerned with single layers of atoms on surfaces. The surface is the edge of a three-dimensional object but in itself it is two-dimensional. If a row of atoms is arranged only in one coordinate, one side of the row of atoms makes contact with the surface but the other side is not in contact with anything. Such structures must have completely different properties from atoms buried in the bulk of the substance, and they behave so. There are in fact two surfaces: one at the edge of the contact material and one at the external edge of atoms on a surface.

In conventional materials most of the atoms are not at a surface. They form part of the bulk of the material, sometimes well crystallized and well laid out, and sometimes full of defects and impurities that destroy the strength of the material. In nanomaterials this bulk does not exist; indeed the principle difference in dealing with nanotechnological materials is the surface-to-bulk ratio. That is, the number of atoms bordering a surface divided by the total number of atoms. Materials with this property are unique and more than anything this is the reason why nanomaterials are different.

1.8 TOP DOWN AND BOTTOM NANO SCALE FORMATION:

Essentially there are two different approaches to creating very small machines or devices. Firstly there is the increasingly precise 'top-down' approach of taking a block of material and whittling it away to the object that is wanted. It is no different from a bronze age scientist working with wood or stone; indeed the solidification of molten metal into shapes is more advanced. The size limit of the smallest features that can be created depends on the tools.

The second approach is called the 'bottom-up' approach, where individual atoms and molecules are placed or are self-assembled precisely where they are needed. Here molecular or atomic building blocks are designed that fit together to produce bigger objects. Scientists have already produced nanoelectronic components, such as molecular switches made of a few molecules, and molecular wires, in order to realise the next challenge of fabricating a molecular transistor.

In parallel, biologists have been rapidly learning how certain mechanisms in nature work, such as understanding how a bacterium is propelled through water using a molecular motor, or understanding how electronic signals are generated across biological membranes (bio-sensors). It is the combination of the understanding gained from biological self-assembly, the chemical development of new molecular structures and the physical development of new tools of nanofabrication.

There are two different ways by which metallic nanoparticles can be formed. These are the “bottom-up" approach and the "top-down" approach. The two can be distinguished in the sense that while the bottom up method is sourced from scientific research including nanoscience, the top-down is not.

The bottom-up approach further comprises of creating nanomaterials and objects within the same nanosphere based on atoms, molecules, and aggregate grouping. This sort of grouping occurs in a clear and manageable manner, which allows for an increase in the functionality of the structure of such materials. The top-down approach which is sourced from microelectronics has to do with a clear reduction or breaking down of systems in their current state by making existing technologies more efficient. This results in a reduction in the size of the devices into nanoscale aspects.

In terms of the size of objects, both methods are very similar. Both approaches tend to converge in terms of the size range of objects. The former approach, however, tends to be more abundant based on the type of material, design varieties, and nanometric control, while the latter approach only makes the acquisition of materials of more importance, however, control may not be as strong.

Synthesis of Metallic Nanoparticles

When it comes to the synthesis of metallic Nanoparticles, two distinct approaches are utilized. The first is the top-down strategy and the second approach is referred to as the bottom-up strategy. While the former deals with the reduction in size of current technological devices, the latter performs an opposite role, which is building of even more complex molecular devices on an atomic arrangement.

While the top-down approach is beneficial in the production of technological structures in a far reached order and for connecting macroscopic devices, the bottom up is suitable for the production and arrangement of short-range order at the nanoscale aspect. The combination of both strategies is expected to form the best integration of equipment for nano-based fabrication.

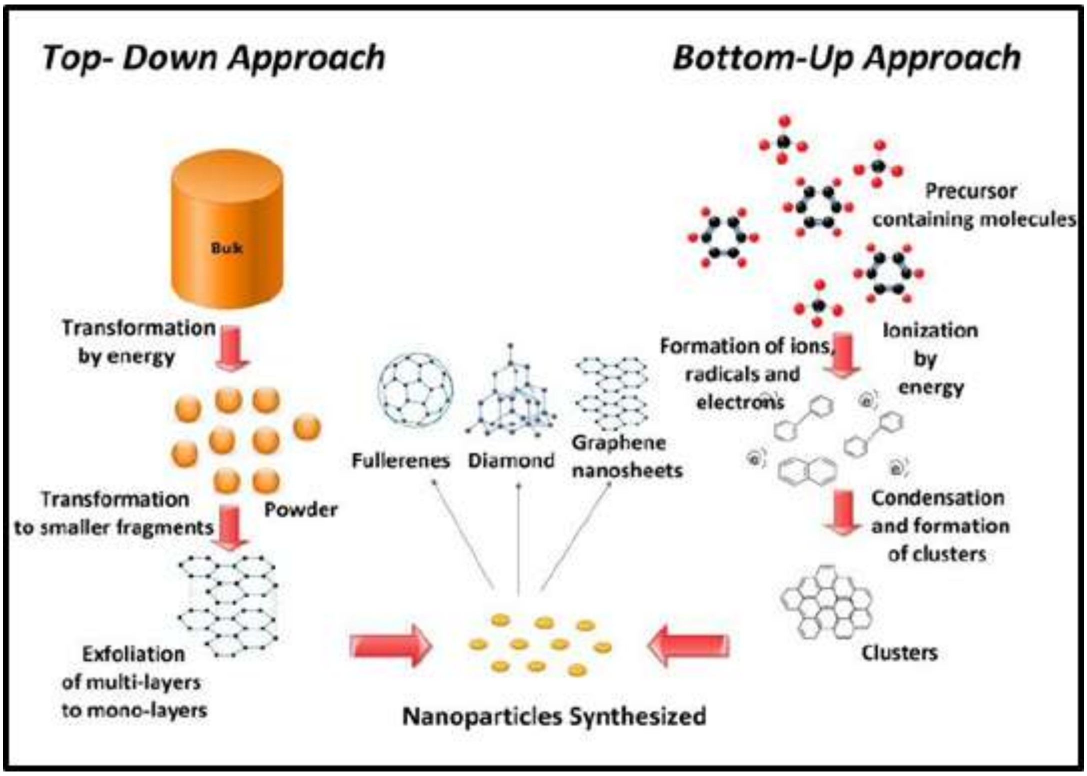
Furthermore, the top-down technique is built up for architectural structures at the micrometer scale (um). The bottom-up strategy is also built up for bringing small collections of atoms together measured in nanometers (nm). What is left is to integrate both approaches to create elongated forms at the nanoscale.

The commonest form of the top-down approach of fabrication is the lithographic technique that utilizes enhanced visual sources of a short wavelength. One main benefit of the top-down technique in fabrication of joint circuits is the fact that all of its parts are created and structured in an orderly form so that no further assemblage is required. The high level of polishing makes visual lithography developed especially in the production of the micro-electric chip with the wavelength reaching a level below 100 nanometers (going by the traditional method).

On the other hand, the sources of shorter wavelengths like intense UV and X-ray, are created to permit the techniques for printing lithography to attain a level between 10-100 nanometers. Beams like the electron lithographic beam make provision for model reaching 20 nanometers. In this technique, the model is stated by flushing a finely patterned electron beam across the surface. Other mire concentrated ionized beams are utilized for the direct processing and modeling of wafers with a lesser effect compared to electron beam lithography.

Printing methods of a mechanical nature, also known as the nanoscale imprinting, stamping, and molding— expands to cover small measurements of 20 to 40 nanometers. Though the details differ, the main aim of this is to create a massive "stamp" by utilizing a high pixel method like the electron beam lithography thereafter adding the stamp or the following ones to the surface layer, thus, producing a model. Each variant comprises the coating of the surface layer of the stamp with the "ink" and then emptying directly on the surface of the stamp's model. Given an example, the model under control of a molecule monolayer can be obtained successfully by depositing the ink directly on the coated surface. Using another technique, the stamp is utilized for the purpose of mechanically pressing the model to the tiny layer of the element.

Typically, the surface layer is a polymeric element that has been patterned for molding by heating during the stamping process. Etching of plasma is then used for masking under the stamped layers; polymers are subsequently removed, while a nanoscale lithography model remains on the surface. Relief models are equally formed from photoresist on a wafer by visual or electro-beam lithography and then emptied on a watery precursor. The effect of this is a solid rubber-like substance that can be easily detached and utilized as a stamp. They can be utilized in any of the ways produced above. A distinguishing feature of the latter technique is the flexibility of the stamp.



Bottom-up and the top-down approaches in synthesis of carbon-based nanomaterials.

UNIT-II

2.1 SYNTHESIS OF METAL NANO PARTICLES AND STRUCTURES:

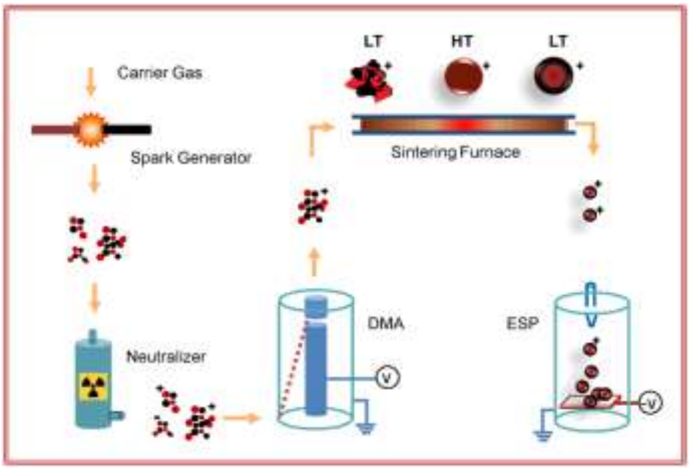
There are generally two routes to preparation of nanosizedmetal particles: top-down and bottom-up. Top-down methods reduce macroscopic particles to the nanosize scale. This route is usually not very well suited to preparing uniformly shaped particles; very small sizes are especially difficult to realize. Top-down routes will not be considered further. Bottom-up procedures are much better suited to generating uniform particles, often of distinct size, shape, and structure, as will be shown in the following sections. Bottom-up methods start with atoms that aggregate in solution or even in the gas phase to form particles of definite size, if appropriate experimental conditions are applied.

2.1.1 GAS PHASE SYNTHESES:

Figure 1 shows a schematic drawing of a so-called cluster-beam generator. It consists of a heating unit where metal targets are evaporated by simple heating or, better, by laser irradiation. The flow of atoms then passes variously constructed slits to focus the beam. Modern techniques use mass spectrometric units to separate different particles according to mass, leading to fractions of very uniform particles. The disadvantage of cluster-beam generated particles is the lack of a protecting skin for the clusters.

Bare metal particles immediately aggregate to polycrystalline powders, owing to the thermodynamically preferred metal-metal bonding, and aggregation of particles means loss of individuality. Solutions to this problem include the deposition of the particles on supports; a more recent promising method uses the spontaneous reaction of bare particles with ligand molecules in solution. The naked particles of a cluster-beam react with molecules, covering their surface faster than they react with each other.

This procedure is similar to chemically based methods that have been known for decades for preparing stabilized nanoparticles in gram amounts. Chemical approaches to nanosized metals are therefore the much more suitable alternative. Some principles will be discussed in the following.



2.1.2CHEMICAL SYNTHESIS:

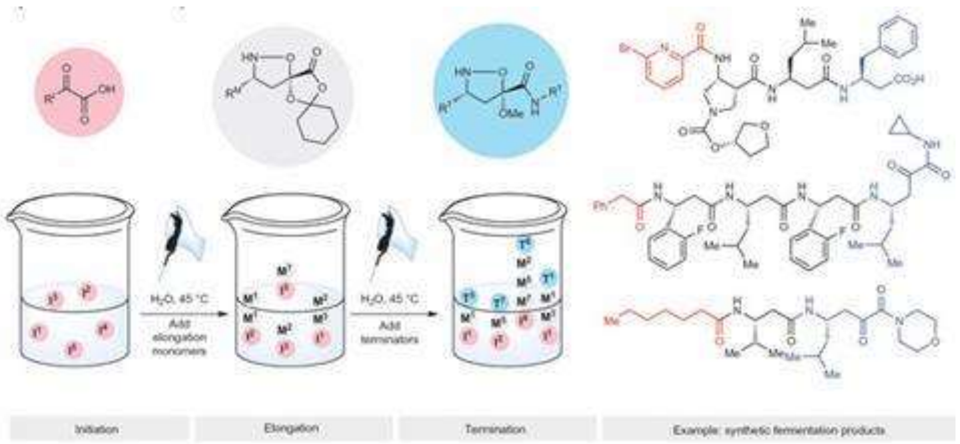
All chemically based synthetic routes to nanosized metal particles start with the reduction of positively charged metal atoms, either as simple ions or as centers of complexes in solution Solvents can vary from water to very nonpolar media such as hydrocarbons, depending on the nature of the salt or the complex used. The nature of the metal compound also determines the kind of reducing agent to be applied. Gaseous hydrogen, hydridic compounds, reducing organics like alcohols, and many other species have been successfully applied. In any case it is essential to generate the particles in the presence of suitable molecules that will cover their surface.

This is an essential, but also the most serious and complicated step in cluster formation: if the ligand molecules are already present when reduction starts, formation of larger particles can be prevented by blocking of growth. If the ligands are added subsequently, it is difficult to determine the right moment for stopping cluster growth; in practice it involves the interplay between the generations of metallic precipitates or mirrors on the one hand and the formation of mono-oroligonuclear complexes on the other hand.

Discussed in the following to show the wide field of preparative possibilities for nanosized. particles based on chemical processes.

The generation of larger metal particles, usually called colloids, can be traced back to Michael Faraday in the mid-nineteenth century. Faraday studied the formation of deep red colloidal gold solutions in water. Even today it is a very convenient procedure to generate gold colloids by Faraday's method using the reduction of $[AuCl_4]^-$ by citric acid. Nowadays numerous additional recipies exist for the preparation of mainly noble metal colloids in dilute solution.

It has been known since Faraday's time that such solutions can be of considerable stability without the addition of stabilizing ligand molecules if impurities are excluded. Why do these large particles not precipitate owing to coalescence processes? As an example, we consider the classical gold sols, prepared by the above-mentioned reduction of [AuCl4]7 by sodium citrate. The particles formed are surrounded by an electric double layer arising from adsorbed citrate and chloride ions and by the corresponding cations. The resulting Coulomb repulsion between the particles prevents aggregation and coalescence.



The Coulomb repulsion between the particles decays approximately exponentially with the particle distance. The weak minimum in the potential energy defines a stable situation. Thus, if the electric potential resulting from the double layers is high enough, electrostatic repulsion prevents aggregation. The surface charge can be reduced if the adsorbed anions are displaced by strong ligand molecules. This enables the formation of colloid patterns as can be seen in Figure 4.

In contrast to the charge-stabilization of colloids, the protection of colloidal particles and of other nanosized metal particles by strongly binding molecules improved their stability and enabled their use for a variety of purposes. Colloidal particles can be generated by very different methods. Salt reduction is one of the most frequently used routes; alcohols have proved very successful reducing agents, due to their a-hydrogen atom; for example,

$$\mathrm{RhCl_3} + {}^{3}{}_{2}\, \mathrm{R^1R^2\,CHOH} \;\square\; \mathrm{Rh_{coll}} + {}^{3}{}_{2}\, \mathrm{R^1R^2C{=}O} + 3\mathrm{HCl}$$

Palladium is another metal that is preferably synthesized in colloidal state using alcohols. Goldis probably the most famous metal with respect to the colloidal state. Faraday prepared it first by using phosphorus vapor to reduce $[AuCl_4]^-$ in aqueous solution. Subsequently, a variety of other compounds have been successfully introduced for making gold colloids; the best-known reducing agent for gold is sodium citrate. Turkevitch and coworkers, in particular, have developed gold colloid syntheses on a broad scale. Citrate is also well-suited to make platinum hydrosols. Another very powerful reducing component for noble metal salts is hydrogen, and borohydrides, hydroxylamine hydrochloride, formaldehyde, carbon monoxide, and other compounds have also been applied successfully.

The formation of metal nanoparticles is not limited to the reduction of cations to the zero-valent state; it can also occur by thermal decomposition of organometallic compounds. However, this technique is fairly limited and has not become as important as salt reduction. The same applies to so-called ligand reaction and displacement from organometallics. Finally, photolysis and radiolysis should also be mentioned as methods that have never achieved the importance of the salt reduction. However, they are used with advantage in some special cases. In principle, the photolytic method has a long tradition in photography, where silver halides are decomposed to silver nuclei and halogen by light. Radiolytic methods start with metal ions and produce solvated electrons that reduce the cations to neutral atoms, for instance.

The generation of metal particles on the nanoscale, independently of the method used, affords their stabilization by a protecting envelope. Without protection, the particles will exist only in diluted solution, weakly stabilized for instance by a shell of electrically charged species. This charge-stabilization, however, will not allow isolation of the particles in solid state and the solutions can be concentrated only to a limited extent.

The protective enveloping of nanoparticles may be achieved by various routes. A very common method is the use of organic polymers such as poly(vinyl pyrrolidone), poly(vinyl alcohol), or poly(methyl vinyl ether). Using these or related functionalized polymers in liquid form, the nanoparticles can be generated directly in the polymer to give liquid composites that are used for catalytic purposes.

Such systems, still relatively dilute, cannot be used for physical investigations of the particles, so various procedures have been developed to protect the particles' surface with strongly bonded molecules. Various syntheses have been devised to make well defined clusters. Colloids, in this chapter on metallic nanoparticles as polycrystalline species with a more or less defined size distribution, are usually generated only as charge-stabilized particles and must be protected after their formation. Clusters, that is, nanocrystalline particles of distinct size, shape, and architecture, are often found in the presence of ligands.

Ligand exchange reactions allow derivatization of the clusters. As the solubility of clusters is exclusively determined by the chemical nature of the ligand molecules, ligand exchange reactions open the possibility of producing clusters of identical metal cores but of completely different solubility, in solvents ranging from nonpolar hydrocarbons to water.

2.2 BACKGROUND ON QUANTUM DOT SEMICONDUCTORS:

In a typical molecular solid, the intermolecular interactions are much weaker than the intramolecular bonding, so the properties of a molecular solid can be analyzed as the sum of individual molecular contributions with small perturbations from the intermolecular forces. Su ch weak intermolecular interactions rarely extend beyond the nearest neighbors and the electronic properties of a molecular crystal are usually independent of the size of the crystal. Inorganic semiconductors consist of a network of ordered atoms with no discernible ``molecular" unit.

For a semiconductor crystal, electronic excitation involves a loosely bound electron±hole pair, usually delocalized over a length much longer than the lattice constant. As the diameter of the semiconductor crystallite approaches this exciton Bohr diameter, its electronic properties start to change. This is the so-called quantum size effect, which can be observed as a blue-shift in the optical bandgap or exciton energy. For CdS, the quantum size effect occurs when crystallite.

Diameter is comparable to or below the exciton diameter of 5-6 nm (3000-4000 atoms). Many terms have been used to describe these ultrasmall particles, such as quantum dots, nanocrystals, Q particles, clusters, and other terms. For nanocrystals in such a small size regime, a large percentage of the atoms are on or near the surface. For example, a 5 nm CdS nanocrystal has 15% of the atoms on the surface.

The existence of this vast interface between the nanocrystal and the surrounding medium can have a profound effect on the nanocrystal properties. For nanocrystals having imperfect surfaces, electron and=or hole traps are observed upon optical excitation. The presence of these trapped electrons and holes can in turn modify the optical properties of the particles.

2.3 BACKGROUND ON REVERSE MICELLER SOLUTION:

Reverse micelles are water-in-oil droplets. Water is readily solubilized in the polar core, forming a so-called ``water pool," characterized by w, the water/surfactant molar ratio (w=$[H_2O]/[S]$. We make no distinction between swollen micelles or microemulsions because there is none. However, some groups call ``reverse micelles" aggregates containing a low amount of water ($w < 15$), reserving ``microemulsion" for larger water content.

2.4 SYNTHESES OF SEMICONDUCTORS:

Mixed reverse micelles are used to make CdS, CdTe, $Cd_{1-y}Zn_yS$, $Cd_{1-y}Mn_yS$, and Ag_2S nanocrystals. It should be noted that functionalized surfactants are needed. When cadmium ions are solubilized in water-in-oil droplets, the crystallinity of the resultant particles is rather low and the size distribution of the nanocrystals is very wide. For alloy nanocrystals, solubilization of reactive ions in the water-in-oil droplet induces formation of a mixture of various nanocrystals and not the alloys; with Ag_2S there is a mixture of silver and Ag_2S.

The composition, y, of prepared samples is determined by energy dispersion spectroscopy (EDS), and the nanocrystal structure is determined by electron diffraction. The particle size, determined from the transmission electron microscopy pattern, is controlled by the size of the water droplets in which syntheses are made. Similar behavior has been observed for various nanoparticles.

Procedure I: Dodecanethiol is immediately added to the micellar solution having a given water content, w. This results in a selective surface reaction between the thio derivative and cadmium and manganese ions. The particles are extracted immediately from micelles and the surfactant is removed by addition of ethanol. The nanocrystallites coated by dodecanethiol are dispersed in a mixture of two solvents (isopentane-methylcyclohexane), 3 v/v, forming an optically clear glass at low temperature. The average size of coated particles increases with increase in the water content in the medium in which the particles are synthesized.

Procedure II : The particles are left in the micellar solution for 48 hours. Dodecanethiol is then added and the particles are immediately extracted.

Procedure III. Immediately after synthesis, dodecanethiol is added and the nanocrystallites remain in the micellar solution for 48 hours. The particles are then extracted from micelles using the same procedure as described above.

Procedure IV. Nanocrystallites are kept in the micellar solution for 90 minutes and then dodecanethiol is added and the particles are extracted as described above.

2.4.1SYNTHESIS OF TRIANGULAR NANOCRYSTALS:

The colloidal self-assembly of $Cd(AOT)_2$ –isooctane-H_2O is used to make CdS nanocrystals. The water content (w) and the surfactant concentration are kept constant (w=30; [Cd $(AOT)_2$ =5 x 10^{-2} M). A mixture of H_2S and N_2 produces cadmium with a sulfide coprecipitation reaction at a molar fraction of 1/3. The gas flow is around 0.05 cm^3s^{-1}. The solution is stirred during the chemical reaction. At the end of the reaction, dodecanthiol (0.5 $\mu l ml^{-1}$) is added to the micellar solution. Procedure II is then used.

2.5. CADMIUM TELLURIDE NANOCRYSTALS:

Cadmium telluride (CdTe) is an important II-VI semiconductor quantum dot because of its large exciton Bohr diameter (15 nm). It has received some attention and its bandgap shift with cluster size has been well mapped. CdTe quantum dots are usually made by RF magnetron sputtering in a glass matrix.

Syntheses are made at various contents under procedures I and II. To prevent the oxidation of telluride, the syntheses were done in the presence of an excess of cadmium (x = $([Cd^{2+}])/[Te^{2-}]=2$) . Procedure I permits a change in the particle size from 2.6 nm to 3.4 nm, whereas it is from 3.4 to 4.1 nm by procedure II. The size distribution is close to 13%. As expected, the CdTe absorption spectrum is redshifted with increasing water content and with increasing the particle size. This is attributed to quantum size effects.

The energy bandgap increases with decreasing CdTe particle size. For a given particle size, the value of the energy bandgap is constant. However, the excitonic peak is better defined for particles produced by procedure II than for those from procedure I.

Photoluminescence (PL) spectra change markedly with the procedure used. Particles made with procedure I (where nanocrystals are extracted from reverse micelles immediately after the synthesis) show a long-tail PL spectrum. This is due to the recombination of charge carriers.

In the surface traps. At the opposite extreme, under procedure II (where the nanocrystals age inside the micellar solution before extraction), Figure 3.1 shows well-defined peaks centered at higher energies. The energy bandgap and the maximum of photoluminescence are similar. This permits the photoluminescence to be attributed to the direct recombination of free electron and hole.

A red-shift is observed in the maximum of the PL spectrum due to the direct transition on increasing the particle size. This is due to a quantum size effect. The relative fluorescence quantum yield of the direct transition, Φ_{PL}, decreases with increase in the particle size. Comparing the photoluminescence spectra obtained with particles differing in their sizes and their fabrication mode, it is concluded that the aging of the crystals permits observation of the direct transition.

This can be explained by formation of a passivated layer due to Oswald ripening, which allows a decrease in the surface defects and then in the trap emissions. These data have to be related to those obtained previously with CdSe nanoparticles produced through inorganic syntheses at 280^0C. A direct transition is observed, at room temperature, when the particles are coated with ZnS.

This has been explained through a decrease in the number of CdSe defects with shell formation. Similarly, direct transition has been observed by addition of adsorbate at the particle interface. The procedu re described permits observation of the direct transition without addition of external adsorbate.

2.6 CADMIUM SULFIDE NANO CRYSTALS:

2.6.1SPHERICAL NANOCRYSTALS:

In our previous work the synthesis of CdS was carried out using procedure I. In these cases no direct fluorescence was observed. To check whether the direct fluorescence of CdS could be observed using procedure II and in the presence of an excess of cadmium ($x=[Cd^{2+}]/[S^{2-}]=2$), syntheses of CdS nanocrystals were performed in the same experimental condition s as described above (syntheses at various water contents). As expected, a shift toward low energy was observed when the average particle size increased.

As observed with CdTe, the excitonic peak was better resolved when the particles were aged. This is probably due to better crystallinity. Photoluminescence spectra of CdS nanocrystals differing in size and mode of fabrication are very broad and correspond to CdS defect states. Hence, contrary to what is observed with CdTe, aging does not permit observation of the direct fluorescence of CdS.

However we know that carrying out the syntheses in an excess of cations increases the sulfur vacancies and the trap emission. To prevent the presence of sulfur vacancies, syntheses have been made in the presence of an excess of sulfur ($x=[Cd^{2+}]/[S^{2-}]=1/2$). A large PL spectrum results due to the trap emission. However, a peak is observed at lower energy and can be attributed to the direct transition. Hence, aging permits observation of the direct transition of CdS nanocrystals that are sulfur-rich.

2.8 NANO MANIPULATOR:

The scanning tunneling electron microscope has a computer-controlled probe that skates across the surface, and the mechanical deflections are transferred to electrical energy like a vinyl record needle. The probe can also be programmed to push against the surface like a finger. When pushing, the charge separating the flexing tip and its fixed mount creates an electrical current that is proportional to the pressure exerted on the tip. By transmitting this current to the proper computer interface a human can actually do the touching.

This instrument is called a Nano manipulator. In its current form it combines a scanning tunneling electron microscope with 3D graphics rendering, a program, and a probe that fits over one finger like a finger bandage. When the scientist gets to a bump on the surface he or she feels it. In this way scientists can feel surfaces. They have even felt viruses. A multipurpose Nano manipulator has been built to perform Nano manipulation studies under vacuum inside a scanning electron microscope as well.

It can also be used to build simple objects and may eventually allow the operator to 'feel' when they pick up and move atoms. If this was virtually converted to fingertips, we could indeed build structures as if we build things in our everyday environment. In other words, we could use atoms as if they were really small objects for building, like Lego bricks. Specific devices for picking up atoms have already been invented and are called nanotweezers. Using nanotweezers is a bit like picking up Lego bricks with chopsticks.

2.9 NANO TWEEZERS:

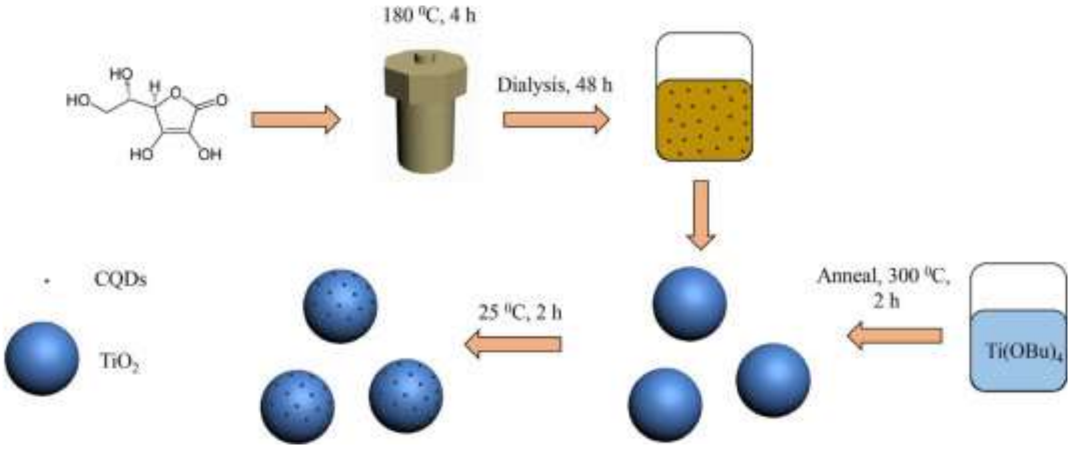
Two researchers at Harvard University have created a nanoscale grasping device ideal for measuring and manipulating molecular structures. The device is used with the scanning-probe microscope and consists of carbon nanotube tips to form tweezer-like structures. The tweezer structure can be closed with an applied electrical field like a pair of chopsticks to produce a device that grasps and moves molecules or atoms.

Nanotubes are specific carbon structures that grow to create hollow tubes only one or two nanometres in diameter. The tubes are mechanically robust and are also good conductors of electricity, making them ideal for scanning- probe techniques. In nanotweezers, nanotubes are connected to a gold electrode. An even finer version of the device is being researched, where the narrowest possible tubes would be directly grown on the gold electrodes using vapour deposition, called chemical vapour deposition or CVD.

However, even with the finest carbon nanotubes the tips are quite crude. The design of tips for the SPM that incorporate individual molecules specifically synthesised for the purpose of lifting atoms is a likely next step, and one that seems essential if we are to make progress in using SPMs to guide chemical reactions in a selective way. Nevertheless, quite a few structures have already been built using the current primitive technology. These include corrals to hold electrons and structures with missing atoms.

2.10 NANO DOTS:

Nanodots and quantum dots are small lifted pieces of raised surface up to several atoms thick that are created by attaching atoms to the SPM tip so that a strip of atoms are lifted and then deposited again. This is a little like pulling a bit of plasticine from a surface to make a bump. Using a platinum tip, nanodots of about 1-2 nm in diameter have been created. Nanodots are useful in molecular computing.



UNIT-III

3.1 TYPES OF NANO TUBES:

A nanotube may consist of one tube of graphite (a single-walled nanotube, SWNT) or a number of concentric tubes, called multiwalled nanotubes (MWNTs). When viewed by transmission electron microscopy these tubes appear as planes. Whereas in SWNTs two planes are observed, representing the edges (Figure 3.2), in MWNTs more than two planes are observed, and these can be seen as a series of parallel lines (Figure 3.2).

There are different types of SWNTs because the graphitic sheet can be rolled in different ways. The conventional way to describe this is by looking at the unrolled sheet and expressing the rolling process by vectors (a_1,a_2), where n and m are integers of the vector equation $R = na_1 + ma_2$ For example, a (10,11) nanotube has n = 10 and m = 11.

Figure 3.3 shows how this is done. This figure has two parallel lines labeled as axes where the graphite is rolled up to create the tube. A is any point on one of the lines that intersects one of the carbon atoms. One vector na_1 is placed horizontally on the graphite sheet along the zigzag bonds. The other vector is placed in any other location. The armchair line (the thin line) is the one that travels across each hexagon, separating them into two equal halves.

It is also shown in the figure. If the tube is rolled directly over this line, the resultant nanotube is an armchair nanotube. In this case, to ensure the vector sum lies over the armchair line, the second vector, ma_2 is placed at an angle such that the armchair line bisects the angle made with the first vector, na1 That is, the sum of the vectors R equates to rolling over the armchair line and $na_1 = ma_2$.

Armchair nanotubes thus have configurations (5,5: 6,6: 7,7 and so on) because the vectors must be the same to bring R over the armchair line. The numbers 5,5, 6,6 and so on reflect the diameter of the nanotube and the pairing of numbers in its stereochemistry.

There are other possible values of the second vector, ma_2. If it is made zero then R lies along and the tube rolls along this line. Zigzag nanotubes have configurations (9,0; 10,0; 11,0 and so on), since one vector must be zero. Other possibilities where and mt2 are not zero or equal result in a chiral nanotube which has left- and right-handed forms.

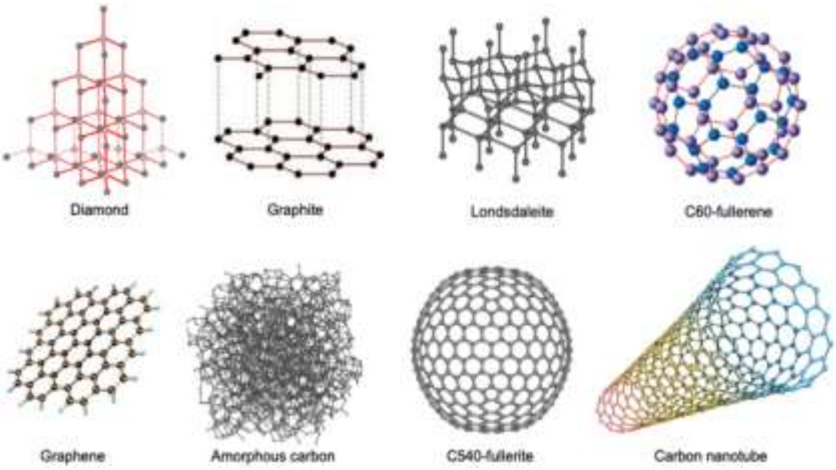
Typical nanotube variants are shown in Figure 3.4. It is possible to recognize zigzag, chiral and armchair nanotubes just by following the pattern across the diameter of the tubes. The void space in these nanotubes varies with different values of n and m so that a range of voids is possible. Values between 1.2 nm and 2 nm are common. Single-walled nanotubes can come as unaligned structures or bundles of ropes. Ropes consist of bundles of tubes packed together in an orderly manner [7, 8]. There are gaps between the nanotube bundles, and these are described as the lattice packing parameter.

Calculations show that the packing depends on the type of nanotube. Armchair (10,10) tubes should have a lattice parameter of 1.678 nm. Zigzag (17, 0) tubes should have a lattice parameter of 1.652 nm and chiral (12,6) SWNTs should have a lattice parameter of 1.652 nm. There are also spaces between the layers of tubes, called interlayer spacings. The inter- layer spacing value between the bundled tubes is also dependent on nanotube structure. For example, for tubes of the same diameter, armchair tubes should have a spacing of 0.338 nm, zigzag tubes 0.341 nm, and chiral tubes 0.339 nm.

These spacings are not very different from those found for the spaces between the different layers in graphite. However, because of the different lattice packing parameters, the densities of the different tubular solids vary. It has been predicted that pure zigzag (17,0), armchair (10,10) and chiral (12,6) SWNTs should have densities of 1.33, 1.34 and 1.40 gem"3 respectively. Preparing pure types of each nanotube is an area of ongoing research but a technique called Raman spectroscopy can detect differences in motion between the bonds in the different nanotubes and can be used to distinguish between them.

MWNTs can come in an even more complex array of forms because each concentric single-walled nanotube can have different structures and hence there are a variety of sequential arrangements. The simplest sequence is when the concentric layers are identical but different in diameter (such as sequence a,a,a,a,a for armchair nanotubes or zigzag nanotubes). However, mixed variants are possible consisting of two or more types of nanotubes arranged in different orders (for example, a,b). These can have regular layering (a,b,a,b,a,b,a) or random layering (such as a,a,b,a,b,b,b,a).

The structure of the nanotube influences its properties, including conductance, density and lattice structure. It is known that some nanotubes are conductors, that is, they are metallic, while some are semiconductors. The conductance of individual single-walled nanotubes have been measured to show that this is true, and connections to each individual type and diameter, such as zigzag, armchair, chiral, and so on, have been made. Both type and diameter are important. The wider the diameter of the nanotube the more it behaves like graphite. The narrower the diameter the more its intrinsic properties depend on type.



3.2 FORMATION OF NANO TUBES:

There are a number of methods of making nanotubes and fullerenes. Fullerenes were first observed by vaporising graphite with a laser (laser ablation) however this was initially not practical for making gram or greater quantities. Carbon nanotubes have probably been around for a lot longer and may have been seen during carbon vapour deposition but electron microscopy was not developed enough to distinguish them from other types of tubes.

The first method for preparing both carbon nanotubes and fullerenes in reasonable quantities — was by putting an electric current across two carbonaceous electrodes in a helium or argon atmosphere This method is called plasma arcing. It involves the evaporation of one electrode (the anode) as cations followed by deposition at the other electrode. Fullerenes and nanotubes are formed by plasma arcing of carbonaceous materials, particularly graphite.

The fullerenes appear in the soot that is formed, while the nanotubes are deposited on the opposing electrode, the cathode. A cheap method, which may be suitable for industrial application, is to make them from coal, especially since fullerenes can be purified on the coal from which they are made.

The products from coal differ from those obtained from graphite. While the ratio of C6 0-fullerene and C70-fullerene appears to be the same for coal as for graphite, other substances called poly cyclic hydrocarbons are formed due to the hydrogen in the coal. The distribution of types of nanotubes appears also to depend on the various minor elements in the coal. They catalyse the growth of different types of nanotubes. Normally nanotubes formed by plasma arcing are multiwalled. However if the electrodes are bored out and cobalt or other metals are included, single-walled nanotubes are formed.

Like the soot from which fullerenes are extracted, the cathode deposit is heterogeneous. Under lowest resolution, cathode deposits consist of two phases. One phase is described here as 'feathers' and the other as 'matrix'. The matrix is composed of nanotubes and nanoparticles (shortened scale-like nanotubes) while the feathers consist of the same mix but with amorphous carbon, called pyrolytic carbon.

Depending on the arcing conditions and the nature of the anode, the ratio of feathers to matrix can change. For coal the ratio of feathers to matrix depends on its hydrogen content. More hydrogen appears to produce more feathers because the additional hydrogen promotes the formation of a disordered carbon material called pyrolytic carbon .

Experiments with coal also produce significant amounts of other types of structures that form on the cathode. These products are microfilaments rather than nanotubes and they come in a variety of forms. Some of them have a uniform central void with graphitic planes aligned at an angle to a central void but not parallel as for nanotubes. The production of these filaments appears to be favoured when coal rather than graphite is used, and even more so when iron sulfides are present in the coal. Iron sulfide is observed at the growing end of the filament where it appears to act as a catalyst for growth. Some microfilaments have a worm-like shape with a nested cup structure while others have collections of different types of voids.

3.3 METHODS AND REACTANTS:

In a chemical reaction, the limiting reagent, also known as the "limiting reactant", is the substance which is totally consumed when the chemical reaction is complete. The amount of product formed is limited by this reagent since the reaction cannot proceed further without it. If one or more other reagents are present in excess of the quantities required to react with the limiting reagent, they are described as excess reagents or excess reactants.

The limiting reagent must be identified in order to calculate the percentage yield of a reaction, since the theoretical yield is defined as the amount of product obtained when the limiting reagent reacts completely.

Given the balanced chemical equation which describes the reaction, there are several equivalent ways to identify the limiting reagent and evaluate the excess quantities of other reagents.

3.4 ARCING IN THE PRESENCE OF COBALT:

The physical nature of the products formed from plasma arcing in the presence of cobalt in about three per cent concentration or more, is quite different to conventional arcing in which no cobalt is used. As noted above, the nanotube product is a compact cathode deposit of rod-like morphology. However when cobalt is added the product changes to a web with strands of 1 mm or so thickness that stretches from the cathode to the walls of the reaction vessel. The web consists of strings of SWNTs that can easily be recognised by Raman spectroscopy.

The mechanism by which cobalt changes this process is unclear, however one possibility is that such metals affect the local electric fields and hence the formation of five-membered rings. If this is true, this process could be simulated in a different way to yield an easier method of preparing the same product or perhaps different products. Cobalt particles are found in independent globules and associated with the strands. They can often be found encapsulated in graphite layers.

Bundles of SWNTs, globular cobalt particles and more amorphous bodies containing vesicles or bladders are also observed . It should be noted that the bladders, vesicles and nodules formed could contain one or more cobalt particles (see the black dots in the bladders and vesicles). The trace amount of cobalt present in coal is not enough to enhance SWNT formation. However, similar processing with cobalt is possible when coal is used as the source of carbon.

From a materials scientist's point of view, it is important to produce a uniform nanotube product. That is, a material consisting of nanotubes which all have the same diameter, are of similar length and have the same number of graphitic sheaths. It is clear that if an arcing process were to be used, cobalt or an element with similar function (such as nickel) would be necessary.

However, elements such as sulfur and iron, which are present in coal, may also play some role here, because they alter the number of layers in the formation of multiwalled nanotubes. Similar work on graphite indicates the importance of sulfur and iron in these roles.

Since the addition of organic substances such as naphthalene can affect multiwall formation, the organic structure of coal (as well as inorganic structures) may play some role. There seems to be scope for making more uniform products by a selective choice of coal Finding out how to do this depends on understanding the mechanism.

The most important tool other than microscopy and spectroscopy is isotopic analysis. Where graphite is used as an anode, individual carbon atoms (C} units) are generated during arcing and migrate to the cathode, producing nanotube and fullerene soot. Fullerene soot contains a greater ratio of 13C to 12C (it is isotopically heavy) compared with the original graphite; and the cathode deposit is isotopically light . The isotope fractionation can be interpreted in terms of the lower diffusion time and higher diffusion velocity of 12C over 13C species of C} or equivalent species in getting to the cathode because of the different charge to mass ratio.

The slower 13C species with less charge per unit mass will have a greater chance of undergoing reactions with other carbon species. Their products also have a smaller charge to mass ratio and may escape the electric field of the plasma arc to form soot or fullerenes In reactions involving species other than C}, the magnitude of this isotope effect can be used to gauge whether molecular entities reach the soot or the cathode.

For coal, there is strong evidence that much of the soot from the char and coal experiments is directly derived from molecular entities in the anode and not solely from C} units. The larger isotopic difference between anode and soot observed for graphite rather than coals is due to the absence of weak bonds which ensures that all the soot-forming process goes via C} or equivalent species.

During arcing, carbon experiences a temperature range from around 1700°C at the centre of the arc to about room temperature at its fringes. If big molecules such as naphthalene from coal are incorporated into fullerenes it is most likely that fullerene synthesis occurs at lower temperatures at the edge of the arc. Likewise, if naphthalene can be incorporated in nanotube formation it must be possible for molecules surviving at the edge of the arc to tumble back into the electrode surface and become incorporated.

In experiments where naphthalene has been added to the anode the average void space of the nanotubes in the cathode deposit increases by up to two nanometres compared with graphite. Presumably the larger void space occurs because there are more six-membered ring structures available when naphthalene is present in the arc and hence the half fullerene or related caps are wider. The wider tubes appear to be more predominant at the outer diameter regions of the anode deposit, possibly because naphthalene survives more readily here and can be incorporated into the structure. Moreover, other process conditions such as pressure can affect both fullerene and nanotube yields and structures, so there is real scope for further development.

3.5 LASER METHODS:

In 1996, a dual-pulsed laser vaporisation technique was used to optimise the laser method to produce SWNT in gram quantities and yields of > 70%. Samples were prepared by laser vaporisation of graphite rods with a 50:50 mixture of Co and Ni powder (particle size ~1 μm) at 1200°C in flowing argon, followed by heat treatment in vacuum at 1000°C to remove the C60 and other fullerenes.

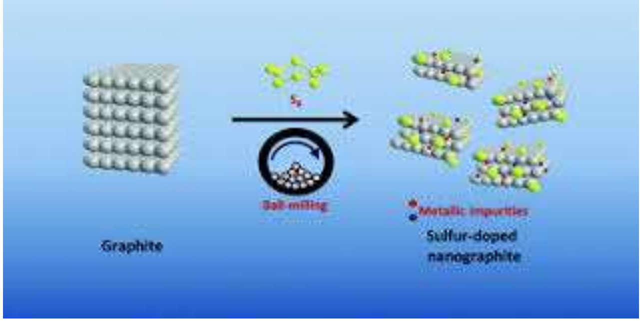
The initial laser vaporisation pulse was followed by a second pulse to vaporise the target more uniformly. The use of two successive laser pulses minimises the amount of carbon deposited as soot. The second laser pulse breaks up the larger particles ablated by the first one, and feeds them into the growing nanotube structure.

The material thus produced appears as a mat of ‘ropes’ 10-20 nm in diameter and up to 100 μm or more in length. Each rope is found to consist primarily of a bundle of SWNTs aligned along a common axis. By varying the growth temperature, the catalyst composition and other process parameters, the average nanotube diameter and distribution can be varied.

3.6 BALL MILLING:

This has been described in Chapter 3.7. Ball milling and subsequent annealing is a simple method for the production of carbon nanotubes and could be the key to cheap methods of production industrially. Although it is well established that mechanical attrition of this type can lead to fully nanoporous microstructures, it was not until recently that nanotubes of carbon and boron nitride were produced from these powders by thermal annealing.

Essentially the method consists of loading graphite powder (99.8% purity) into a stainless steel container along with four hardened steel balls. The container is purged and argon gas (300 kPa) is introduced. The milling is carried out at room temperature for up to 150 hours. Following milling, the powder is annealed under a nitrogen (or argon) gas flow at temperatures of 1400°C for six hours. The mechanism of this process is not known but it is thought that the ball milling process forms nanotube nuclei and the annealing process activates the nanotube growth. Work has shown that multiwalled nanotubes are formed but single-walled nanotubes are more difficult to prepare.



3.7 CHEMICAL VAPOUR DEPOSITION METHOD:

Arc-discharge and laser vaporization are currently the principal methods for obtaining quantities of high quality carbon nanotubes. However, both methods suffer from some drawbacks. The first is that both methods involve evaporating the carbon source so that it has been unclear how to scale up nanotube production to the industrial level using these approaches. The second issue relates to the fact that vaporization methods grow nanotubes in highly tangled forms mixed with unwanted forms of carbon or metal species. The nanotubes are difficult to purify, manipulate, and assemble for building nanotube-device architectures.

Chemical vapor deposition, and Figure 3.2 shows some pictures of aligned nanotubes. Chemical vapor deposition of hydrocarbons over metal catalysts is a classical method that has been used to produce various carbon materials such as carbon fibres, filaments, and whiskers for over twenty years . However, there was no evidence that this technique could be used to synthesis carbon nanotubes until relatively recently . The method consists of the catalytic decomposition of acetylene over iron particles at 700°C.

Using this method, four structural forms of carbon are formed: amorphous carbon layers on the surface of the catalyst, filaments of amorphous carbon, graphitic layers covering metal particles, and MWNTs. The MWNTs are usually covered with amorphous carbon on their outer layer. These carbon nanotubes have been studied by high-resolution TEM in both their as-grown form and after heat treatment. The as-grown nanotubes generally do not look fully formed. However, the structure is much improved after heat treatment to 2500-3000°C in argon.

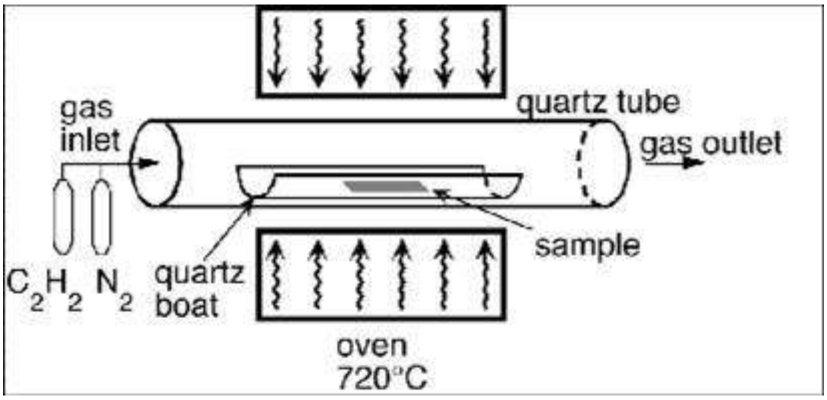
Large amounts of carbon nanotubes can be formed by catalytic deposition of acetylene over Co and Fe catalysts supported on silica or zeolite . (A zeolite is a caged structure with large voids into which molecules can enter). The carbon deposition activity seems to relate to the cobalt content of the catalysts, whereas the nanotubes' selectivity seems to be a function of the pH in catalyst preparation. Fullerenes and bundles of SWNTs were also found among the MWNTs produced on Co/zeolite catalysts.

Some researchers have studied the formation of nanotubes from ethylene . Supported catalysts (Fe, Co, Ni) containing either a single metal or a mixture of metals seem to induce the growth of isolated SWNTs or SWNT bundles in the ethylene atmosphere. The production of SWNTs, including double-walled nanotubes (DWNTs) on Mo and Mo-Fe alloy has also been demonstrated. Chemical vapour deposition of carbon within the pores of a thin alumina template called a membrane with or without a Ni catalyst has been achieved. Ethylene was used with reaction temperatures of 545°C for Ni-catalysed chemical vapour deposition and 900°C for an uncatalysed process. The resultant carbon nanostructures have open ends. That is, they have no caps.

Methane has also been used as carbon feedstock. In particular it has been used to obtain 'nanotube chips' containing isolated SWNTs at controlled locations . High yields (70-80%) of SWNTs have been obtained by catalytic decomposition of a H2 / CH4 mixture over well-dispersed metal particles (Co, Ni, Fe) on MgO at 1000°C. It has been reported that the synthesis of composite powders containing well- dispersed carbon nanotubes can be achieved by selective reduction in H2 / CH4 of oxide solid solutions between a non-reducible oxide such as A12Os or MgAl204 and one or more transition metal oxide(s).

The reduction produces very small transition metal (Fe, Co, Ni and their alloys) nanoparticles at a temperature of usually > 800°C. The decomposition of CH4 over the freshly formed nanoparticles prevents their further growth and thus results in a very high proportion of SWNTs and less MWNTs.

The disproportionation reaction of carbon monoxide has also been used to produce aligned carbon nanotubes.



A comprehensive study of the production of carbon nanotubes by the catalytic decomposition of various carbon-containing compounds over supported transition metal catalysts has been reported. It has been found that iron-containing compounds make good nanotube arrays . For example, acetylene, ethylene, propylene, acetone, n- pentane, methanol, toluene, and methane were tested with iron-con- taining compounds and each resulted in the formation of carbon nanotubes.

3.8 PROPERTIES OF NANO TUBES:

There has been considerable interest in the conductivity of nanotubes. As noted earlier, nanotubes with particular combinations of n and m are believed to be conducting and hence metallic. Conductivity has also been shown to be a function of diameter.

Conductivity in multiwalled nanotubes is quite complex. Frank and Poncharalp carefully contacted multiwalled nanotube fibres with a mercury surface. The conductance of MWNTs jumped by increments as additional nanotubes were touched to the mercury surface. This quantised conductance was found in all sizes of nanotubes and is also observed in metal nanowires. Some types of armchair nanotubes appear to conduct better than other metallic nanotubes. Furthermore, interwall reactions of MWNTs were found to redistribute the current over individual tubes across the structure non-uniformly.

Atomic force microscopy tips have been used to investigate the electronic properties of individual single-walled nanotubes. There is no change in current across different parts of metallic single- walled nanotubes. However, the behaviour of ropes of semi-conducting SWNTs is different in that the transport current changes abruptly at various positions on the nanotubes.

The conductivity and resistivity of ropes of SWNTs has been measured directly with a technique in which four electrodes have been placed at different parts of the nanotubes (Plate

3). The resistivity of these SWNT ropes was in the order of 10 4 ohms per cm at 27°C. This means that the ropes are the most highly conductive carbon fibres known. Measurements showed the current density in the tube was greater than 107 A/cm2. However, this may have been underestimated as theory demonstrates nanotubes could sustain stable current densities as high as 1013 A/cm2.

It has been reported that individual SWNTs may contain defects. Fortuitously these defects allow the SWNTs to act as transistors. Likewise, joining nanotubes together may form transistor-like devices . A single nanotube with a natural junction (that is, where a straight section is joined to a chiral section (Figure 3.8), behaves as a rectifying diode — a half-transistor in a single molecule.

The properties of bent nanotubes have been explored. Nanotubes that are suspended and then deflected from an equilibrium position can be described as springs. Their conductivity is reduced when they are stressed.

3.8.2STRENGTH AND ELASTICITY:

SWNTs are stiffer than steel and are resistant to damage from physical forces. Pressing on the tip of the nanotube will cause it to bend with out damage to the tip. When the force is removed, the tip of the nanotube will recover to its original state. Quantification of these effects, however, is rather difficult and an exact numerical value cannot be agreed upon. Using an AFM, unanchored ends of freestanding nanotubes can be pushed out of their equilibrium position and the force required to push the nanotube can be measured.

The current Young's Modulus value (Chapter 3.9) of SWNTs is about 1 TPa but this value is disputed and a value as high as 1.8 TPa has been reported. Other workers have also reported different values. A (10,10) armchair nanotube had a Young's Modulus of 640.30 GPa; for a (17,0) zigzag tube it was 648.43 GPa, and a (12,6) gave a value of 673.94 GPa. The differences probably arise through different experimental measurement techniques.

Others have shown theoretically that the Young's Modulus depends on the size and chirality of the SWNT, ranging from 1.22 TPa for the (10,0) and (6, 6) to 1.26 TPa for the large (20,0) SWNT. They calculated a value of 1.09 TPa for a generic nanotube. However, when working with different MWNTs, others have noted that modulus measurements of MWNTs using AFM do not strongly depend on the diameter. Instead, they argue that the modulus of MWNTs correlates to the amount of disorder in the nanotube walls. Not surprisingly when multiwalled nanotubes break, the outermost layers break first.

3.9 PLASMA ARCING:

Plasma is an ionised gas. Plasma is achieved by making a gas conduct electricity by providing a potential difference across the two electrodes so that the gas yields up its electrons and thus ionises. In a vacuum or in an inert gas the electrodes can be made volatile. Heat is produced and the electrodes or even other materials can be volatilised and ionised using this heat. Plasma arcing has been important in forming carbon nanotubes (Chapter 4). A typical plasma arcing device consists of two electrodes. An arc passes from one electrode to the other. The first electrode (anode) vaporises as electrons are taken from it by the potential difference. To make carbon nanotubes, carbon electrodes are used. Atomic carbon cations are produced. These positively charged ions pass to the other electrode, pick up electrons and are deposited to form nanotubes.

The electrodes can be made of other materials but they must be able to conduct electricity. An interesting variation is to make the electrodes from a mixture of conducting and non-conducting materials. During heating, the non-conducting material is vaporised and ionised so that it also becomes part of the plasma arc and is transported and deposited on the cathode.

Plasma arcing can be used to make deposits on surfaces rather than new structures. In this way it resembles chemical vapour deposition (see below) except that the species involved are ionised. As a surface deposit, the nanomaterial can be as little as a few atoms in depth. It is not a nano- material unless at least one dimension of the bulk particle of the surface deposit is of nanometre scale. If this is not true, it is a thin film and not a nanomaterial.

Each particle must be nanosized and independent, other than interacting by hydrogen bonding or van der Waals forces A variation on plasma arcing is flame ionisation. If a material is sprayed into a flame ions are produced, and these can also be collected and deposited in nanocrystallite form.

3.10 ELECTRO DEPOSITION:

Electodeposition has been used for a long time to make electroplated materials. By carefully controlling the number of electrons transferred, the weight of material transferred can be determined in accordance with Faraday's law of electrolysis. This states that the number of moles of product formed by an electric current is directly proportional to the number of moles of electrons supplied.

Since the quantity of electricity passed (measured in coulombs) is current (amps) x time (sec) and Faraday's constant F (96 485 coulombs is currently the most accurate estimate) is the charge per mole of electrons (1 mole of electrons = 96 485 coulombs), then the number of moles of electrons is charge supplied /F.

Thus if we wished to copper plate an object with 5 g of copper, we would need 5 / 63.546 (atomic weight of copper) = 0.07868 moles of copper or 2 x 0.07868 moles of electrons if we were reducing Cu2+ ions. This is 1.52 x 104 coulombs or 4.2 amps for one hour. If the surface of the object to be coated is 2 m2, each m2 would have 2.5 g of copper or 0.03934 x 6.022 x 1023 (Avogadro's number) atoms = 0.237 x 10^{23} atoms. Each nm2 would therefore have 0.237x 1023/ 1018 = 23 700 Cu atoms.

If the surface was perfectly flat, then knowing the diameter (Chapter 1, Figure 1.6) of a copper atom it should be possible to calculate the height and number of atoms in the copper layer. In practice the surface is rocky, so a coverage factor needs to be included which is related to root-mean-squared roughness or average roughness (Chapter 2.5).

In nanotechnology the aim is to place only a single layer or more of coverage on a surface by electrodeposition in a very controlled way. Thus, hypothetically if an atom of 10 nm diameter, which packs cubi- cally (that is, at the corners of a square), is to be deposited as a monolayer at 50% coverage of a 1 cm2 surface, then 0.5 x 1012 atoms are needed. If it is prepared from a divalent cation this requires lx 1012 electrons or 0.166 x 10 11 moles (=16 016 x 10 11 coulombs) or 160.16 milliamps per microsecond. The current and time must be carefully measured and any other factors involved in consuming current, such as impurities, must be known in great detail. Hence the necessity for super clean rooms.

Nevertheless, nanostructured films of platinum can be produced by electrodeposition from liquid crystalline mixtures. The films obtained are mechanically robust, remarkably flat, uniform, and shiny in appearance. They also have surface areas comparable with those of the platinum blacks deposited from conventional electroplating baths, and exhibit quite different and favourable electrical properties than conventional platinum deposits.

The concept of electroplating from liquid crystalline mixtures can be used for other metals including Pd, Ni, and Au, organic polymers (for example, polyaniline), oxides and semiconductors. The unique nature of nanostructured films from liquid crystals makes them of considerable interest for a very wide range of applications. These include batteries, fuel cells, solar cells, windows that can disperse heat and change properties depending on the environment (electrochromic windows), sensors, field emitters, and photonic devices.

An electrochromic device consists of materials in which an optical absorption band can be introduced, or an existing band can be altered by passing a current through the materials, or by the application of an electric field. Nanocrystalline materials, such as tungstic oxide (W03.xH20) gel, are used in very large electrochromic display devices.

The reaction governing electrochromism (a reversible colouration process under the influence of an electric field) is the double-injection of ions (or protons, H+) and electrons, which combine with the nanocrystalline tungstic acid to form a tungsten bronze.

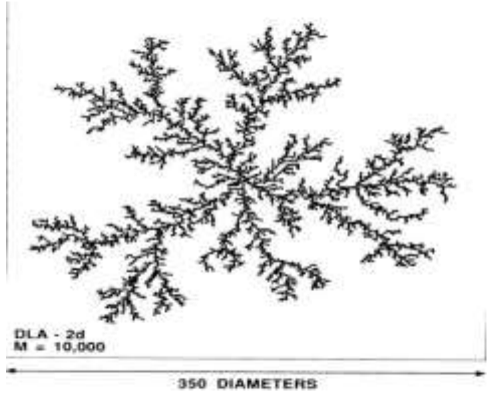
These devices are mostly used in public billboards and ticker boards to convey information. Electrochromic devices are similar to the liquid-crystal displays (LCDs) commonly used in calculators and watches. However, electrochromic devices display information by changing colour when a voltage is applied. When the polarity is reversed, the colour is bleached. The resolution, brightness, and contrast of these devices greatly depend on the grain size of the tungstic acid gels. Hence, nanomateri- als are being explored for this purpose. More optical uses of nanoma- terials are described in Chapter 7.

Electrodeposition can be used to fill holes to make dispersed nano- materials. Nanoholes have been strategically placed in membranes. These materials start with the bombardment of a polymer sheet by energetic heavy ions accelerated by a cyclotron. The heavy ions pass through the sheet and leave minuscule damage tracks. Chemical etching is used to turn these tracks into holes (nanoholes) with diameters in the 10 to 100 nanometre range. Filling nanosized holes in polymer membranes with various combinations of metals (Figure 3.7) produces nanocomposites, which have different uses.

For example, if some holes are filled with a conducting metal like gold, then they can be charged and this can influence the nature of ions that will go through the unfilled holes. If there is a device at the other end that responds to charge then the device becomes a specific ion detector. Other nanocomposite materials can be produced with designer optical, electrical, magnetic or chemical properties. Such materials can be used as screening materials for heat, light or radiation, for example as thermo liners in ovens and utensils, and in mobile phones.

However, if they are compound-specific they can be used as the active sensing material in so-called intelligent materials for 'artificial noses' or sensors of biological material. The most important development is the manufacture of multipurpose chips, which will be able to sense a host of substances at once and thus provide very specific and effective diagnoses.

Certain non-carbon types of nanotubes can be made by electrodeposition and also by sol-gel processes.



The transformation of sol to gel takes place via hydrolysis and condensation reactions of the precursors. The hydrolysis reaction is represented as (taking an example of Silicon):

$$Si\,(OR)_4 + n\,H_2O \rightarrow (HO)_n\text{-}Si\,(OR)_{4-n} + ROH.$$

In case of metal alkoxide precursors, R represents an alkyl group. The metal is totally hydrolyzed when n = 4. For any other value of n, partial hydrolysis takes place.

In the condensation reaction, the two partially hydrolyzed molecules link together and liberate a small molecule as H_2O or ROH. The general reaction is represented as:

$$(OR)_{4-n}\,Si\,(OH)_n + (HO)_n\,Si\,(OR)_{4-n} \rightarrow (OR)_{4-n}\,(OH)_{n-1}\,Si\text{-}O\text{-}Si\,(HO)_{n-1}\,(OR)_{4-n} + H_2O$$

The condensation takes place in such a way as to maximize the number of M-O-M (metal-metal linkage through oxygen) bonds and minimize terminal hydroxyl groups through internal condensation. Initially monomers add to form rings, and creating 3-D structures. These compact structures are formed by leaving the hydroxyl groups outside, as shown in figure 2.

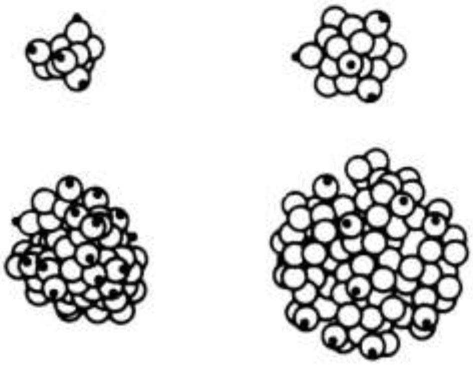
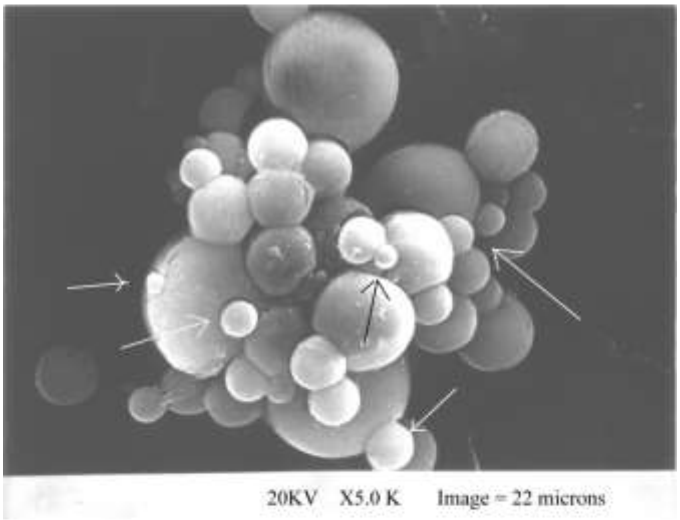


Figure 2. Colloidal particles formed by condensing monomers to form closed rings.

These 3-D structures serve as the nuclei for further particle growth[2]. Further particle growth is by Ostwald ripening mechanism (Figure 3) i.e. particles grow in size decrease in number. The highly soluble small particles precipitate on the relatively larger, insoluble particles.



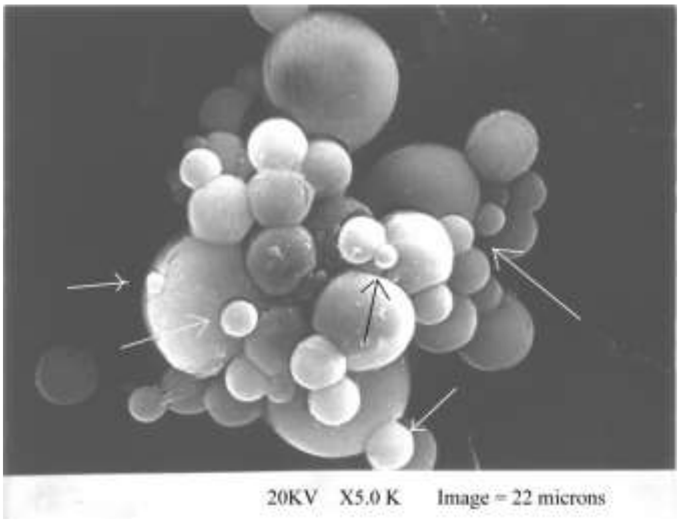
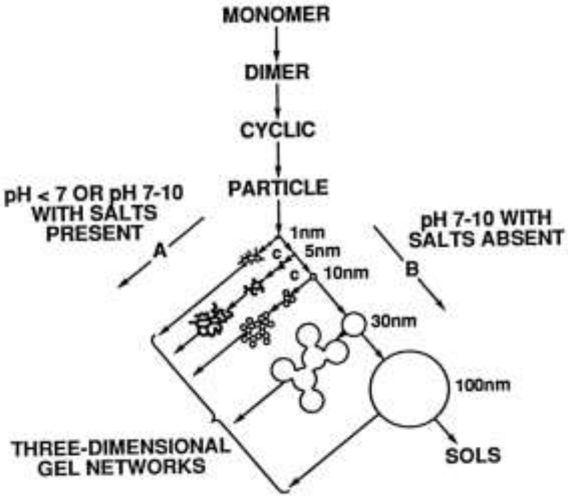


Figure 3: SEM showing Ostwald ripening. The arrowheads indicated the smaller particles precipitated on the larger particles.

The figure 4 shows the general representation of the sol-gel process, carried out at different pH and additives[2].



3.12.2 SOL-GEL PROCESSING:

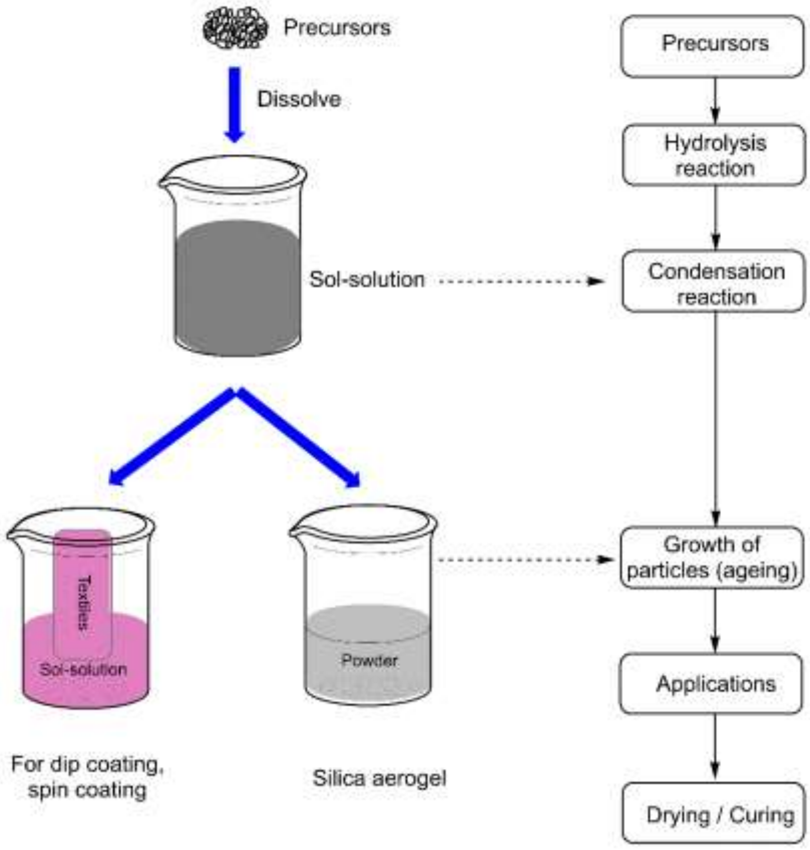
In section 1.1 the general sol-gel processing was described in brief. The formation of zeolites will be discussed here. The hydrolysis and condensation proceeds with conversion of tetrahedrally coordinated Al atoms to octahedrally coordinated Al atoms[1]. The inorganic polymerization is due primarily to the formation of Al-O-Al linkages, first involving tetrahedrally coordinated Al and later octahedrally coordinated Al, leading to 3-D structure.

The polymer growth occurs by chain polymerization mechanism involving tetrahedrally coordinated Al.

The existence of the sol can be verified by measuring the fractal dimension of the solution. This can be achieved by small angle X-ray scattering (SAXS), small angle neutron scattering or small angle light scattering (SALS). The zeolite synthesis takes in two steps: nucleation and crystallization. Nucleation is a process where small aggregates of precursors give rise to germ nuclei (embryos), which become larger with time. The formation of these nuclei is discussed earlier. The rate of nucleation of a new phase from a melt increase by decreasing the temperature of the system.

Crystallization starts by involving nuclei and ingredients from the solution mixture. Following are the characteristics of the zeolite crystallization:

1. The deposition on a seed or stable nucleus increases with the extent of stirring and temperature.
2. High index faces grow more rapidly and they tend to disappear.
3. As the overall rate of crystallization increases, the difference in the growth rate of the various phases tends to decrease.



UNIT-IV

4.1 SCANNING ELECTRON MICROSCOPE:

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam ofelectrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum, low vacuum and in environmental SEM specimens can be observed in wet conditions

History:

An account of the early history of SEM has been presented by McMullan. Although Max Knoll produced a photo with a 50 mm object-field-width showing channeling contrast by the use of an electron beam scanner, it was Manfred von Ardenne who in 1937 invented a true microscope with high magnification by scanning a very small raster with a demagnified and

Finely focused electron beam. Ardenne applied the scanning principle not only to achieve magnification but also to purposefully eliminate the chromatic aberration otherwise inherent in the electron microscope. He further discussed the various detection modes, possibilities and theory of SEM, together with the construction of the first high magnification instrument of a SEM. Further work was reported by Zworykin's group, followed by the Cambridge groups in the 1950s and early 1960s headed by Charles Oatley, all of which finally led to the marketing of the first commercial instrument by Cambridge Scientific Instrument Company as the "Stereoscan" in 1965 (delivered to DuPont).

Principles and capacities:

The types of signals produced by a SEM include secondary electrons (SE), back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence) (CL), specimen current and transmitted electrons. Secondary electron detectors are standard equipment in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details less than 1 nm in size. Due to the very narrow electron beam, SEM micrographs have a largedepth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample.

This is exemplified by the micrograph of pollen shown above. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes.

Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays, because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen. BSE images can provide information about the distribution of different elements in the sample.

For the same reason, BSE imaging can imagecolloidal gold immuno-labels of 5 or 10 nm diameter, which would otherwise be difficult or impossible to detect in secondary electron images in biological specimens. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher-energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.

Sample preparation:

All samples must also be of an appropriate size to fit in the specimen chamber and are generally mounted rigidly on a specimen holder called a specimen stub. Several models of SEM can examine any part of a 6-inch (15 cm) semiconductor wafer, and some can tilt an object of that size to 45°.

For conventional imaging in the SEM, specimens must be electrically conductive, at least at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface. Metal objects require little special preparation for SEM except for cleaning and mounting on a specimen stub. Nonconductive specimens tend to charge when scanned by the electron beam, and especially in secondary electron imaging mode, this causes scanning faults and other image artifacts. They are therefore usually coated with an ultrathin coating of electrically conducting material, deposited on the sample either by low-vacuum sputter coating or by high-vacuum evaporation. Conductive materials in current use for specimen coating include gold, gold/palladium alloy, platinum, osmium, iridium, tungsten, chromium, and graphite. Additionally, coating may increase signal/noise ratio for samples of low atomic number (Z). The improvement arises because secondary electron emission for high-Z materials is enhanced.

An alternative to coating for some biological samples is to increase the bulk conductivity of the material by impregnation with osmium using variants of the OTO staining method (O-osmium, T-thiocarbohydrazide, O-osmium).

Nonconducting specimens may be imaged uncoated using environmental SEM (ESEM) or low-voltage mode of SEM operation. Environmental SEM instruments place the specimen in a relatively high-pressure chamber where the working distance is short and the electron optical column is differentially pumped to keep vacuum adequately low at the electron gun. The high-pressure region around the sample in the ESEM neutralizes charge and provides an amplification of the secondary electron signal.

Low-voltage SEM is typically conducted in an FEG-SEM because the field emission guns (FEG) is capable of producing high primary electron brightness and small spot size even at low accelerating potentials. Operating conditions to prevent charging of non-conductive specimens must be adjusted such that the incoming beam current was equal to sum of outcoming secondary and backscattered electrons currents. It usually occurs at accelerating voltages of 0.3–4 kV.

Embedding in a resin with further polishing to a mirror-like finish can be used for both biological and materials specimens when imaging in backscattered electrons or when doing quantitative X-ray microanalysis.

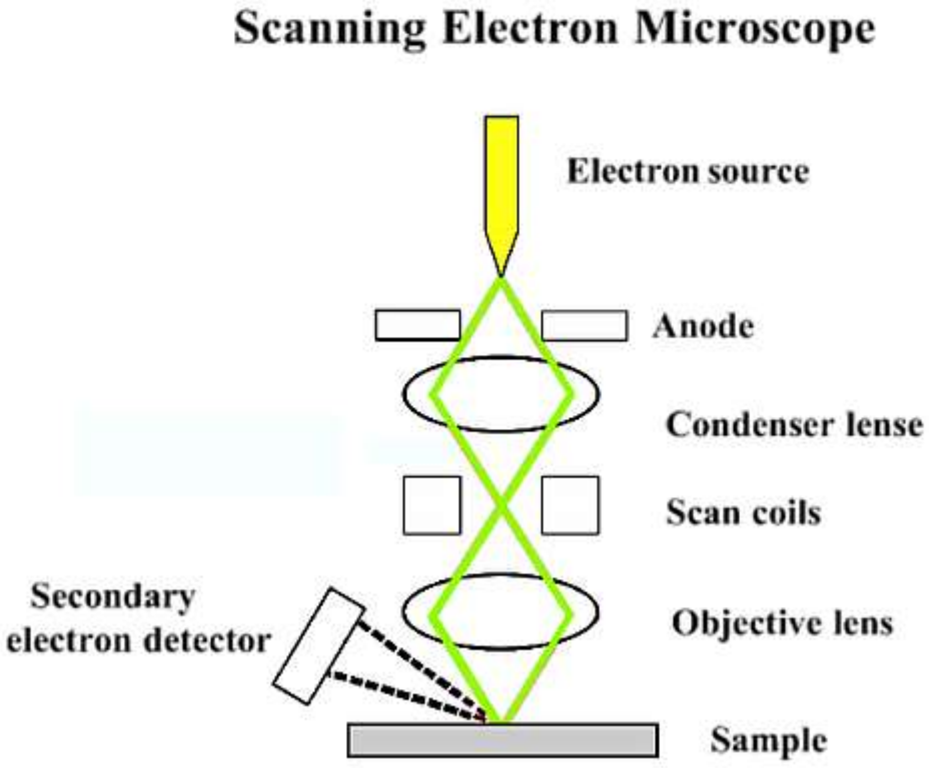
The main preparation techniques are not required in the environmental SEM outlined below, but some biological specimens can benefit from fixation

Biological samples:

For SEM, a specimen is normally required to be completely dry, since the specimen chamber is at high vacuum. Hard, dry materials such as wood, bone, feathers, dried insects, or shells can be examined with little further treatment, but living cells and tissues and whole, soft-bodied organisms usually require chemical fixation to preserve and stabilize their structure.

Fixation is usually performed by incubation in a solution of a buffered chemical fixative, such as glutaraldehyde, sometimes in combination with formaldehyde and other fixatives, and optionally followed by postfixation with osmium tetroxide. The fixed tissue is then dehydrated. Because air-drying causes collapse and shrinkage, this is commonly achieved by replacement of water in the cells with organic solvents such as ethanol or acetone, and replacement of these solvents in turn with a transitional fluid such as liquid carbon dioxide by critical point drying.

The carbon dioxide is finally removed while in a supercritical state, so that no gas-liquid interface is present within the sample during drying. The dry specimen is usually mounted on a specimen stub using an adhesive such as epoxy resin or electrically conductive double-sided adhesive tape, and sputter-coated with gold or gold/palladium alloy before examination in the microscope.



If the SEM is equipped with a cold stage for cryo microscopy, cryofixation may be used and low-temperature scanning electron microscopy performed on the cryogenically fixed specimens. Cryo-fixed specimens may be cryo-fractured under vacuum in a special apparatus to reveal internal structure, sputter-coated, and transferred onto the SEM cryo-stage while still frozen.

Low-temperature scanning electron microscopy is also applicable to the imaging of temperature-sensitive materials such as ice and fats.

Freeze-fracturing, freeze-etch or freeze-and-break is a preparation method particularly useful for examining lipid membranes and their incorporated proteins in "face on" view. The preparation method reveals the proteins embedded in the lipid bilayer.

Materials:

Back scattered electron imaging, quantitative X-ray analysis, and X-ray mapping of specimens often requires that the surfaces be ground and polished to an ultra smooth surface. Specimens that undergo WDS or EDS analysis are often carbon coated. In general, metals are not coated prior to imaging in the SEM because they are conductive and provide their own pathway to ground.

Fractography is the study of fractured surfaces that can be done on a light microscope or commonly, on an SEM. The fractured surface is cut to a suitable size, cleaned of any organic residues, and mounted on a specimen holder for viewing in the SEM.

Integrated circuits may be cut with a focused ion beam (FIB) or other ion beam milling instrument for viewing in the SEM. The SEM in the first case may be incorporated into the FIB.

Metals, geological specimens, and integrated circuits all may also be chemically polished for viewing in the SEM.

Special high-resolution coating techniques are required for high-magnification imaging of inorganic thin films.

4.3 SCANNING PROCESS AND IMAGE FORMATION:

In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission, and because of its low cost. Other types of electron emitters include lanthanum hexaboride (LaB6) cathodes, which can be used in a standard tungsten filament SEM if the vacuum system is upgraded and FEG, which may be of the cold-cathode type using tungsten single crystal emitters or the thermally assistedSchottky type, using emitters of zirconium oxide.

The electron beam, which typically has an energy ranging from 0.2 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface.

When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 µm into the surface. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density.

The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals, which are displayed as variations in brightness on a computer monitor (or, for vintage models, on a cathode ray tube).

Each pixel of computer videomemory is synchronized with the position of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. In older microscopes image may be captured by photography from a high-resolution cathode ray tube, but in modern machines image is saved to a computer data storage.

Microscopes, image magnification in the SEM is not a function of the power of the objective lens. SEMs may have condenser and objective lenses, but their function is to focus the beam to a spot, and not to image the specimen. Provided the electron gun can generate a beam with sufficiently small diameter, a SEM could in principle work entirely without condenser or objective lenses, although it might not be very versatile or achieve very high resolution.

In a SEM, as inscanning probe microscopy, magnification results from the ratio of the dimensions of the raster on the specimen and the raster on the display device. Assuming that the display screen has a fixed size, higher magnification results from reducing the size of the raster on the specimen, and vice versa. Magnification is therefore controlled by the current supplied to the x, y scanning coils, or the voltage supplied to the x, y deflector plates, and not by objective lens power.

The most common configuration for an SEM produces a single value per pixel, with the results usually rendered as black-and-white images. However, often these images are then colorized through the use of feature-detection software, or simply by hand-editing using a graphics editor. This is usually for aesthetic effect or for clarifying structure, and generally does not add.

In some configurations more information is gathered per pixel, often by the use of multiple detectors. The attributes of topography and material contrast can be obtained by a pair of backscattered electron detectors and such attributes can be superimposed on a single color image by assigning a different primary color to each attribute. Similarly, a combination of backscattered and secondary electron signals can be assigned to different colors and superimposed on a single color micrograph displaying simultaneously the properties of the specimen.

Some types of detectors used in SEM have analytical capabilities, and can provide detectors it is common to color code the signals and superimpose them in a single color image, so that differences in the distribution of the various components of the specimen can be seen clearly and compared.

Optionally, the standard secondary electron image can be merged with the one or more compositional channels, so that the specimen's structure and composition can be compared. Such images can be made while maintaining the full integrity of the original signal, which is not modified in any way

Detection of secondary electrons:

The most common imaging mode collects low-energy (<50 eV) secondary electrons that are ejected from the k-orbitals of the specimen atoms by inelastic scattering interactions with beam electrons. Due to their low energy, these electrons originate within a few nanometers from the sample surface. The electrons are detected by an Everhart-Thornley detector, which is a type of scintillator-photomultiplier system. The secondary electrons are first collected by attracting them towards an electrically biased grid at about +400 V, and then further accelerated towards a phosphor or scintillator positively biased to about +2,000 V.

The accelerated secondary electrons are now sufficiently energetic to cause the scintillator to emit flashes of light (cathodoluminescence), which are conducted to a photomultiplier outside the SEM column via a light pipe and a window in the wall of the specimen chamber. The amplified electrical signal output by the photomultiplier is displayed as a two-dimensional intensity distribution that can be viewed and photographed on an analogue video display, or subjected toanalog-to-digital conversion and displayed and saved as a digital image.

This process relies on a raster-scanned primary beam. The brightness of the signal depends on the number of secondary electrons reaching the detector. If the beam enters the sample perpendicular to the surface, then the activated region is uniform about the axis of the beam and a certain number of electrons "escape" from within the sample.

As the angle of incidence increases, the "escape" distance of one side of the beam will decrease, and more secondary electrons will be emitted. Thus steep surfaces and edges tend to be brighter than flat surfaces, which results in images with a well-defined, three-dimensional appearance. Using the signal of secondary electrons image resolution less than 0.5 nm is possible.

Detection of backscattered electrons:

Backscattered electrons (BSE) consist of high-energy electrons originating in the electron beam, that are reflected or back-scattered out of the specimen interaction volume by elastic scattering interactions with specimen atoms. Since heavy elements (high atomic number) backscatter electrons more strongly than light elements (low atomic number), and thus appear brighter in the image, BSE are used to detect contrast between areas with different chemical compositions.

The Everhart-Thornley detector, which is normally positioned to one side of the specimen, is inefficient for the detection of backscattered electrons because few such electrons are emitted in the solid angle subtended by the detector, and because the positively biased detection grid has little ability to attract the higher energy BSE electrons. Dedicated backscattered electron detectors are positioned above the sample in a "doughnut" type arrangement, concentric with the electron beam, maximizing the solid angle of collection. BSE detectors are usually either ofscintillator or of semiconductor types. When all parts of the detector are used to collect electrons symmetrically about the beam, atomic number contrast is produced. However, strong topographic contrast is produced by collecting back-scattered electrons from one side above the specimen using an asymmetrical, directional BSE detector; the resulting contrast appears as illumination of the topography from that side. Semiconductor detectors can be made in radial segments that can be switched in or out to control the type of contrast produced and its directionality.

Backscattered electrons can also be used to form an electron backscatter diffraction (EBSD) image that can be used to determine the crystallographic structure of the specimen.

Stain not required:

The improved contrast allows for the significant reduction, or elimination, of the heavy metalnegative staining step for TEM imaging of light elements (H, C, N, O, S, P).While staining is beneficial for experiments aimed at high resolution structure determination, it is highly undesirable in certain protein sample preparations, because it could destabilize the protein sample due to its acid pH and relatively high heavy metal concentration. The addition of stain to sectioned samples such as biological materials or polymers can also introduce imaging artifacts.

LVEM experiments carried out on an extracted membrane protein sample that was analyzed with and without the staining procedure show a marked improvement in the appearance of the sample.

Resolution:

Present low voltage electron microscopes are capable of spatial resolutions of about 2.5 nm in TEM 2.0 nm in STEM and 3.0 nm in SEM.

As of 2013, technological advancements have shown low voltage electron microscopes with resolutions better than 1.2nm in TEM mode.

Limitations:

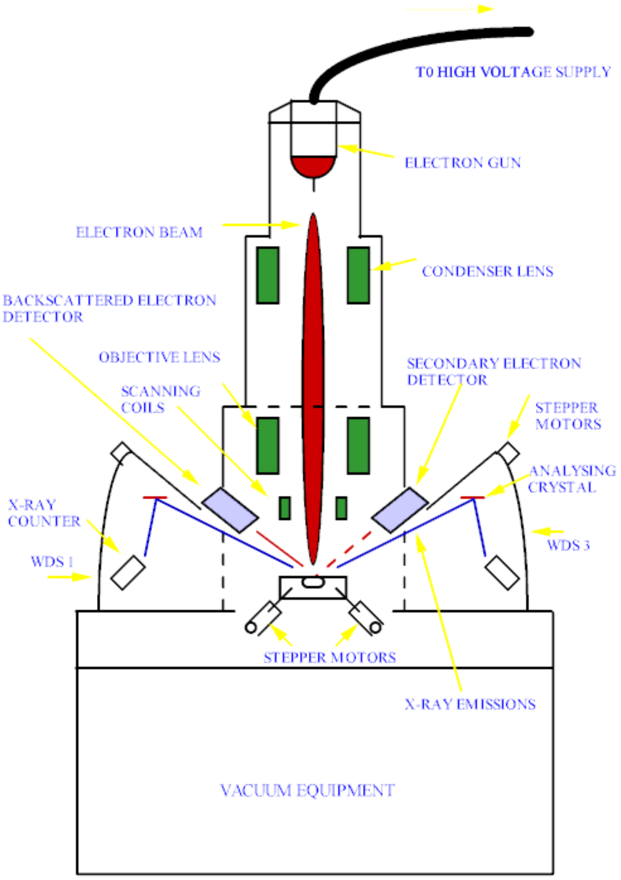
Currently available low voltage microscopes are only able to obtain resolutions of 1.2–3 nanometers. While this is well beyond resolutions possible from optical (light) microscopes, they are not yet able to compete with the atomic resolution obtainable from conventional (higher voltage) electron microscopes

Low voltage limits the maximum thickness of samples which can be studied in the TEM or STEM mode. Whereas it is about 50-90 nm in conventional TEM, it decreases to around 20– 65 nanometers for LVEM. However, thicknesses of the order of 20 nm or less are required to attain the maximal resolution in the TEM and STEM modes. These thickness are sometimes achievable with the use of an ultramicrotome.

4.4 ELECTRON MICROPROBE:

An electron microprobe (EMP), also known as an electron probe microanalyzer (EPMA) or electron micro probe analyzer (EMPA), is an analytical tool used to non-destructively determine the chemical composition of small volumes of solid materials. It works similarly to a scanning electron microscope: the sample is bombarded with an electron beam, emitting x-rays at wavelengths characteristic to the elements being analyzed.

This enables the abundances of elements present within small sample volumes (typically 10-30 cubic micrometers or less) to be determined. The concentrations of elements from boron to plutonium can be measured at levels as low as 100 parts per million (ppm). Recent improvements on EMPAs (e.g. the CamecaSX100 with five oversized PET crystals for trace element analysis) can accurately measure elemental concentrations of approximately 10 ppm.



History:

Development of the electron microprobe was preceded by that of the closely related analytical technique of X-ray fluorescence spectrometry (XRF). This technique was first proposed by Georg von Hevesy in 1923 and applied by other workers in the following few years

In 1944, MIT built an electron microprobe, combining an electron microscope and an energy-loss spectrometer. Electron energy-loss spectrometry is very good for light element analysis and they obtained spectra of C-Kα, N-Kα and O-Kα radiation. In 1947, Hiller patented the idea of using an electron beam to produce analytical X-rays, but never constructed a working model.

His design proposed using Bragg diffraction from a flat crystal to select specific X-ray wavelengths and a photographic plate as a detector. In 1948-1950, Raymond Castaing, supervised by André Guinier, built the first electron “microsonde électronique” (electron microprobe) at the University of Paris.

This microprobe produced an electron beam diameter of 1-3 µm with a beam current of ~10 nanoamperes (nA) and used a Geiger counter to detect the X-rays produced from the sample. However, the Geiger counter could not distinguish X-rays produced from specific elements and in 1950, Castaing added a quartz crystal between the sample and the detector to permit wavelength discrimination. He also added an optical microscope to view the point of beam impact. The resulting microprobe was described in Castaing's 1951 Ph.D. thesis, in which he laid the foundations of the theory and application of quantitative analysis by electron microprobe, establishing the theoretical framework for the matrix corrections of absorption and fluorescence effects. Casting (1921-1999) is considered the "father" of electron microprobe analysis.

Cameca (France) produced the first commercial microprobe, the “MS85,” in 1956. It was soon followed by many microprobes from other companies; however, all companies except Cameca andJEOL, are now out of business. In addition, many researchers build electron microprobes in their labs. Significant subsequent improvements and modifications to microprobes included scanning the electron beam to make X-ray maps (1960), the addition of

solid state EDS detectors (1968) and the development of synthetic multilayer diffracting crystals for analysis of light elements (1984).

How it works:

A beam of electrons is fired at a sample. The beam causes each element in the sample to emit X-rays at a characteristic frequency; the X-rays can then be detected by the electron microprobe. The size of the electron beam determines the trade-off between resolution and scan time.

Thousand electron volts (keV). The anode plate has central aperture and electrons that pass through it are collimated and focused by a series of magnetic lenses and apertures. The resulting electron beam (approximately from 5 nm to 10 micrometre diameter) may be rastered across the sample or used in spot mode to excite various effects from the sample.

Among these effects are: phonon excitation (heat),cathodoluminescence (visible light fluorescence), continuum X-ray radiation (bremsstrahlung), characteristic X-ray radiation, secondary electrons (plasmon production), backscattered electron production, and Auger electron production The characteristic X-rays are used for chemical analysis. Specific X-ray wavelengths are selected and counted, either by wavelength dispersive X-ray spectroscopy (WDS) or energy dispersive X-ray spectroscopy (EDS).

WDS utilizes Bragg diffraction from crystals to select X-ray wavelengths of interest and direct them to gas-flow or sealed proportional detectors. In contrast, EDS uses a solid state semiconductor detector to accumulate X-rays of all wavelengths produced from the sample. While EDS yields more information and typically requires a much shorter counting time, WDS is the more precise technique because its superior X-ray peak resolution.

Chemical composition is determined by comparing the intensities of characteristic X-rays from the sample material with intensities from known composition (standards). Count from the sample must be corrected for matrix effects (absorption and secondary fluorescence) to yield quantitative chemical compositions. The resulting chemical information is gathered in textural context. Variations in chemical composition within a material (zoning), such as a mineral grain or metal, can be readily determined.

Volume from which chemical information is gathered (volume of X-rays generation) is 0.3 – 3 cubic micrometers.

USES:

Materials science and engineering:

The technique is commonly used for analyzing the chemical composition of metals, alloys, ceramics, and glasses. It is particularly useful for assessing the composition of individual particles or grains and chemical changes on the scale of a few micrometres to millimeters. The electron microprobe is widely used for research, quality control, and failure analysis

Mineralogy and Petrology:

This technique is most commonly used by mineralogists and petrologists. Most rocks are aggregates of small mineral grains. These grains may preserve chemical information adopted during their formation and subsequent alteration. This information may illuminate geologic processes, such as crystallization, lithification, volcanism, metamorphism, orogenic events (mountain building), plate tectonics. This technique is also used for the study of extraterrestrial rocks (i.e. meteorites), and provides chemical data which is vital to understanding the evolution of the planets, asteroids, and comets.

The change in elemental composition from the center (also known as core) to the edge (or rim) of a mineral can yield information about the history of the crystal's formation, including the temperature, pressure, and chemistry of the surrounding medium. Quartz crystals, for example, incorporate a small, but measurable amount of titanium into their structure as a function of temperature, pressure, and the amount of titanium available in their environment. Changes in these parameters are recorded by titanium as the crystal grows.

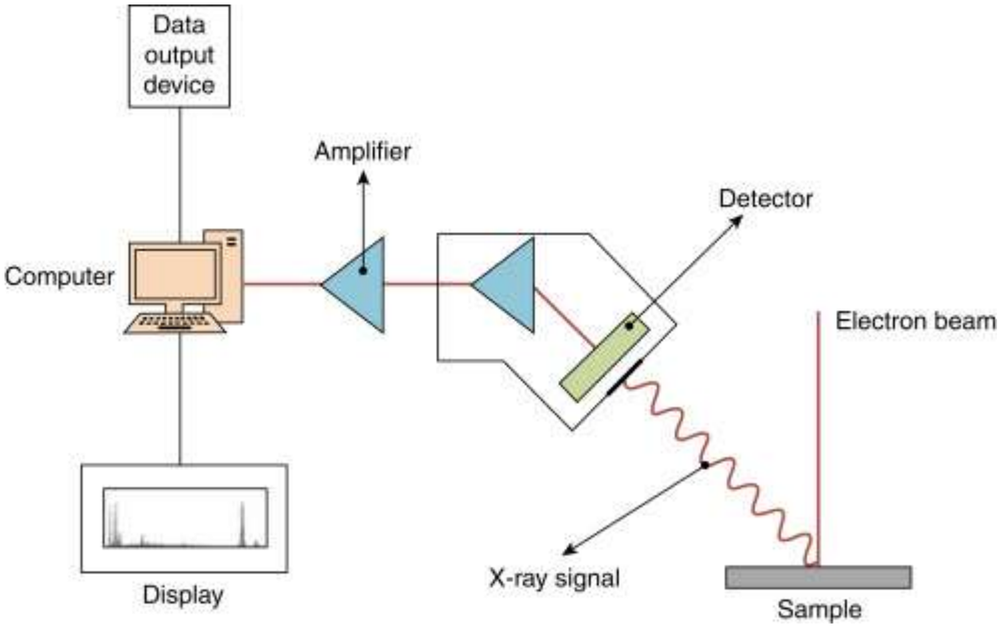
Paleontology:

In exceptionally preserved fossils, such as those of the Burgess shale, soft parts of organisms may be preserved. Since these fossils are often compressed into a 2D film, it can be difficult to deduce what features were what: a famous example is that of triangular extensions in Opabinia, which were interpreted as either legs or extensions of the gut. Elemental mapping showed that they had a similar composition to the gut, favouring the second interpretation. Because of the thin nature of the carbon films, only low voltages (5-15V) can be used in such specimens.

4.5 ENERGY-DISPERSIVE X-RAY SPECTROSCOPY:

Energy-dispersive X-ray spectroscopy (EDS, EDX, or XEDS) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on the investigation of an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum. To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons, or a beam of X-rays, is focused into the sample being studied.

At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energy of the X-rays are characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured.



X-ray measurement:

The equipment measures the energy and number of emitted X-rays.

Equipment:

Four primary components of the EDS setup are

(I) the excitation source (electron beam or x-ray beam)
(II) the X-ray detector
(III) the pulse processor
(IV) the analyzer

Excitation is used in X-ray fluorescence (XRF) spectrometers. A detector is used to convert X-ray energy into voltage signals; this information is sent to a pulse processor, which measures the signals and passes them onto an analyzer for data display and analysis. The most common detector now is Si(Li) detector cooled to cryogenic temperatures with liquid nitrogen; however newer systems are often equipped with silicon drift detectors (SDD) with Peltier cooling systems.

Technological variants:

The excess energy of the electron that migrates to an inner shell to fill the newly created hole can do more than emit an X-ray. Often, instead of X-ray emission, the excess energy is transferred to a third electron from a further outer shell, prompting its ejection. This ejected species is called an Auger electron, and the method for its analysis is known as Auger electron spectroscopy (AES).

X-ray photoelectron spectroscopy (XPS) is another close relative of EDS, utilizing ejected electrons in a manner similar to that of AES. Information on the quantity and kinetic energy of ejected electrons is used to determine the binding energy of these now-liberated electrons, which is element-specific and allows chemical characterization of a sample.

EDS is often contrasted with its spectroscopic counterpart, WDS (wavelength dispersive X-ray spectroscopy). WDS differs from EDS in that it uses the X-rays diffraction on special crystals as its raw data. WDS has a much finer spectral resolution than EDS. WDS also avoids the problems associated with artifacts in EDS (false peaks, noise from the amplifiers, and microphonics). In WDS, only one element can be analyzed at a time, while EDS gathers a spectrum of all elements, within limits, of a sample.

Accuracy of EDS:

Accuracy of EDS spectrum can be affected by various factors. Many elements will have overlapping peaks (e.g., Ti Kβ and V Kα, Mn Kβ and Fe Kα). The accuracy of the spectrum can also be affected by the nature of the sample. X-rays can be generated by any atom in the sample that is sufficiently excited by the incoming beam. These X-rays are emitted in any direction, and so they may not all escape the sample. The likelihood of an X-ray escaping the specimen, and thus being available to detect and measure, depends on the energy of the X-ray and the amount and density of material it has to pass through. This can result in reduced accuracy in inhomogeneous and rough samples.

Emerging technology:

There is a trend towards a newer EDS detector, called the silicon drift detector (SDD). The SDD consists of a high-resistivity silicon chip where electrons are driven to a small collecting anode. The advantage lies in the extremely low capacitance of this anode, thereby utilizing shorter processing times and allowing very high throughput. Benefits of the SDD include:

(I) High count rates and processing,
(II) Better resolution than traditional Si(Li) detectors at high count rates,
(III) Lower dead time (time spent on processing X-ray event),
(IV) Faster analytical capabilities and more precise X-ray maps or particle data collected in seconds, Ability to be stored and operated at relatively high temperatures, eliminating the need for liquid nitrogen cooling.
(V) Because the capacitance of the SDD chip is independent of the active area of the detector, much larger SDD chips can be utilized (40 mm2 or more). This allows for even higher count rate collection. Further benefits of large area chips include:
(VI) Minimizing SEM beam current allowing for optimization of imaging under analytical conditions,
(VII) Reduced sample damage and
(VIII) Smaller beam interaction and improved spatial resolution for high speed maps.

In recent years, a different type of EDS detector, based upon a microcalorimeter, has become commercially available. This new model allegedly has the simultaneous detection capabilities of EDS as well as the high spectral resolution of WDS. The EDS microcalorimeter relies highly on two components: an absorber, and a thermistor. The former absorbs X-rays emitted from the sample and converts this energy into heat; the latter measures the subsequent change in temperature due to the influx of heat (in essence, a thermometer).

The EDS microcalorimeter has suffered from a number of drawbacks; including low count rates, poor collection efficiencies and small detector areas. The count rate is hampered by its reliance on the time constant of the calorimeter’s electrical circuit. The collection efficiency is a function of the absorber material and remains to be optimized. The detector area must be small in order to keep the heat capacity as small as possible and maximize thermal sensitivity (resolution).

4.6 ORGANIC OPTOELECTRONIC MATERIALS AND DEVICES:

Organic optoelectronics has developed into a new interdisciplinary research field involving organic chemistry, physics, electronic engineering and materials science. Organic optoelectronic devices, such as organic electroluminescent device (OLED), organic photovoltaic (OPV) and organic thin film transistors (OTFT), have attracted significant attention in academics and industries due to their great application potential in flat-panel and flexible display, solid-state lighting, information transport and storage, new generation energy, photocatalyst and so on.

Owing to the advantages of solid-state, self-emission, full color capability and flexibility, OLED has been recognized as one of the most promising flat-panel display technology and has stepped into commercialization. OPV has been considered as rapid-developing green energy technology because of its low cost, large area capability and simple processing.

And now the conversion efficiency of OPV is approaching the requirement for practical applications. OTFT has grown into a hotspot in organic electronics as it also possesses the merits of low cost, flexibility, low temperature processing and large area capability. And its performance is already comparable to that of the amorphous silicon based thin film transistors.

Accordingly, FUNSOM will dedicate itself to the studies of organic optoelectronic materials, devices and related manufacturing techniques along the chain of "molecular design à material synthesis à device fabrication à technology application", and be prepared for the commercialization of any scientific research achievements.

Fundamental studies: clarifying the mechanisms of conversion efficiency, energy transfer, charge injection and trasport in organic optoelectronic devices; further understanding the physical and chemical properties at device interfaces; providing the fundamental basis for new organic optoelectronic device development.

Applied studies: white OLED for solid-state lighting application, full-color OLED for large area display application, and flexible OLED technology; high-performance OPV with high conversion efficiency and low cost; high-performance OTFT with high field effect mobility and high ON/OFF ratio.

UNIT-V

5.1APPLICATIONS OF NANOTECHNOLOGY:

The driving force behind the fundamental research into nanocrystals is the perceived and demonstrated properties that can be exploited into applications. The application of these properties falls largely into two broad categories: improved properties and unique properties. The improved, or incremental, group covers those applications that have already been conceived but can benefit from the use of nanocrystals in terms of either particle size or surface area.

Many of these types of applications have found nearly instant commercial success and have opened the door to larger use. The ―unique‖ group of applications is a smaller set but holds the greatest potential. This group consists of properties that are exclusively attributed to nanostructuring and includes electronic and optical quantum confinement effects, superparamagnetism, and ceramic superplasticity, to name a few. To date, these have created niche commercial opportunities, but acceptance and interest are growing.

HISTORICAL:

One might ask, whether nanocrystals are really new. The answer would have to be yes and no, with a qualification for each. For over a century the properties of small particles have been exploited in applications ranging from catalysis to the colors of stained glass. Some of the earliest recorded evidence came in 1856 when Michael Faraday discovered that nanometer-sized particles create the color variations of metal-particle colloids through surface charge effects.

He found that colloids of 6 nm gold particles are red and those of 12 nm particles are blue. There is even evidence that nature has made use of nanoparticles in areas of biomineralization that take place in bones and teeth. The reason we might say that nanostructuring is new is largely attributable to the developments of modern science as it has investigated the ever-shrinking world of matter.

Advances in theoretical and experimental tools and techniques have increased our understanding of matter in both the micro and the nano regimes, largely motivated by the development of applications and technology. Consider the development of atomic force and scanning tunneling microscopy that has led to sophisticated machines that change the landscape of surfaces atom byatom.

An obvious example of this revolution is in the world of semiconductor electronics, which is driven by the demand to reduce the size of circuits, pushing the envelope ofboth science and technology. This applies not only to materials, but to a host of areas including optics, manufacturing, chemicals, and electronic design.

5.2. STRUCTURAL AND MECHANICAL MATERIALS:

The initial investigation of nanostructuring began with the property enhancements of bulk materials that were assembled entirely or partially from nanoparticles. The earliest work began with metals that demonstrated a transfer from normal, soft ductility to a hard, brittle nature when nanostructuring occurred. A similar property reversal effect was later discovered in brittle ceramic materials that could be made ductile at temperatures near one-half their melting point.

Some of the earliest commercial development in nanostructuring was focused on these unique properties. For example, improved properties of cutting tool materials have been achieved through the nanostructuring of materials like tungsten carbide (WC), which benefits in hardness and toughness via nanoscale distribution of tungsten particles throughout the matrix. Increases in tool life and performance have been commercially established as aresult of this technology.

In the case ofa technical ceramic material, usually desired for their mechanical and chemical features, the fabrication of shapes or components is largely through traditional ``whiteware" processing followed by extensive machining and finishing. In some cases, the machining and finishing operations are not only costly but can also introduce defects and flaws that lower the predictable strength of the component. Nanostructuring is changing the way in which ceramic components can be fabricated, by making use of the enhanced ductility property.

This is due to the fact that plastic flow rate (strain rate) of ceramics is inversely proportional to the cube of the grain dimensions. Plastic shaping of metals is applied to several aluminum metal alloys used in aerospace applications. These metals are superplastically formed to net shape components, at strain rates of5-6% per minute, in a closed die system, allowing full replication of the die geometry.

To date, several ceramic compositions are achieving or approaching these strain rates, through the use of nanostructuring, making use of the inverse relation to particle size. Parts with high dimensional tolerances can be forged from nanostructured ceramic performs in less than half an hour. Figure 1 shows an engine valve seat that was superplastically stamped in a manner of minutes.

To achieve the benefits of ceramics (wear, hardness, corrosion resistance) while maintaining the ambient ductility of metals, several methods of coating metals with ceramics have been developed. In many ofthese methods, nanostructuring or nanocrystals have played a major role in improving the end-use properties. For example, oxide nanocrystals have been thermal-plasma sprayed onto metal surfaces, forming dense, hard coatings that are superior to coatings made with conventional micron size particulates.

Nearly fourfold increases in wear resistance of nanocrystal plasma spray coatings have been observed. Other nanocrystal coatings have been formulated for a variety of uses including wear-resistant laminate floorings, where thin layers of aluminum oxide are bound to synthetic material surfaces in thin layers.

5.3. COLORANTS AND PIGMENTS:

Significant research and development of ultraviolet (UV) ligh t-attenuating pigments has taken place in the past decade, due to an increased awareness of the degradation effects of solar radiation. Protection of synthetic and natural substances has been the focus of a host of industrial applications; ranging from colored fabrics to human skin. Inorganic particles have long served as optical opacifiers and ―whiteners‖ in a wealth of commercial and industrial products, where particle sizes can be tailored to provide the highest degree of optical light scattering.

For example, thousands of tons of titanium dioxide (TiO) are synthesized every year to provide whitening of a variety of products ranging from paint coatings to low-fat dairy substitutes. When the same material, and others like it, are reduced to the nanometer size regime it has been discovered that the scattering efficiency shifts to the higher-frequency UV light range, in particular to the UVA and UVB regions (200-400 nm), which produces the highest degradation of organic materials.

In addition to a more efficient scattering in the UV range the nanosizing reduces optical scattering and allows for the passage of visible light. Therefore, coatings made from these nanometer pigments form optically transparent films that attenuate harmful UV radiation. This effect is most obvious from the photograph (Figure 2) that shows two powder consolidated disks.

The transparent disk was formed by the ambient consolidation of nanocrystals that are 10 nm in dimension. Both pores and solid grains are well below the wavelength of visible light and thus allow light to pass through. The opaque disk was formed by the ambient consolidation of 100 nm particles that easily scatter visible light, thus forming an optically opaque system.

Inkjet printer inks generally make use ofdyes or pigments to provide color. Dye-based inks provide a high chroma, while pigmented inks offer a high lightfastness but poor hue and saturation. This effect is generally attributed to the particle size distributions that overlap the dimen sions ofthe optical wavelengths. New, nanometer-sized pigments are being developed to overcome the limitations of conventional pigment technology.

Pigments with average particle sizes in the 10-20 nm range, creating the standard cyan, magenta, and yellow colors, display a greatly improved printed color that is superior to that of commercially available dye-based inks. In addition, the color fastness can be dramatically improved due to the UV-attenuating effects discussed above.

5.4. BIOMEDICAL APPLICATIONS:

A wealth of interest has developed for nanocrystals as applied to health and biological systems. In the area of medical diagnostics, colloidal or imbedded iron-based particles are being used to separate specific substances present in body fluid samples. Antibodies can be attached to magnetic colloidal particles, typically silica-coated iron oxides or polystyrene spheres with embedded iron oxides; when these are mixed with a blood sample the antibody reacts and binds with the target hormone.

Because the nanoparticle size creates both high surface area for reaction and a tendency to move rapidly in solution due to thermal Brownian motion, reactions can be quite rapid. The magnetic functionality of the particle permits detection of the antibody=hormone complex by separating and concentrating the reacted material from the blood sample. Even DNA detection through colorimetric techniques has been developed through the use of oligonucleotide-functionalized gold nanocrystals that can be assembled into periodic network materials.

Similar particles are also being developed for drug delivery. In this application, biochemical drugs can be bound to the magnetic nanocrystals and with applied magnetic fields can be steered into regions of the body where they are required. For example, malignant tumors can be attached with targeted drug delivery and concentration through the use of magnetic fields.

Rare, tumor-causing cells can also be targeted by nanocrystals with attached chemicals that bind to the cells and sweep them from the bloodstream before they have had a chance to degrade. Some previous examples showed that 100 tumor cells could be captured and removed from 50 million blood cells in less than one hour.

5.5 TYPES OF OPTO ELECTRONICS DEVICES ABD THEIR APPLICATIONS:

Optoelectronics is the communication between optics and electronics which includes the study, design and manufacture of a hardware device that converts electrical energy into light and light into energy through semiconductors. This device is made from solid crystalline materials which are lighter than metals and heavier than insulators. Optoelectronics device is basically an electronic device involving light. This device can be found in many optoelectronics applications like military services, telecommunications, automatic access control systems and medical equipments.

This academic field covers a wide range of devices including LEDs and elements, image pick up devices, information displays, optical communication systems, optical storages and remote sensing systems, etc. Examples of optoelectronic devices include telecommunication laser, blue laser, optical fiber, LED traffic lights, photo diodes and solar cells. Majority of the optoelectronic devices (direct conversion between electrons and photons) are LEDs, laser diodes, photo diodes and solar cells.

Types of Optoelectronics Devices:

Optoelectronics are classified into different types such as

(I) Photodiode
(II) Solar Cells
(III) Light Emitting Diodes
(IV) Optical Fiber
(V) Laser Diodes

Photo Diode:

A photo diode is a semiconductor light sensor that generates a voltage or current when light falls on the junction. It consists of an active P-N junction, which is operated in reverse bias. When a photon with plenty of energy strikes the semiconductor, an electron or hole pair is created. The electrons diffuse to the junction to form an electric field.

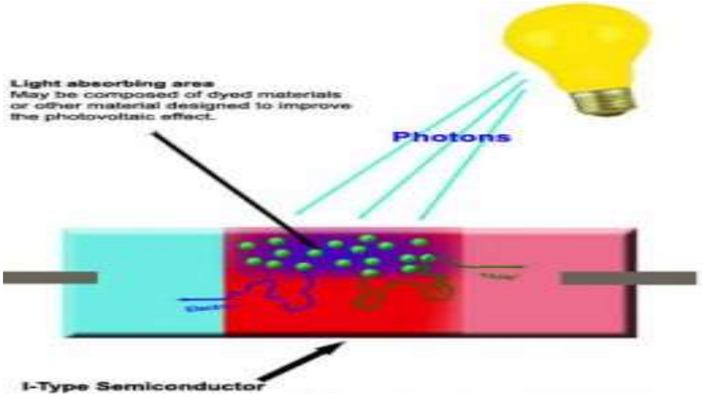
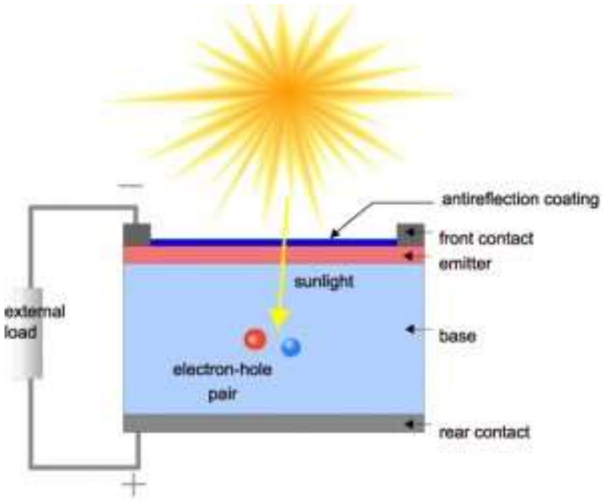


Photo Diode

This electric field across the depletion zone is equal to a negative voltage across the unbiased diode. This method is also known as the inner photoelectric effect. This device can be used in three modes: photovoltaic as a solar cell, forward biased as an LED and reverse biased as a photo detector. Photodiodes are used in many types of circuits and different applications such as cameras, medical instruments, safety equipments, industries, communication devices and industrial equipments.

Solar Cells:

A solar cell or photo-voltaic cell is an electronic device that directly converts sun’s energy into electricity. When sunlight falls on a solar cell, it produces both a current and a voltage to produce electric power. Sunlight, which is composed of photons, radiates from the sun. When photons hit the silicon atoms of the solar cell, they transfer their energy to lose electrons; and then, these high-energy electron flow to an external circuit.



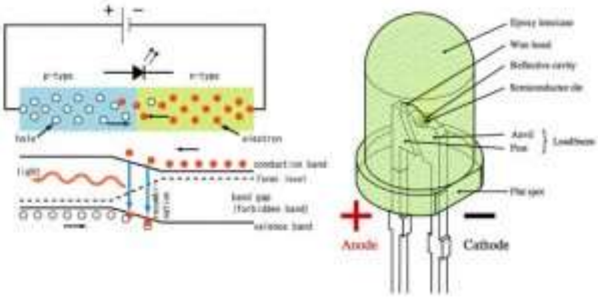
Solar Cells

The solar cell is composed of two layers which are struck together. The first layer is loaded with electrons, so these electrons are ready to jump from the first layer to the second layer. The second layer has some electrons taken away, and therefore, it is ready to take more electrons. The advantages of solar cells are that, there is no fuel supply and cost problem. These are very dependable and require little maintenance.

The solar cells are applicable in rural electrification, telecommunication systems, ocean navigation aids, electric power generation system in space and remote monitoring and control systems.

Light-Emitting Diodes:

Light-emitting diode is a P-N semiconductor diode in which the recombination of electrons and holes yields a photon. When the diode is electrically biased in the forward direction, it emits incoherent narrow spectrum light. When a voltage is applied to the leads of the LED, the electrons recombine with the holes within the device and release energy in the form of photons. This effect is called as electroluminescence. It is the conversion of electrical energy into light. The color of the light is decided by the energy band gap of the material.

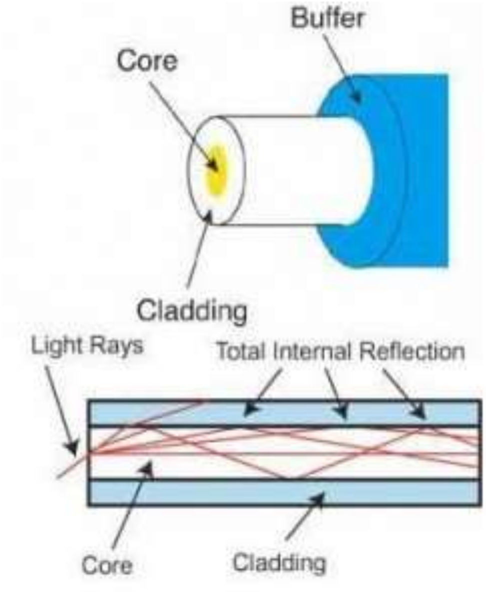


Light Emitting Diode

The usage of LED is advantageous as it consumes less power and produces less heat. LEDs last longer than incandescent lamps. LEDs could become the next generation of lighting and used anywhere like in indication lights, computer components, medical devices, watches, instrument panels, switches, fiber-optic communication, consumer electronics, household appliances, etc.

Optical Fiber:

An optical fiber or optic fibre is a plastic and transparent fiber made of plastic or glass. It is somewhat thicker than a human hair. It can function as a light pipe or waveguide to transmit light between the two ends of the fiber. Optical fibers usually include three concentric layers: a core, a cladding and a jacket. The core, a light transmitting region of the fiber, is the central section of the fiber, which is made of silica. Cladding, the protective layer around the core, is made of silica.This creates an optical waveguide that limits the light in the core by total reflection at the interface of the core-cladding. Jacket, the non-optical layer around the cladding, typically consists of one or more layers of a polymer that protect the silica from the physical or environmental damage.



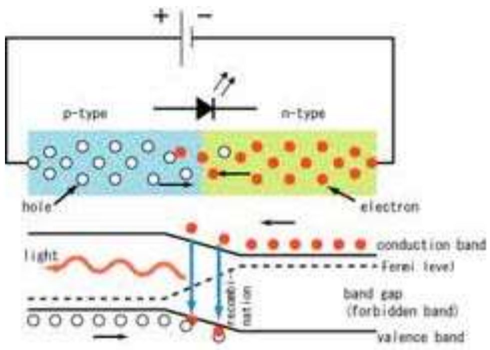
Optical Fiber

Along with the fiber-optic cable, jackets are available in different colors. These colors allow the recognition of the fiber-optic cable and the type of cable one is dealing with. For example, an orange-color cable clearly indicates a single-mode fiber, while a yellow one indicates a multimode fiber. In the single-mode fiber, one mode propagates and the light rays travel straight through the cable. In a multimode cable, the light rays travel through the cable following different modes.

These cables are used in telecommunications, sensors, fiber lasers, bio-medicals and in many other industries. The advantages of using optical-fiber cable include their higher bandwidth, less signal degradation, weightlessness and thinness than a copper wire, cost-effectiveness, flexibility, and hence they are used in medical and mechanical imaging systems.

Laser Diodes:

Laser (light amplification by stimulated emission of radiation) is a source of highly monochromatic, coherent and directional light. It operates under stimulated emission condition. The function of a laser diode is to convert electrical energy into light energy like infrared diodes or LEDs. The beam of a typical laser has 4×0.6mm extending at a distance of 15 meters. The most common lasers used are injection lasers or semiconductor lasers. The semiconductor laser changes from other lasers like solid, liquid and gas lasers.



Laser Diodes

When a voltage is applied across the P-N junction, the population inversion of the electrons is produced, and then the laser beam is available from the semiconductor region. The ends of the P-N junction of the laser diode have polished surface, and hence, the emitted photons reflect back to create more electron pairs. Thus, the photons generated will be in phase with the previous photons.

Applications of Optoelectronics Devices:

1. LEDs could become the next generation of lighting and used anywhere like in indication lights, computer components, medical devices, watches, instrument panels, switches, fiber-optic communication, consumer electronics, household appliances, traffic signals, automobile brake lights, 7 segment displays and inactive displays, and also used in different electronic and electrical engineering projects such as

Propeller Display of Message by Virtual LEDs

LED Based Automatic Emergency Light

Mains Operated LED Light

Display of Dialed Telephone Numbers on Seven Segment Display

Solar Powered Led Street Light with Auto Intensity Control

2. The solar cells are applicable in rural electrification, telecommunication systems, ocean navigation aids, and electric power generation in space and remote monitoring and control systems and also used in different solar energy based projects such as

Solar Energy Measurement System

Arduino based Solar Street Light

Solar Powered Auto Irrigation System

Solar Power Charge Controller

Sun Tracking Solar Panel

Solar based Project from edgefxkits.com

3. Photodiodes are used in many types of circuits and different applications such as cameras, medical instruments, safety equipments, industries, communication devices and industrial equipments.

4. Optical fibers are used in telecommunications, sensors, fiber lasers, bio-medicals and in many other industries.

5. The laser diodes are used in fiber optic communication, optical memories, military applications, CD players, surgical procedures, Local Area Networks, long distance communications, optical memories, fiber optic communications and in electrical projects such as RF Controlled Robotic Vehicle with Laser Beam Arrangement and so on.

Thus, this is all about the optoelectronic devices which include laser diodes, photo diodes, solar cells, LEDs, optical fibers.These optoelectronic devices are used in different electronic project kits as well as in telecommunications, military services and in medical applications. For more information regarding the same, please post your queries by commenting below.

5.6. CNTs:

Many electronic applications of carbon nanotubes crucially rely on techniques of selectively producing either semiconducting or metallic CNTs, preferably of a certain chirality. Several methods of separating semiconducting and metallic CNTs are known, but most of them are not yet suitable for large-scale technological processes. The most efficient method relies on density-gradient ultracentrifugation, which separates surfactant-wrapped nanotubes by the minute difference in their density.

This density difference often translates into difference in the nanotube diameter and (semi)conducting properties. Another method of separation uses a sequence of freezing, thawing, and compression of SWNTs embedded in agarose gel. This process results in a solution containing 70% metallic SWNTs and leaves a gel containing 95% semiconducting SWNTs. The diluted solutions separated by this method show various colors. Moreover, SWNTs can be separated by the column chromatography method. Yield is 95% in semiconductor type SWNT and 90% in metallic type SWNT.

In addition to separation of semiconducting and metallic SWNTs, it is possible to sort SWNTs by length, diameter, and chirality. The highest resolution length sorting, with length variation of <10%, has thus far been achieved by size exclusion chromatography (SEC) of DNA-dispersed carbon nanotubes (DNA-SWNT). SWNT diameter separation has been achieved by density-gradient ultracentrifugation (DGU) using surfactant-dispersed SWNTs and by ion-exchange chromatography (IEC) for DNA-SWNT.

Purification of individual chiralities has also been demonstrated with IEC of DNA-SWNT: specific short DNA oligomers can be used to isolate individual SWNT chiralities. Thus far, 12 chiralities have been isolated at purities ranging from 70% for (8,3) and (9,5) SWNTs to 90% for (6,5), (7,5) and (10,5)SWNTs. There have been successful efforts to integrate these purified nanotubes into devices, e. g. FETs.

An alternative to separation is development of a selective growth of semiconducting or metallic CNTs. Recently, a new CVD recipe that involves a combination of ethanol and methanol gases and quartz substrates resulting in horizontally aligned arrays of 95–98% semiconducting nanotubes was announced.

Nanotubes are usually grown on nanoparticles of magnetic metal (Fe, Co), which facilitates production of electronic (spintronic) devices. In particular, control of current through a field-effect transistor by magnetic field has been demonstrated in such a single-tube nanostructure.

Structural:

Because of the carbon nanotube's superior mechanical properties, many structures have been proposed ranging from everyday items like clothes and sports gear to combat jackets and space elevators. However, the space elevator will require further efforts in refining carbon nanotube technology, as the practical tensile strength of carbon nanotubes can still be greatly improved.

For perspective, outstanding breakthroughs have already been made. Pioneering work led by Ray H. Baughman at the NanoTech Institute has shown that single and multi-walled nanotubes can produce materials with toughness unmatched in the man-made and natural worlds.

Carbon nanotubes are also a promising material as building blocks in bio-mimetic hierarchical composite materials given their exceptional mechanical properties (~1TPa in modulus, and ~100 GPa in strength). Initial attempts to incorporate CNTs into hierarchical structures led to mechanical properties that were significantly lower than these achievable limits. Windle et al. have used an *in situ* chemical vapor deposition (CVD) spinning method to produce continuous CNT yarns from CVD grown CNT aerogels.

With this technology, they fabricated CNT yarns with strengths as high as ~9 GPa at small gage lengths of ~1 mm, however, defects resulted in a reduction of specific strength to ~1 GPa at 20 mm gage length. Espinosa et al. developed high performance DWNT-polymer composite yarns by twisting and stretching ribbons of randomly oriented bundles of DWNTs thinly coated with polymeric organic compounds.

These DWNT-polymer yarns exhibited unusually high energy to failure of ~100 $J \cdot g^{-1}$ (comparable to one of the toughest natural materials – spider silk), and strength as high as ~1.4 GPa. Effort is ongoing to produce CNT composites that incorporate tougher matrix materials, such as Kevlar, to further improve on the mechanical properties toward those of individual CNTs.

Because of the high mechanical strength of carbon nanotubes, research is being made into weaving them into clothes to create stab-proof and bulletproof clothing. The nanotubes would effectively stop the bullet from penetrating the body, although the bullet's kinetic energy would likely cause broken bones and internal bleeding.

In electrical circuits:

Nanotube-based transistors, also known as carbon nanotube field-effect transistors (CNFETs), have been made that operate at room temperature and that are capable of digital switching using a single electron. However, one major obstacle to realization of nanotubes has been the lack of technology for mass production. In 2001 IBM researchers demonstrated how metallic nanotubes can be destroyed, leaving semiconducting ones behind for use as transistors. Their process is called "constructive destruction," which includes the automatic destruction of defective nanotubes on the wafer. This process, however, only gives control over the electrical properties on a statistical scale.

The potential of carbon nanotubes was demonstrated in 2003 when room-temperature ballistic transistors with ohmic metal contacts and high-k gate dielectric were reported, showing 20–30x higher ON current than state-of-the-art Si MOSFETs. This presented an important advance in the field as CNT was shown to potentially outperform Si. At the time, a major challenge was ohmic metal contact formation. In this regard, palladium, which is a high-work function metal was shown to exhibit Schottky barrier-free contacts to semiconducting nanotubes with diameters >1.7 nm.

The first nanotube integrated memory circuit was made in 2004. One of the main challenges has been regulating the conductivity of nanotubes. Depending on subtle surface features a nanotube may act as a plain conductor or as a semiconductor. A fully automated method has however been developed to remove non-semiconductor tubes.

Another way to make carbon nanotube transistors has been to use random networks of them. By doing so one averages all of their electrical differences and one can produce devices in large scale at the wafer level. This approach was first patented by Nanomix Inc. (date of original application June 2002). It was first published in the academic literature by the United States Naval Research Laboratory in 2003 through independent research work. This approach also enabled Nanomix to make the first transistor on a flexible and transparent substrate.

Large structures of carbon nanotubes can be used for thermal management of electronic circuits. An approximately 1 mm–thick carbon nanotube layer was used as a special material to fabricate coolers, this materials has very low density, ~20 times lower weight than a similar copper structure, while the cooling properties are similar for the two materials.

Overall, incorporating carbon nanotubes as transistors into logic-gate circuits with densities comparable to modern CMOS technology has not yet been demonstrated.

As electrical cables and wires:

Wires for carrying electrical current may be fabricated from pure nanotubes and nanotube-polymer composites. Recently small wires have been fabricated with specific conductivity exceeding copper and aluminum; these cables are the highest conductivity carbon nanotube and also highest conductivity non-metal cables.

As paper batteries:

A paper battery is a battery engineered to use a paper-thin sheet of cellulose (which is the major constituent of regular paper, among other things) infused with aligned carbon nanotubes. The nanotubes act as electrodes; allowing the storage devices to conduct electricity. The battery, which functions as both a lithium-ion battery and a supercapacitor, can provide a long, steady power output comparable to a conventional battery, as well as a supercapacitor’s quick burst of high energy—and while a conventional battery contains a number of separate components, the paper battery integrates all of the battery components in a single structure, making it more energy efficient.

Solar cells:

Solar cells developed at the New Jersey Institute of Technology use a carbon nanotube complex, formed by a mixture of carbon nanotubes and carbon buckyballs (known as fullerenes) to form snake-like structures. Buckyballs trap electrons, although they can't make electrons flow. Add sunlight to excite the polymers, and the buckyballs will grab the electrons. Nanotubes, behaving like copper wires, will then be able to make the electrons or current flow.

Medical:

In the Kanzius cancer therapy, single-walled carbon nanotubes are inserted around cancerous cells, then excited with radio waves, which causes them to heat up and kill the surrounding cells.

Researchers at Rice University, Radboud University Nijmegen Medical Centre and University of California, Riverside have shown that carbon nanotubes and their polymer nanocomposites are suitable scaffold materials for bone cell proliferation and bone formation.

Other applications:

Carbon nanotubes have been implemented in nanoelectromechanical systems, including mechanical memory elements (NRAM being developed by Nantero Inc.) and nanoscale electric motors (see Nanomotor or Nanotube nanomotor).

In May 2005, Nanomix Inc. placed on the market a hydrogen sensor that integrated carbon nanotubes on a silicon platform. Since then, Nanomix has been patenting many such sensor applications, such as in the field of carbon dioxide, nitrous oxide, glucose, DNA detection, etc.

Eikos Inc of Franklin, Massachusetts and Unidym Inc. of Silicon Valley, California are developing transparent, electrically conductive films of carbon nanotubes to replace indium tin oxide (ITO). Carbon nanotube films are substantially more mechanically robust than ITO films, making them ideal for high-reliability touchscreens and flexible displays. Printable water-based inks of carbon nanotubes are desired to enable the production of these films to replace ITO Nanotube films show promise for use in displays for computers, cell phones, PDAs, and ATMs.

A nanoradio, a radio receiver consisting of a single nanotube, was demonstrated in 2007. In 2008 it was shown that a sheet of nanotubes can operate as a loudspeaker if an alternating current is applied. The sound is not produced through vibration but thermoacoustically.

A flywheel made of carbon nanotubes could be spun at extremely high velocity on a floating magnetic axis in a vacuum, and potentially store energy at a density approaching that of conventional fossil fuels. Since energy can be added to and removed from flywheels very efficiently in the form of electricity, this might offer a way of storing electricity, making the electrical grid more efficient and variable power suppliers (like wind turbines) more useful in meeting energy needs. The practicality of this depends heavily upon the cost of making massive, unbroken nanotube structures, and their failure rate under stress.

Carbon nanotube springs have the potential to indefinitely store elastic potential energy at ten times the density of lithium-ion batteries with flexible charge and discharge rates and extremely high cycling durability.

Ultra-short SWNTs (US-tubes) have been used as nanoscaled capsules for delivering MRI contrast agents in vivo.

Nitrogen-doped carbon nanotubes may replace platinum catalysts used to reduce oxygen in fuel cells. A forest of vertically-aligned nanotubes can reduce oxygen in alkaline solution more effectively than platinum, which has been used in such applications since the 1960s. The nanotubes have the added benefit of not being subject to carbon monoxide poisoning.

5.7. NANOLITHOGRAPHY:

Nanolithography is a term used to describe a number of techniques for creating incredibly small structures. The sizes involved are on the order of tens of nanometers (nm). A nanometer is a billionth of a meter, much smaller than the width of a single human hair. The word lithography is used because the method of pattern generation is essentially the same as writing, only on a much smaller scale

One common method of nanolithography, used particularly in the creation of microchips, is known as photolithography. This technique is a parallel method of nanolithography in which the entire surface is drawn on in a single moment. Photolithography is limited in the size it can reduce to, however, because if the wavelength of light used is made too small the lens simply absorbs the light in its entirety. This means that photolithography cannot reach the super-fine sizes of some alternate technologies

A technology that allows for smaller sizes than photolithography is that of electron-beam lithography. Using an electron beam to draw a pattern nanometer by

Nanometer, incredibly small sizes (on the order of 20nm) may be achieved. Electron-beam lithography is much more expensive and time consuming than photolithography, however, making it a difficult sell for industry applications of nanolithography. Since electron-beam lithography functions more like a dot-matrix printer than a flash-photograph, a job that would take five minutes using photolithography will take upwards of five hours with electron-beam lithography.

New nanolithography technologies are constantly being researched and developed, leading to smaller and smaller possible sizes. Extreme ultraviolet lithography, for example, is capable of using light at wavelengths of 13.5nm. While hurdles still exist in this new field, it promises the possibility of sizes far below those produced by current industry standards. Other nanolithography techniques include dip-pen nanolithography, in which a small tip is used to deposit molecules on a surface. Dip-pen nanolithography can achieve very small sizes, but cannot currently go below 40nm.

Funding for nanolithography research comes from a number of places, including the private academic world, futurist companies with an eye towards next-generation nanotechnology, and established computer chip manufacturers looking to shrink their chips far below their current sizes. As interest in nanotechnology grows within industrial sectors, funding and research will no doubt expand in the field of nanolithography, leading to more adept technologies and even lower limits on size

Optical lithography:

Optical lithography, which has been the predominant patterning technique since the advent of the semiconductor age, is capable of producing sub-100-nm patterns with the use of very short wavelengths (currently 193 nm). Optical lithography will require the use of liquid immersion and a host of resolution enhancement technologies (phase-shift masks (PSM), optical proximity correction (OPC)) at the 32 nm node. Most experts feel that traditional optical lithography techniques will not be cost effective below 22 nm. At that point, it may be replaced by a next-generation lithography (NGL) technique.

Other nanolithography techniques:

X-ray lithography can be extended to an optical resolution of 15 nm by using the short wavelengths of 1 nm for the illumination. This is implemented by the proximity printing approach. The technique is developed to the extent of batch processing. The extension of the method relies on Near Field X-rays in Fresnel diffraction: a clear mask feature is "demagnified" by proximity to a wafer that is set near to a "Critical Condition". This Condition determines the mask-to-wafer Gap and depends on both the size of the clear mask feature and on the wavelength. The method is simple because it requires no lenses.

A method of pitch resolution enhancement which is gaining acceptance is **double patterning**. This technique increases feature density by printing new features in between pre-printed features on the same layer. It is flexible because it can be adapted for any exposure or patterning technique. The feature size is reduced by non-lithographic techniques such as etching or sidewall spacers.

Work is in progress on an optical **maskless lithography** tool. This uses a digital micro-mirror array to directly manipulate reflected light without the need for an intervening mask. Throughput is inherently low, but the elimination of mask-related production costs - which are rising exponentially with every technology generation - means that such a system might be more cost effective in the case of small production runs of state of the art circuits, such as in a research lab, where tool throughput is not a concern.

The most common nanolithographic technique is Electron-Beam Direct-Write Lithography (EBDW), the use of a beam of electrons to produce a pattern — typically in a polymeric resist such as PMMA.

Extreme ultraviolet lithography (EUV) is a form of optical lithography using ultrashort wavelengths (13.5 nm). It is the most popularly considered NGL technique.

Charged-particle lithography, such as ion- or electron-projection lithographies (PREVAIL, SCALPEL, LEEPL), are also capable of very-high-resolution patterning.

Ion beam lithography uses a focused or broad beam of energetic lightweight ions (like He^+) for transferring pattern to a surface. Using Ion Beam Proximity Lithography (IBL) nano-scale features can be transferred on non-planar surfaces

Neutral Particle Lithography:

(NPL) uses a broad beam of energetic neutral particle for pattern transfer on a surface.

Nanoimprint lithography:

(NIL), and its variants, such as Step-and-Flash Imprint Lithography, LISA and LADI are promising nanopattern replication technologies. This technique can be combined with **contact printing**and **cold welding**.

Scanning probe lithography:

(SPL) is a promising tool for patterning at the deep nanometer-scale. For example, individual atoms may be manipulated using the tip of a scanning tunneling microscope (STM). Dip-Pen Nanolithography (DPN) is the first commercially available SPL technology based on atomic force microscopy.

Atomic Force Microscopic Nanolithography:

(AFM) is a chemomechanical surface patterning technique that uses an atomic force microscope.

Magnetolithography:

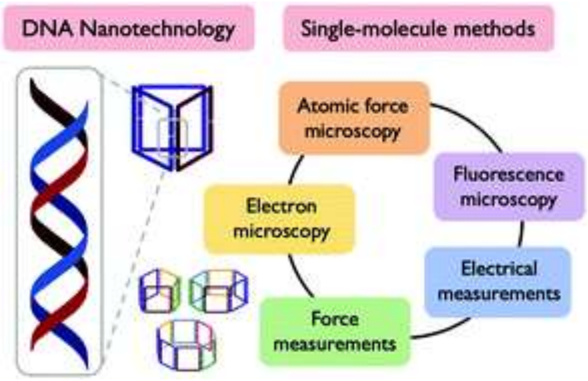
(ML) based on applying a magnetic field on the substrate using paramagnetic metal masks call "magnetic mask". Magnetic mask which is analog to photomask define the spatial distribution and shape of the applied magnetic field. The second component is ferromagnetic nanoparticles (analog to the photoresist) that are assembled onto the substrate according to the field induced by the magnetic mask.

5.8. DNA NANOTECHNOLOGY:

DNA nanotechnology is a branch of nanotechnology which uses the molecular recognition properties of DNA and other nucleic acids to create designed, artificial structures out of DNA for technological purposes. In this field, DNA is used as a structural material rather than as a carrier of genetic information, making it an example of bionanotechnology. DNA nanotechnology has applications in molecular self-assembly and in DNA computing.

Although DNA is usually considered in the context of molecular biology as the carrier of genetic information in living cells, DNA nanotechnology considers DNA solely as a chemical and as a material, and is usually pursued outside of any biological context. DNA nanotechnology makes use of the fact that, due to the specificity of Watson-Crick base pairing, only portions of the strands which are complementary to each other will bind to each other to form duplex DNA. DNA nanotechnology attempts to rationally design sets of DNA strands so that desired portions of each strand will assemble in the correct positions to for some desired target structure, a process called nucleic acid design.

Although the field is usually called DNA nanotechnology, its principles apply equally well to other nucleic acids such as RNA and PNA, and structures incorporating these have been made. For this reason the field is occasionally referred to as nucleic acid nanotechnology.



DNA nanotechnology creates complex structures out of nucleic acids by making use of the specificity of base pairing in nucleic acid molecules. The structure of a nucleic acid molecule consists of a sequence of nucleotides, distinguished by which nucleobase they contain. In DNA, the four bases used are adenine (A), cytosine (C), guanine (G), and thymine (T).

Nucleic acids have the property that two molecules will bind to each other to form a double helix only if the two sequences are complementary, meaning that they form matching sequences of base pairs, with A's only binding to T's, and C's only to G's. Because the formation of correctly matched base pairs is energetically favorable, nucleic acid strands are expected in most cases to bind to each other in the conformation that maximizes the number of correctly paired bases.

This property, that the sequence determines the pattern of binding and the overall structure, is used by the field of DNA nanotechnology in that sequences are artificially designed so that a desired structure is favored to form.

Fundamental concepts:

These four strands associate into a DNA four-arm junction because this structure maximizes the number of correct base pairs, with A's matched to T's and C's matched to G's. See this image for a more realistic model of the four-arm junction showing its tertiary structure.

A double-crossover (DX) molecule. This molecule consists of five DNA single strands which form two double-helical domains, on the left and the right in this image. There are two crossover points where the strands cross from one domain into the other.

Nearly all structures in DNA nanotechnology make use of branched DNA structures containing junctions, as opposed to most biological DNA which exists in a linear double helix form. One of the simplest branched structures, and the first made, is a four-arm junction which can be made using four individual DNA strands which are complementary to each other in the correct pattern. Unlike in natural Holliday junctions, in the artificial immobile four-arm junction shown below, the base sequence of each arm is different, meaning that the junction point is fixed in a certain position.

Junctions can be used in more complex molecules. One of the more widely-used of these is the "double-crossover" or DX motif. A DX molecule can be thought of as two DNA duplexes positioned parallel to each other, with two crossover points where strands cross from one duplex into the other.

Each junction point is itself topologically a four-arm junction. This molecule has the advantage that the junction points are now constrained to a single orientation as opposed to being flexible as in the four-arm junction. This makes the DX motif suitable as a structural building block for larger DNA complexes

Design:

DNA nanostructures must be rationally designed so that the individual nucleic acid strands will assemble into the desired structures. The design process of such nanostructures usually begins with the specification of a desired target structure and/or functionality. Then, the overall secondary structure of the target molecule is designed, meaning the arrangement of nucleic acid strands within the structure, and which portions of those strands should be bound to each other. The last step is the primary structure design, the specification of the actual base sequences of each nucleic acid strand.

Structural design:

The first step in designing a nucleic acid nanostructure is to decide how a given structure should be represented by a specific arrangement of nucleic acid strands. This design step thus determines the secondary structure, or the series of base pairs which hold the individual strands together in the desired shape. There are several approaches which have been demonstrated:

Tile-based structures. This approach breaks the target structure into smaller units with strong binding between the strands contained in each unit, and relatively weaker interactions between the units. It is often used to make periodic lattices, but can also be used to implement algorithmic self-assembly, making them one platform for DNA computing

Folding structures. An alternative to the tile-based approach, folding approaches make the nanostructure out of a single long strand. This long strand can either have a designed sequence which folds due to its interactions with itself, or it can be folded into the desired shape by using shorter, "staple" strands. This latter method is called DNA origami, which allows the creation of two- and three-dimensional shapes at the nanoscale using DNA (see #Arbitrary shapes below).

Kinetic assembly. Recently, there has been interest in controlling the kinetics of DNA self-assembly, so that transient dynamics can also be programmed into the assembly. Such a method also has the advantage of proceeding isothermally and thus not requiring a thermal annealing step required by solely thermodynamic approaches.

Sequence design:

After any of the above approaches are used to design the secondary structure of a target molecule, an actual sequence of nucleotides must be devised which will form into the desired structure. Nucleic acid design is the process of assigning a specific nucleic acid base sequence to each strand so that they will associate into a desired conformation. Nucleic acid design is central to the field of DNA nanotechnology.

Most methods seek to designing sequences so that the target structure is a thermodynamic minimum, and mis-assembled structures have higher energies and are thus disfavored. This is done either through heuristic methods such as sequence symmetry minimization and coding theory based approaches, or by explicitly using a full nearest-neighbor thermodynamic model. Geometric models are also used to examine tertiary structure of the nanostructures and ensure that the complexes are not overly strained.

Nucleic acid design has similar goals to protein design: in both, the sequence of monomers is designed to favor the desired folded or associated structure and to disfavor alternate structures. Nucleic acid design has the advantage of being a much computationally simpler problem, since the simplicity of Watson-Crick base pairing rules leads to simple heuristic methods which yield experimentally robust designs. However, nucleic acid structures are less versatile than proteins in their functionality

Structural DNA nanotechnology:

Structural DNA nanotechnology, sometimes abbreviated as SDN, focuses on synthesizing and characterizing nucleic acid complexes and materials with various nanoscale structures. Structural DNA nanotechnology is largely based on the fact that the three-dimensional structure of DNA—the nucleic acid double helix— has a robust, defined geometry which makes it possible to predict and design the structures of more complex DNA molecules. Many such structures have been created, including two- and three-dimensional structures; and periodic, aperiodic, and discrete structures.

Periodic lattices:

Smaller nucleic acid assemblies can be equipped with sticky ends in order to combine them into a two-dimensional periodic lattice. The earliest example of this was the array of DX, or double-crossover, molecules. Each DX molecule can be designed with four sticky ends, one at each end of the two double-helical domains, and these sticky ends can be designed with sequences that cause the DX units to combine into a specific tessellated pattern. They thus form extended flat sheets which are essentially rigid two-dimensional crystals of DNA.

Two-dimensional arrays have been made out of other motifs as well, including the Holliday junction rhombus array as well as various DX-based arrays making use of a double-cohesion scheme

Creating three-dimensional lattices out of DNA was the earliest goal of DNA nanotechnology, but proved to be one of the most difficult to realize. Success in constructing three-dimensional DNA lattices was finally reported in 2009 using a motif based on the concept of tensegrity, a balance between tension and compression forces

Nanotubes:

In addition to flat sheets, DX arrays have been made to form hollow nanotubes of 4–20 nm diameter. These DNA nanotubes are somewhat similar in size and shape to carbon nanotubes, but the carbon nanotubes are stronger and better conductors, whereas the DNA nanotubes are more easily modified and connected to other structures.

There have been multiple schemes for constructing DNA nanotubes, one of which uses the inherent curvature of DX tiles to form a DX lattice to curl around itself and close into a tube. An alternative design uses single-stranded "tiles" for which the rigidity of the tube is an emergent property. This method also has the benefit of being able to determine the circumference of the nanotube in a simple, modular fashion

Algorithmic self-assembly:

DNA nanotechnology has been applied to the related field of DNA computing. The DX tiles can have their sticky end sequences chosen so that they act as Wang tiles, allowing them to perform computation. A DX array has been demonstrated whose assembly encodes an XOR operation; this allows the DNA array to implement a cellular automaton which generates a fractal called the Sierpinski gasket. Another system has the function of a binary counter, displaying a representation of increasing binary numbers as it grows. These results show that computation can be incorporated into the assembly of DNA arrays, increasing its scope beyond simple periodic arrays.

Note that DNA computing overlaps with, but is distinct from, DNA nanotechnology. The latter uses the specificity of Watson-Crick basepairing to make novel structures out of DNA. These structures can be used for DNA computing, but they do not have to be. Additionally, DNA computing can be realized without using the types of molecules made possible by DNA nanotechnology

Nanomechanical devices:

DNA complexes have been made which change their conformation upon some stimulus. These are intended to have applications in nanorobotics. DNA machines have also been made which show a twisting motion. The first such device made use of the transition between the B-DNA and Z-DNA forms to respond to a change in buffer conditions. This reliance on buffer conditions, however, caused all devices to change state at the same time. A subsequent system, called "molecular tweezers," changes from an open to a closed state based upon the presence of control strands, allowing multiple devices to be individually operated in solution.

This was followed up by another system which relies on the presence of control strands to switch from a paranemic-crossover (PX) conformation to a double-junction (JX2) conformation.

Nucleic acid nanomachines have been made which exhibit directional motion along a linear track, called DNA walkers. A large number of schemes have been demonstrated. One strategy is to control the motion of the walker along the track using control strands which need to be manually added in sequence. Another approach is to make use of restriction enzymes or deoxyribozymes to cleave the strands and cause the walker to move forward, which has the advantage of running autonomously.

A later system extended the concept of DNA walkers to walk upon a two-dimensional surface rather than a linear track, and demonstrated the ability to selectively pick up and move molecular cargo. Additionally, a linear walker has been demonstrated which performs DNA-templated synthesis as the walker advances along the track, allowing autonomous multistep chemical synthesis directed by the walker.

5.9. DRUG DELIVERY SYSTEM:

Drug delivery is the method or process of administering a pharmaceutical compound to achieve a therapeutic effect in humans or animals. Drug delivery technologies modify drug release profile, absorption, distribution and elimination for the benefit of improving product efficacy and safety, as well as patient convenience and compliance. Drug release is from: diffusion, degradation, swelling, and affinity-based mechanisms. Most common routes of administration include the preferred non-invasive peroral (through the mouth), topical (skin), transmucosal (nasal, buccal/sublingual, vaginal, ocular and rectal) and inhalation routes.

Many medications such as peptide and protein, antibody, vaccine and gene based drugs, in general may not be delivered using these routes because they might be susceptible to enzymatic degradation or cannot be absorbed into the systemic circulation efficiently due to molecular size and charge issues to be therapeutically effective. For this reason many protein and peptide drugs have to be delivered by injection or a nanoneedle array. For example, many immunizations are based on the delivery of protein drugs and are often done by injection.

Current efforts in the area of drug delivery include the development of targeted delivery in which the drug is only active in the target area of the body (for example, in cancerous tissues) and sustained release formulations in which the drug is released over a period of time in a controlled manner from a formulation. Types of sustained release formulations include liposomes, drug loaded biodegradable microspheres and drug polymer conjugates.

Drug delivery:

Nanomedical approaches to drug delivery center on developing nanoscale particles or molecules to improve drug bioavailability. Bioavailability refers to the presence of drug molecules where they are needed in the body and where they will do the most good. Drug delivery focuses on maximizing bioavailability both at specific places in the body and over a period of time. This can potentially be achieved by molecular targeting by nanoengineered devices.

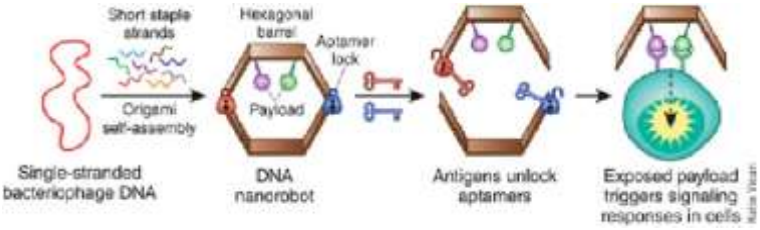
It is all about targeting the molecules and delivering drugs with cell precision. More than $65 billion are wasted each year due to poor bioavailability. *In vivo* imaging is another area where tools and devices are being developed. Using nanoparticle contrast agents, images such as ultrasound and MRI have a favorable distribution and improved contrast.

The new methods of nanoengineered materials that are being developed might be effective in treating illnesses and diseases such as cancer. What nanoscientists will be able to achieve in the future is beyond current imagination. This might be accomplished by self assembled biocompatible nanodevices that will detect, evaluate, treat and report to the clinical doctor automatically.

Drug delivery systems, lipid- or polymer-based nanoparticles, can be designed to improve the pharmacological and therapeutic properties of drugs. The strength of drug delivery systems is their ability to alter the pharmacokinetics and biodistribution of the drug. Nanoparticles have unusual properties that can be used to improve drug delivery. Where larger particles would have been cleared from the body, cells take up these nanoparticles because of their size.

Complex drug delivery mechanisms are being developed, including the ability to get drugs through cell membranes and into cell cytoplasm. Efficiency is important because many diseases depend upon processes within the cell and can only be impeded by drugs that make their way into the cell. Triggered response is one way for drug molecules to be used more efficiently. Drugs are placed in the body and only activate on encountering a particular signal.

For example, a drug with poor solubility will be replaced by a drug delivery system where both hydrophilic and hydrophobic environments exist, improving the solubility. Also, a drug may cause tissue damage, but with drug delivery, regulated drug release can eliminate the problem. If a drug is cleared too quickly from the body, this could force a patient to use high doses, but with drug delivery systems clearance can be reduced by altering the pharmacokinetics of the drug.



Poor biodistribution is a problem that can affect normal tissues through widespread distribution, but the particulates from drug delivery systems lower the volume of distribution and reduce the effect on non-target tissue. Potential nanodrugs will work by very specific and well-understood mechanisms; one of the major impacts of nanotechnology and nanoscience will be in leading development of completely new drugs with more useful behavior and less side effects.

Protein and peptide delivery:

Protein and peptides exert multiple biological actions in human body and they have been identified as showing great promise for treatment of various diseases and disorders. These macromolecules are called biopharmaceuticals. Targeted and/or controlled delivery of these biopharmaceuticals using nanomaterials like nanoparticles and Dendrimers is an emerging field called nanobiopharmaceutics, and these products are called nanobiopharmaceuticals.

Cancer:

The small size of nanoparticles endows them with properties that can be very useful in oncology, particularly in imaging. Quantum dots (nanoparticles with quantum confinement properties, such as size-tunable light emission), when used in conjunction with MRI (magnetic resonance imaging), can produce exceptional images of tumor sites. These nanoparticles are much brighter than organic dyes and only need one light source for excitation. This means that the use of fluorescent quantum dots could produce a higher contrast image and at a lower cost than today's organic dyes used as contrast media. The downside, however, is that quantum dots are usually made of quite toxic elements.

Another nanoproperty, high surface area to volume ratio, allows many functional groups to be attached to a nanoparticle, which can seek out and bind to certain tumor cells. Additionally, the small size of nanoparticles (10 to 100 nanometers), allows them to preferentially accumulate at tumor sites (because tumors lack an effective lymphatic drainage system). A very exciting research question is how to make these imaging nanoparticles do more things for cancer. For instance, is it possible to manufacture

multifunctional nanoparticles that would detect, image, and then proceed to treat a tumor? This question is under vigorous investigation; the answer to which could shape the future of cancer treatment. A promising new cancer treatment that may one day replace radiation and chemotherapy is edging closer to human trials. Kanzius RF therapy attaches microscopic nanoparticles to cancer cells and then "cooks" tumors inside the body with radio waves that heat only the nanoparticles and the adjacent (cancerous) cells.

Sensor test chips containing thousands of nanowires, able to detect proteins and other biomarkers left behind by cancer cells, could enable the detection and diagnosis of cancer in the early stages from a few drops of a patient's blood.

The basic point to use drug delivery is based upon three facts: a) efficient encapsulation of the drugs, b) successful delivery of said drugs to the targeted region of the body, and c) successful release of that drug there.

Researchers at Rice University under Prof. Jennifer West, have demonstrated the use of 120 nm diameter nanoshells coated with gold to kill cancer tumors in mice. The nanoshells can be targeted to bond to cancerous cells by conjugating antibodies or peptides to the nanoshell surface.

By irradiating the area of the tumor with an infrared laser, which passes through flesh without heating it, the gold is heated sufficiently to cause death to the cancer cells.

Nanoparticles of cadmium selenide (quantum dots) glow when exposed to ultraviolet light. When injected, they seep into cancer tumors. The surgeon can see the glowing tumor, and use it as a guide for more accurate tumor removal.

In photodynamic therapy, a particle is placed within the body and is illuminated with light from the outside. The light gets absorbed by the particle and if the particle is metal, energy from the light will heat the particle and surrounding tissue. Light may also be used to produce high energy oxygen molecules which will chemically react with and destroy most organic molecules that are next to them (like tumors).

This therapy is appealing for many reasons. It does not leave a ―toxic trail‖ of reactive molecules throughout the body (chemotherapy) because it is directed where only the light is shined and the particles exist. Photodynamic therapy has potential for a noninvasive procedure for dealing with diseases, growth and tumors.

Surgery:

At Rice University, a flesh welder is used to fuse two pieces of chicken meat into a single piece. The two pieces of chicken are placed together touching. A greenish liquid containing gold-coated nanoshells is dribbled along the seam. An infrared laser is traced along the seam, causing the two sides to weld together. This could solve the difficulties and blood leaks caused when the surgeon tries to restitch the arteries that have been cut during a kidney or heart transplant. The flesh welder could weld the artery perfectly.

Visualization:

Tracking movement can help determine how well drugs are being distributed or how substances are metabolized. It is difficult to track a small group of cells throughout the body, so scientists used to dye the cells. These dyes needed to be excited by light of a certain wavelength in order for them to light up. While different color dyes absorb different frequencies of light, there was a need for as many light sources as cells. A way around this problem is with luminescent tags.

These tags are quantum dots attached to proteins that penetrate cell membranes. The dots can be random in size, can be made of bio-inert material, and they demonstrate the nanoscale property that color is size-dependent. As a result, sizes are selected so that the frequency of light used to make a group of quantum dots fluoresce is an even multiple of the frequency required to make another group incandesce. Then both groups can be lit with a single light source.

Nanoparticle targeting:

It is greatly observed that nanoparticles are promising tools for the advancement of drug delivery, medical imaging, and as diagnostic sensors. However, the biodistribution of these nanoparticles is mostly unknown due to the difficulty in targeting specific organs in the body. Current research in the excretory systems of mice, however, shows the ability of gold composites to selectively target certain organs based on their size and charge.

These composites are encapsulated by a dendrimer and assigned a specific charge and size. Positively-charged gold nanoparticles were found to enter the kidneys while negatively-charged gold nanoparticles remained in the liver and spleen. It is suggested that the positive surface charge of the nanoparticle decreases the rate of opsonization of nanoparticles in the liver, thus affecting the excretory pathway. Even at a relatively small size of 5 nm , though, these particles can become compartmentalized in the peripheral tissues, and will therefore accumulate in the body over time. While advancement of research proves that targeting and distribution can be augmented by nanoparticles, the dangers of nanotoxicity become an important next step in further understanding of their medical uses.

Neuro-electronic interfaces

Neuro-electronic interfacing is a visionary goal dealing with the construction of nanodevices that will permit computers to be joined and linked to the nervous system This idea requires the building of a molecular structure that will permit control and detection of nerve impulses by an external computer. The computers will be able to interpret, register, and respond to signals the body gives off when it feels sensations. The demand for such structures is huge because many diseases involve the decay of the nervous system (ALS and multiple sclerosis).

Also, many injuries and accidents may impair the nervous system resulting in dysfunctional systems and paraplegia. If computers could control the nervous system through neuro-electronic interface, problems that impair the system could be controlled so that effects of diseases and injuries could be overcome. Two considerations must be made when selecting the power source for such applications.

They are refuelable and nonrefuelable strategies. A refuelable strategy implies energy is refilled continuously or periodically with external sonic, chemical, tethered, magnetic, or electrical sources. A nonrefuelable strategy implies that all power is drawn from internal energy storage which would stop when all energy is drained.

One limitation to this innovation is the fact that electrical interference is a possibility. Electric fields, electromagnetic pulses (EMP), and stray fields from other *in vivo* electrical devices can all cause interference. Also, thick insulators are required to prevent electron leakage, and if high conductivity of the *in vivo* medium occurs there is a risk of sudden power loss and ―shorting out.‖ Finally, thick wires are also needed to conduct substantial power levels without overheating. Little practical progress has been made even though research is happening.

The wiring of the structure is extremely difficult because they must be positioned precisely in the nervous system so that it is able to monitor and respond to nervous signals. The structures that will provide the interface must also be compatible with the body's immune system so that they will remain unaffected in the body for a long time. In addition, the structures must also sense ionic currents and be able to cause currents to flow backward. While the potential for these structures is amazing, there is no timetable for when they will be available.

Nanorobots:

The somewhat speculative claims about the possibility of using nanorobots in medicine, advocates say, would totally change the world of medicine once it is realized. Nanomedicine would make use of these nanorobots (e.g., Computational Genes), introduced into the body, to repair or detect damages and infections.

According to Robert Freitas of the Institute for Molecular Manufacturing, a typical blood borne medical nanorobot would be between 0.5-3 micrometres in size, because that is the maximum size possible due to capillary passage requirement. Carbon could be the primary element used to build these nanorobots due to the inherent strength and other characteristics of some forms of carbon (diamond/fullerene composites), and nanorobots would be fabricated in desktop nanofactories specialized for this purpose.

Nanodevices could be observed at work inside the body using MRI, especially if their components were manufactured using mostly ^{13}C atoms rather than the natural ^{12}C isotope of carbon, since ^{13}C has a nonzero nuclear magnetic moment. Medical nanodevices would first be injected into a human body, and would then go to work in a specific organ or tissue mass.

The doctor will monitor the progress, and make certain that the nanodevices have gotten to the correct target treatment region. The doctor will also be able to scan a section of the body, and actually see the nanodevices congregated neatly around their target (a tumor mass, etc.) so that he or she can be sure that the procedure was successful.

Cell repair machines:

Using drugs and surgery, doctors can only encourage tissues to repair themselves. With molecular machines, there will be more direct repairs. Cell repair will utilize the same tasks that living systems already prove possible. Access to cells is possible because biologists can insert needles into cells without killing them. Thus, molecular machines are capable of entering the cell. Also, all specific biochemical interactions show that molecular systems can recognize other molecules by touch, build or rebuild every molecule in a cell, and can disassemble damaged molecules. Finally, cells that replicate prove that molecular systems can assemble every system found in a cell. Therefore, since nature has demonstrated the basic operations needed to perform molecular-level cell repair, in the future, nanomachine based systems will be built that are able to enter cells, sense differences from healthy ones and make modifications to the structure.

The healthcare possibilities of these cell repair machines are impressive. Comparable to the size of viruses or bacteria, their compact parts would allow them to be more complex. The early machines will be specialized. As they open and close cell membranes or travel through tissue and enter cells and viruses, machines will only be able to correct a single molecular disorder like DNA damage or enzyme deficiency. Later, cell repair machines will be programmed with more abilities with the help of advanced AI systems.

Nanocomputers will be needed to guide these machines. These computers will direct machines to examine, take apart, and rebuild damaged molecular structures. Repair machines will be able to repair whole cells by working structure by structure. Then by working cell by cell and tissue by tissue, whole organs can be repaired. Finally, by working organ by organ, health is restored to the body. Cells damaged to the point of inactivity can be repaired because of the ability of molecular machines to build cells from scratch. Therefore, cell repair machines will free medicine from reliance on self repair alone.