

4. Basics of nanopackaging

4.1 Introduction

Microtechnology has changed our lives dramatically. The most striking impact is apparent in computer technology, which is essential for today's industry, and also for our individual life styles. Apart from microelectronics, microtechnology influences many other areas. The size of typical structures that is accessible is in the sub-micrometer range, which is at the limits of optical resolution and barely visible with a light microscope. This is about 1/1000 smaller than structures resolvable by the naked eye, but still 1000 times larger than an atom. Today's developments are addressing the size range below these dimensions. Because a typical structure size is in the nanometer range, the methods and techniques are defined as nanotechnology.

The consequent extension of the resolution limit of microscopes led to instruments with the capacity to resolve features below the wavelength of light: the field ion microscope, the electron microscope, and finally the family of scanning probe microscopes. Now it is possible to image individual molecules, and even single atoms. Although chemistry and microtechnology appear to be fundamentally different, they are somehow related. They have mutual interests in the area of properties of materials. Microtechnology is not a simple extrapolation of conventional precise mechanical methods down to smaller dimensions. Chemical methods, such as plasma processes, wet chemical etching and photo resist techniques, are predominant compared with cutting or reshaping processes. However, microtechnology follows physical principles. As in classical chemistry, chemical processes in microtechnology use a relatively high number of similar particles. Individual particles play no dominant role, whether in fabrication methods or in applications.

In nanotechnology, the primary role of classical physical principles is replaced as molecular and atomic dimensions are approached. Physical-technical and chemical aspects influence the fabrication and the use and application of nanotechnical structures on an equal basis. The effects of mesoscopic physics, a field that is influenced by and uses quantum phenomena, complement these aspects. In contrast to classical chemistry, small ensembles or even individual particles can play a decisive role.

Truly *revolutionary* nanotechnology products, materials and applications, such as nanorobotics, are years in the future (some say only a few years; some say many years). What qualifies as "nanotechnology" today is basic research and development that is happening in laboratories all over the world. "Nanotechnology" products that are on the market today are mostly gradually improved products (using *evolutionary* nanotechnology) where some form of nanotechnology enabled material (such as carbon nanotubes, nanocomposite structures or nanoparticles of a particular substance) or nanotechnology process (e.g. nanopatterning or quantum dots for medical imaging) is used in the manufacturing process. In their ongoing quest to improve existing products by creating smaller components and better performance materials, all at a lower cost, the number of companies that will manufacture "nanoproducts" (by this definition) will grow very fast and soon make up the majority of all companies across many industries. Evolutionary nanotechnology should therefore be viewed as a process that gradually will affect most companies and industries.

Nanotechnology is a new word, but it is not an entirely new field. Nature has many objects and processes that function on a micro to nanoscale. The understanding of these functions can guide us in imitating and producing nanodevices and nanomaterials.

Billions of years ago, molecules began organizing themselves into the complex structures that could support life. Molecular ensembles are present in plants, which include light harvesting molecules, such as chlorophyll, arranged within the cells on the nanometer to micrometer scales. These structures capture light energy, and convert it into the chemical energy that drives the biochemical machinery of plant cells. Live organs use chemical energy in the body. The flagella, a type of bacteria, rotate at over 10,000RPM. This is an example of a biological molecular machine. The flagella motor is driven by the proton flow caused by the electrochemical potential differences across the membrane. The diameter of the bearing is about 20–30 nm, with an estimated clearance of about 1 nm.

So what exactly is nanotechnology? One of the problems facing nanotechnology is the confusion about its definition. Most definitions revolve around the study and control of phenomena and materials at length scales below 100 nm and quite often they make a comparison with a human hair, which is about 80,000 nm wide. Some definitions include a reference to molecular systems and devices and nanotechnology ‘purists’ argue that any definition of nanotechnology needs to include a reference to “functional systems”.

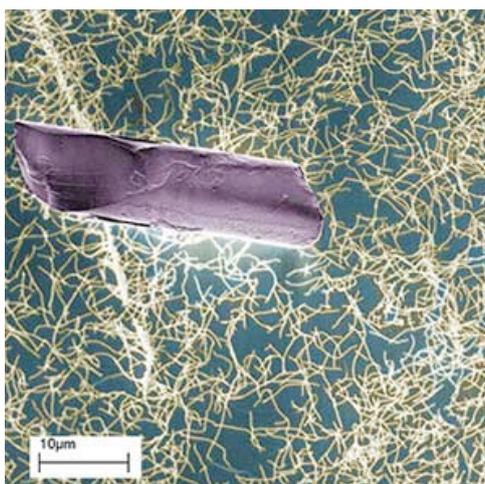


Fig. 4.1.1 Human hair fragment and a network of single-walled carbon nanotubes (image: Jirka Cech)

It seems that a size limitation of nanotechnology to the 1-100 nm range, the area where size-dependant quantum effects come to bear, would exclude numerous materials and devices, especially in the pharmaceutical area, and some experts caution against a rigid definition based on a sub-100 nm size.

Another important criterion for the definition is the requirement that the nanostructure is man-made. Otherwise you would have to include every naturally formed biomolecule and material particle, in effect redefining much of chemistry and molecular biology as ‘nanotechnology’.

The most important requirement for the nanotechnology definition is that the nanostructure has special properties that are exclusively due to its nanoscale proportions.

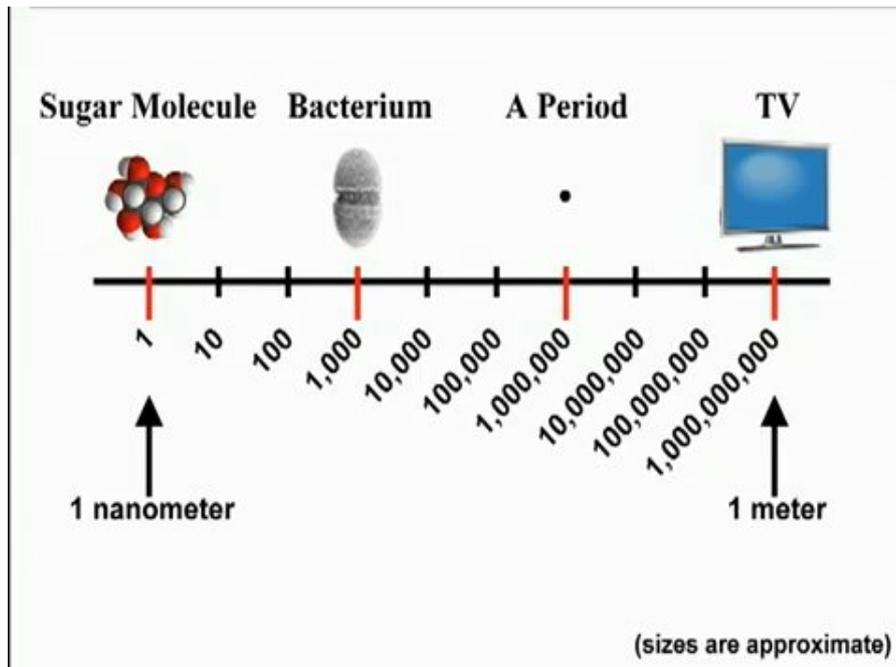
A good definition that is practical and unconstrained by any arbitrary size limitations: **the design, characterization, production, and application of structures, devices, and systems by controlled manipulation of size and shape at the nanometer scale (atomic, molecular, and macromolecular scale) that produces structures, devices, and systems with at least one novel/superior characteristic or property.**

The micro and nanosystems include micro/nanoelectromechanical systems (MEMS/NEMS) (e.g. sensors, actuators, and miniaturized systems comprising sensing, processing, and/or actuating functions), micromechatronics, optoelectronics, microfluidics, and systems integration. These systems can sense, control, and activate on the micro/nanoscale and function individually or in arrays to generate effects on the macroscale. The nanosystems market in 2001 was about \$100 million and the integrated nanosystems market was more than \$30 billion at the end of last year. Due to the enabling nature of these systems, and because of the significant impact they can have on the commercial and defence applications, venture capitalists, industry, as well as the federal government have taken a special interest in nurturing growth in this field. Micro and nanosystems are likely to be the next logical step in the “silicon revolution”.

The significance of the nanoscale

A nanometer (nm) is one thousand millionth of a meter. A nanometer, 10^{-9} m, is about ten times the size of the smallest atoms, such as hydrogen and carbon, while a micron is barely larger than the wavelength of visible light, thus invisible to the human eye. A millimetre, the size of a pinhead, is roughly the smallest size available in present day machines. The range of scales from millimetres to nanometers is one million, which is also about the range of scales in present day mechanical technology, from the largest skyscrapers to the smallest conventional mechanical machine parts. For comparison, a red blood cell is approximately 7,000nm wide and a water molecule is almost 0.3nm across. People are interested in the nanoscale (which we define to be from 100nm down to the size of atoms (approximately 0.2nm)) because it is at this scale that the properties of materials can be very different from those at a larger scale. We define nanoscience as the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale; and nanotechnologies as the design, characterisation, production and application of structures, devices and systems by controlling shape and size at the nanometer scale. In some senses, nanoscience and nanotechnologies are not new. Chemists have been making polymers, which are large molecules made up of nanoscale subunits, for many decades and nanotechnologies have been used to create the tiny features on computer chips for the past 20 years. However, advances in the tools that now allow atoms and molecules to be examined and probed with great precision have enabled the expansion and development of nanoscience and nanotechnologies.

In order to understand the significance of the nanoscale and the carbon nanotubes technology, watch the presentation film from below, created by the Center for Integrated Systems, Stanford University, as an introduction in nanopackaging.



Carbon nanotubes electronics (<http://www.youtube.com/watch?v=ikYhyjPjKBs>)

The bulk properties of materials often change dramatically with nano ingredients. Composites made from particles of nano-size ceramics or metals smaller than 100 nanometers can suddenly become much stronger than predicted by existing materials-science models. For example, metals with a so-called grain size of around 10 nanometers are as much as seven times harder and tougher than their ordinary counterparts with grain sizes in the hundreds of nanometers. The causes of these drastic changes stem from the weird world of quantum physics. The bulk properties of any material are merely the average of all the quantum forces affecting all the atoms. As you make things smaller and smaller, you eventually reach a point where the averaging no longer works.

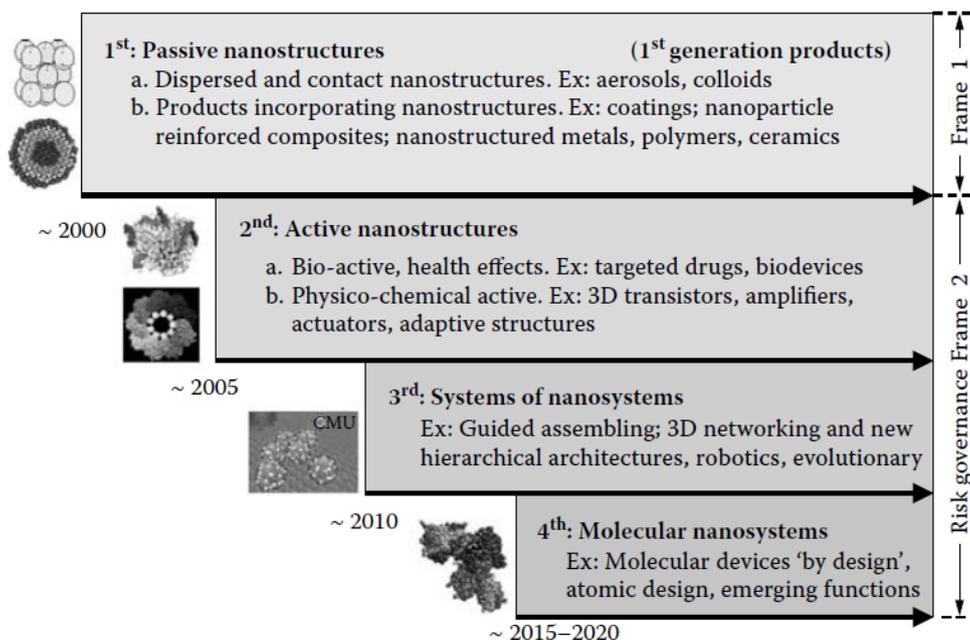


Fig. 4.1.2 Timeline for beginning of industrial prototyping and nanotechnology commercialization: four generations of nanoproducts

The properties of materials can be different at the nanoscale for two main reasons:

First, nanomaterials have a relatively larger surface area when compared to the same mass of material produced in a larger form. This can make materials more chemically reactive (in some cases materials that are inert in their larger form are reactive when produced in their nanoscale form), and affect their strength or electrical properties.

Second, quantum effects can begin to dominate the behaviour of matter at the nanoscale -particularly at the lower end - affecting the optical, electrical and magnetic behaviour of materials. Materials can be produced that are nanoscale in one dimension (for example, very thin surface coatings), in two dimensions (for example, nanowires and nanotubes) or in all three dimensions (for example, nanoparticles).

4.2 Nanomaterials

Much of nanoscience and many nanotechnologies are concerned with producing new or enhanced materials. Nanomaterials can be constructed by 'top down' techniques, producing very small structures from larger pieces of material, for example by etching to create circuits on the surface of a silicon microchip. They may also be constructed by 'bottom up' techniques, atom by atom or molecule by molecule. One way of doing this is self-assembly, in which the atoms or molecules arrange themselves into a structure due to their natural properties. Crystals grown for the semiconductor industry provide an example of self assembly, as does chemical synthesis of large molecules. A second way is to use tools to move each atom or molecule individually. Although this 'positional assembly' offers greater control over construction, it is currently very laborious and not suitable for industrial applications.

The 'top-down' approach tries to enhance the methods from microtechnology to achieve structure sizes in the medium and also lower nanometer range. This approach is based on a physical and microlithographic philosophy, which is in contrast to the other approach, where atomic or molecular units are used to assemble molecular structures, ranging from atomic dimensions up to supramolecular structures in the nanometer range. This 'bottom-up' approach is mainly influenced by chemical principles.

The challenge of modern nanotechnology is the realization of syntheses by the 'top down' and 'bottom up' approaches. This task is not driven entirely by the absolute structure dimensions, because today macro and supramolecules extending up to hundreds of nanometers or even micrometers can already be synthesized or isolated from biological systems. So the overlap of both approaches is not a problem. Both techniques provide specific capabilities that can be implemented by the other. The lithographic techniques ('top down') offer the connection between structure and technical environment. The interface with the surrounding system is given in this approach, but it is not really possible with the chemical ('bottom up') approach. At the same time, the integration of nanostructures into a functional microtechnical environment is realized. On the other hand, chemical technologies provide adjustment of chemical binding strength and preferred orientation of bonds, together with a fine tuning according to the numbers of bound atoms or atomic groups and a classification of the spatial orientation based on the number of bonds and their angles.

It has been 25 years since the scanning tunnelling microscope (STM) was invented, followed four years later by the atomic force microscope, and that's when nanoscience and nanotechnology really started to take off. Various forms of scanning probe microscopes based on these discoveries are essential for many areas of today's research. Scanning probe techniques have become the workhorse of nanoscience and nanotechnology research. Here is a Scanning Electron Microscope (SEM) image of a gold tip for Near-field Scanning Optical Microscopy (SNOM) obtained by Focussed Ion Beam (FIB) milling. The small tip at the centre of the structure measures some tens of nanometers.

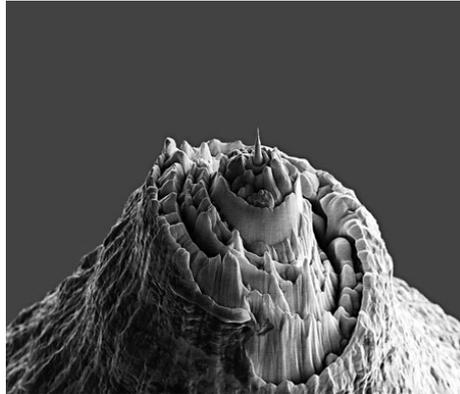
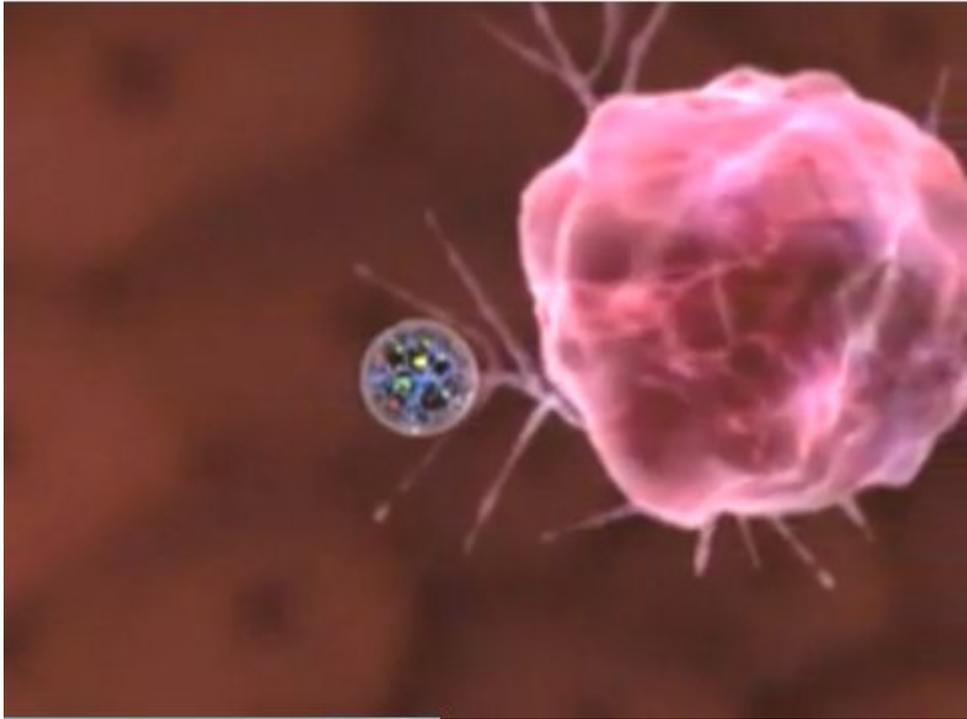


Fig. 4.2.1 Gold Tip for SNOM, imaged by SEM, 2006, Gian Carlo Gazzadi and Pietro Gucciardi, with Lucia Covi (www.s3.infm.it/blowup)

Current applications of nanoscale materials include very thin coatings used, for example, in electronics and active surfaces (for example, self-cleaning windows). In most applications the nanoscale components will be fixed or embedded but in some, such as those used in cosmetics and in some pilot environmental remediation applications, free nanoparticles are used. The ability to machine materials to very high precision and accuracy (better than 100 nm) is leading to considerable benefits in a wide range of industrial sectors, for example in the production of components for the information and communication technology, automotive and aerospace industries.

The documentation film from below, created by the National Cancer Institute, presents the use of nanotechnology in cancer diagnosis and treatment. The nanotechnology, the science of building small, is changing the way we look at cancer. The National Cancer Institute built new tools that are actually smaller than molecules giving us the chance to attack cancer at the genetic level.



The use of nanotechnology in cancer diagnosis and treatment
(<http://www.youtube.com/watch?v=5jqQxuVncmc>)

4.2.1 Definition

Nanostructured materials have been known for a long time and have been used for specific applications without any knowledge of the tiny size of the particles involved. For example, colloidal gold (which can be considered as belonging to this broad class of materials) has been used in coloured glass since ancient times, but its particular character was only explained in the middle of the 19th century by Michael Faraday.

Although a broad definition, we categorise nanomaterials as those which have structured components with at least one dimension less than 100nm. Materials that have one dimension in the nanoscale (and are extended in the other two dimensions) are layers, such as thin films or surface coatings. Some of the features on computer chips come in this category. Materials that are nanoscale in two dimensions (and extended in one dimension) include nanowires and nanotubes. Materials that are nanoscale in three dimensions are particles, for example precipitates, colloids and quantum dots (tiny particles of semiconductor materials). Nanocrystalline materials, made up of nanometre-sized grains, also fall into this category. Some of these materials have been available for some time; others are genuinely new.

The term “nanomaterial” is nowadays applied to very different classes of materials, including:

- dry solid nanoparticles and clusters;
- dispersions of nanoparticles in liquids (“nanosuspensions” and “colloidal solutions”);
- nanocrystalline materials held together by glassy material or embedded in a glassy;
- matrix, such as ceramics or glass ceramics with nanosized phases;
- nanocomposite materials including organic as well as inorganic components;

- stiff macromolecular or supermolecular aggregates composed of fullerenes, nanorods, nanotubes, or similar rigid molecular objects.

Two principal factors cause the properties of nanomaterials to differ significantly from other materials: increased relative surface area, and quantum effects. These factors can change or enhance properties such as reactivity, strength and electrical characteristics. As a particle decreases in size, a greater proportion of atoms are found at the surface compared to those inside. For example, a particle of size 30 nm has 5% of its atoms on its surface, at 10 nm 20% of its atoms, and at 3 nm 50% of its atoms. Thus nanoparticles have a much greater surface area per unit mass compared with larger particles. As growth and catalytic chemical reactions occur at surfaces, this means that a given mass of material in nanoparticulate form will be much more reactive than the same mass of material made up of larger particles.

To understand the effect of particle size on surface area, consider a U.S. silver dollar. The silver dollar contains 26.96 grams of coin silver, has a diameter of about 40mm, and has a total surface area of approximately 27.70 square centimetres. If the same amount of coin silver were divided into tiny particles – say 1 nanometer in diameter – the total surface area of those particles would be 11,400 square meters. When the amount of coin silver contained in a silver dollar is rendered into 1 nm particles, the surface area of those particles is 4.115 million times greater than the surface area of the silver dollar!

Normally not included in the term “nanomaterials” are nanopolycrystalline materials, partially crystalline polymers, and emulsions with nanodroplets. However, such materials fall within the focus of nanotechnology when they are to be used for functional nanostructures or as materials with special properties in the framework of planar technology.

4.2.2 Properties of nanomaterials

In tandem with surface-area effects, quantum effects can begin to dominate the properties of matter as size is reduced to the nanoscale. These can affect the optical, electrical and magnetic behaviour of materials, particularly as the structure or particle size approaches the smaller end of the nanoscale. Materials that exploit these effects include quantum dots, and quantum well lasers for optoelectronics.

For other materials such as crystalline solids, as the size of their structural components decreases, there is much greater interface area within the material; this can greatly affect both mechanical and electrical properties. For example, most metals are made up of small crystalline grains; the boundaries between the grain slow down or arrest the propagation of defects when the material is stressed, thus giving it strength. If these grains can be made very small, or even nanoscale in size, the interface area within the material greatly increases, which enhances its strength. For example, nanocrystalline nickel is as strong as hardened steel. Understanding surfaces and interfaces is a key challenge for those working on nanomaterials, and one where new imaging and analysis instruments are vital.

From the present knowledge of materials it is understood that the beautiful colours of stained glass windows originate in nanometer scale metal particles present in the glass. These metal particles have scattering resonances for light of specific wavelengths, depending on the particle size L . The particle size distribution, in turn, will depend upon the choice of metal impurity, its concentration, and the heat treatment of the glass. When the metallic particles in

the glass are illuminated, they preferentially scatter light of particular colours. Neutral density filters marketed for photographic application also have distributions of small particles embedded in glass.

Carbon black, commonly known as soot, which contains nanometer-sized particles of carbon, was used very early as an additive to the rubber in automobile tires. (As we now know, carbon black contains small amounts of 60C (Buckminsterfullerene), other fullerenes, and graphitic nanotubes of various types.)

The AgBr and AgI crystals of conventional photography are nanometer-sized single crystals embedded in a thin gelatine matrix. It appears that the fundamental light absorption in these crystals is close to the quantum sensitivity limit. It further appears that the nanoscopic changes in these tiny crystals, which occur upon absorption of one or more light photons, enable them to be turned into larger metallic silver particles in the conventional photographic development process. The conventional photographic negative image is an array of solid silver grains embedded in a gelatine matrix. As such it is remarkably stable as a record, over decades or more.

The drugs that are so important in everyday life (and are also of huge economic importance), including caffeine, aspirin and many more, are specific molecules of nanometer size, typically containing fewer than 100 atoms. Controlled precipitation chemistry for example is employed to produce uniform nanometer spheres of polystyrene, which have long been marketed as calibration markers for transmission electron microscopy.

4.2.3 Nanoscale in one dimension

- **Thin films, layers and surfaces**

One-dimensional nanomaterials, such as thin films and engineered surfaces, have been developed and used for decades in fields such as electronic device manufacture, chemistry and engineering. In the silicon integrated-circuit industry, for example, many devices rely on thin films for their operation, and control of film thicknesses approaching the atomic level is routine. Monolayers (layers that are one atom or molecule deep) are also routinely made and used in chemistry. The formation and properties of these layers are reasonably well understood from the atomic level upwards, even in quite complex layers (such as lubricants). Advances are being made in the control of the composition and smoothness of surfaces, and the growth of films.

Engineered surfaces with tailored properties such as large surface area or specific reactivity are used routinely in a range of applications such as in fuel cells and catalysts. The large surface area provided by nanoparticles, together with their ability to self assemble on a support surface, could be of use in all of these applications.

Although they represent incremental developments, surfaces with enhanced properties should find applications throughout the chemicals and energy sectors. The benefits could surpass the obvious economic and resource savings achieved by higher activity and greater selectivity in reactors and separation processes, to enabling small-scale distributed processing (making chemicals as close as possible to the point of use). There is already a move in the chemical industry towards this. Another use could be the small-scale, on-site production of high value chemicals such as pharmaceuticals.

4.2.4 Nanoscale in two dimensions

Two dimensional nanomaterials such as tubes and wires have generated considerable interest among the scientific community in recent years. In particular, their novel electrical and mechanical properties are the subject of intense research.

- **Carbon Nanotubes**

Carbon nanotubes (CNTs) were first observed by Sumio Iijima in 1991. CNTs are extended tubes of rolled graphene sheets. There are two types of CNTs: single-walled (one tube) or multi-walled (several concentric tubes). Both of these are typically a few nanometres in diameter and several micrometres to centimetres long. CNTs have assumed an important role in the context of nanomaterials, because of their novel chemical and physical properties. They are mechanically very strong (their Young's modulus is over 1 terapascal, making CNTs as stiff as diamond), flexible (about their axis), and can conduct electricity extremely well (the helicity of the graphene sheet determines whether the CNT is a semiconductor or metallic). All of these remarkable properties give CNTs a range of potential applications: for example, in reinforced composites, sensors, nanoelectronics and display devices.

CNTs are now available commercially in limited quantities. They can be grown by several techniques. However, the selective and uniform production of CNTs with specific dimensions and physical properties is yet to be achieved. The potential similarity in size and shape between CNTs and asbestos fibres has led to concerns about their safety.

- **Inorganic Nanotubes**

Inorganic nanotubes and inorganic fullerene-like materials based on layered compounds such as molybdenum disulphide were discovered shortly after CNTs. They have excellent tribological (lubricating) properties, resistance to shockwave impact, catalytic reactivity, and high capacity for hydrogen and lithium storage, which suggest a range of promising applications. Oxide-based nanotubes (such as titanium dioxide) are being explored for their applications in catalysis, photo-catalysis and energy storage.

- **Nanowires**

Nanowires are ultrafine wires or linear arrays of dots, formed by self-assembly. They can be made from a wide range of materials. Semiconductor nanowires made of silicon, gallium nitride and indium phosphide, have demonstrated remarkable optical, electronic and magnetic characteristics (for example, silica nanowires can bend light around very tight corners). Nanowires have potential applications in high-density data storage; either as magnetic read heads or as patterned storage media, and electronic and opto-electronic nanodevices, for metallic interconnects of quantum devices and nanodevices. The preparation of these nanowires relies on sophisticated growth techniques, which include self-assembly processes, where atoms arrange themselves naturally on stepped surfaces, chemical vapour deposition (CVD) onto patterned substrates, electroplating or molecular beam epitaxy (MBE). The 'molecular beams' are typically from thermally evaporated elemental sources.

4.2.5 Nanoscale in three dimensions

- **Nanoparticles**

We classify nanoparticles to be particles less than 100nm in diameter that exhibit new or enhanced size-dependent properties compared with larger particles of the same material. Nanoparticles exist widely in the natural world: for example as the products of photochemical and volcanic activity, and created by plants and algae. They have also been created for thousands of years as products of combustion and food cooking, and more recently from vehicle exhausts. Deliberately manufactured nanoparticles, such as metal oxides, are by comparison in the minority.

Nanoparticles are of interest because of the new properties (such as chemical reactivity and optical behaviour) that they exhibit compared with larger particles of the same materials. For example, titanium dioxide and zinc oxide become transparent at the nanoscale, however are able to absorb and reflect UV light, and have found application in sunscreens. Nanoparticles have a range of potential applications: in the short-term in new cosmetics, textiles and paints; in the longer term, in methods of targeted drug delivery where they could be used to deliver drugs to a specific site in the body. Nanoparticles can also be arranged into layers on surfaces, providing a large surface area and hence enhanced activity, relevant to a range of potential applications such as catalysts.

Manufactured nanoparticles are typically not products in their own right, but generally serve as raw materials, ingredients or additives in existing products. Nanoparticles are currently in a small number of consumer products such as cosmetics and their enhanced or novel properties may have implications for their toxicity. For most applications, nanoparticles will be fixed (for example, attached to a surface or within a composite) although in others they will be free or suspended in fluid. Whether they are fixed or free will have a significant affect on their potential health, safety and environmental impacts.

- **Fullerenes (carbon 60)**

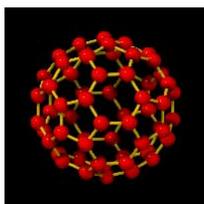


Fig. 4.2.2 Model C60

In the mid-1980s a new class of carbon material was discovered called carbon 60 (C60). Harry Kroto and Richard Smalley, the experimental chemists who discovered C60 named it “buckminsterfullerene”, in recognition of the architect Buckminster Fuller, who was well-known for building geodesic domes, and the term fullerenes was then given to any closed carbon cage. C60 are spherical molecules about 1nm in diameter, comprising 60 carbon atoms arranged as 20 hexagons and 12 pentagons: the configuration of a football. In 1990, a technique to produce larger quantities of C60 was developed by resistively heating graphite rods in a helium atmosphere. Several applications are envisaged for fullerenes, such as miniature ‘ball bearings’ to lubricate surfaces, drug delivery vehicles and in electronic circuits.

- **Dendrimers**

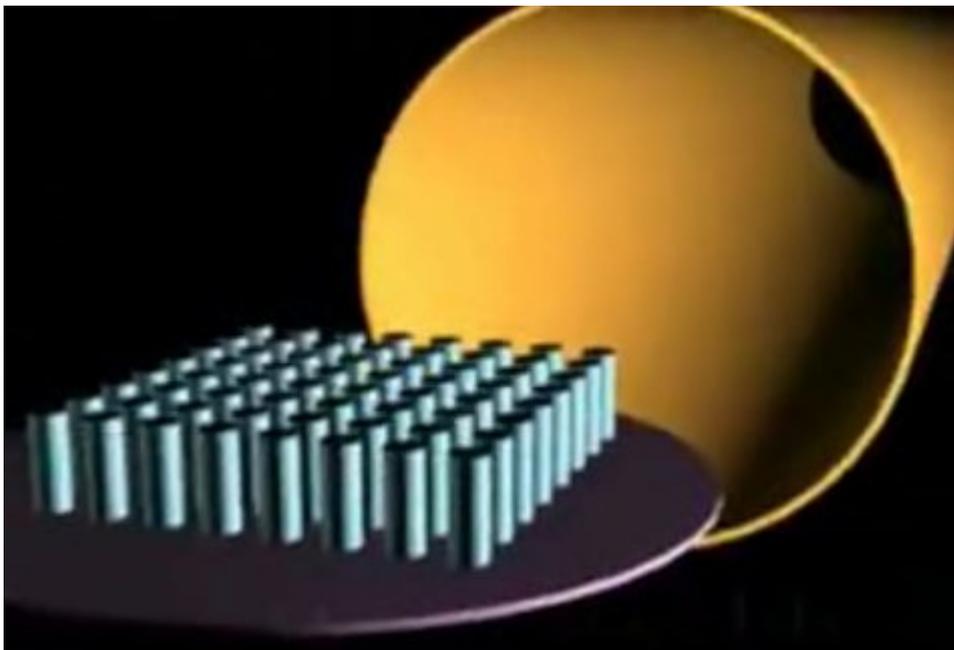
Dendrimers are spherical polymeric molecules, formed through a nanoscale hierarchical self-assembly process. There are many types of dendrimer; the smallest is several nanometres in size. Dendrimers are used in conventional applications such as coatings and inks, but they also have a range of interesting properties which could lead to useful applications. For example, dendrimers can act as nanoscale carrier molecules and as such could be used in drug delivery. Environmental clean-up could be assisted by dendrimers as they can trap metal ions, which could then be filtered out of water with ultra-filtration techniques.

- **Quantum Dots**

Nanoparticles of semiconductors (quantum dots) were theorized in the 1970s and initially created in the early 1980s. If semiconductor particles are made small enough, quantum effects come into play, which limit the energies at which electrons and holes (the absence of an electron) can exist in the particles. As energy is related to wavelength (or colour), this means that the optical properties of the particle can be finely tuned depending on its size. Thus, particles can be made to emit or absorb specific wavelengths (colours) of light, merely by controlling their size. Recently, quantum dots have found applications in composites, solar cells (Gratzel cells) and fluorescent biological labels (for example to trace a biological molecule) which use both the small particle size and tuneable energy levels. Recent advances in chemistry have resulted in the preparation of monolayer-protected, high-quality, monodispersed, crystalline quantum dots as small as 2nm in diameter, which can be conveniently treated and processed as a typical chemical reagent.

4.3 Carbon Nanotubes

As an example of carbon structures arrays and the manufacturing process, see the documentation film from below, created by Dr. Madou's BioMEMS LAB.



C-MEMS Process (<http://www.youtube.com/watch?v=tzKHC-SICXE>)

4.3.1 History

In 1980 we knew of only three forms of carbon, namely diamond, graphite, and amorphous carbon. Today we know there is a whole family of other forms of carbon. The first to be discovered was the hollow, cage-like buckminsterfullerene molecule - also known as the buckyball, or the C₆₀ fullerene. There are now thirty or more forms of fullerenes, and also an extended family of linear molecules, carbon nanotubes. C₆₀ is the first spherical carbon molecule, with carbon atoms arranged in a soccer ball shape. In the structure there are 60 carbon atoms and a number of five-membered rings isolated by six-membered rings. The second, slightly elongated, spherical carbon molecule in the same group resembles a rugby ball, has seventy carbon atoms and is known as C₇₀. C₇₀'s structure has extra six-membered carbon rings, but there are also a large number of other potential structures containing the same number of carbon atoms. Their particular shapes depend on whether five-membered rings are isolated or not, or whether seven-membered rings are present. Many other forms of fullerenes up to and beyond C₁₂₀ have been characterized, and it is possible to make other fullerene structures with five-membered rings in different positions and sometimes adjoining one another.

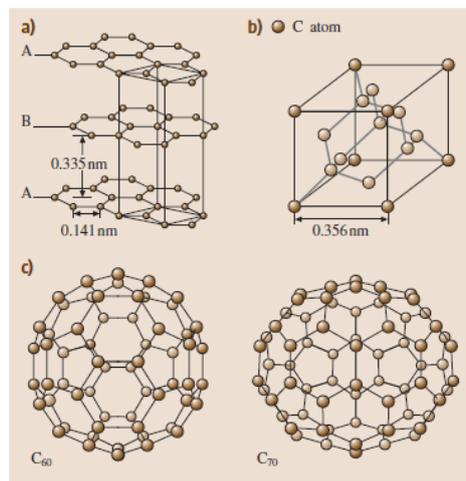


Fig. 4.3.1 The structure of three known forms of crystalline carbon (a) hexagonal structure of graphite, (b) modified face-centered cubic (fcc) structure, two interpenetrating fcc lattices displaced by one-quarter of the cube diagonal, of diamond (each atom is bonded to four others that form the corners of the pyramidal structure called tetrahedron), and (c) the structure of the two most common forms of fullerenes-soccer ball C₆₀ and rugby ball C₇₀ molecules

The important fact for nanotechnology is that useful dopant atoms can be placed inside the hollow fullerene ball. Atoms contained within the fullerene are said to be endohedral. Of course they can also be bonded to fullerenes outside the ball as salts, if the fullerene can gain electrons.

Endohedral fullerenes can be produced in which metal atoms are captured within the fullerene cages. Theory shows that the maximum electrical conductivity is to be expected for endohedral metal atoms, which will transfer three electrons to the fullerene. Fullerenes can be dispersed on the surface as a monolayer. That is, there is only one layer of molecules, and they are said to be mono dispersed. Provided fullerenes can be placed in very specific locations, they may be aligned to form a fullerene wire. Systems with appropriate material inside the fullerene ball are conducting and are of particular interest because they can be deposited to produce bead-like conducting circuits. Combining endohedrally doped structures

with non-doped structures changes the actual composition of a fullerene wire, so that it may be tailored in-situ during patterning. Hence within a single wire, insulating and conducting regions may be precisely defined. One-dimensional junction engineering becomes realistic with fullerenes.

Possibly more important than fullerenes are Carbon Nanotubes, which are related to graphite. The molecular structure of graphite resembles stacked, one-atom-thick sheets of chicken wire - a planar network of interconnected hexagonal rings of carbon atoms. In conventional graphite, the sheets of carbon are stacked on top of one another, allowing them to easily slide over each other. That is why graphite is not hard, but it feels greasy, and can be used as a lubricant. When graphene sheets are rolled into a cylinder and their edges joined, they form CNTs. Only the tangents of the graphitic planes come into contact with each other, and hence their properties are more like those of a molecule.

CNTs come in a variety of diameters, lengths, and functional group content. CNTs today are available for industrial applications in bulk quantities up metric ton quantities from Cheap Tubes. Several CNT manufacturers have >100 ton per year production capacity for multi walled nanotubes.

A nanotube may consist of one tube of graphite, a one-atom thick single-wall nanotube, or a number of concentric tubes called multiwalled nanotubes. When viewed with a transmission electron microscope these tubes appear as planes. Whereas single walled nanotubes appear as two planes, in multi walled nanotubes more than two planes are observed, and can be seen as a series of parallel lines. There are different types of CNTs, because the graphitic sheets can be rolled in different ways. The three types of CNTs are Zigzag, Armchair, and Chiral. It is possible to recognize zigzag, armchair, and chiral CNTs just by following the pattern across the diameter of the tubes, and analyzing their cross-sectional structure.

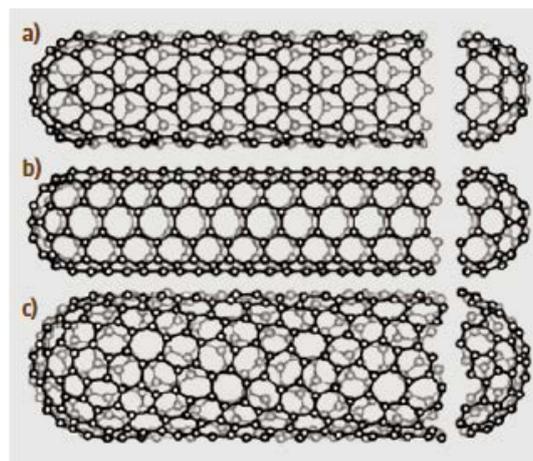


Fig. 4.3.2 Sketch of three different SWNT structures as examples for (a) a zig-zag-type nanotube, (b) an armchairtype nanotube, (c) a helical nanotube

Multi walled nanotubes 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 concentric layers are identical but different in diameter. However, mixed variants are possible, consisting of two or more types of concentric CNTs arranged in different orders. These can have either regular layering or random layering. The structure of the nanotube influences its properties -

including electrical and thermal conductivity, density, and lattice structure. Both type and diameter are important. The wider the diameter of the nanotube, the more it behaves like graphite. The narrower the diameter of the nanotube, the more its intrinsic properties depends upon its specific type.

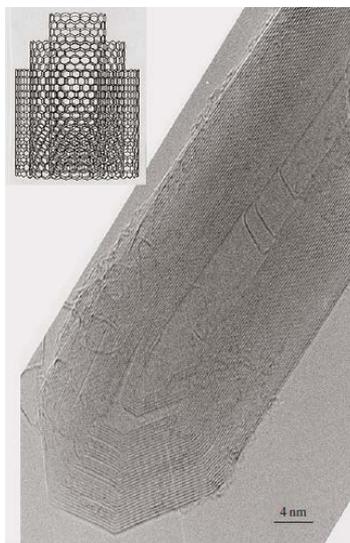


Fig. 4.3.3 High resolution transmission electron microscopy image (longitudinal view) of a concentric multiwall carbon nanotube (c-MWNT) prepared by electric arc. In *insert*, sketch of the Russian-doll-like display of graphenes

The integration of metal nanostructures, inorganic semiconductor nanostructures, and single CNTs is of particular interest in relation to nanoelectronic and nanooptoelectronic devices. Carbon nanotubes can be directly coupled with metals by combining the CVD synthesis of CNTs with electrochemical deposition. In this way, Ag/Si and Pt₆Si₅/Si nanostructures have been directly coupled with CNTs. These heterojunctions can be formed in perpendicular orientation to the substrate plane and arranged into arrays.

The conversion of discrete CNTs into complex networks of nanotubes is of interest with regard to the formation of three-dimensional wires and of nanoscale, complex topologies of coupled nanoelectronic functions. In principle, the impact of high-energy particles (40 keV Si ion beams, for example) on assemblies of CNTs can cause the formation of tube connections and the appearance of nanotube networks.

Fullerenes are not only interesting as individual nanoobjects, but also as material for structures in the medium nanometer range. So regular structures in this dimension can be realized by a self-organization process during the thermal activation of fullerene crystals. Single crystals of C₆₀ exhibit a photon-induced surface reconstruction that leads to periodic structures with dimensions of 30–40 nm.

4.3.2 Production methods

There are a number of methods of making CNTs and fullerenes. Fullerenes were first observed after vaporizing graphite with a short-pulse, high-power laser, however this was not a practical method for making large quantities. CNTs have probably been around for a lot longer than was first realized, and may have been made during various carbon combustion

and vapour deposition processes, but electron microscopy at that time was not advanced enough to distinguish them from other types of tubes. The first method for producing CNTs and fullerenes in reasonable quantities – was by applying an electric current across two carbonaceous electrodes in an inert gas atmosphere. This method is called plasma arcing. It involves the evaporation of one electrode as cations followed by deposition at the other electrode. This plasma-based process is analogous to the more familiar electroplating process in a liquid medium. Fullerenes and CNTs are formed by plasma arcing of carbonaceous materials, particularly graphite. The fullerenes appear in the soot that is formed, while the CNTs are deposited on the opposing electrode. Another method of nanotube synthesis involves plasma arcing in the presence of cobalt with a 3% or greater concentration. As noted above, the nanotube product is a compact cathode deposit of rod like morphology. However when cobalt is added as a catalyst, the nature of the product changes to a web, with strands of 1 mm or so thickness that stretch from the cathode to the walls of the reaction vessel. 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 the five-membered rings.

- **Arc Method**

The carbon arc discharge method, initially used for producing C₆₀ fullerenes, is the most common and perhaps easiest way to produce CNTs, as it is rather simple. However, it is a technique that produces a complex mixture of components, and requires further purification - to separate the CNTs from the soot and the residual catalytic metals present in the crude product. This method creates CNTs through arc-vaporization of two carbon rods placed end to end, separated by approximately 1 mm, in an enclosure that is usually filled with inert gas at low pressure. Recent investigations have shown that it is also possible to create CNTs with the arc method in liquid nitrogen. A direct current of 50 to 100 A, driven by a potential difference of approximately 20 V, creates a high temperature discharge between the two electrodes. The discharge vaporizes the surface of one of the carbon electrodes, and forms a small rod-shaped deposit on the other electrode. Producing CNTs in high yield depends on the uniformity of the plasma arc, and the temperature of the deposit forming on the carbon electrode.

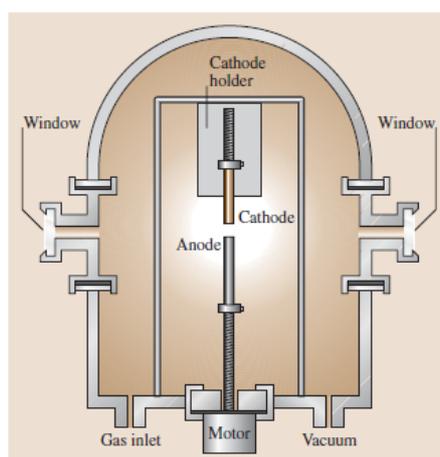


Fig. 4.3.4 Sketch of an electric arc reactor

- **Laser Method**

In 1996 CNTs were first synthesized using a dual-pulsed laser and achieved yields of >70wt% purity. Samples were prepared by laser vaporization of graphite rods with a 50:50 catalyst mixture of Cobalt and Nickel at 1200°C in flowing argon, followed by heat treatment

in a vacuum at 1000°C to remove the C60 and other fullerenes. The initial laser vaporization pulse was followed by a second pulse, to vaporize the target more uniformly. The use of two successive laser pulses minimizes 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 produced by this method 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 single walled nanotubes, aligned along a common axis. By varying the growth temperature, the catalyst composition, and other process parameters, the average nanotube diameter and size distribution can be varied. Arc-discharge and laser vaporization are currently the principal methods for obtaining small quantities of high quality CNTs. However, both methods suffer from drawbacks. The first is that both methods involve evaporating the carbon source, so it has been unclear how to scale up production to the industrial level using these approaches. The second issue relates to the fact that vaporization methods grow CNTs in highly tangled forms, mixed with unwanted forms of carbon and/or metal species. The CNTs thus produced are difficult to purify, manipulate, and assemble for building nanotube-device architectures for practical applications.

- **Chemical Vapour Deposition**

Chemical vapour deposition of hydrocarbons over a metal catalyst is a classical method that has been used to produce various carbon materials such as carbon fibers and filaments, for over twenty years. Large amounts of CNTs can be formed by catalytic CVD of acetylene over Cobalt and iron catalysts supported on silica or zeolite. The carbon deposition activity seems to relate to the cobalt content of the catalyst, whereas the CNTs' selectivity seems to be a function of the pH in catalyst preparation. Fullerenes and bundles of single walled nanotubes were also found among the multi walled nanotubes produced on the carbon/zeolite catalyst. Some researchers are experimenting with the formation of CNTs from ethylene. Supported catalysts such as iron, cobalt, and nickel, containing either a single metal or a mixture of metals, seem to induce the growth of isolated single walled nanotubes or single walled nanotubes bundles in the ethylene atmosphere. The production of single walled nanotubes, as well as double-walled CNTs, on molybdenum and molybdenum-iron alloy catalysts has also been demonstrated. CVD of carbon within the pores of a thin alumina template with or without a Nickel catalyst has been achieved. Ethylene was used with reaction temperatures of 545°C for Nickel-catalyzed CVD, and 900°C for an uncatalyzed process. The resultant carbon nanostructures have open ends, with no caps. Methane has also been used as a carbon source. In particular it has been used to obtain ‘nanotube chips’ containing isolated single walled nanotubes at controlled locations. High yields of single walled nanotubes have been obtained by catalytic decomposition of an H₂/CH₄ mixture over well-dispersed metal particles such as Cobalt, Nickel, and Iron on magnesium oxide at 1000°C. It has been reported that the synthesis of composite powders containing well-dispersed CNTs can be achieved by selective reduction in an H₂/CH₄ atmosphere of oxide solid solutions between a non-reducible oxide such as Al₂O₃ or MgAl₂O₄ and one or more transition metal oxides. The reduction produces very small transition metal particles 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 single walled nanotubes and fewer multi walled nanotubes.

- **Ball Milling**

Ball milling and subsequent annealing is a simple method for the production of CNTs. Although it is well established that mechanical attrition of this type can lead to fully nano porous microstructures, it was not until a few years ago that CNTs of carbon and boron nitride

were produced from these powders by thermal annealing. Essentially the method consists of placing graphite powder into a stainless steel container along with four hardened steel balls. The container is purged, and argon is introduced. The milling is carried out at room temperature for up to 150 hours. Following milling, the powder is annealed under an inert 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 nanotube growth. Research has shown that this method produces more multi walled nanotubes and few single walled nanotubes.

- **Other Methods**

CNTs can also be produced by diffusion flame synthesis, electrolysis, use of solar energy, heat treatment of a polymer, and low-temperature solid pyrolysis. In flame synthesis, combustion of a portion of the hydrocarbon gas provides the elevated temperature required, with the remaining fuel conveniently serving as the required hydrocarbon reagent. Hence the flame constitutes an efficient source of both energy and hydrocarbon raw material. Combustion synthesis has been shown to be scalable for high-volume commercial production.

4.3.3 Functionalization

Pristine nanotubes are unfortunately insoluble in many liquids such as water, polymer resins, and most solvents. Thus they are difficult to evenly disperse in a liquid matrix such as epoxies and other polymers. This complicates efforts to utilize the nanotubes' outstanding physical properties in the manufacture of composite materials, as well as in other practical applications which require preparation of uniform mixtures of CNTs with many different organic, inorganic, and polymeric materials.

To make nanotubes more easily dispersible in liquids, it is necessary to physically or chemically attach certain molecules, or functional groups, to their smooth sidewalls without significantly changing the nanotubes' desirable properties. This process is called functionalization. The production of robust composite materials requires strong covalent chemical bonding between the filler particles and the polymer matrix, rather than the much weaker van der Waals physical bonds which occur if the CNTs are not properly functionalized.

Functionalization methods such as chopping, oxidation, and "wrapping" of the CNTs in certain polymers can create more active bonding sites on the surface of the nanotubes. For biological uses, CNTs can be functionalized by attaching biological molecules, such as lipids, proteins, biotins, etc. to them. Then they can usefully mimic certain biological functions, such as protein adsorption, and bind to DNA and drug molecules. This would enable medially and commercially significant applications such as gene therapy and drug delivery. In biochemical and chemical applications such as the development of very specific biosensors, molecules such as carboxylic acid (COOH), poly m-aminobenzoic sulfonic acid (PABS), polyimide, and polyvinyl alcohol (PVA) have been used to functionalize CNTs, as have amino acid derivatives, halogens, and compounds. Some types of functionalized CNTs are soluble in water and other highly polar, aqueous solvents.

4.3.4 Properties

- **Electrical Conductivity**

CNTs can be highly conducting, and hence can be said to be metallic. Their conductivity has been shown to be a function of their chirality, the degree of twist as well as their diameter. CNTs can be either metallic or semi-conducting in their electrical behavior. Conductivity in MWNTs is quite complex. Some types of “armchair”-structured CNTs appear to conduct better than other metallic CNTs. Furthermore, interwall reactions within multi walled nanotubes have been found to redistribute the current over individual tubes non-uniformly. However, there is no change in current across different parts of metallic single-walled nanotubes. The behaviour of the ropes of semi-conducting single walled nanotubes is different, in that the transport current changes abruptly at various positions on the CNTs.

The conductivity and resistivity of ropes of single walled nanotubes has been measured by placing electrodes at different parts of the CNTs. The resistivity of the single walled nanotubes ropes was of the order of 10^{-4} ohm-cm at 27°C. This means that single walled nanotube ropes are the most conductive carbon fibres known. The current density that was possible to achieve was 10^{-7} A/cm², however in theory the single walled nanotube ropes should be able to sustain much higher stable current densities, as high as 10^{-13} A/cm². It has been reported that individual single walled nanotubes may contain defects. Fortunately, these defects allow the single walled nanotubes to act as transistors. Likewise, joining CNTs together may form transistor-like devices. A nanotube with a natural junction (where a straight metallic section is joined to a chiral semiconducting section) behaves as a rectifying diode – that is, a half-transistor in a single molecule. It has also recently been reported that single walled nanotubes can route electrical signals at speeds up to 10 GHz when used as interconnects on semi-conducting devices.

- **Strength and Elasticity**

The carbon atoms of a single sheet of graphite form a planar honeycomb lattice, in which each atom is connected via a strong chemical bond to three neighbouring atoms. Because of these strong bonds, the basal plane elastic modulus of graphite is one of the largest of any known material. For this reason, CNTs are expected to be the ultimate high-strength fibres. Single walled nanotubes are stiffer than steel, and are very resistant to damage from physical forces. Pressing on the tip of a nanotube will cause it to bend, but without damage to the tip. When the force is removed, the nanotube returns to its original state. This property makes CNTs very useful as probe tips for very high-resolution scanning probe microscopy. Quantifying these effects has been rather difficult, and an exact numerical value has not been agreed upon.

Using atomic force microscopy, the unanchored ends of a freestanding nanotube 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 of single walled nanotubes is about 1 TeraPascal, but this value has been widely disputed, and a value as high as 1.8TPa has been reported. Other values significantly higher than that have also been reported. 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 single walled nanotubes, ranging from 1.22TPa to 1.26TPa. They have calculated a value of 1.09TPa for a generic nanotube. However, when working with different multi walled nanotubes, others have

noted that the modulus measurements of multi walled nanotubes using AFM techniques do not strongly depend on the diameter. Instead, they argue that the modulus of the multi walled nanotubes correlates to the amount of disorder in the nanotube walls. Not surprisingly, when multi walled nanotubes break, the outermost layers break first.

- **Thermal Conductivity and Expansion**

CNTs have been shown to exhibit superconductivity below 20°K (approx. -253°C). Research suggests that these exotic strands, already heralded for their unparalleled strength and unique ability to adopt the electrical properties of either semiconductors or perfect metals, may someday also find applications as miniature heat conduits in a host of devices and materials. The strong in-plane graphitic carbon - carbon bonds make them exceptionally strong and stiff against axial strains. The almost zero in-plane thermal expansion but large inter-plane expansion of single walled nanotubes implies strong in-plane coupling and high flexibility against non-axial strains.

Many applications of CNTs, such as in nanoscale molecular electronics, sensing and actuating devices, or as reinforcing additive fibres in functional composite materials, have been proposed. Reports of several recent experiments on the preparation and mechanical characterization of CNT-polymer composites have also appeared. These measurements suggest modest enhancements in strength characteristics of CNT-embedded matrixes as compared to bare polymer matrixes. Preliminary experiments and simulation studies on the thermal properties of CNTs show very high thermal conductivity. It is expected, therefore, that nanotube reinforcements in polymeric materials may also significantly improve the thermal and thermomechanical properties of the composites.

- **Field Emission**

Field emission results from the tunneling of electrons from a metal tip into vacuum, under application of a strong electric field. The small diameter and high aspect ratio of CNTs is very favourable for field emission. Even for moderate voltages, a strong electric field develops at the free end of supported CNTs because of their sharpness. This was observed by de Heer and co-workers at EPFL in 1995. He also immediately realized that these field emitters must be superior to conventional electron sources and might find their way into all kind of applications, most importantly flat-panel displays. It is remarkable that after only five years Samsung actually realized a very bright colour display, which will be shortly commercialized using this technology. Studying the field emission properties of multi walled nanotubes, Bonard and co-workers at EPFL observed that together with electrons, light is emitted as well. This luminescence is induced by the electron field emission, since it is not detected without applied potential. This light emission occurs in the visible part of the spectrum, and can sometimes be seen with the naked eye.

- **High Aspect Ratio**

CNTs represent a very small, high aspect ratio conductive additive for plastics of all types. Their high aspect ratio means that a lower loading of CNTs is needed compared to other conductive additives to achieve the same electrical conductivity. This low loading preserves more of the polymer resins' toughness, especially at low temperatures, as well as maintaining other key performance properties of the matrix resin. CNTs have proven to be an excellent additive to impart electrical conductivity in plastics. Their high aspect ratio, about 1000:1 imparts electrical conductivity at lower loadings, compared to conventional additive materials such as carbon black, chopped carbon fibre, or stainless steel fibre.

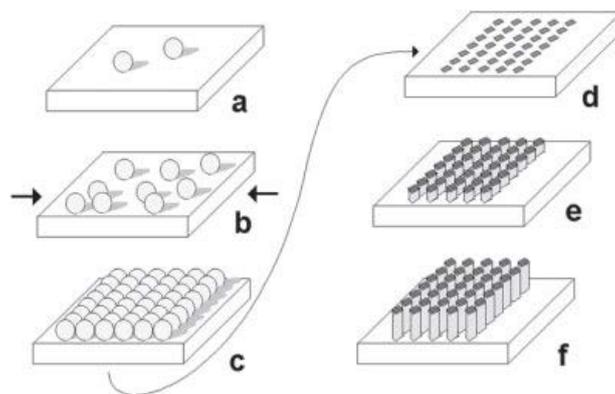


Fig. 4.3.5 Formation of arrays of high aspect ratio ZnO nanostructures by means of microsphere assembly: a) adsorption of microspheres at a clean, smooth substrate surface, b) increasing microsphere density by increasing particle adsorption and lateral compression, c) regular microsphere array formed after compression at substrate surface, d) gold deposition from gas phase using the microsphere array as mask; obtained gold spot array after removal of microspheres, e) gold-catalyzed growth of ZnO piles, f) obtained array with high aspect ratio ZnO nanostructures and gold capping

- **Highly Absorbent**

The large surface area and high absorbency of CNTs make them ideal candidates for use in air, gas, and water filtration. A lot of research is being done in replacing activated charcoal with CNTs in certain ultra high purity applications.

4.4 Applications of nanomaterials

- **Composites**

An important use of nanoparticles and nanotubes is in composites, materials that combine one or more separate components and which are designed to exhibit overall the best properties of each component. This multi-functionality applies not only to mechanical properties, but extends to optical, electrical and magnetic ones. Currently, carbon fibres and bundles of multi-walled CNTs are used in polymers to control or enhance conductivity, with applications such as antistatic packaging. The use of individual CNTs in composites is a potential long-term application. A particular type of nanocomposite is where nanoparticles act as fillers in a matrix; for example, carbon black used as a filler to reinforce car tyres. However, particles of carbon black can range from tens to hundreds of nanometres in size, so not all carbon black falls within our definition of nanoparticles.

- **Clays**

Clays containing naturally occurring nanoparticles have long been important as construction materials and are undergoing continuous improvement. Clay particle based composites – containing plastics and nano-sized flakes of clay – are also finding applications such as use in car bumpers.

- **Coatings and Surfaces**

Coatings with thickness controlled at the nano or atomic scale have been in routine production for some time, for example in molecular beam epitaxy or metal oxide chemical vapor deposition for optoelectronic devices, or in catalytically active and chemically

functionalized surfaces. Recently developed applications include the self-cleaning window, which is coated in highly activated titanium dioxide, engineered to be highly hydrophobic (water repellent) and antibacterial, and coatings based on nanoparticulate oxides that catalytically destroy chemical agents. Wear and scratch-resistant hard coatings are significantly improved by nanoscale intermediate layers (or multilayers) between the hard outer layer and the substrate material. The intermediate layers give good bonding and graded matching of elastic and thermal properties, thus improving adhesion. A range of enhanced textiles, such as breathable, waterproof and stainresistant fabrics, have been enabled by the improved control of porosity at the nanoscale and surface roughness in a variety of polymers and inorganics.

- **Tougher and Harder Cutting Tools**

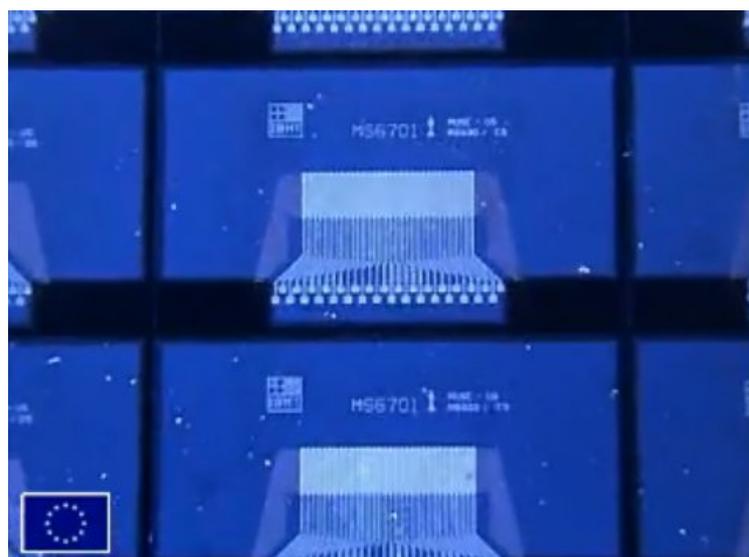
Cutting tools made of nanocrystalline materials, such as tungsten carbide, tantalum carbide and titanium carbide, are more wear and erosion-resistant, and last longer than their conventional (large-grained) counterparts. They are finding applications in the drills used to bore holes in circuit boards.

- **Sunscreens and Cosmetics**

Nanosized titanium dioxide and zinc oxide are currently used in some sunscreens, as they absorb and reflect ultraviolet (UV) rays and yet are transparent to visible light and so are more appealing to the consumer. Nanosized iron oxide is present in some lipsticks as a pigment but it is our understanding that it is not used by the European cosmetics sector. The use of nanoparticles in cosmetics has raised a number of concerns about consumer safety.

The documentation film from below presents the work of some scientists regarding the use of micro and nanotechnologies in medicine. They create real labs on a chip being able to detect cancer cells early or different kinds of chemical ingredients.

Combining microsystems and nanostructures (medicine and the environment) they check if the food is fresh or not by measuring the level of gases. In theory it can detect only one type of molecule at a time. The detection system can exist on a single chip. We can integrate these devices in mobile instruments which can be hand-held.



Micro- and nanotechnologies in medicine
(<http://www.youtube.com/watch?v=K3DREmTiAqA&feature=related>)

Another application of nanotechnology is presented in the documentation film from below, created by the Society of Manufacturing Engineers. It presents the nanomanufacturing (or molecular nanotechnology) insights. The molecular nanotechnology is the process of assembling complex structures with atomic precision.



Applications of Nanotechnology - Nanomanufacturing
(http://www.youtube.com/watch?v=9yuTM_EOtHY)

Applications of carbon nanotubes

The carbon nanotube is a nanoscale element with several useful properties, from an electrical point of view, but it is not envisioned that such elements, which can form individual devices, can be integrated to make a “carbon” computer. The electrical and also the mechanical properties are outstanding, which can be traced to the perfect periodicity, lack of defects inherent in a single molecule, and the consequent lack of scattering for carriers. More likely are applications in the direction of extending Moore’s Law in silicon: hybrid configurations of nanotube arrays attached to an underlying silicon configuration, perhaps a CMOS array.

Stand-alone applications, however, do seem likely in the role of the carbon nanotube as a sensor. Some such sensors exploit the small nanotube diameter, to allow generation of a large electric field easily at low voltage.

The special nature of carbon combined with the molecular perfection of single-walled nanotubes to endow them with exceptional material properties, such as very high electrical and thermal conductivity, strength, stiffness, and toughness. No other element in the periodic table bonds to itself in an extended network with the strength of the carbon-carbon bond. The delocalized pi-electron donated by each atom is free to move about the entire structure, rather than remain with its donor atom, giving rise to the first known molecule with metallic-type electrical conductivity. Furthermore, the high-frequency carbon-carbon bonds vibrations provide an intrinsic thermal conductivity higher than even diamond. In most conventional materials, however, the actual observed material properties - strength, electrical conductivity, etc. - are degraded very substantially by the occurrence of defects in their structure. For example, high-strength steel typically fails at only about 1% of its theoretical breaking

strength. CNTs, however, achieve values very close to their theoretical limits because of their molecular perfection of structure.

This aspect is part of the unique story of CNTs. CNTs are examples of true nanotechnology: they are under 100 nanometers in diameter, but are molecules that can be manipulated chemically and physically in very useful ways. They open an incredible range of applications in materials science, electronics, chemical processing, energy management, and many other fields. CNTs have extraordinary electrical conductivity, heat conductivity, and mechanical properties. They are probably the best electron field-emitter possible. They are polymers of pure carbon and can be reacted and manipulated using the well-known and the tremendously rich chemistry of carbon. This provides opportunity to modify their structure, and to optimize their solubility and dispersion. Very significantly, CNTs are molecularly perfect, which means that they are normally free of property-degrading flaws in the nanotube structure. Their material properties can therefore approach closely the very high levels intrinsic to them. These extraordinary characteristics give CNTs potential in numerous applications.

- **Field Emission**

CNTs are the best known field emitters of any material. This is understandable, given their high electrical conductivity, and the incredible sharpness of their tip. The smaller the tip's radius of curvature, the more concentrated the electric field will be, leading to increased field emission. The sharpness of the tip also means that they emit at especially low voltage, an important fact for building low-power electrical devices that utilize this feature. CNTs can carry an astonishingly high current density. Furthermore, the current is extremely stable. An immediate application of this behaviour receiving considerable interest is in field-emission flat-panel displays. Instead of a single electron gun, as in a traditional cathode ray tube display, in CNT-based displays there is a separate nanotube electron gun for each individual pixel in the display. Their high current density, low turn-on and operating voltages, and steady, long-lived behaviour make CNTs very attractive field emitters in this application. Other applications utilizing the field-emission characteristics of CNTs include general types of low-voltage cold-cathode lighting sources, lightning arrestors, and electron microscope sources.

- **Conductive or Reinforced Plastics**

Much of the history of plastics over the last half-century has involved their use as a replacement for metals. For structural applications, plastics have made tremendous headway, but not where electrical conductivity is required, because plastics are very good electrical insulators. This deficiency is overcome by loading plastics up with conductive fillers, such as carbon black and larger graphite fibres. The loading required to provide the necessary conductivity using conventional fillers is typically high, however, resulting in heavy parts, and more importantly, plastic parts whose structural properties are highly degraded. It is well-established that the higher the aspect ratio of the filler particles, the lower the loading required to achieve a given level of conductivity.

CNTs are ideal in this sense, since they have the highest aspect ratio of any carbon fibre. In addition, their natural tendency to form ropes provides inherently very long conductive pathways even at ultra-low loadings. Applications that exploit this behaviour of CNTs include EMI/RFI shielding composites; coatings for enclosures, gaskets, and other uses such as electrostatic dissipation; antistatic materials, transparent conductive coatings; and radar-absorbing materials for stealth applications.

A lot of automotive plastics companies are using CNTs as well. CNTs have been added into the side mirror plastics on automobiles in the US since the late 1990s.

- **Energy Storage**

CNTs have the intrinsic characteristics desired in material used as electrodes in batteries and capacitors, two technologies of rapidly increasing importance. CNTs have a tremendously high surface area, good electrical conductivity, and very importantly, their linear geometry makes their surface highly accessible to the electrolyte.

Research has shown that CNTs have the highest reversible capacity of any carbon material for use in lithium ion batteries. In addition, CNTs are outstanding materials for super capacitor electrodes and are now being marketed for this application. CNTs also have applications in a variety of fuel cell components. They have a number of properties, including high surface area and thermal conductivity, which make them useful as electrode catalyst supports in PEM fuel cells. Because of their high electrical conductivity, they may also be used in gas diffusion layers, as well as current collectors. CNTs' high strength and toughness-to-weight characteristics may also prove valuable as part of composite components in fuel cells that are deployed in transport applications, where durability is extremely important.

- **Conductive Adhesives and Connectors**

The same properties that make CNTs attractive as conductive fillers for use in electromagnetic shielding, ESD materials, etc., make them attractive for electronics packaging and interconnection applications, such as adhesives, potting compounds, coaxial cables, and other types of connectors.

- **Molecular Electronics**

The idea of building electronic circuits out of the essential building blocks of materials - molecules - has seen a revival the past few years, and is a key component of nanotechnology. In any electronic circuit, but particularly as dimensions shrink to the nanoscale, the interconnections between switches and other active devices become increasingly important. Their geometry, electrical conductivity, and ability to be precisely derived, make CNTs the ideal candidates for the connections in molecular electronics. In addition, they have been demonstrated as switches themselves.

There are already companies such as Nantero from Woburn, MA that are already making CNT based non-volatile random access memory for PC's. A lot of research is being done to design CNT based transistors as well.

- **Thermal Materials**

The record-setting anisotropic thermal conductivity of CNTs is enabling many applications where heat needs to move from one place to another. Such an application is found in electronics, particularly heat sinks for chips used in advanced computing, where uncooled chips now routinely reach over 100°C. The technology for creating aligned structures and ribbons of CNTs [D.Walters, et al., Chem. Phys. Lett. 338, 14 (2001)] is a step toward realizing incredibly efficient heat conduits. In addition, composites with CNTs have been shown to dramatically increase their bulk thermal conductivity, even at very small loadings.

- **Structural Composites**

The superior properties of CNTs are not limited to electrical and thermal conductivities, but also include mechanical properties, such as stiffness, toughness, and strength. These properties lead to a wealth of applications exploiting them, including advanced composites requiring high values of one or more of these properties.

- **Fibers and Fabrics**

Fibres spun of pure CNTs have recently been demonstrated and are undergoing rapid development, along with CNT composite fibres. Such super-strong fibres will have many applications including body and vehicle armour, transmission line cables, woven fabrics and textiles.

- **Catalyst Support**

CNTs intrinsically have an enormously high surface area; in fact, for single walled nanotubes every atom is not just on one surface - each atom is on two surfaces, the inside and the outside of the nanotube! Combined with the ability to attach essentially any chemical species to their sidewalls this provides an opportunity for unique catalyst supports. Their electrical conductivity may also be exploited in the search for new catalysts and catalytic behaviour.

- **CNT Ceramics**

A ceramic material reinforced with carbon nanotubes has been made by materials scientists at UC Davis. The new material is far tougher than conventional ceramics, conducts electricity and can both conduct heat and act as a thermal barrier, depending on the orientation of the nanotubes. Ceramic materials are very hard and resistant to heat and chemical attack, making them useful for applications such as coating turbine blades, but they are also very brittle.

The researchers mixed powdered alumina (aluminium oxide) with 5 to 10 percent carbon nanotubes and a further 5 percent finely milled niobium. The researchers treated the mixture with an electrical pulse in a process called spark-plasma sintering. This process consolidates ceramic powders more quickly and at lower temperatures than conventional processes.

The new material has up to five times the fracture toughness -- resistance to cracking under stress -- of conventional alumina. The material shows electrical conductivity seven times that of previous ceramics made with nanotubes. It also has interesting thermal properties, conducting heat in one direction, along the alignment of the nanotubes, but reflecting heat at right angles to the nanotubes, making it an attractive material for thermal barrier coatings.

- **Biomedical Applications**

The exploration of CNTs in biomedical applications is just underway, but has significant potential. Since a large part of the human body consists of carbon, it is generally thought of as a very biocompatible material. Cells have been shown to grow on CNTs, so they appear to have no toxic effect. The cells also do not adhere to the CNTs, potentially giving rise to applications such as coatings for prosthetics and surgical implants. The ability to functionalize the sidewalls of CNTs also leads to biomedical applications such as vascular stents, and neuron growth and regeneration. It has also been shown that a single strand of

DNA can be bonded to a nanotube, which can then be successfully inserted into a cell; this has potential applications in gene therapy.

- **Air, Water and Gas Filtration**

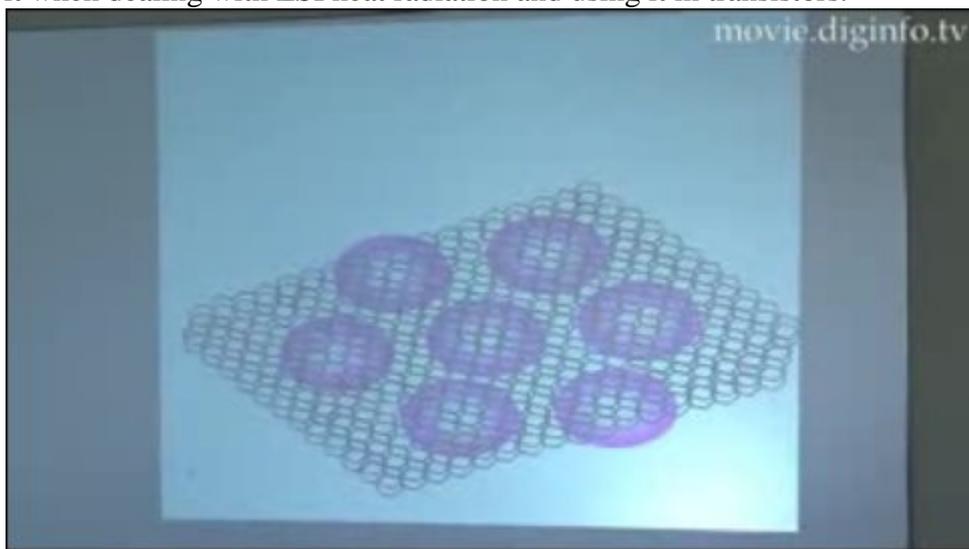
Many researchers and corporations have already developed CNT based air and water filtration devices. It has been reported that these filters can not only block the smallest particles but also kill most bacteria. This is another area where CNTs have already been commercialized and products are on the market now. Someday CNTs may be used to filter other liquids such as fuels and lubricants as well.

A lot of research is being done in the development of CNT based air and gas filtration. Filtration has been shown to be another area where it is cost effective to use CNTs already. The research I've seen suggests that 1 gram of MWNTs can be dispersed onto 1 sq ft of filter media. Manufacturers can get their cost down to 35 cents per gram of purified MWNTs when purchasing ton quantities.

- **Other Applications**

Some commercial products on the market today utilizing CNTs include stain resistant textiles, CNT reinforced tennis rackets and baseball bats. Companies like Kraft foods are heavily funding CNT based plastic packaging. Food will stay fresh longer if the packaging is less permeable to atmosphere. Coors Brewing Company has developed new plastic beer bottles that stay cold for longer periods of time. Samsung already has CNT based flat panel displays on the market. A lot of companies are looking forward to being able to produce transparent conductive coatings and phase out ITO coatings. Samsung uses align SWNTs in the transparent conductive layer of their display manufacturing process.

Fujitsu Laboratories has made a breakthrough in carbon nanotube research. Watch the presentation film from below to see how the company has combined carbon nanotubes and graphene, both of which are nano-scale carbon structures, to self-form a new nano-scale carbon composite, at the relatively low temperature of 510 degrees Celsius. As an electronics company, Fujitsu Labs aims to use the new structure to improve today's LSI performance by applying it when dealing with LSI heat radiation and using it in transistors.



New Carbon Nanotube Composite (<http://www.youtube.com/watch?v=2HJIMyB7FsM>)

4.5 Nanotechnology images

The nanoworld cannot be portrayed with a camera, nor can it be seen even with the most powerful optical microscope. Only special instruments have access to images of the nanoworld. A fascinating new exhibition “Blow-up: images from the nanoworld” in Modena/Italy. This exhibition brings to the public images that are usually accessible to few, because they remain confined in the research laboratories, on the scientists’ desks.

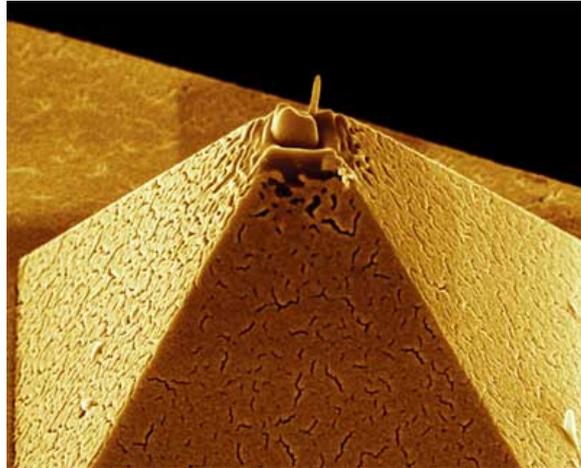


Fig. 4.5.1 Developing new instruments to be able to “see” at the nanoscale is a research field in itself. Shown here is the tip of an atomic force microscope (AFM), one of the foremost tools for imaging, measuring and manipulating matter at the nanoscale. Here, a platinum electrode measuring one hundredth of a nanometer has been deposited on the tip of this pyramid shaped AFM tip via focused ion beam (FIB) deposition. (image: C. Menozzi, G.C. Gazzadi, S3 (INFM-CNR), Modena. Artwork: Lucia Covi)

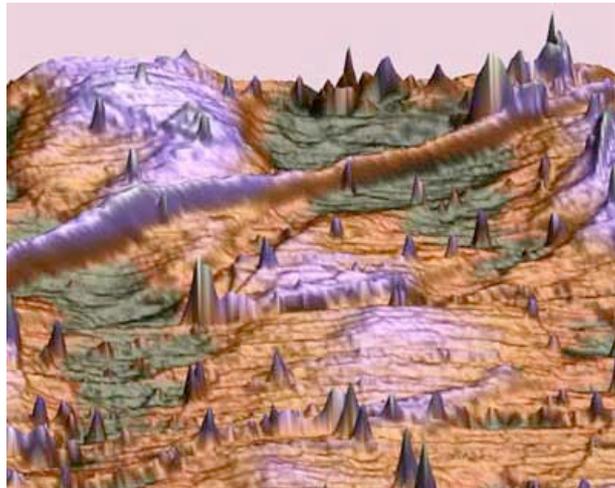


Fig. 4.5.2 Climatic change on carbon nanotubes – Carbon nanotubes have many characteristics that promise to revolutionize the world of structural materials. There are different ways to grow carbon nanotubes, especially the CVD technique, which allows obtaining SWCNT’s on a silicon surface. These SWCNT can be carried from the silicon surface to another surface, as HOPG, without suffering changes on their properties. That means nanomanipulation of carbon nanotubes. (Mr Miguel Ángel Fernández Vindel, Universidad Autonoma de Madrid/Spain)



Fig. 4.5.3 Nanoflower: The crystalline wurtzite indium nitride (InN) nanoflower was synthesized via molecular beam epitaxy (MBE) processes, using pure indium and a high efficient nitrogen source, hydrazoic acid (HN₃). (image: PaiChun Wei, Center for Condensed Matter Science, National Taiwan University, Taipei, Taiwan)

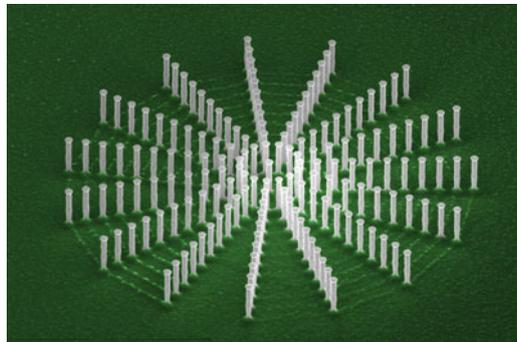


Fig. 4.5.4 Modern Stonehenge: Colorized SEM image of silicon nanopillar formation created by Gallium implantation and DRIE-etching. (Image: Nikolai Chekurov)



Fig. 4.5.5 Top view of a hole carved in a polyethylene surface. During a series of experiments the use of a FIB has proven to be very versatile and capable of carving various materials, including plastic. (Image: G.C. Gazzadi, S3 (INFM-CNR), Modena. Artwork: Lucia Covi)

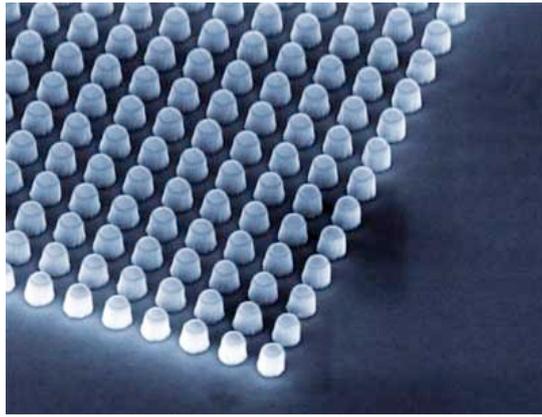


Fig. 4.5.6 Scanning electron microscope (SEM) image of quantum dots fabricated through electron beam lithography and subsequent dry-chemical etching on a quasi bidimensional layer (GaAl heterostructure). These structures are used to study the behavior of electrons, which are confined into tiny spaces – approximate. 10 electrons per dot. The diameter of each quantum dot is 200 nm (which means that a billion of these structure easily fit on the tip of your finger). (Image: C.P. Garcia, V. Pellegrini , NEST (INFM), Pisa. Artwork: Lucia Covi)

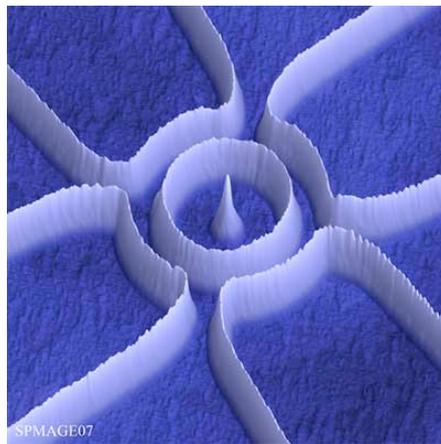


Fig. 4.5.7 Nano Rings: The image shows a four-terminal quantum ring structure defined in a two-dimensional electron gas (2DEG) with local anodic oxidation using an atomic force microscope tip. The elevated white lines represent the oxide on the surface of the GaAlAs heterostructure containing the 2DEG. These oxide lines are on average 15nm high and penetrate just as deep into the sample surface, forming barriers in the electron gas below. The ring has an average diameter of 1 micron and the four outer rectangular areas enclosed by oxide lines are used as in-plane gates to tune the electron density of the four arms of the ring.

Measuring Aharonov-Bohm oscillations in the ring conductance this device is used to interferometrically detect the relative phaseshift of Coulomb blockade resonances in two quantum dots induced in the arms of the ring. (Dr Andreas Fuhrer, Nanophysics Group of Prof. Ensslin at ETH Zürich/Switzerland)

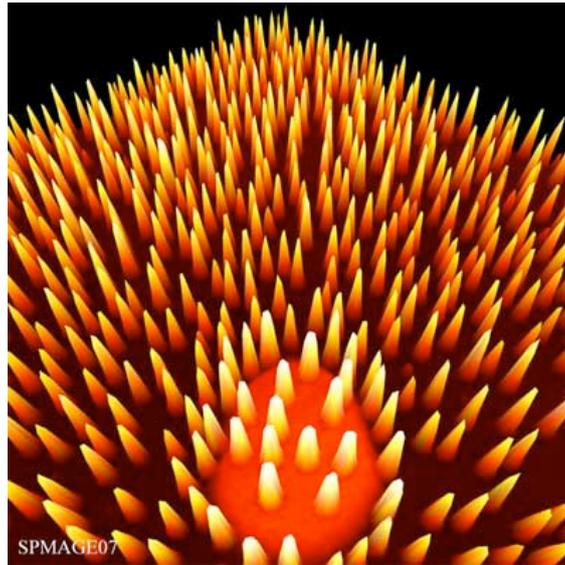


Fig. 4.5.8 Quantum Forest: GeSi quantum dots on Si, average diameter approx. 70nm, typical height approx. 15 nm. (Mr Thorsten Dziomba. Physikalisch-Technische Bundesanstalt, Germany)