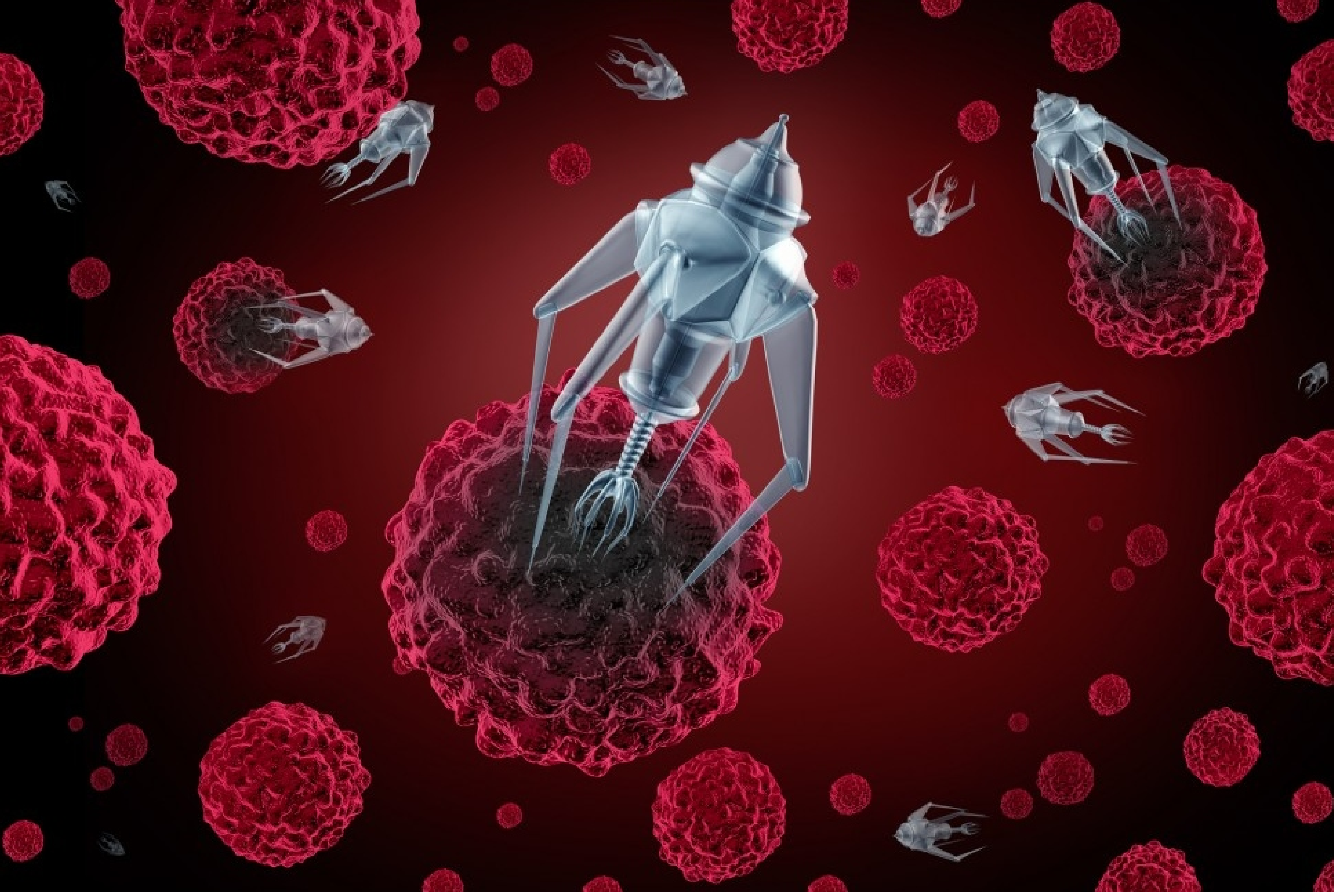

BASIC OF NANO CHEMISTRY

Eric McDonald

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Introduction

Nano in Water Industry

A lot of the water today is transported via public supply. Public supply covers the water that is transported by water departments whether government owned, or private. These departments withdraw water from lakes, rivers, and reservoirs to wherever it needs to be, for domestic or industrial use, or any other use necessary.

Uses

Around thirteen per cent of fresh water is affected by public supply:

- *The first of these is domestic use*: This covers water that is used in the home for private reasons, such as showering, toilets, cooking, washing and cleaning, and, when it happens, drinking. This can be either obtained from public supply or can be self supplied.

- *The second use is commercial use*: This is water for motels, hotels, restaurants, office buildings, and other commercial facilities, and institutions. This can also include fountain displays.
- *The third use for water and one of the most common is industrial use*: This includes water used in fabrication, processing, washing and cooling, and also can cover steel, chemical and allied products, paper and allied products, mining, and petroleum refining. This covers around five per cent of all water used. Industrial water use can sometimes use saline water, but 89% of the time its the same fresh water that we drink in our homes.
- *The fourth use is irrigation*: This is the when land is watered. This can cover the growing of crops, pastures, and maintaining vegetative growth in recreational lands, such as parks and golf courses.
- *The fifth use is thermoelectric power*: This is basically electrical power generation that it is not hydroelectric. Water is merely used in the process of creating this electricity.
- *The sixth use is mining*: This is not a huge use of water, however, often water is used to create a slurry something which allows the gold to be separated from the dirt.
- *The seventh use is livestock*: Livestock need water, and lots of it. One per cent of all fresh water used is used for livestock.
- *The eighth use is hydroelectric power*: This is power that is produced through falling water. The great

thing about this however, is that the water does not have to be fresh. It does have to fall from a great hight at a high speed though. A great example of this is the snowy mountain scheme.

Industry

The annual water volume used by industry is estimated to rise from 752 km 3/year in 1995 to an estimated 1,170 km 3/year in 2025. In 2025, the industrial component is expected to represent about 24% of total freshwater withdrawal. Some 300-500 million tons of heavy metals, solvents, toxic sludge, and other wastes accumulate each year from industry. Industries based on organic raw materials are the most significant contributors to the organic pollutant load with the food sector being the most important polluter.

Energy

World energy demand, especially for electricity, will increase greatly during this 21st century. Hydropower is the most important and widely-used renewable source of energy it represents 19% of total electricity production. Worldwide there are now about 45,000 large dams in operation. Canada is the largest producer of hydroelectricity, followed by the United States and Brazil. Built to provide hydropower and irrigation water and to regulate river flow to prevent floods and draughts, they have had a disproportionate impact on the environment. Collectively, they have inundated more than 400,000 square kilometers of mostly productive land. Somewhere between 40 and 80 million people have been displaced by dams, forced to relocate to other, often less productive, land. A study by the World Commission on Dams, published in 2000, found that large dams have a very mixed record. In 140 countries, dams provide cheap hydroelectric power. On a global scale, dams account for 19 per cent of the world's electricity generation and supply, through irrigation, almost 16 per cent of the world's food. Some dams continue to operate after 30-40 years, providing water and electricity. Hydropower plays a major role in reducing greenhouse gas emissions: developing ½ of the world's economically feasible hydropower potential could reduce greenhouse gases emissions by about 13%.

On the other hand large dams have led to the loss of forests and wildlife habitat and the loss of aquatic biodiversity - both upstream and downstream. Large dams have, in most cases, systematically failed to assess and account for the range of potential negative impacts on displaced and resettled communities. With up to 80 million people displaced from their homes and many more living downstream suffering from unintended effects (eg. Loss of fisheries), mitigation efforts have, for the most part, been cosmetic and ineffective. According to the Commission, large dams may be on their way out: Mini-hydropower plants have proved to be far cheaper to build and more economical to run than originally forecast; plus they have minimal impacts on the environment. Better management to reduce the demand for water has great potential to reduce water stress and hydropower requirements.

Improved systems management, particularly for irrigated agriculture, has tremendous potential for reducing waste, while increasing the efficiency of irrigation systems. Demand for Water Increasing While freshwater supply is limited, demand risen as populations grow and consumption per capita increases. Global consumption of water is doubling every 20 years, more than twice the rate of human population growth, while pollution and over-extraction in many regions of the world has reduced the ability of supplies to meet demand.

During the last 70 years, the global population has tripled, but water withdrawals have increased over six times. Since 1940, annual global water withdrawals have increased by an average of nearly 3 per cent per year, while population growth has averaged between 1.5 and 2 per cent. According to the United Nations, more than one billion people on earth already lack access to fresh drink water. If current trends persists, by 2025 the demand for freshwater is expected to rise to 56 per cent more than the amount that is currently available.

More people mean increased water use and less available on a per capita basis. In 1989 there was some 9,000 cubic meters of freshwater per person available for human use. By 2000, that figures had dropped to 7,800 cubic meters and is expected to plummet to 5,100 cubic meters per person by 2025, when the global population is projected to reach 8 billion.

The world's six billion people are already using about 54 per cent of all the accessible freshwater contained in rivers, lakes and underground aquifers. By 2025 the human's share will be 70 per cent, based on the population increase. If per capita consumption of water resources continues to rise at its current rate, humankind could be using over 90 per cent of all available freshwater within 25 years.

Water Shortages

A country experiences water stress when annual supplies drop below 1,700 cubic meters per person. When annual water supplies drop below 1,000 cubic meters per person, the country faces water scarcity for all or part of the year.

- In 1995, 31 countries containing 458 million people faced either water stress or scarcity.
- By 2025, according to projections made by Population Action International, more than 2.8 billion people in 48 countries will be facing water stress or scarcity.
- By 2050, the number of water short countries soars to 54, affecting 4 billion people, or 40 per cent of the projected global population.

Measurement of nano appratus

steel

Steel reinforcements are the backbone of any concrete structure and provide tensile strength to complement the compressive strength of concrete. Together they provide strength to the structure. Concrete under ideal conditions is maintenance free and has almost infinite life. However, the presence of steel makes it vulnerable to the attack of corrosion and in the process reduces the useful, maintenance free life of the RCC structures.

The corrosion of steel used in buildings, bridges and other concrete structures (especially in coastal and marine environment) in the form of reinforcement bars leads to the deterioration of concrete. This in turn reduces the load bearing capacity of concrete thereby rendering it vulnerable to failure. This effectively creates the need for undertaking expensive maintenance and restoration work, the cost of which at times runs into many times the original cost of construction.

This is more severe and conspicuous in the coastal regions. Hence there is an urgent need to protect the steel against corrosion, especially in the future projects coming up across the country accounting for crores of rupees in investments and ensure that the useful life of these projects are enhanced substantially to serve the nation with many more years of service life.

Corrosion induced damage to reinforced concrete often necessitates early repair and occasionally complete replacement of the structure or element well before its design life is reached. Worldwide, the costs associated with such remedial work are massive and are expected to increase in the future at an alarming rate. Estimates of these costs vary widely. For example, as early as 1977 in the USA, the cost of major repair and replacement of damaged bridge decks, which was rapidly becoming a systemic problem, was about $23 billion.

Broomfield reported that in the late 1980s the UK Department of Transport estimated repair costs of some £616 million for motorway bridges in England and Wales. Over the same period in the USA, annual costs associated with bridge deck repairs due to deicing salts alone was in the range 50-200 million, plus an additional 100 million for substructures and 50-100 million on multi-level parking garages. India has a large coastal belt starting from Gujarat, Goa and Maharashtra in the west to Tamil Nadu, Karnataka and Kerala in the south, and Andhra Pradesh, West Bengal and Orissa to the east. It has one of the largest coastlines and highly aggressive environments, leading to accelerated corrosion of the steel being used in these regions. The Indian Lead Zinc Development Association and CECRI figures put the total annual loss due to corrosion at an amount equal to 2 per cent of the GDP of nation.

Clearly, such costs are an enormous drain on finances and resources which could otherwise be allocated to new construction. What has also become evident is that while the repair of reinforced concrete may make good the surface deterioration of the structure, it usually does not address the root causes of the problem.

Corrosion rates

The corrosion map of India developed by the Corrosion Advisory Bureau, NML (CSIR), indicates the corrosion rate across the country. The different regions are classified into severe corrosion, high corrosion, moderate corrosion and least corrosion and minimal corrosion belts, depending on the local environment. It is seen that a major part of the coastal regions including Chennai, Mumbai, Kolkata and Visakhapatnam fall in the severe corrosion area. These regions especially require precautions to be taken to prevent corrosion of steel thereby necessitating the need for steel protection. The remaining areas would not require this level of protection.

Protection

Corrosion of steel reinforcement in concrete is an electrochemical process which requires access of an electrolyte and oxygen to steel. Rust-stained surfaces and cracking and spelling of concrete in recently completed structures demonstrate the imperative need to protect steel reinforcement. Protective measures against corrosion rely on minimizing or preventing the corrosion (electrochemical) process. Out of the above mentioned alternatives, coating of rebars has been proved to be the best one and galvanizing has emerged as technically superior to all the other forms of coating, as it isolates the steel from direct contact with the external corrosive environment while maintaining the other factors like bond strength and strength of steel, constant.

Galvanized coatings provide important advantages for the protection of reinforcement. Research and practical experience since the 1950s have established that the corrosion resistance of galvanized steel reinforcement is superior to uncoated steel and any other type of protective measure. The corrosion protection by the galvanized coating ensures that the design strength of concrete is maintained and the possibility of surface rust staining and eventual corrosion of reinforcement and spelling of concrete are removed.

Galvanising

Galvanising process is basically the process of formation of series of alloy layers formed as a result of a metallurgical reaction between steel and zinc. Also, these alloy layers impart the hardness and abrasion resistance to the galvanised rebar which prevents peeling off of the layers in handling, and storage unlike in other coatings. This protects the steel not only inside the concrete but also in handling and storage at site. The galvanising bath is typically 8 to 13 metres in length;

also double dipping can be done for longer bars. Approved galvanizes are present across India who caters to the demand in individual geographical areas.

Aggressive Corrosion

Background

The corrosion effect of the Cowper gases can be explained as follows: It has to be seen that the Cowper work regeneratively *i.e.* at least one of the air preheaters is heated by flue gas (spent gas) up to a temperature of about 1450° C and that this flue gas contains SO_2 and SO_3 and water vapour which may form sulfuric acid by condensation. The chance for this condensation is high if the refractory lining is not sealed and so the corrosive parts of the gas have the chance to condense on the cold steel shell.

The acid-resisting cement proposed there as a protective measure against corrosion should be applied onto the steel surfaces in danger of corroding in the form of a coating without joints of for example 10 - 25 mm according to the type of fireclay spraying process. It is known that these acid-resisting cements contain quartz sand, silicate binder and hardener. The quartz sand may be present as pure SiO_2.

However, quartz sand in the natural state will be generally used. Normally, a sodium or potassium silicate binder is introduced as the binder. The dry acid-resisting cement contains about 2 - 7 vol.% silicate binder, the addition of hardener is co-ordinated to this amount and the remainder is essentially quartz sand. The hardener can be a condensed aluminum phosphate as disclosed in the German

Auslegeschrift 1,571,485 and German Patent 1,252,835 of the Hoechst Company, in amount of 0.5 to 6 vol.%, preferably 1.0 to 4 vol.%.

It has surprisingly been proved that the durability of the protective layer against corrosion, with the given purpose of usage and particularly in the case of great fluctuations in temperature, can be considerably improved if 10 - 40% vol. of the total amount of quartz is replaced by refractory materials in the form of hollow spheres. An acid-resisting cement is preferably used in which 15 to 35% vol. of the total amount of quartz, in particular 22 to 28% vol, is replaced by refractory materials in the form of hollow spheres. The amount of binder can be 2 to 7 vol.%, preferably 4 to 6 vol.%. The amount of hardener can be 0.5 to 6 vol.%, preferably 1 to 4 vol.%. The composition of the binder and hardener can be as is disclosed above for prior art cements.

Refractory materials in the form of hollow spheres belong in another context to the prior art. German Auslegeschrift 1,086,614 describes a refractory, sintered bonding body which contains a layer composed of refractory material in the form of hollow spheres for heat insulation. It can be further seen from this publication that it has been known for a long time that granules in the form of hollow spheres composed of refractory material are produced. Thus, alumina, quartz, mixtures of alumina and quartz and similar refractory materials are mentioned as material for the production of the hollow spheres.

An acid-resisting cement is preferably used according to the invention in which the refractory materials present in the form of hollow spheres of corundum (hollow sphere corundum). It remains to bear in mind that the refractory material added in the form of hollow spheres corresponds to the volume amount which was removed from the known acid-resisting cement in the form of quartz sand. This means in other words that the thickness of the layer applied does not change, however, the structure does. The thickness of the layer amounts in practice to between 5 and 15 mm. Very good results have been achieved with layer thickness of up to 8 mm.

The particular advantages of the subject of the invention is to be seen in that the proposed acid-resisting cement is more flexible to fluctuations in temperature and therefore the movements of the refractory material and the steel shell are better absorbed. It is evident that the layer does not only act as a protection against corrosion but as an insulating layer for the movements which are caused by fluctuations in temperature. The layer consequently is very flexible. It has moreover been shown that this layer is less sensitive to subsequent moisture (wetting).

On the contrary, the known acid-resisting cement becomes relatively moist after spraying so that according to the prior art technique it may result in the sprayed-on elements falling, rolling or sliding away during overhead work, *e.g.* in the cupola of the blast preheater. This subsequent wetting is known to the specialist by the term “ionisation effect” and occurs on a considerably lower scale with the subject of the application.

The acid-resisting cement proposed according to the invention is preferably used for the steel shell of the blast heating apparatus of a blast furnace and for the hot-air pipe system appertaining thereto. An acid-resisting cement according to the invention was used as protective means against corrosion to protect the cupola and the upper portion of the shaft of the blast preheater. The said acid-resisting cement, comprising quartz sand, a sodium silicate binder, a usual hardener and hollow sphere corundum, was composed as follows: 70 vol.% quartz sand; 4 vol.% sodium silicate binder, 1 vol.% of hardener, and 25 vol.% as hollow sphere corundum. The diameter of the hollow sphere corundum used was between about 0.06 and 2 mm. The diameter of the greater part of the hollow sphere corundum was about 1mm.

The acid-resisting cement serving as a protective means against corrosion was applied by the spraying process to the surface of the steel without anchorage by means of a rotor machine, which works continuously according to a revolving system. The dry means is mixed shortly before spraying with 14 wt.% water, based on the total weight of the dry means.

The surfaces which were to be protected were continuously covered with the protective means against corrosion without seams, the thickness of the layer amounting to about 8mm. The sprayed-on means was set after about 12 hours with the temperature of the sheet metal at about 20° C. Further lining comprising insulating layers and a refractory layer was then applied. Preferably the further lining consists of bricks.

With comparable positive result the blast air steel pipes belonging to the blast heating apparatus of the blast furance were sprayed with the protective means against corrosion according to the invention and then lined with two insulating layers and a refractory layer.

The invention has been explained in detail by the example blast furnace and regeneration air preheaters as for this example the fluctuations in temperature during the regenerative phases amount to about 500° C.. It has to be recognized that the invention is also suitable for protecting the steel shell if the preheated is used to preheat reduction gas as in necessary for alternative processes for the blast furnace process.

Nano Cycle

In the water-use cycle, water moves from a source to a point of use, and then to a point of disposition. The sources of water are either surface water or groundwater. Water is withdrawn and moved from a source to a point of use, such as an industry, restaurant, home, or farm. After water is used, it must be disposed of (or sometimes, reused). Used water is either directly returned to the environment or passes through a treatment processing plant before being returned.

The Geological Survey compiles nationwide water-use data every 5 years. Even though discussions of water use typically focus on fresh-water use, saline water use also is important in countries. Some categories of water use, such as thermoelectric, industrial, and mining, use saline water, mainly for cooling generators in thermoelectric power plants. Industries and mines use saline water to cool machinery and to wash and transport products, mainly for cooling of machinery.

After continual increases in the nation’s total water withdrawals (fresh water and saline water) for the years reported from 1950 to 1980, withdrawals declined from 1980 to 1985 and remained fairly constant from 1985 to 1995. The 1995 estimate of total withdrawals (402,000 MGD) is about 2 per cent less than the 1990 estimate and nearly 10 per cent less than the peak year of 1980. Likewise, total freshwater withdrawals for 1995 were about 8 per cent less than in 1980.

The decline in withdrawals is especially significant in light of the fact that population posted an increase of 16 per cent during the same period. Clearly as a nation, the countries are using its surface water and groundwater resources more efficiently. This decline signals that water use responds to economic and regulatory factors, and that the general public has an enhanced awareness of water resources and conservation issues.

The public supply, domestic, and livestock categories are the only categories to show continual increases from 1950 to 1995, largely because of continual increases in population. The increase of 4 per cent in public supply withdrawals from 1990 to 1995, compared to the population increase of 7 per cent served by public supply, indicates that conservation programmes have been effective in lowering public supply per capita use from about 184 gallons per day (GPD) in 1990 to 179 GPD in 1995. More water continues to be withdrawn for thermoelectric power generation than for any other category. Withdrawals for thermoelectric power generation peaked in 1980 at 210,000 MGD and fluctuated around 190,000 MGD during 1985, 1990, and 1995.

Industrial withdrawals declined from 1980 to 1995 after remaining about the same for the years reported between 1965 and 1980. Lower industrial withdrawals are the result of new industries and technologies that require less water, improved plant efficiencies, increased water recycling; changes in laws and regulations to reduce the discharge of pollutants; and conservation measures.

Nano Softening

Hardness

Carbon dioxide reacts with water to form carbonic acid which at ordinary environmental pH exists mostly as bicarbonate ion. Microscopic marine organisms take this up as carbonate to form calcite skeletons which, over millions of years, have built up extensive limestone deposits. Groundwater, made slightly acidic by CO_2 (both that absorbed from the air and from the respiration of soil bacteria) dissolve the limestone, thereby acquiring calcium and bicarbonate ions and becoming "hard". These "hardness ions" cause two major kinds of problems. First, the metal captions react with soaps, causing them to form an unsightly precipitate— the familiar "bathtub ring". More seriously, the calcium and magnesium carbonates tend to precipitate out as adherent solids on the surfaces of pipes and especially on the hot heat exchanger surfaces of boilers. The resulting scale buildup can impede water flow in pipes. In boilers, the deposits act as thermal insulation that impedes the flow of heat into the water; this not only reduces heating efficiency, but allows the metal to overheat, which in pressurized systems can lead to catastrophic failure.

Temporary Hardness

Most conventional water-softening devices depend on a process known as *ion-exchange* in which "hardness" ions trade places with sodium and chloride ions that are loosely bound to an *ion-exchange resin* or a *zeolite* (many zeolite minerals occur in nature, but specialized ones are often made artificially.)

In a similar way, positively-charged zeolites bind negatively-charged chloride ions (Cl^-), which get displaced by bicarbonate ions in the water. As the zeolites become converted to their Ca^{2+} and HCO_3^- forms they gradually lose their effectiveness and must be regenerated. This is accomplished by passing a concentrated brine solution though them, causing the above reaction to be reversed. Herein lies one of the drawbacks of this process: most of the salt employed in the regeneration process gets flushed out of the system and is usually released into the soil or drainage system something that can have damaging consequences to the environment, especially in arid regions. For this reason, many jurisdictions prohibit such release, and require users to dispose of the spent brine at an approved site or to use a commercial service company.

The great economic importance of water softening has created a large and thriving industry that utilizes a number of proven methods based on well established scientific principles. It has also unfortunately attracted a variety of operators offering technologies that are purported to be better, less expensive, easier to install, or “chemical-free”, but which have never been validated scientifically and whose principles of operation are largely unexplained by the known laws of chemistry.

This does not mean that such schemes cannot work (after all, we can use theory to show that under idealized conditions, water can never boil and it can never rain!), but it should inspire a good degree of skepticism. Most of the statements supporting alternative water treatment methods come from those who have a commercial interest in these devices, they are not supported by credible and independently verifiable performance data, and the explanations they offer for how they work reveal such a weak understanding of basic chemistry on the part of their authors that it is difficult to have much confidence in them.

Against this, there is some anecdotal evidence that certain magnetic and electromagnetic devices can be effective in preventing scale formation in hard water systems. It is very difficult to judge such claims, which are almost never based on tests that are well enough described to allow others to evaluate them and to verify the results. While the lack of "scientific" evidence does not in itself invalidate a claim for the efficacy of a device, it should make one hesitate to accept it without some guarantee of performance.

Nano device and method

The invention is concerned with a water softening device for application in automatic washing machines, more particularly, a water softening device based on capacitive deionization in a flow-through capacitor for obtaining water that is suitable for use with detergent products having low environmental impact.

In recent years one has become increasingly aware of the impact of human activities on the environment and the negative consequences this may have. Ways to reduce, reuse and recycle resources are becoming more important. Fabric cleaning is one of the many household activities with a significant environmental impact. This is partly caused by the use of conventional detergent products, which tend to be relatively complex compositions with a variety of ingredients.

Over the years some ingredients have been banned by legislation in certain countries because of their adverse environmental effects. Examples include certain nonionic surfactants and builders such as phosphates. The use of phosphates in detergents has been linked to increased levels of phosphates in surface waters. The resulting eutrophication is thought to cause an increased growth of algae. The increased algae growth in stagnant surface water leads to oxygen depletion in lower water layers, which in turn causes general reduction of overall water quality.

Although some ingredients in conventional laundry detergent products may have a limited environmental effect, the energy involved in the production thereof influences the environmental impact during their life cycle negatively. Life cycle analysis typically estimates the environmental impact of a product during the different phases such as production of raw material, production of the product itself, distribution to the end user, use of the product by for example the consumer and the disposal after use.

Environmental impact may include factors like eutrophication, green house effect, acidification and photo-chemical oxidant formation. With respect to laundry detergent products, extra ingredients necessarily add cost, volume and weight to the product, which in turn requires more packaging material and transport costs. Extra ingredients usually require a more complex production process.

However, it is difficult to reduce the number and/or amount of the ingredients without reducing the cleaning efficiency. One of the most bulky ingredients of common laundry detergents are so-called builders like for example zeolites, phosphates, soaps and carbonates. Builders are added to laundry detergent formulations for their ability to sequester hardness-ions like Ca^{2+} and Mg^{2+}. The reduction of hardness ions is required in order to prevent the deposition of calcium soaps in the soil, to prevent the precipitation of anionic surfactants, to maximise colloid stability and to reduce the calcium-soil-substrate-interaction and soil-soil interaction and hence to improve soil removal.

Apart from their positive effects, common builders also may have negative effects on laundry cleaning processes. Builders often generate insoluble materials in the wash either as such or by formation of precipitates. For example, zeolites are insoluble and may cause incrustation of fabrics and precipitates of calcium-builder-complex result in higher redepositioning.

In short, builders are required for sequestering hardness ions to improve wash efficiency, but have a negative environmental effect and generate insoluble precipitates that may cause redepositioning on the fabric articles and thereby reduce the wash efficiency. However, the requirement for builder material may be reduced when soft water is used in the washing process.

Different methods are known in the art to produce soft water by sequestering hardness-ions like Ca^{2+} and Mg^{2+} from tap water, for instance by ion-exchange. In WO01/30229, a system is described, which utilizes a built-in ion-exchange system to remove calcium and magnesium ions from the water supply. However, the ion-exchange material requires regular regeneration. For application in a common type of automatic washing machine, vast amounts of *e.g.* salt solution would be required for the regeneration of the ion-exchanger, thereby undoing the effect of the reduction of builder chemicals in the detergent. Further disadvantages of ion-exchange are the limited life-time of the ion-exchange resin and/or the required volume of resin for the production of the amount of soft water required in a washing machine.

Another water softening method is electronic deionization (EDI), which combines ion exchange and electro dialysis, as described in co-pending application 04076353.4. Although this method does not require regeneration chemicals, the other disadvantages of the ion-exchange resin remain as indicated above. Furthermore, EDI is a complicated technology, that is difficult to operate in a robust manner over a long time period, as required in house-hold appliances.

A known method for water treatment is capacitive deionization, using a flow through capacitor (FTC) as among others described in U.S. Said method comprises the use of an electrically regenerable electrochemical cell for capacitive deionization and electrochemical purification and regeneration of the electrodes including two end plates, one at each end of the cell. By polarizing the cell, ions are removed from the electrolyte and are held in the electric double layers at the electrodes. The cell can be (partially) regenerated electrically to desorbs such previously removed ions. The regeneration could be carried out without added chemical substances. The term charge barrier refers to a layer of material which is permeable or semi-permeable and is capable of holding an electric charge. Pore volume ions are retained, or trapped, on the side of the charge barrier towards which the like-charged ions migrate.

Generally, a charge barrier functions by forming a concentrated layer of ions. The effect of forming a concentrated layer of ions balances out, or compensates for, the losses ordinarily associated with pore volume ions. This effect allows a large increase in ionic efficiency, which in turn allows energy efficient purification of concentrated fluids. Using the charge barrier flow-through capacitor in the purification of water has been observed at an energy level of less than 1 joules per coulomb ions purified, for example, 0.5 joules per coulomb ions purified, with an ionic efficiency of over 90%.

It is an object of the present invention to find a cost-effective method having low environmental impact for removing hardness ions from tap water. It is another object of the invention to find a cost-effective method having low environmental impact both for removing hardness ions from tap water and for modifying the pH. Another object of the present invention is to find a method for removing hardness ions from tap water and for modifying the pH of said water in a manner that is robust, long lasting, and convenient and user friendly to consumers.

It is a further object of the invention to find a method to remove hardness ions from the tap water, without the need for added chemicals or vast amounts of water. It is another object of the invention to find a method to remove hardness ions from a softening device, without the need for added chemicals or vast amounts of water.

Yet another object of the invention is to find a suitable method for treating tap water such that water is obtained that is suitable for use with a low environmental impact detergent product (LEIP, as defined herein), in fabric cleaning methods. A still further object of the invention is to find a cleaning method wherein water obtained from such a water treatment method can be suitably used with a LEIP in in-home cleaning appliances, such as a fabric washing machine.

Nano corrosion

The process of corrosion however is a complex electro chemical reaction and it takes many forms. Corrosion may produce general attach over a large metal surface or it may result in pinpoint penetration of metal. Corrosion is a relevant problem caused by water in boilers. Corrosion can be of widely varying origin and nature due to the action of dissolved oxygen, to corrosion currents set up as a result of heterogeneities on metal surfaces, or to the iron being directly attacked by the water.

While basic corrosion in boilers may be primarily due to reaction of the metal with oxygen, other factors such as stresses, acid conditions, and specific chemical corrodents may have an important influence and produce different forms of attack. It is necessary to consider the quantity of the various harmful substances that can be allowed in the boiler water without risk of damage to the boiler. Corrosion may occur in the feed-water system as a result of low pH water and the presence of dissolved oxygen and carbon dioxide.

Starting form these figures and allowing the amount that can be blown down, the permitted concentration in the make-up water is thus defined. Corrosion is caused principally by complex oxide-slag with low melting points. High temperature corrosion can proceed only if the corroding deposit is in the liquid phase and the liquid is in direct contact with the metal. Deposits also promote the transport of oxygen to the metal surface. Corrosion in the boiler proper generally occurs when the boiler water alkalinity is low or when the metal is exposed to oxygen bearing water either during operation or idle periods.

High temperatures and stresses in the boiler metal tend to accelerate the corrosive mechanisms. In the steam and condensate system corrosion is generally the result of contamination with carbon dioxide and oxygen. Specific contaminants such as ammonia or sulphur bearing gases may increase attack on copper alloys in the system.

Metals

Cracking in boiler metal may occur by two different mechanisms. In the first mechanism, cyclic stresses are created by rapid heating and cooling and are concentrated at points where corrosion has roughened or pitted the metal surface. This is usually associated with improper corrosion prevention. The second type of corrosion fatigue cracking occurs in boilers with properly treated water.

In these cases corrosion fatigue is probably a misnomer. These cracks often originate where a dense protective oxide film covers the metal surfaces and cracking occurs from the action of applied cyclic stresses. Corrosion fatigue cracks are usually thick, blunt and cross the metal grains. They usually start at internal tube surfaces and are most often circumferential on the tube.

Corrosion control techniques vary according to the type of corrosion encountered. Major methods include maintenance of the proper pH, control of oxygen, control of deposits, and reduction of stresses trough design and operational practices. Deaeration and recently the use of membrane contractors are the best and most diffused ways to avoid corrosion removing the dissolved gasses (mainly O_2 and CO_2).

Foaming

Bubbles or froth actually build up on the surface of the boiler water and pass out with the steam. This is called foaming and it is caused by high concentration of any solids in the boiler water. It is generally believed, however, that specific substances such as alkalis, oils, fats, greases, certain types of organic matter and suspended solids are particularly conducive to foaming. In theory suspended solids collect in the surface film surrounding a steam bubble and make it tougher. The steam bubble therefore resists breaking and builds up foam. It is believed that the finer the suspended particles the greater their collection in the bubble.

Priming is the carryover of varying amounts of droplets of water in the steam (foam and mist), which lowers the energy efficiency of the steam and leads to the deposit of salt crystals on the super heaters and in the turbines. Priming may be caused by improper construction of boiler, excessive ratings, or sudden fluctuations in steam demand. Priming is sometimes aggravated by impurities in the boiler-water.

Some mechanical entertainment of minute drops of boiler water in the steam always occurs. When this boiler water carryover is excessive, steam-carried solids produce turbine blade deposits. The accumulations have a composition similar to that of the dissolved solids in the boiler water. Priming is common cause of high levels of boiler water carryover. These conditions often lead to super heater tube failures as well. Priming is related to the viscosity of the water and its tendency to foam. These properties are governed by alkalinity, the presence of certain organic substances and by total salinity or TDS. The degree of priming also depends on the design of the boiler and its steaming rate.

The most common measure to prevent foaming and priming is to maintain the concentration of solids in the boiler water at reasonably low levels. Avoiding high water levels, excessive boiler loads, and sudden load changes also helps. Very often contaminated condensate returned to the boiler system causes carry-over problems. In these cases the condensate should be temporarily wasted until the source of contamination is found and eliminated. The use of chemical anti-foaming and anti-priming agents, mixtures of surface-active agents that modify the surface tension of a liquid, remove foam and prevent the carry-over of fine water particles in the stream, can be very effective in preventing carry-over due to high concentrations of impurities in the boiler-water.

Nano energy meters

Sourcing fresh water from streams, rivers, lakes and underground aquifers and adhering to strict water conservation measures are much more viable for both economic and environmental reasons in most situations, although some desert regions with thirsty and growing populations may not have many such options. The relationship between desalinization and climate change is complex. Global warming has increased droughts around the world and turned formerly verdant landscapes into near deserts. Some long held fresh water sources are simply no longer reliably available to hundreds of millions of people around the world.

Meanwhile, expanding populations in desert areas are putting intense pressure on existing fresh water supplies, forcing communities to turn to desalinization as the most expedient way to satisfy their collective thirst. But the process of desalinization burns up many more fossil fuels than sourcing the equivalent amount of fresh water from fresh water bodies. As such, the very proliferation of desalinization plants around the world, some 13,000 already supply fresh water in 120 nations, primarily in the Middle East, North Africa and Caribbean, is both a reaction to and one of many contributors to global warming.

Beyond the links to climate problems, marine biologists warn that widespread desalinization could take a heavy toll on ocean biodiversity; as such facilities' intake pipes essentially vacuum up and inadvertently kill millions of plankton, fish eggs, fish larvae and other microbial organisms that constitute the base layer of the marine food chain. And, according to Jeffrey Graham of the Scripps Institute of Oceanography's Center for Marine Biotechnology and Biomedicine, the salty sludge leftover after desalinization for every gallon of freshwater produced, another gallon of doubly concentrated salt water must be disposed of can wreak havoc on marine ecosystems if dumped willy-nilly offshore. For some desalinization operations, says Graham, it is thought that the disappearance of some organisms from discharge areas may be related to the salty outflow.

Sources

The world's water consumption rate is doubling every 20 years, outpacing by two times the rate of population growth. It is projected that by the year 2025 water demand will exceed supply by 56%, due to persistent regional droughts, shifting of the population to urban coastal cities, and water needed for industrial growth. The supply of fresh water is on the decrease. Water demand for food, industry and people is on the rise. Lack of fresh water reduces economic development and lowers living standards. Clearly, there is a critical worldwide need to better manage this increasingly valuable resource. Desalination systems from GE Water and Process Technologies can make abundant fresh water both from seawater and from challenging brackish sources.

Oceans make up 97% of the world's supply of water. Desalination using seawater reverse osmosis (SWRO) membrane technology has become a viable option for the development of new regional water supplies. GE Water and Process Technologies is the world leader in the supply of reliable seawater SWRO membrane desalination systems. GE's desalination projects range in size from small 2,000 cubic meter/day (370 gpm) plants — providing potable water to hotels and resort complexes — all the way up to projects like the 200,000 cubic meter/day (53 MGD) Hamma Desalination Plant, the largest of its kind in Africa. Hamma supplies desperately-needed drinking water to over 20% of the population of Algeria's capital city.

Effective mineral and salt removal converts previously unusable waters to high-purity resources for drinking, irrigation or industrial process uses. GE pioneered brackish water desalination in the early 1950s and continues to lead the way withcost-effective, environmentally friendly treatment systems for groundwater and surface water sources. Our global installed capacity includes approximately 250 mgd (950,000 m3/day) of EDR systems and 600 mgd (2.3 million m3/day) of RO systems.

Nano Environment

The oxygen can come from air or water. Iron oxide is actually more stable than pure iron or steel and therefore rusting is very common. Prevention of rust is actually a means of retaining a less stable or higher energy, state. Humans have most likely been trying to understand and control corrosion for as long as they have been using metal objects. The most important periods of prerecorded history are named for the metals that were used for tools and weapons. With a few exceptions, metals are unstable in ordinary aqueous environments. Metals are usually extracted from ores through the application of aconsiderable amount of energy.

Certain environments offer opportunities for these metals to combine chemically with elements to form compounds and return to their lower energy levels. Corrosion is the primary means by which metals deteriorate. Most metals corrode on contact with water (and moisture in the air), acids, bases, salts, oils, aggressive metal polishes, and other solid and liquid chemicals. Metals will also corrode when exposed to gaseous materials like acid vapours, formaldehyde gas, ammonia gas, and sulfur containing gases. Corrosion specifically refers to any process involving the deterioration or degradation of metal components. The best known case is that of the *rusting of steel*. Corrosion processes are usually electrochemical in nature, having the essential features of a battery.

When metal atoms are exposed to an environment containing water molecules they can give up electrons, becoming themselves positively charged ions, provided an electrical circuit can be completed. This effect can be concentrated locally to *form a pit* or, *sometimes a crack*, or it can extend across a wide area to produce general wastage. *Localized corrosion* that leads to pitting may provide sites for fatigue initiation and, additionally, corrosive agents like seawater may lead to greatly enhanced growth of the fatigue crack. *Pitting corrosion* also occurs much faster in areas where *microstructural changes* have occurred due to welding operations. The corrosion process (anodic reaction) of the metal dissolving as ions generates some electrons, as shown in the simple model on the left, that are consumed by a secondary process (cathodic reaction). These two processes have to balance their charges.

Reaction

The anodic reaction may occur uniformly over a metal surface or may be localized to a specific area. If the dissolved metal ion can react with the solution to form an insoluble compound, then a buildup of corrosion products may accumulate at the anodic site. In the absence of any applied voltage, the electrons generated by the anodic reaction are consumed by the cathodic reaction. For most practical situations, the cathodic reaction is either the hydrogen-evolution reaction or the oxygen-reduction reaction. The hydrogen-evolution reaction can be summarized as reaction.

Reactions above represent the overall reactions which, in practice, may occur by a sequence of reaction steps. In addition, the reaction sequence may be dependent upon the metal surface, resulting in significantly different rates of the overall reaction.

The cathodic reactions are important to corrosion processes since many methods of corrosion control depend on altering the cathodic process. Although the cathodic reactions may be related to corrosion processes which are usually unwanted, they are essential for many applications such as energy storage and generation.

Corrosion rates are usually expressed in terms of loss of thickness per unit time. General corrosion rates may vary from on the order of centimeters per year to micrometers per year. Relatively large corrosion rates may be tolerated for some large structures, whereas for other structures small amounts of corrosion may result in catastrophic failure. For example, with the advent of technology for making extremely small devices, future generations of integrated circuits will contain components that are on the order of nanometers (10^{-9} m) in size, and even small amounts of corrosion could cause a device failure.

In some situations, corrosion may occur only at localized regions on a metal surface. This type of corrosion is characterized by regions of locally severe corrosion, although the general loss of thickness may be relatively small. Pitting corrosion is usually associated with passive metals, although this is not always the case. Pit initiation is usually related to the local breakdown of a passive film and can often be related to the presence of halide ions in solution.

Crevice corrosion occurs in restricted or occluded regions, such as at a bolted joint, and is often associated with solutions that contain halide ions. Crevice corrosion is initiated by a depletion of the dissolved oxygen in the restricted region. As the supply of oxygen within the crevice is depleted, because of cathodic oxygen reduction, the metal surface within the crevice becomes activated, and the anodic current is balanced by cathodic oxygen reduction from the region adjacent to the crevice. The ensuing reactions within the crevice are the same as those described for pitting corrosion: halide ions migrate to the crevice, where they are then hydrolyzed to form metal hydroxides and hydrochloric acid.

Corrosion can also be accelerated in situations where two dissimilar metals are in contact in the same solution. This form of corrosion is known as galvanic corrosion. The metal with the more negative potential becomes the anode, while the metal with the more positive potential sustains the cathodic reaction. In many cases the table of equilibrium potential can be used to predict which metal of galvanic couple will corrode. For example, aluminum-graphite composites generally exhibit poor corrosion resistance since graphite has a positive potential and aluminum exhibits a highly negative potential. As a result, in corrosive environments the aluminum will tend to corrode while the graphite remains unaffected.

Stress corrosion cracking and hydrogen embrittlement are corrosion-related phenomena associated with the presence of a tensile stress. Stress corrosion cracking results from a combination of stress and specific environmental conditions so that localized corrosion initiates cracks that propagate in the presence of stress. Mild steels are susceptible to stress corrosion cracking in environments containing hydroxyl ions (O≈; often called caustic cracking) or nitrate ions ($NO_3^{''}$). Austenitic stainless steels are susceptible in the presence of chloride ions ($Cl^{”}$) and hydroxyl ions (O≈).

Other alloys that are susceptible under specific conditions include certain brasses, aluminum and titanium alloys. Hydrogen embrittlement is caused by the entry of hydrogen atoms into a metal or alloy, resulting in a loss of ductility or cracking if the stress level is sufficiently high. The source of the hydrogen is usually from corrosion (that is, cathodic hydrogen evolution) or from cathodic polarization. In these cases the presence of certain substances in the metal or electrolyte can enhance the amount of hydrogen entry into the alloy by poisoning the formation of molecular hydrogen. Metals and alloys that are susceptible to hydrogen embrittlement include certain carbon steels, high-strength steels, nickel-based alloys, titanium alloys, and some aluminum alloys.

A reduction in the rate of corrosion is usually achieved through consideration of the materials or the environment. Materials selection is usually determined by economic constraints. The corrosion resistance of a specific metal or alloy may be limited to a certain range of pH, potential, or anion concentration. As a result, replacement metal or alloy systems are usually selected on the basis of cost for an estimated service lifetime.

Electron Transfer

Wet corrosion of metals occurs through electron transfer, involving two processes, oxidation and reduction. In oxidation, the metal atoms lose electrons. The surrounding environment then gains the electrons in reduction. The metal, where electrons are lost, is called the anode. The other metal, liquid or gas which gains the electrons is called the cathode.

The corrosion resistance of aluminium varies widely depending on alloy, environment, design and protective measures taken. However, it is possible to give some general guide-lines.

A clean aluminium surface is reactive and will react spontaneously with water or air and form aluminium oxide. This oxide is very stable and has in addition a very good adhesion to the metal surface and thus protects aluminium from corrosion or further oxidation. This means that aluminium has good corrosion resistance in environments where the oxide layer is stable. Aggressive ions will break down the oxide layer locally and start local corrosion attacks. Among the aggressive ions, chloride (Cl-), is the one with the most practical importance, because it is present in large amounts in both sea-water, road salts and some soils and in lower concentrations in other natural sources.

A so called general corrosion attack proceeds at about the same rate on the entire metal surface. Because of the stability of the oxide layer, general corrosion will rarely be a problem on aluminium, except in very alkaline or acidic environments. Aluminium may however experience local attacks in connection with formation of small anodic areas as a result of a local breakdown of the oxide layer. Some of the most typical local attacks on aluminium are pitting corrosion, crevice corrosion, intergranular corrosion and galvanic corrosion.

When there is a relative movement between the corrosive liquid and the metal surface, the metal may be exposed to mechanical wear which removes the protective oxide layer and enhances the corrosion. This is called flow influenced corrosion and can be further divided into;

Erosion

Pure erosion is caused by a shear force from a flowing liquid which is higher than the adhesion of the oxide layer on the aluminium surface. The shear force from the liquid may be increased by turbulence or dissolved or suspended solids causing abrasion. The shear force from the liquid is not necessarily caused by liquid flow, but can also be induced by a moving surface for example a propeller.

If the removal of the oxide layer occurs in a corrosive liquid, the corrosion will be enhanced because a bare aluminium surface will be exposed to the liquid for a while until the oxide layer is healed. This is called erosion-corrosion. The rapid self healing of the oxide layer on aluminium is a great advantage with regards to erosion-corrosion, but because aluminium is a fairly soft material, erosion-corrosion can be a serious problem.

The shear force from the liquid on the metal surface is the main design criteria with regards to erosion corrosion. In practice, this is often transferred to flow rate limits. For the same flow rate, the shear force in a small diameter tube will be higher than in a large diameter tube, but the differences will be small for normal flow rates. If the liquid contains no solids and in smooth pipes, with undisturbed flow, the tolerable flow rate will be fairly high, but normally some turbulence must be expected and the flow rate limitations must be decided, based on these critical areas. Crevice corrosion occurs in narrow metal to metal or non-metal to metal gaps where the convection of water is hampered and a specific crevice chemistry different from the environment is allowed to develop. Aggressive ions like chlorides must be present in the electrolyte. The oxygen in the bottom of the crevice is consumed and an anodic area is developed adjacent to the oxygen depleted zone. Crevice corrosion develops quite similar to pitting corrosion after the initiation stage, with a gradual decrease of the pH and an increase of the chloride concentration within the crevice.

Crevice corrosion is normally not a serious problem on aluminium in the absence of aggressive ions, because of the very stable aluminiumoxide. However in a crevice there will be a possibility for accumulation of moisture because of capillary forces and deposits with corrosive or hygroscopic species. In this way there will be a constant corrosive environment in the crevice which eventually can break down the oxide layer.

Crevice corrosion can occur during storage of aluminium such as water-staining which creates dark stains as a result of a surface etching caused by water trapped between the adjacent surfaces. It is most commonly seen on sheet products and is mainly an aesthetic problem as the mechanical integrity of the water stained aluminium is rarely impaired.

Stress Corrosion

Stress corrosion is another form of corrosion that is important to many fields including civil structures. Stress-corrosion occurs when a material exists in a relatively inert environment but corrodes due to an applied stress. The stress may be externally applied or residual. This form of corrosion is particularly dangerous because it may not occur under a particular set of conditions until there is an applied stress. The corrosion is not clearly visible prior to fracture and can result in catastrophic failure. Many alloys can experience stress corrosion, and the applied stress may also be due to a residual stress in the material. An example of a residual stress could be a stress remaining in a material after forming, or a stress due to welding.

Stress corrosion cracking will usually cause the material to fail in a brittle manner, which can have grave consequences as there is usually little or no warning before the failure occurs. Stress corrosion is a form of galvanic corrosion, where stressed areas of the material are anodic to the unstressed areas of the material. Practically the best way to control stress corrosion cracking is to limit or reduce the stresses a material is under while it is in a corrosive atmosphere.

Room Temperature

Introduction

At room temperature, most metals carry a thin oxide layer as a result of the reaction of metals with oxygen in the atmosphere. Increase of temperature may cause formation of a heavier layer, or the layer may detach. Zinc and zinc coatings carry a fairly protective zinc hydroxide or carbonate layer (zinc patina) which increases in thickness very slowly. Aluminium carries a thin, highly protective oxide layer. Some corrosion takes place even under completely dry conditions.

Recently, we invented novel nanocrystalline metal-base nanocomposites distributing nanoparticles of Cr or/and Al through co-electrodeposition of metal matrix with nanoparticles These nanocomposites containing appropriate contents of Cr or/and Al can quickly form protective films, when they are suffered the attack of corrosive species at ambient or high temperatures. Hence, they exhibit excellent corrosion resistance, as compared to conventionally coarse-grained (CG) alloys. These kinds of nanocomposites are proposed as surface coatings for metals against liquid corrosion hot corrosion and high temperature oxidation Moreover, the nanocomposites contain numerous grain boundaries (GBs); this causes highly enhanced diffusion kinetics of atoms in them with respect to in the CG alloy counterparts. For this reason, the nanocomposites may be applied to metals as precursor films for chemical heat treatment such as nitridation to further improve their surface properties for various proposes.

This improvement of surface properties would be more significantly, if the chemical treatment on the nanocomposites is conducted at temperatures greatly lower than normal temperatures adopted by similar treatment on conventional CG alloys. In this paper, the fabrication, wet and dry corrosion behaviours, and plasma nitridation performance of the types of electrodeposited nanocomposites (ENCs) are we briefly reviewed taking ENC Ni-Cr as an example.

Atmospheric conditions

Components exposed to the elements will inevitably experience damage due to atmospheric corrosion. The severity of the corrosion and the rate at which corrosion will take place are dependant primarily upon the properties of the surface formed electrolytes, which in turn are dependant upon factors such as the humidity and pollution levels in the atmosphere.

Mechanism

Atmospheric corrosion is an electrochemical process, requiring the presence of an electrolyte. Thin film “invisible” electrolytes tend to form on metallic surfaces under atmospheric corrosion conditions, when a certain critical humidity level is reached.

For iron, this level is around 60%, in unpolluted atmospheres. The critical humidity level is not a constant - it depends on the corroding material, the hygroscopic nature of corrosion products and surface deposits and the presence of atmospheric pollutants.

Conditions

A defining feature of atmospheric corrosion is the thin aqueous layer between the surface of the corroding material and the atmosphere.

Three phases (solid [corroding substrate], liquid [thin aqueous layer] and gaseous [atmosphere]) and the interfaces between these phases are therefore important and can be used in corrosion monitoring principles..Corrosion monitoring in outdoor and indoor atmospheres poses specific challenges related to characterizing corrosion damage (generally taking place at a low rate) in a short (practical) time frame.

Category

The main drawbacks of the direct measurement approach are the lengthy exposure time period usually required and that only a “snapshot” of cumulative damage is obtained when detailed analysis of corrosion damage is performed periodically.

The approach of atmospheric corrosivity classification is generally one of a simple, low-cost measurement in a short time frame. Ultimately, such simplistic measurements require correlation to actual long term service performance and therefore need to be linked to the other measurement methodologies. Atmospheric corrosion monitoring is generally employed to quantify this type of damage and corrosion risk, rather than merely resorting to broadly descriptive atmospheric classifications such as “industrial”, “rural”, etc.

Chemical Reactions

Introduction

Chemical reactions involving almost each of the existing elements are known to take place in soils, many of which are not yet fully understood. The relative importance of variables changes for different materials, making a universal guide to corrosion impossible. Variations in soil properties and characteristics across three dimensions can have a major impact on corrosion of buried structures.

In the presence of thin film electrolytes, atmospheric corrosion proceeds by balancing anodic and cathodic reactions. The anodic oxidation reaction involves the dissolution of the metal in the electrolyte, while the cathodic reaction is often assumed to be the oxygen reduction reaction. Oxygen from the atmosphere is readily supplied to the electrolyte, under thin film corrosion conditions. Variations in soil properties and characteristics across three dimensions can have a major impact on corrosion of buried structures.

The response of carbon steel to soil corrosion depends primarily on the nature of the soil and certain other environmental factors, such as the availability to moisture and oxygen.

These factors can lead to extreme variations in the rate of the attack. For example, under the worst condition a buried vessel may perforate in less than one year, although archaeological digs in arid desert regions have uncovered iron tools that are hundreds of years old.

Some general rules can be formulated. Soils with high moisture content, high electrical conductivity, high acidity, and high dissolved salts will be most corrosive.

The effect of aeration on soils is somewhat different from the effect of aeration in water because poorly aerated conditions in water can lead to accelerated attack by sulfate-reducing anaerobic bacteria.

Classification

Soil texture refers to the size distribution of mineral particles in a soil. Sand (rated from coarse to very fine), silt and clay refer to textures of decreasing particle coarseness. Soils with a high proportion of sand have very limited storage capacity for water, whereas clays are excellent in retaining water. A newer soil classification system has evolved in the country that can be utilized to classify soils globally, at any location. In this “universal” classification system soils are considered as individual three- dimensional entities that can be grouped according to similar physical, chemical and mineralogical properties.

2

Nanoelectronic Devices

Radios

Nanoradios have been developed structured around carbon nanotubes.

Computers

Nanoelectronics holds the promise of making computer processors more powerful than are possible with conventional semiconductor fabrication techniques. A number of approaches are currently being researched, including new forms of nanolithography, as well as the use of nanomaterials such as nanowires or small molecules in place of traditional CMOS components. Field effect transistors have been made using both semiconducting carbon nanotubes and with heterostructured semiconductor nanowires.

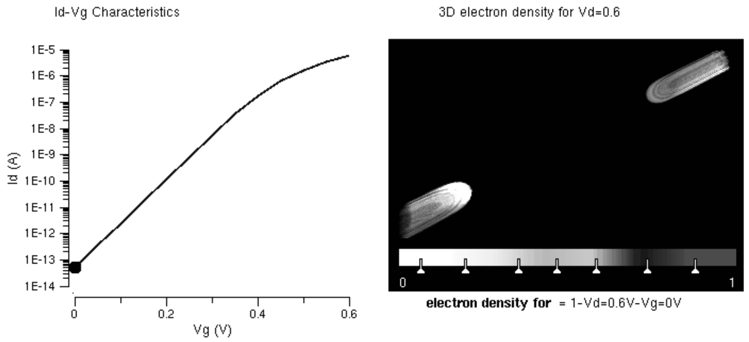


Fig. Simulation result for formation of inversion channel (electron density) and attainment of threshold voltage (IV) in a nanowire MOSFET. Note that the threshold voltage for this device lies around 0.45V.

Energy Production

Research is ongoing to use nanowires and other nanostructured materials with the hope to create cheaper and more efficient solar cells than are possible with conventional planar silicon solar cells. It is believed that the invention of more efficient solar energy would have a great effect on satisfying global energy needs.

There is also research into energy production for devices that would operate *in vivo*, called bio-nano generators. A bio-nano generator is a nanoscale electrochemical device, like a fuel cell or galvanic cell, but drawing power from blood glucose in a living body, much the same as how the body generates energy from food. To achieve the effect, an enzyme is used that is capable of stripping glucose of its electrons, freeing them for use in electrical devices. The average person's body could, theoretically, generate 100 watts of electricity (about 2000 food calories per day) using a bio-nano generator. However, this estimate is only true if all food was converted to electricity, and the human body needs some energy consistently, so possible power generated is likely much lower. The electricity generated by such a device could power devices embedded in the body (such as pacemakers), or sugar-fed nanorobots. Much of the research done on bio-nano generators is still experimental, with Panasonic's Nanotechnology Research Laboratory among those at the forefront.

Medical Diagnostics

There is great interest in constructing nanoelectronic devices that could detect the concentrations of biomolecules in real time for use as medical diagnostics, thus falling into the category of nanomedicine. A parallel line of research seeks to create nanoelectronic devices which could interact with single cells for use in basic biological research. These devices are called nanosensors. Such miniaturization on nanoelectronics towards in vivo proteomic sensing should enable new approaches for health monitoring, surveillance, and defense technology.

Molecular Scale Electronics

Molecular scale electronics, also called single molecule electronics, is a branch of nanotechnology that uses single molecules, or nanoscale collections of single molecules, as electronic components. Because single molecules constitute the smallest stable structures imaginable this miniaturization is the ultimate goal for shrinking electrical circuits. The field is often referred to as simply “molecular electronics”, but this term is also used to refer to the distantly related field of conductive polymers and organic electronics, which uses the properties of molecules to affect the bulk properties of a material. A nomenclature distinction has been suggested so that *molecular materials for electronics* refers to this latter field of bulk applications, while *molecular scale electronics* refers to the nanoscale single-molecule applications discussed here.

Fundamental Concepts

Conventional electronics have traditionally been made from bulk materials. Ever since its invention in 1958 the performance and complexity of integrated circuits has been growing exponentially (a trend also known as Moore's law) and has forced the feature sizes of the embedded components to shrink accordingly. As the structures become smaller, the sensitivity for deviations increases and in a few generations, when the minimum feature sizes reaches 13 nm, the composition of the devices must be controlled to a precision of a few atoms for the devices to work. With the bulk approach having inherent limitations in addition to becoming increasingly demanding and expensive, the idea was born that the components could instead be built up atom for atom in a chemistry lab (bottom up) as opposed to carving them out of bulk material (top down). This idea is the reasoning behind molecular electronics with the ultimate miniaturization being components contained in single molecules.

In single molecule electronics, the bulk material is replaced by single molecules. That is, instead of creating structures by removing or applying material after a pattern scaffold, the atoms are put together in a chemistry lab. This way billions of billions of copies are made simultaneously (typically more than 10^{20} molecules are made at once) while the composition of molecules are controlled down to the last atom. The molecules utilized have properties that resemble traditional electronic components such as a wire, transistor or rectifier.

Single molecule electronics is an emerging field, and entire electronic circuits consisting exclusively of molecular sized compounds are still very far from being realized. However, the continuous demand for more computing power together with the inherent limitations of the present day lithographic methods make the transition seem unavoidable. Currently, the focus is on discovering molecules with interesting properties and on finding ways to obtaining reliable and reproducible contacts between the molecular components and the bulk material of the electrodes.

Theoretical Basis

Molecular electronics operates in the quantum realm of distances less than 100 nanometers. The miniaturization down to single molecules brings the scale down to a regime where quantum effects are significant. As opposed to the case in conventional electronic components, where electrons can be filled in or drawn out more or less like a continuous flow of charge, the transfer of a single electron alters the system significantly. This means that when an electron has been transferred from the source electrode to the molecule, the molecule gets charged up and makes it much harder for the next one to transfer. The significant amount of energy due to charging must be taken into account when making calculations about the electronic properties of the setup and is highly sensitive to distances to conducting surfaces nearby.

The theory of single molecule devices is particularly interesting since the system under consideration is an open quantum system in nonequilibrium (driven by voltage). In the low bias voltage regime, the nonequilibrium nature of the molecular junction can be ignored, and the current-voltage characteristics of the device can be calculated using the equilibrium electronic structure of the system.

However, in stronger bias regimes a more sophisticated treatment is required, as there is no longer a variational principle. In the elastic tunneling case (where the passing electron does not exchange energy with the system), the formalism of Rolf Landauer can be used to calculate the transmission through the system as a function of bias voltage, and hence the current.

In inelastic tunneling, an elegant formalism based on the non-equilibrium Green's functions of Leo Kadanoff and Gordon Baym, and independently by Leonid Keldysh was put forth by Ned Wingreen and Yigal Meir. This Meir-Wingreen formulation has been used to great success in the molecular electronics community to examine the more difficult and interesting cases where the transient electron exchanges energy with the molecular system (for example through electron-phonon coupling or electronic excitations).

Further, connecting single molecules reliably to a larger scale circuit has proven a great challenge, and constitutes a significant hindrance to commercialization.

Examples

Common for molecules utilized in molecular electronics is that the structures contain a lot of alternating double and single bonds. The reason for this is that such a pattern delocalizes the molecular orbitals making it possible for electrons to move freely over the conjugated area.

Wires

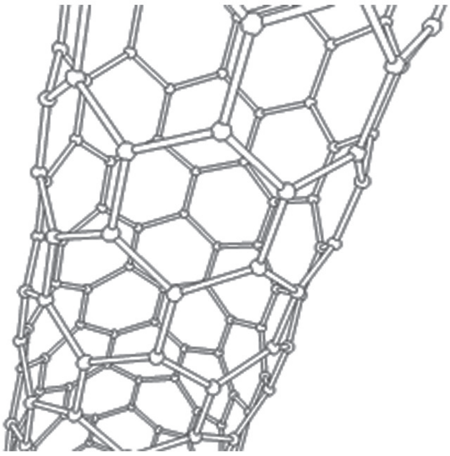


Fig. This animation of a rotating carbon nanotube shows its 3D structure.

The sole purpose of molecular wires is to electrically connect different parts of a molecular electrical circuit. As the assembly of these and their connection to a macroscopic circuit is still not mastered, the focus of research in single molecule electronics is primarily on the functionalized molecules: molecular wires are characterized by containing no functional groups and are hence composed of plain repetitions of a conjugated building block.

Among these are the carbon nanotubes that are quite large compared to the other suggestions but have shown very promising electrical properties.

The main problem with the molecular wires is to obtain good electrical contact with the electrodes so that the electrons can move freely in and out of the wire.

Transistors

Single molecule transistors are fundamentally different than the ones known from bulk electronics. The gate in a conventional (field-emission) transistor determines the conductance between the source and drain electrode by controlling the density of charge carriers between them, whereas the gate in a single molecule transistor controls the feasibility of a single electron to jump on and off the molecule by modifying the energy of the molecular orbitals. One of the effects of this difference is that the single molecule transistor is almost binary: it is either ON or OFF. This opposes its bulk counterparts, which have quadratic responses to gate voltage.

It is the quantization of charge into electrons that is responsible for the markedly different behavior compared to bulk electronics. Because of the size of a single molecule, the charging due to a single electron is significant and provides a mean to turn the transistor ON or OFF. For this to work, the electronic orbitals on the transistor molecule cannot be too well integrated with the orbitals on the electrodes. If they are, an electron cannot be said to be located on the molecule or the electrodes and the molecule will function as a wire.

A popular group of molecules, that can work as the semiconducting channel material in a molecular transistor, is the oligopolyphenylenevinylenes (OPVs) that works by the Coulomb blockade mechanism when placed between the source and drain electrode in an appropriate way. Fullerenes work by the same mechanism and have also been commonly utilized.

Semiconducting carbon nanotubes have also been demonstrated to work as channel material but although molecular, these molecules are sufficiently large to behave almost as bulk semiconductors.

The size of the molecules and the low temperature the measurements are being conducted at makes the quantum mechanical states well defined. It is therefore being researched if the quantum mechanical properties can be used for more advanced purposes than simple transistors (e.g. spintronics).

Physicists at the University of Arizona, in collaboration with chemists from the University of Madrid, have designed a single molecule transistor using a ring-shaped molecule similar to benzene.

Physicists at Canada's National Institute for Nanotechnology have designed a single-molecule transistor using styrene. Both groups expect (their designs have yet to be experimentally verified) their respective devices to function at room temperature, and to be controlled by a single electron.

Rectifiers (Diodes)

Molecular rectifiers are mimics of their bulk counterparts and have an asymmetric construction so that the molecule can accept electrons in one end but not the other. The molecules have an electron donor (D) in one end and an electron acceptor (A) in the other. This way, the unstable state $D^+ - A^-$ will be more readily made than $D^- - A^+$. The result is that an electric current can be drawn through the molecule if the electrons are added through the acceptor end, but not so easily if the reverse is attempted. An example of a molecular rectifier was made by Geoffrey J. Ashwell's Ph.D. students.

Techniques

One of the biggest problems with measuring on single molecules is to establish reproducible electrical contact with only one molecule and doing so without shortcutting the electrodes. Because the current photolithographic technology is unable to produce electrode gaps small enough to contact both ends of the molecules tested (in the order of nanometers) alternative strategies are put into use.

Molecular Gaps

One way to produce electrodes with a molecular sized gap between them is break junctions, in which a thin electrode is stretched until it breaks. Another is electromigration. Here a current is lead through a thin wire until it melts and the atoms migrate to produce the gap. Further, the reach of conventional photolithography can be enhanced by chemically etching or depositing metal on the electrodes.

Probably the easiest way to conduct measurements on several molecules is to use the tip of a scanning tunneling microscope (STM) to contact molecules adhered at the other end to a metal substrate.

Anchoring

A popular way to anchor molecules to the electrodes is to make use of sulfurs' high affinity to gold. In these setups, the molecules are synthesized so that sulfur atoms are placed strategically to function as crocodile clips connecting the molecules to the gold electrodes. Though useful, the anchoring is non-specific and thus anchors the molecules randomly to all gold surfaces. Further, the contact resistance is highly dependent on the precise atomic geometry around the site of anchoring and thereby inherently compromises the reproducibility of the connection.

To circumvent the latter issue, experiments has shown that fullerenes could be a good candidate for use instead of sulfur because of the large conjugated π-system that can electrically contact many more atoms at once than a single atom of sulfur.

Fullerene nanoelectronics

In polymers, classical organic molecules are composed of both carbon and hydrogen (and sometimes additional compounds such as nitrogen, chlorine or sulphur). They are obtained from petrol and can often be synthesized in large amounts.

Most of these molecules are insulating when their length exceeds a few nanometers. However, naturally occurring carbon is conducting. In particular, graphite (recovered from coal or encountered naturally) is conducting.

From a theoretical point of view, graphite is a semi-metal, a category in between metals and semi-conductors. It has a layered structure, each sheet being one atom thick. Between each sheet, the interactions are weak enough to allow an easy manual cleavage.

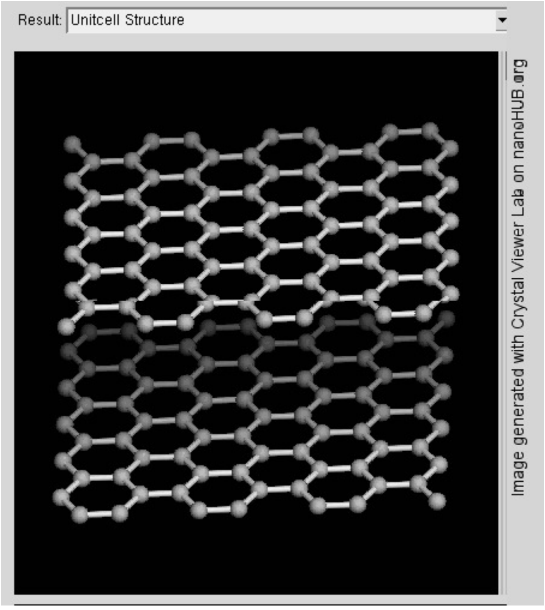


Fig. Rotating view of a graphite crystal (2 graphene layers)

Tailoring the graphite sheet to obtain well defined nanometer-sized objects remains a challenge. However, by the close of the twentieth century, chemists were exploring methods to fabricate extremely small graphitic objects that could be considered single molecules.

After studying the interstellar conditions under which carbon is known to form clusters, Richard Smalley's group (Rice University, Texas) set up an experiment in which graphite was vaporized using laser irradiation. Mass spectrometry revealed that clusters containing specific "magic numbers" of atoms were stable, in particular those clusters of 60 atoms.

Harry Kroto, an English chemist who assisted in the experiment, suggested a possible geometry for these clusters – atoms covalently bound with the exact symmetry of a soccer ball. Coined buckminsterfullerenes, buckyballs or C_{60}, the clusters retained some properties of graphite, such as conductivity. These objects were rapidly envisioned as possible building blocks for molecular electronics.

Problems

Artifacts

When trying to measure electronic characteristics of molecules, artificial phenomena can occur that can be hard to distinguish from truly molecular behavior. Before they were discovered these artifacts have mistakenly been published as being features pertaining to the molecules in question. Applying a voltage drop in the order of volts across a nanometer sized junction results in a very strong electrical field. The field can cause metal atoms to migrate and eventually close the gap by a thin filament, which can be broken again when carrying a current. The two levels of conductance imitate molecular switching between a conductive and an isolating state of a molecule. Another encountered artifact is when the electrodes undergo chemical reactions due to the high field strength in the gap. When the bias is reversed the reaction will cause hysteresis in the measurements that can be interpreted as being of molecular origin. A metallic grain between the electrodes can act as a single electron transistor by the mechanism described above thus resembling the characteristics of a molecular transistor. This artifact is especially common with nanogaps produced by the electromigration technique.

Commercialization

One of the biggest hindrances for single molecule electronics to be commercially exploited is the lack of techniques to connect a molecular sized circuit to bulk electrodes in a way that gives reproducible results. At the current state, the difficulty of connecting single molecules vastly outweighs any possible performance increase that could be gained from such shrinkage. The picture becomes even worse if the molecules are to have a certain spatial orientation and/or have multiple poles to connect.

Also problematic is the fact that some measurements on single molecules are carried out in cryogenic temperatures (close to absolute zero), which is very energy consuming. This is done to reduce signal noise enough to measure the faint currents of single molecules.

History and Recent Progress

In their 1940's discussion of so-called “donor-acceptor” complexes, Robert Mulliken and Albert Szent-Gyorgi advanced the concept of charge transfer in molecules. They subsequently further refined the study of both charge transfer and energy transfer in molecules. Likewise, a 1974 paper from Mark Ratner and Ari Aviram illustrated a theoretical molecular rectifier.

In 1988, Aviram described in detail a theoretical single-molecule field-effect transistor. Further concepts were p roposed by Forrest Carter of the Naval Research Laboratory, including single-molecule logic gates. A wide range of ideas were presented, under his aegis, at a conference entitled *Molecular Electronic Devices* in 1988. These were all theoretical constructs and not concrete devices. The *direct* measurement of the electronic characteristics of individual molecules awaited the development of methods for making molecular-scale electrical contacts. This was no easy task. Thus, the first experiment directly-measuring the conductance of a single molecule was only reported in 1997 by Mark Reed and co-workers. Since then, this branch of the field has progressed rapidly. Likewise, as it has become possible to measure such properties directly, the theoretical predictions of the early workers have been substantially confirmed.

Recent progress in nanotechnology and nanoscience has facilitated both experimental and theoretical study of molecular electronics. In particular, the development of the scanning tunneling microscope (STM) and later the atomic force microscope (AFM) have facilitated manipulation of single-molecule electronics. In addition, theoretical advances in molecular electronics have facilitated further understanding of non-adibatic charge transfer events at electrode-electrolyte interfaces.

The concept of molecular electronics was first published in 1974 when Aviram and Ratner suggested an organic molecule that could work as a rectifier. Having both huge commercial and fundamental interest much effort was put into proving its feasibility and 16 years later in 1990 the first demonstration of an intrinsic molecular rectifier was realized by Ashwell and coworkers for a thin film of molecules.

The first measurement of the conductance of a single molecule was realised in 1994 by C. Joachim and J. K. Gimzewski and published in 1995. This was the conclusion of 10 years of research started at IBM TJ Watson, using the scanning tunnelling microscope tip apex to switch a single molecule as already explored by A. Aviram, C. Joachim and M. Pomerantz at the end of the 80's. The trick was to use an UHV Scanning Tunneling microscope to allow the tip apex to gently touch the top of a single C_{60} molecule adsorbed on a Au(110) surface. A resistance of 55 MOhms was recorded together with a low voltage linear I-V. The contact was certified by recording the I-z current distance characteristic, which allows the measurement of the deformation of the C_{60} cage under contact. This first experiment was followed by the reported result using a mechanical break junction approach to connect two gold electrodes to a sulfur-terminated molecular wire by Mark Reed and James Tour in 1997.

A single-molecule amplifier was implemented by C. Joachim and J.K. Gimzewski in IBM Zurich. This experiment involving a single C_{60} molecule demonstrated that a single C_{60} molecule can provide gain in a circuit just by playing with through C_{60} intramolecular quantum interference effects. A collaboration of researchers at HP and UCLA, led by James Heath, Fraser Stoddart, R. Stanley Williams, and Philip Kuekes, has developed molecular electronics based on rotaxanes and catenanes.

Work is also being done on the use of single-wall carbon nanotubes as field-effect transistors. Most of this work is being done by IBM.

Some specific reports of a field-effect transistor based on molecular self-assembled monolayers were shown to be fraudulent in 2002 as part of the Schön scandal.

Until recently entirely theoretical, the Aviram-Ratner model for a unimolecular rectifier has been unambiguously-confirmed in experiments by a group led by Geoffrey J. Ashwell at Bangor University, UK. Many rectifying molecules have so far been identified, and the number and efficiency of these systems is expanding rapidly.

Supramolecular electronics is a new field that tackles electronics at a supramolecular level.

An significant issue in molecular electronics is the determination of the resistance of a single molecule (both theoretical and experimental). For example, Bumm, et al. used STM to analyze a single molecular switch in a self-assembled monolayer to determine how conductive such a molecule can be. Another problem faced by this field is the difficulty of performing direct characterization since imaging at the molecular scale is often difficult in many experimental devices.

Existing Nanosensors

Currently, the most common mass-produced functioning nanosensors exist in the biological world as natural receptors of outside stimulation. For instance, sense of smell, especially in animals in which it is particularly strong, such as dogs, functions using receptors that sense nanosized molecules.

Certain plants, too, use nanosensors to detect sunlight; various fish use nanosensors to detect minuscule vibrations in the surrounding water; and many insects detect sex pheromones using nanosensors.

Certain electromagnetic sensors have also been in use in photoelectric systems. These work because the specific sensors called, aptly, photosensors are easily influenced by light of various wavelengths.

The electromagnetic source transfers energy to the photosensors and energizes them into an excited state which causes them to release an electron into a semiconductor. At that point, it is relatively easy to detect the electricity coming from the sensors, and thus easy to know if the sensors are receiving light.

Though more advanced uses of photosensors incorporating other forms of nanotechnology have yet to be implemented into consumer society, most film cameras have used photosensors at the nano size for years. Traditional film uses a layer of silver ions that become excited by solar energy and clump into groups, as small as four atoms apiece in some cases, that scatter light and appear dark on the frame.

Various other types of film can be made using a similar process to detect other specific wavelengths of light, including x-rays, infrared, and ultraviolet.

One of the first working examples of a synthetic nanosensor was built by researchers at the Georgia Institute of Technology in 1999. It involved attaching a single particle onto the end of a carbon nanotube and measuring the vibrational frequency of the nanotube both with and without the particle. The discrepancy between the two frequencies allowed the researchers to measure the mass of the attached particle.

Chemical sensors, too, have been built using nanotubes to detect various properties of gaseous molecules. Carbon nanotubes have been used to sense ionization of gaseous molecules while nanotubes made out of titanium have been employed to detect atmospheric concentrations of hydrogen at the molecular level.

Many of these involve a system by which nanosensors are built to have a specific pocket for another molecule. When that particular molecule, and only that specific molecule, fits into the nanosensor, and light is shone upon the nanosensor, it will reflect different wavelengths of light and, thus, be a different colour.

Production Methods

There are currently several hypothesized ways to produce nanosensors. Top-down lithography is the manner in which most integrated circuits are now made. It involves starting out with a larger block of some material and carving out the desired form. These carved out devices, notably put to use in specific microelectromechanical systems used as microsensors, generally only reach the micro size, but the most recent of these have begun to incorporate nanosized components.

Another way to produce nanosensors is through the bottom-up method, which involves assembling the sensors out of even more minuscule components, most likely individual atoms or molecules.

This would involve moving atoms of a particular substance one by one into particular positions which, though it has been achieved in laboratory tests using tools such as atomic force microscopes, is still a significant difficulty, especially to do en masse, both for logistic reasons as well as economic ones.

Most likely, this process would be used mainly for building starter molecules for self-assembling sensors. he third way, which promises far faster results, involves self-assembly, or "growing" particular nanostructures to be used as sensors. This most often entails one of two types of assembly.

The first involves using a piece of some previously created or naturally formed nanostructure and immersing it in free atoms of its own kind.

After a given period, the structure, having an irregular surface that would make it prone to attracting more molecules as a continuation of its current pattern, would capture some of the free atoms and continue to form more of itself to make larger components of nanosensors.

The second type of self-assembly starts with an already complete set of components that would automatically assemble themselves into a finished product. Though this has been so far successful only in assembling computer chips at the micro size, researchers hope to eventually be able to do it at the nanometer size for multiple products, including nanosensors.

Accurately being able to reproduce this effect for a desired sensor in a laboratory would imply that scientists could manufacture nanosensors much more quickly and potentially far more cheaply by letting numerous molecules assemble themselves with little or no outside influence, rather than having to manually assemble each sensor.

What are Nanorobots

Nanorobotics is emerging as a demanding field dealing with miniscule things at molecular level. Nanorobots are quintessential nanoelectromechanical systems designed to perform a specific task with precision at nanoscale dimensions.

Its advantage over conventional medicine lies on its size. Particle size has effect on serum lifetime and pattern of deposition. This allows drugs of nanosize to be used in lower concentration and has an earlier onset of therapeutic action.

It also provides materials for controlled drug delivery by directing carriers to a specific location. The typical medical nanodevice will probably be a micron-scale robot assembled from nanoscale parts.

These nanorobots can work together in response to environment stimuli and programmed principles to produce macro scale results.

Elements of Nanorobots

Carbon will likely be the principal element comprising the bulk of a medical nanorobot, probably in the form of diamond or diamondoid/fullerene nanocomposites. Many other light elements such as hydrogen, sulfur, oxygen, nitrogen, fluorine, silicon, etc. will be used for special purposes in nanoscale gears and other components.

The chemical inertness of diamond is proved by several experimental studies. One such experiment conducted on mouse peritoneal macrophages cultured on DLC showed no significant excess release of lactate dehydrogenase or of the lysosomal enzyme beta N-acetyl-D-glucosaminidase an enzyme known to be released from macrophages during inflammation.

Morphological examination revealed no physical damage to either fibroblasts or macrophages, and human osteoblast like cells confirming the biochemical indication that there was no toxicity and that no inflammatory reaction was elicited in vitro. The smoother and more flawless the diamond surface, the lesser is the leukocyte activity and fibrinogen adsorption. Interestingly, on the rougher "polished" surface, a small number of spread and fused macrophages were present, indicating that some activation had occurred.

The exterior surface with near-nanometer smoothness results in very low bioactivity. Due to the extremely high surface energy of the passivated diamond surface and the strong hydrophobicity of the diamond surface, the diamond exterior is almost completely chemically inert.

Constituents and Design of Nanorobots

Nanorobots will possess full panoply of autonomous subsystems whose design is derived from biological models. Drexler evidently was the first to point out, in 1981, that complex devices resemble biological models in their structural components. The various components in the nanorobot design may include onboard sensors, motors, manipulators, power supplies, and molecular computers.

Perhaps the best-known biological example of such molecular machinery is the ribosome the only freely programmable nanoscale assembler already in existence. The mechanism by which protein binds to the specific receptor site might be copied to construct the molecular robotic arm.

The manipulator arm can also be driven by a detailed sequence of control signals, just as the ribosome needs mRNA to guide its actions. These control signals are provided by external acoustic, electrical, or chemical signals that are received by the robot arm via an onboard sensor using a simple "broadcast architecture a technique which can also be used to import power. the biological cell may be regarded as an example of a broadcast architecture in which the nucleus of the cell send signals in the form of mRNA to ribosomes in order to manufacture cellular proteins.

Assemblers are molecular machine systems that could be described as systems capable of performing molecular manufacturing at the atomic scale which require control signals provided by an onboard nanocomputer This programmable nanocomputer must be able to accept stored instructions which are sequentially executed to direct the manipulator arm to place the correct moiety or nanopart in the desired position and orientation, thus giving precise control over the timing and locations of chemical reactions or assembly operations.

Cellular RF and Microwave Oscillations

Starting in 1968, H. Frohlich, observing that millivolt electrical potentials maintained across cell membranes ~10 nm thick give rise to huge fields ~10^7 volts/m possibly producing an electret state, theorized that membrane molecules must be highly electrically polarized and thus could interact to produce coherent surface acoustic vibrational modes in the 10-100 GHz (microwave) frequency range; the longest wavelength is about twice the membrane thickness.

Interestingly, this frequency span is very close to the maximum trigger/reset frequency for bioelectronic molecules. Note that (~100 mV) (1.6 x 10^{-19} coul) ~ 4 kT, so a membrane molecule with a single charge on either end should be reliably reoriented by a depolarization wave, coupling pressure waves and electrostatic field fluctuations. However, the direct detection of 10-100 GHz millimeter radiation by non-nanotechnological means is experimentally difficult and controversial because the tests must be performed in vivo in close proximity to an actively metabolizing cell in water — and water strongly absorbs microwaves over macroscale ranges. Nevertheless, active cells have shown enhanced Raman anti-Stokes scattering, an effect ascribed to the converse of the Frohlich oscillations.

In one study, the normalized growth rate of yeast cultures was enhanced or inhibited when irradiated by CW microwave fields of ~30 watts/m^2 of various frequencies; growth rate data spanning 62 separate runs revealed a repeatable frequency-dependent spectral fine structure with six distinct peaks of width ~10 MHz near 42 GHz.

Investigations of related phenomena are ongoing and voluminous; the interested reader should peruse *Bioelectromagnetics*, the archival journal of this field. 100 GHz waves attenuate only ~1% after passing through ~3 microns of soft tissue.

A single electron injected into an integral membrane protein could act as an oscillating dipole, making a 300 volt/m signal 10 nm from the protein antenna with an energy transfer of ~0.004 kT per cycle; ~1000 oscillating electrons could produce a measurable field.

A 20-micron diameter cell modeled as a nonuniform spherical dipole layer with transmembrane dipoles located 10 nm apart and embedded in a dissipative medium could produce $10^2 – 10^5$ volt/m microwave fields 1-10 microns from the cell surface.

Thus, a variety of rf and microwave electromagnetic emanations may in theory be detectable both within and nearby living cells which could prove diagnostic of numerous internal states.

Such states may include cytoskeletal dynamics, metabolic rates, plasmon-type excitations due to the collective motion of ions freed in chemical reactions, positional, rotational or conformational changes in biological macromolecules and membranes, internal movements of organelles and nerve traffic conduction, cellular pinocytosis, cellular reproduction events, cell membrane identity, and cell-cell interactions.

Macrosensing

Macrosensing is the detection of global somatic states (inside the human body) and extrasomatic states (sensory data originating outside the human body). While the treatment here is necessarily incomplete, the discussion nevertheless gives a good feel for the kinds of environmental variables that internally-situated nanodevices could sense.

Not all capabilities outlined here need be available on every nanorobot, since injection of a cocktail of numerous distinct but mutually cooperative machine species allows designers to take full advantage of the benefits of functional specialization.

In many cases, a given environmental variable can be measured by several different classes of sensor device. However, since these devices are microscopic it is in theory possible to operationalize almost all of the macrosensing capabilities described below in one patient using just a billion devices (~10 mm^{-3} whole-body deployment density), a total volume of ~1 mm^3 of nanorobots or ~0.1% of the typical ~1 cm^3 therapeutic dose.

Cyto-Auscultation

Can sounds generated by a single cell be detected, and thus be useful for diagnosis? Probably not, given that low frequency acoustic radiators are notoriously inefficient. For example, mitochondrion organelles of the giant amoeba *Reticulomyxa* are shuttled back and forth by 1–4 cytoplasmic dynein motors while riding on the outside of a bundle of 1–6 microtubules.

Each dynein motor generates 2.6 pN of force and drives the mitochondria at up to ~10 micron/sec, developing 0.3–1.0 × 10^{-16} watts of mechanical power within each 320-nm diameter organelle.

Taking each organelle as a cylindrical acoustic radiator with a mechanical input power of $P_{in} \sim 10^{-16}$ watts at $\nu \sim 1000$ Hz, the output acoustic pressure at the organelle surface is only ~10^{-9} atm, an acoustic power intensity I ~ 10^{-15} watts/m^2 which is not detectable by micron-sized nanorobots.

Nevertheless, cells and intracellular elements are capable of vibrating in a dynamic manner with complex harmonics that can be altered by growth factors and by the process of carcino-genesis, so the possibility cannot be completely ruled out.

Blood Pressure and Pulse Detection

Blood pressure ranges from 0.1– 0.2 atm in the arteries to as low as 0.005 atm in the veins. The systolic/diastolic differential ranges from 0.05–0.07 atm in the aorta and 0.01–

0.02 atm in the pulmonary artery, falling to 0.001–0.003 atm in the microvessels, or 0.003–0.005 atm if the precapillary sphincter is dilated.

In venous vessels, pulse fluctuations are 0.002–0.010 atm in the superior vena cava, 0.004 – 0.006 atm in the subclavian vein, ~0.004 atm in venules generally, and ~0.0005 atm in the brachial vein.

There is also a ~0.05 Hz random fluctuation in the microvessels with amplitude on the order of 0.004 – 0.007 atm. Both blood pressure and pulse rate can be reliably monitored by a medical nanodevice virtually anywhere in the vascular system using a $(68\ \mathrm{nm})^3$ pressure sensor with ~0.001 atm sensitivity.

Pulse propagation through body tissue is somewhat muted due to absorption in compressible fatty membranes, but most cells lie within 1 – 3 cell-widths of a capillary so the cardiac acoustic signal should still be measurable using more sensitive detectors. The time-averaged interstitial pressure in subcutaneous tissue is 0.001–0.004 atm. Arterial pulse waves (vascular oscillations) carry subtle messages about the health of internal organs and the arterial tree. The idea of using pulse waves for diagnosis has a long history dating back 2000 years in China.

Waves detected by manual probing are classified using such subjective and qualitative descriptors as floating, deep, hidden, rapid, slow, moderate, feeble, replete, full, thready, faint, weak, soft, slippery, hesitant, hollow, firm, long, short, swift, running, intermittent, uneven, taut, string-tight, gigantic, or tremulous.

Abnormal waves were empirically related to disease states. Wave data gathered by nanodevices could make possible a theoretically sound, quantitative system of noninvasive observation, classification, and diagnosis as a supplement to other nanomedical tools.

Respiratory Audition

The variation of mechanical pressure over a complete respiratory cycle is ~0.003 atm in the pleura, ~0.002 atm at the alveoli, detectable by nanomedical pressure sensors positioned in the vicinity of the respiratory organs.

Holding a deep breath further stretches the pulmonary elastic tissue, up to 0.02 atm. However, turbulent flows at Reynolds number $N_R > 2300$ in the trachea, main bronchus and lobar bronchus produce a whooshing noise that may be the loudest noncardiac sound in the human torso during conventional auscultation.

The energy dissipation for turbulent flow in a tube is

(watts)

where P_{lam} is the dissipation for laminar (Poiseuillean) flow in a long circular cylindrical tube of length L, v is the mean flow velocity, and turbulence factor $Z = 0.005 (N_R^{3/4} - (2300)^{3/4})$, a well-known empirical formula.

For $\eta_{air} = 1.83 \times 10^{-5}$ kg/m-sec for room-temperature air (20°C), $P_{turb} = 0.87$ milliwatts for the trachea; $P_{turb} = 0.66$ milliwatts for the main bronchus (L = 0.167 m, v = 4.27 m/sec and $N_R = 3210$); and $P_{turb} = 0.09$ milliwatts for the lobar bronchus (L = 0.186 m, v = 4.62 m/sec and $N_R = 2390$), totalling ~1.6 milliwatts acoustic emission from a ~120 cm^3 upper tracheobroncheal volume.

This is a power density of 13 watts/m^3 corresponding to a pressure of 4×10^{-5} atm assuming a 300 millisecond measurement window at the maximum respiration rate. The amplitude of an acoustic plane wave propagating through tissue attenuates exponentially with distance due to absorption, scattering and reflection. The amplitude is given approximately by

$$A_x = A_D e^{-\alpha F x}$$

where A_0 is the initial wave amplitude in atm, A_x is the amplitude a distance x from the source, and α is the amplitude absorption coefficient. The function F expresses the frequency dependence of the attenuation. For pure liquids, $F = F_{liq} = \nu^2$ (Hz^2); for example, $\alpha_{liq} = 2.5 \times 10^{-14}$ sec^2/m for water at room temperature. However, for soft tissues, $F = F_{tiss} \sim \nu$ (Hz).

Mechanical Body Noises

Many other mechanical body noises should be globally audible to properly instrumented medical nanodevices. If normal chewing motions (of hard foods) release 1–10 milliwatts in a ~100 cm^3 oral volume with a ~1 sec jawstroke, power density is ~10 watts/m^3 or ~10^{-4} atm of toothcrunching noise.

A stomach growl registering 45 dB (vs. 30 dB whisper, 60 dB normal conversation) at 2 meters has a source power of 160 milliwatts; released from a 10 cm^3 gastric sphincter volume gives a ~2×10^{-6} atm acoustic wave, detectable throughout the body.

Walking and running releases 20-100 joules/footfall for a 70 kg man; assuming the energy is absorbed within a ~1 cm thickness or within ~1 second by the sole of the foot, Eqn. implies an upward-moving planar compression wave of 0.4-2.0 atm, easily detectable by acoustically instrumented nanodevices body-wide. Hand-clapping generates 0.02-0.2 atm pulses, also easily detectable.

Lesser noises including ~30 millisec hiccups at (4–60)/ min, intestinal and ureteral peristalsis, sloshing of liquid stomach contents, heart murmurs, a tap on the shoulder by a friend, nasal sniffling and swallowing, clicks from picking or drumming fingernails, crepitations, manustuprations and ejaculations, the rustling noise of clothing against the skin, flapping eyelids, anal towelling, bruits (including murmurs and thrills) due to vascular lesions, dermal impact of water while showering, copulatory noises, urethral flow turbulence during urination, transmitted vibrations from musical instruments, creaking joints, and squeaking muscles can be detected locally if not globally.

Implantation of significant interconnected in vivo diamondoid structures may produce increased sensitivity to internal noises, due to the extremely low acoustic absorption coefficient of diamond.

Vocalizations

Average source power for conversational speech in air is ~10 microwatts at the vocal cords (60 dB), up to ~1000 microwatts for shouting (90 dB) and as little as 0.1 microwatts (30 dB) for whispering. Vocal cord surface area ~1 cm^2, giving an acoustic intensity I ~ 0.001–10 watts/m^2. (Using the decibel notation, dB = 10 $\log_{10}(I/I_0)$, where $I_0 \sim 5 \times 10^{-13}$ watts/m^2

in air, $I_0 \sim 1 \times 10^{-16}$ watts/m^2 in water.) In a planar traveling wave, pressure amplitude A_p (N/m^2) is related to power intensity I by (N/m^2) For water at 310 K, $\rho = 993.4$ kg/m^3 and $v_{sound} = 1500$ m/sec, therefore $A_p = 0.0005–0.05$ atm for speech, detectable by nanodevices throughout the body due to minimal attenuation at audible frequencies.

Other easily detectable vocalizations include whistling, humming, coughing, sneezing, rales, wheezing, expectorating, eructations, flatus, vomiting, hawking and noseblowing.

Environmental Sources

Can in vivo nanodevices directly detect sounds emanating from the environment outside of the body, such as other people talking in the same room or a door slamming? The waves from an external acoustic source of power P_R watts travel through the air and, upon arriving at the air/skin interface a distance x_R from the source with amplitude $A_{incident}$, are transmitted through the interface with amplitude $A_{transmit}$.

For a specular reflector — interface dimensions (human body ~ 2 m) > acoustic wavelength (~0.03–3.0 m for typical audible sounds in air) — with acoustic impedance Z_1 and Z_2 on either side of the interface and perpendicular incidence,

Acoustic impedance, like the speed of sound, is essentially frequency-independent over the nanomedically-relevant range of ultrasonic frequencies. For $Z_{air} = 400$ kg/m^2-sec and assuming $Z_{skin} \sim 1.6 \times 10^6$ kg/m^2-sec, then $A_{transmit} = (5 \times 10^{-4})\ A_{incident}$.

In other words, there is ~99.95% reflection from the air-skin interface, which is why coupling mediums like gels and oils are commonly employed in ultrasound imaging. If an immediately subdermal nanodevice can detect a minimum $A_{transmit} \sim 10^{-6}$ atm, then from simple geometry:

For STP (1 atm, 0°C) air, $\rho = 1.29$ kg/m^3 and v_{sound} = 331 m/sec. If the minimum detectable pressure $\sim 10^{-6}$ atm $\sim A_{transmit}$, then at a distance of $x_R = 2$ meters the acoustic source must have a power of ~2000 watts, far exceeding the ~1 milliwatt output of a person loudly shouting.

To hear normal conversation at $x_R = 2$ m, minimum nanodevice detector sensitivity falls to 7×10^{-11} atm requiring a subdermal pressure nanosensor ~(17 micron)^3 in size, roughly the dimensions of a single human cell; other methods may prove more efficient.

Of course, an ex vivo acoustic nanosensor may receive sound that has passed through no interface, hence may detect pressure waves ~3 orders of magnitude lower in amplitude. Assuming $A_{transmit} = A_{incident}$, $P_R \sim 600$ microwatts, so ex vivo nanorobots with a 0.3 micron^3 sensor could hear people shouting at $x_R = 2$ meters.

To hear talking (~10 microwatt source) requires a 2.4 micron^3 ex vivo pressure sensor (limit $\sim 10^{-7}$ atm). Optimally positioned and calibrated nanomedical pressure sensors could directly measure changes in the ambient barometric pressure to within $\pm 10^{-6}$ atm.

Normal atmospheric variation due to weather ranges from 0.94–1.05 atm; such slow moving changes are readily monitored. Very near the Earth's surface, the air pressure P at altitude h above sea level is approximated by $P = e^{-kp\ h}$ (atm), where $k_p = 1.16 \times 10^{-4}\ m^{-1}$ at 20°C; at sea level, a 10^{-6} atm change in pressure reflects a change in altitude of only ~1 cm.

However, the opening or closing of a door inside a $(\sim 5\ m)^3$ room that displaces $>125\ cm^3$ of air also causes a minimally detectable $>10^{-6}$ atm pressure pulse.

Other sources of environmental pressure variation such as infrasonic (~0.2 Hz) microbaroms from offshore ocean storms, wind entering through open windows, forced-air currents from central heating or A/C systems, or even the movements of nearby people and pets may be detectable and thus may further confuse the measurement, reducing absolute accuracy unless suitable corrections are made.

Tools for Measuring Nanostructures

Scanning Probe Instruments

Some of the first tools to help launch the nanoscience revolution were the so-called scanning probe instruments. All types of scanning probe instruments are based on an idea first developed at the IBM Laboratory in Zurich in the 1980s. Essentially, the idea is a simple one: if you rub your finger along a surface, it is easy to distinguish velvet from steel or wood from tar. The different materials exert different forces on your finger as you drag it along the different surfaces. In these experiments, your finger acts like a force measurement structure. It is easier to slide it across a satin sheet than across warm tar because the warm tar exerts a stronger force dragging back the finger. This is the idea of the scanning force microscope, one of the common types of scanning probe. In scanning probe measurements, the probe, also called a tip, slides along a surface in the same way your finger does. The probe is of nanoscale dimensions, often only a single atom in size where it scans the target. As the probe slides, it can measure several different properties, each of which corresponds to a different scanning probe measurement. For example, in atomic force microscopy (AFM), electronics are used to measure the force exerted on the probe tip as it moves along the surface. This is exactly the measurement made by your sliding finger, reduced to the nanoscale.

In scanning tunneling microscopy (STM), the amount of electrical current flowing between a scanning tip and a surface is measured. Depending on the way the measurement is done, STM can be used either to test the local geometry (how much the surface protrudes locally) or to measure the local electrical conducting characteristics. STM was actually the first of the scanning probe methods to be developed, and Gerd Binnig and Heinrich Rohrer shared the 1986 Nobel Prize for its development.

In magnetic force microscopy (MFM), the tip that scans across the surface is magnetic. It is used to sense the local magnetic structure on the surface. The MFM tip works in a similar way to the reading head on a hard disk drive or audio cassette player.

Computer enhancement is often used to get a human-usable picture from any scanning probe instrument. It takes a great deal of enhancement just to make the raw results look as good as the ghostly x-ray pictures taken of your luggage at the airport. Scanning probe instruments can't image anything as large as luggage, however; they are more useful for measuring structures on length scales from the single atom level to the microscale. Nanotechnology will offer us other ways of catching baggage offenders.

Other types of scanning microscopies also exist. They are referred to as scanning probe microscopies because all are based on the general idea of the STM. In all of them, the important idea is that a nanoscale tip that slides or scans over the surface is used to investigate nanoscale structure by measuring forces, currents, magnetic drag, chemical identity, or other specific properties. Figure shows an example of one of these tips.

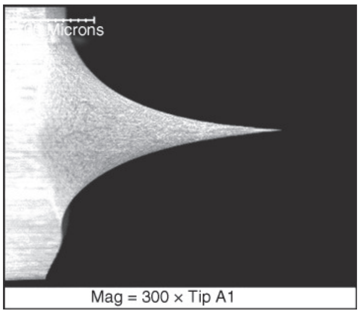


Fig. An STM tip Made of Tungsten.

Scanning probe microscopy made it possible to see things of atomic dimensions for the first time. It has been critical for measuring and understanding nanoscale structures.

Spectroscopy

Spectroscopy refers to shining light of a specific colour on a sample and observing the absorption, scattering, or other properties of the material under those conditions. Spectroscopy is a much older, more general technique than scanning probe microscopy and it offers many complementary insights. Some types of spectroscopy are familiar from the everyday world. X-ray machines, for example, pass very high-energy radiation through an object to be examined and see how the radiation is scattered by the heavy nuclei of things like steel or bone. Collecting the x-ray light that passes through yields an image that many of us have seen in the doctor's office after a slip on the ice or in the bathtub. Magnetic resonance imaging, or MRI, is another type of spectroscopy that may be familiar from its medical applications.

Many sorts of spectroscopy using different energies of light are used in the analysis of nanostructures. The usual difficulty is that all light has a characteristic wavelength and isn't of much use in studying structures smaller than its wavelength.

Since visible light has a wavelength of between approximately 400 and 900 nanometers, it is clear that it isn't too much help in looking at an object only a few nanometers in size. Spectroscopy is of great importance for characterizing nanostructures en masse, but most types of spectroscopy do not tell us about structures on the scale of nanometers.

Electrochemistry

Electrochemistry deals with how chemical processes can be changed by the application of electric currents, and how electric currents can be generated from chemical reactions. The most common electrochemical devices are batteries that produce energy from chemical reactions. The opposite process is seen in electroplating, wherein metals are made to form on surfaces because positively charged metal ions absorb electrons from the current flowing through the surface to be plated and become neutral metals.

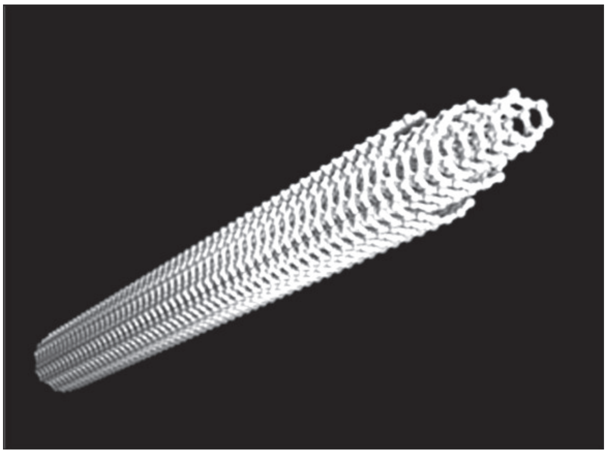
Electrochemistry is broadly used in the manufacturing of nanostructures, but it can also be used in their analysis. The nature of the surface atoms in an array can be measured directly using electrochemistry, and advanced electrochemical techniques (including some scanning probe electrochemical techniques) are often used both to construct and to investigate nanostructures.

3

Carbon Nanotube Synthesis

What is Carbon Nanotube Synthesis, and What are its Implications for Modern Science? While the mystery and implications for science surrounding carbon nanotubes in modern science have gained them immense popularity with scientists and researchers in myriad fields. The age old question-what is carbon nanotube synthesis? is quickly gaining ground in modern science as well. And its implications may far outweigh and outreach those of just carbon nanotubes, since this process of synthesis may very well open doors for science and for the use of carbon nanotubes that no one ever thought possible. Carbon nanotubes are essentially constructed of a lattice work sheet of graphite that is rolled into a cylindrical shape. These carbon nanotubes are feather light in their construction and much stronger than many other properties used in not only nanotechnology but also in electronics, optics, additional areas of materials science, architecture and even the construction of motor vehicles, space vehicles and other materials useful in a wide array of traditional fields of research and modern living.

Carbon nanotubes are also known to have any unique electrical properties and have even been tested and proven as super efficient conductors of heat, otherwise referred to as thermal conductors. It is only their potential to have some toxic properties that has limited their widespread use and distribution for construction and other purposes.



Carbon nanotubes come in a variety of forms, including single walled carbon nanotubes, double walled carbon nanotubes and multi walled carbon nanotubes. Each type of carbon nanotubes has its own set of unique properties that make it useful for different areas of science. For instance, the single walled carbon nanotube has especially strong electric properties that the other varieties lack.

Carbon nanotube synthesis is incredibly important to the research of the potential uses of carbon nanotubes because nanotube synthesis is the method of production used to create carbon nanotubes. The faster the rate of synthesis, or production, the more carbon nanotubes available for researches and scientists to use in testing for the various possible uses of carbon nanotubes in standard modern day living, current science and potential future applications. Although carbon nanotube synthesis can occur naturally through flame synthesis, the most common methods of used in modern science include laser ablation, arc discharge and chemical vapour deposition.

The arc discharge method of nanotube synthesis was initially developed by accident. In 1991, an arc discharge that was meant for producing fullerenes, produced, along with the fullerenes, carbon nanotubes. In 1992, the experiment was reproduced by two researchers at the Fundamental Research Laboratory of the NEC. This process involves high temperatures for discharge which cause the negative electrode in the arc to force sublimate the carbon nanotubes contained within. Additionally, this process has a yield by weight of more than 30 percent and it is able to produce both multi walled (including double walled) and single walled carbon nanotubes.

This method for carbon nanotube synthesis is most popular because it was the first method discovered and used. The carbon nanotubes produced through this method of synthesis often have few defects, if any, and lengths of more than 50 micrometers are able to be produced. But arc discharge is not the only type of nanotube synthesis available to researchers and scientists. Other methods have been developed in order to provide a wide variety of acceptable outcomes—acceptable outcomes being defined as producing usable carbon nanotubes in large quantities with minimal defects.

One of the additional methods of nanotube synthesis is laser ablation method. When scientists use laser ablation synthesis method for carbon nanotubes, both a pulsing laser and an inert gas are paired together in a tightly sealed reactor with high temperatures. The pulsed laser is used to vaporize the graphite as the gas is allowed to slowly seep into the reactor chamber. The graphite vapour condenses as the reactor surfaces of the chamber cool down and nanotubes form out of the vapours.

In the laser ablation method, scientists most often produce single walled carbon nanotubes and the yield is approximately 70 percent by weight. Although this method yields much more by weight than the other two available methods, it is much more expensive to use and many scientists and researchers opt in favour of the less expensive methods. The final popular method of carbon nanotube synthesis is the chemical vapour desposition method. Although this method has been used to synthesize carbon since 1959, the chemical catalytic vapour deposition method of producing carbon nanotubes was not first used until 1993, nearly forty years after its first use for synthesis and two years after the first nanotubes were synthesized using the arc discharge method.

This method was further developed in 2007 by University of Cincinnati researchers and at that time began producing carbon nanotubes at lengths of 18 millimetres, much longer than those produced by the arc discharge method at only fifty micrometers.

In chemical vapour desposition, a substrate made of iron, cobalt, nickel or a combination of any of these metals is heated to precisely 700 degrees Celsius inside a chemical reactor.

Process gases such as hydrogen, nitrogen or ammonia along with a carbon gas like methane, ethanol or acetylene, is leaked into the reactor chamber. The meeting of the gases at the substrate cause a reaction that breaks the carbon gases apart and forces the particles to the sides of the chamber, where the carbon nanotubes are formed. This method of nanotube synthesis is the most popular for commercial production because it allows for nanotubes to be grown from and on a specified substrate. The most important factors relating to nanotube synthesis are how fast the nanotubes can be grown, how many can be made at any one time, how much the process to be used will cost and most importantly, how few structural defects will be present in the new carbon nanotubes that have been synthesized. All of these factors determine the future of carbon nanotubes and the development of better method for synthesis will determine the future application of carbon nanotubes in everything that surrounds us.

The Phase Diagram of Carbon

The stable bonding configuration of carbon at NTP is graphite, with an energy difference between the graphite and the diamond of 0.02 eV per atom. Due to the high energetic barrier between the two phases of carbon, the transition from diamond to the most stable phase of graphite at normal conditions is extremely slow. This transition can also occurs more rapidly, when diamond is exposed to ion bombardment or high temperature for example. Due to the high anisotropy in the graphite structure as compared to that of diamond, the electronic, mechanical and optical properties of these two phases of carbon are very different. Some properties of diamond and graphite crystals are presented. In the column related to graphite, the in-plane properties appears on the left and the transverse one between planes on the right.

Table : Properties of diamond and graphite.

Property	***Graphite***	***Diamond***
Lattice constant (RT) [Å]	2.462 6.708	3.567
Bond length (RT) [Å]	1.421	1.545
Atomic density [cm^{-3}]	1.14×10^{23}	1.77×10^{23}
Thermal conductivity [W/cm-K]	30 0.06	25
Debye temperature [K]	2500 950	1860
Electron mobility [cm^2/V-sec]	20×10^3 100	1800
Hole mobility [cm^2/V-sec]	15×10^3 90	1500
Melting point K	4200	4500
Band gap [eV]	-0.04	5.47

Bridging between these two allotropes of carbon lie a whole variety of carbon materials which include, among others, amorphous sp^2 bonded carbon (such as thermally evaporated carbon), micropolycrystalline sp^2 bonded graphite (such as glassy carbon), nanodiamond films, and amorphous sp^3 bonded carbon (sometimes referred to as amorphous diamond), which is structurally analogous to amorphous Si and is formed during low energy carbon ions deposition.

Nanodiamond films, for example, can been grown by different deposition techniques such as dc assisted plasma chemical vapour deposition (CVD) from a methane-hydrogen mixture and others. The criteria of quality of the nanodiamond films include low-contents of nondiamond phases, nano-sizes crystallites, uniform nanocrystallinity throughout thick films and random grain orientation.

Another polymorphic form of carbon was discovered in 1985. It exists in discrete molecular form, and consists of a hollow spherical cluster of carbon atoms. Each molecule is composed of groups of carbon atoms that are bonded to one another form both hexagons and pentagons geometrical configuration. The material composed of C^{60} is known as buckminsterfullerene, named in honour of R.

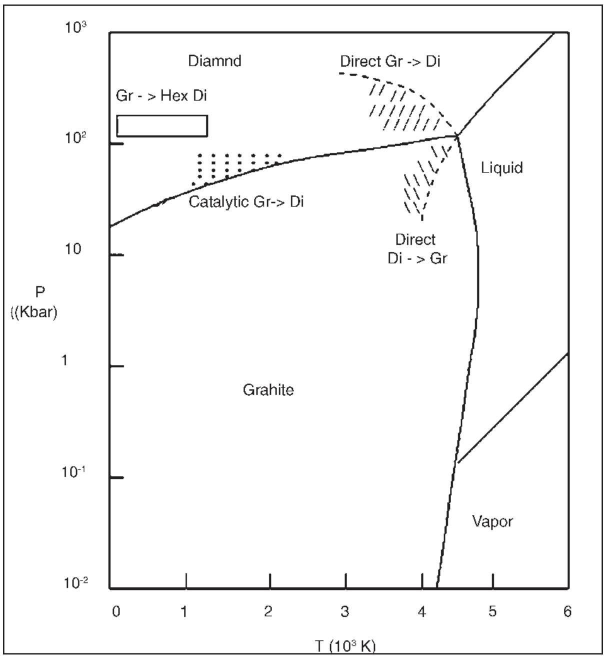


Figure : P, T Phase Diagram of Carbon Reproduced.

Buckminster Fuller, who invented the geodesic dome. In the solid state, the C^{60} units form a crystalline structure and pack together in a face-centred cubic array.

Molecular shapes other than the ball clusters recently have been discovered: these include nanoscale tubular and polyhedral structures. It is anticipated that, with further developments, the fullerenes will become technologically important materials.

Extreme Carbon Nanotubes

The observation of the *longest* carbon nanotubes (18.5 cm long) was reported in 2009. These nanotubes were grown on Si substrates using an improved chemical vapour deposition

(CVD) method and represent electrically uniform arrays of single-walled carbon nanotubes.

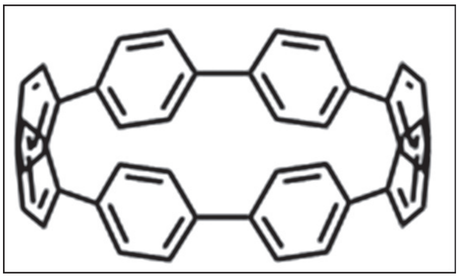


Figure: Cycloparaphenylene

The *shortest* carbon nanotube is the organic compound cyclopara-phenylene, which was synthesized in early 2009.

The *thinnest* carbon nanotube is armchair (2,2) CNT with a diameter of 3 Å. This nanotube was grown inside a multi-walled carbon nanotube. Assigning of carbon nanotube type was done by combination of high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy and density functional theory (DFT) calculations.

The *thinnest freestanding* single-walled carbon nanotube is about 4.3 Å in diameter. Researchers suggested that it can be either SWCNT, but exact type of carbon nanotube remains questionable. Carbon nanotubes (all about 4 Å in diameter) were unambiguously identified using more precise aberration-corrected high-resolution transmission electron microscopy. However, they were found inside of double-walled carbon nanotubes.

Properties

Strength

Carbon nanotubes are the strongest and stiffest materials yet discovered in terms of tensile strength and elastic modulus respectively. This strength results from the covalent sp^2 bonds formed between the individual carbon atoms. In 2000, a multi-walled carbon nanotube was tested to have a tensile strength of 63 gigapascals (GPa). (For illustration, this translates into the ability to endure tension of a weight equivalent to 6422 kg on a cable with cross-section of 1 mm^2.) Further studies, conducted in 2008, revealed that individual CNT shells have strengths of up to ~100 GPa, which is in good agreement with quantum/atomistic models. Since carbon nanotubes have a low density for a solid of 1.3 to 1.4 g/cm^3, its specific strength of up to 48,000 $kN{\cdot}m{\cdot}kg^{-1}$ is the best of known materials, compared to high-carbon steel's 154 $kN{\cdot}m{\cdot}kg^{-1}$.

Under excessive tensile strain, the tubes will undergo plastic deformation, which means the deformation is permanent. This deformation begins at strains of approximately 5% and can increase the maximum strain the tubes undergo before fracture by releasing strain energy.

Although the strength of individual CNT shells is extremely high, weak shear interactions between adjacent shells and tubes leads to significant reductions in the effective strength of multi-walled carbon nanotubes and carbon nanotube bundles down to only a few GPa's.

This limitation has been recently addressed by applying high-energy electron irradiation, which crosslinks inner shells and tubes, and effectively increases the strength of these materials to ~60 GPa for multi-walled carbon nanotubes and ~17 GPa for double-walled carbon nanotube bundles.

CNTs are not nearly as strong under compression. Because of their hollow structure and high aspect ratio, they tend to undergo buckling when placed under compressive, torsional, or bending stress.

Comparison of mechanical properties

Material	***Young's modulus (TPa)***	***Tensile strength (GPa)***	***Elongation at break (%)***
SWNT^E	~1 (from 1 to 5)	13–53	16
Armchair SWNT^T	0.94	126.2	23.1
Zigzag SWNT^T	0.94	94.5	15.6–17.5
Chiral SWNT	0.92		
MWNT^E	0.2–0.8–0.95	11–63–150	
Stainless steel^E	0.186–0.214	0.38–1.55	15–50
Kevlar–29&149^E	0.06–0.18	3.6–3.8	~2

^{E}Experimental observation; ^{T}Theoretical prediction.

To axial properties of the nanotube, whereas simple geometrical considerations suggest that carbon nanotubes should be much softer in the radial direction than along the tube axis. Indeed, TEM observation of radial elasticity suggested that even the van der Waals forces can deform two adjacent nanotubes.

Nanoindentation experiments, performed by several groups on multiwalled carbon nanotubes and tapping/contact mode atomic force microscope measurement performed on single-walled carbon nanotube, indicated Young's modulus of the order of several GPa confirming that CNTs are indeed rather soft in the radial direction.

Hardness

Standard single-walled carbon nanotubes can withstand a pressure up to 24GPa without deformation. They then undergo a transformation to superhard phase nanotubes. Maximum pressures measured using current experimental techniques are around 55GPa. However, these new superhard phase nanotubes collapse at an even higher, albeit unknown, pressure. The bulk modulus of superhard phase nanotubes is 462 to 546 GPa, even higher than that of diamond(420 GPa for single diamond crystal).

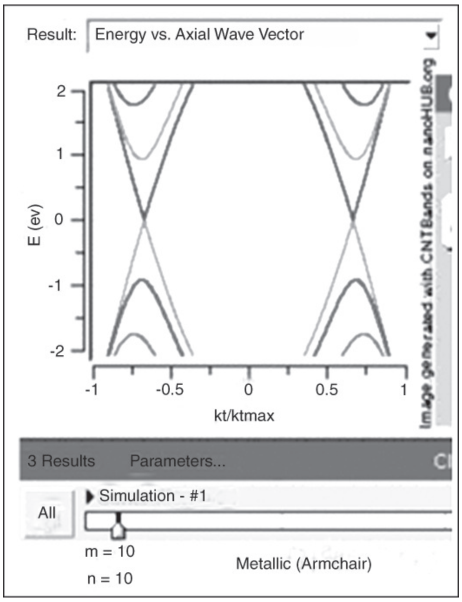
Kinetic Properties

Multi-walled nanotubes are multiple concentric nanotubes precisely nested within one another. These exhibit a striking telescoping property whereby an inner nanotube core may slide, almost without friction, within its outer nanotube shell, thus creating an atomically perfect linear or rotational bearing. This is one of the first true examples of molecular nanotechnology, the precise positioning of atoms to create useful machines. Already, this property has been utilized to create the world's smallest rotational motor. Future applications such as a gigahertz mechanical oscillator are also envisaged.

Electrical Properties

Because of the symmetry and unique electronic structure of graphene, the structure of a nanotube strongly affects its electrical properties. For a given (n,m) nanotube, if $n = m$, the nanotube is metallic; if n “ m is a multiple of 3, then the nanotube is semiconducting with a very small band gap, otherwise the nanotube is a moderate semiconductor. Thus all armchair $(n = m)$ nanotubes are metallic, and nanotubes etc. are semiconducting.

However, this rule has exceptions, because curvature effects in small diameter carbon nanotubes can strongly influence electrical properties. Thus, a SWCNT that should be semiconducting in fact is metallic according to the calculations. Likewise, *vice-versa*— zigzag and chiral SWCNTs with small diameters that should be metallic have finite gap (armchair nanotubes remain metallic). In theory, metallic nanotubes can carry an electric current density of 4 × 10^9 A/cm^2, which is more than 1,000 times greater than those of metals such as copper, where for copper interconnects current densities are limited by electromigration.



m = 10
n = 10
Metallic (Armchair)

Figure: Band Structures Computed using Tight Binding Approximation for (6,0) CNT (Zigzag, Metallic) (10,2) CNT (Semiconducting) and (10,10) CNT (Armchair, Metallic).

Because of their nanoscale cross-section, electrons propagate only along the tube's axis and electron transport involves quantum effects. As a result, carbon nanotubes are frequently referred to as one-dimensional conductors. The maximum electrical conductance of a single-walled carbon nanotube is $2G_0$, where $G_0 = 2e^2/h$ is the conductance of a single ballistic quantum channel.

There have been reports of intrinsic superconductivity in carbon nanotubes. Many other experiments, however, found no evidence of superconductivity, and the validity of these claims of intrinsic superconductivity remains a subject of debate.

Optical Properties

Wave Absorption

One of the more recently researched properties of multi-walled carbon nanotubes (MWNTs) is their wave absorption characteristics, specifically microwave absorption. Interest in this research is due to the current military push for radar absorbing materials (RAM) to better the stealth characteristics of aircraft and other military vehicles. There has been some research on filling MWNTs with metals, such as Fe, Ni, Co, etc., to increase the absorption effectiveness of MWNTs in the microwave regime.

Thus far, this research has shown improvements in both maximum absorption and bandwidth of adequate absorption. The reason the absorptive properties changed when filled is that the complex permeability (μ_r) and complex permitivity (ε_r), have been shown to vary depending on how the MWNTs are called and what medium they are suspended in. The direct relationship between μ_r, ε_r, and the other system parameters that affect the absorption sample thickness, d, and frequency, f,, where Z_{in} is the normalized input impedance. These characteristics vary by frequency. Because of this, it is convenient to set a baseline reflection loss (R.L.) that is deemed effective and determine the bandwidth within a given frequency that produces the desired reflection loss. A common R.L. to use for this bandwidth determination is “10 dB, which corresponds to a loss of over 90% of the incoming wave. This bandwidth is usually maximized at the same time as the absorption is. This is done by satisfying the impedance matching condition, getting $Z_{in} = 1$. In the work done at Beijing Jiaotong University it was found that Fe filled MWNTs exhibited a maximum reflection loss of –22.73 dB and had a bandwidth of 4.22 GHz for a reflection loss of –10 dB.

$$R.L.(dB) = 20\log_{10}\left[\frac{Z_{in}-1}{Z_{in}+1}\right]$$

$$Z_{in} = \sqrt{\frac{\mu_r}{\varepsilon_r}}\tanh\left[j\left(\frac{2\pi fd}{c}\right)\sqrt{\mu_r\varepsilon_r}\right]$$

Thermal Properties

All nanotubes are expected to be very good thermal conductors along the tube, exhibiting a property known as "ballistic conduction", but good insulators laterally to the tube axis. Measurements show that a SWNT has a room-temperature thermal conductivity along its axis of about 3500 $W\cdot m^{-1}\cdot K^{-1}$; compare this to copper, a metal well known for its good thermal conductivity, which transmits 385 $W\cdot m^{-1}\cdot K^{-1}$. A SWNT has a room-temperature thermal conductivity across its axis (in the radial direction) of about 1.52 $W\cdot m^{-1}\cdot K^{-1}$, which is about as thermally conductive as soil. The temperature stability of carbon nanotubes is estimated to be up to 2800 °C in vacuum and about 750 °C in air.

Defects

As with any material, the existence of a crystallographic defect affects the material properties. Defects can occur in the form of atomic vacancies. High levels of such defects can lower the tensile strength by up to 85%. An important example is the Stone Wales defect, which creates a pentagon and heptagon pair by rearrangement of the bonds. Because of the very small structure of CNTs, the tensile strength of the tube is dependent on its weakest segment in a similar manner to a chain, where the strength of the weakest link becomes the maximum strength of the chain.

Crystallographic defects also affect the tube's electrical properties. A common result is lowered conductivity through the defective region of the tube. A defect in armchair-type tubes (which can conduct electricity) can cause the surrounding region to become semiconducting, and single monoatomic vacancies induce magnetic properties.

Crystallographic defects strongly affect the tube's thermal properties. Such defects lead to phonon scattering, which in turn increases the relaxation rate of the phonons. This reduces the mean free path and reduces the thermal conductivity of nanotube structures.

Phonon transport simulations indicate that substitutional defects such as nitrogen or boron will primarily lead to scattering of high-frequency optical phonons. However, larger-scale defects such as Stone Wales defects cause phonon scattering over a wide range of frequencies, leading to a greater reduction in thermal conductivity.

Toxicity

The toxicity of carbon nanotubes has been an important question in nanotechnology. Such research has just begun. The data are still fragmentary and subject to criticism. Preliminary results highlight the difficulties in evaluating the toxicity of this heterogeneous material. Parameters such as structure, size distribution, surface area, surface chemistry, surface charge, and agglomeration state as well as purity of the samples, have considerable impact on the reactivity of carbon nanotubes. However, available data clearly show that, under some conditions, nanotubes can cross membrane barriers, which suggests that, if raw materials reach the organs, they can induce harmful effects such as inflammatory and fibrotic reactions.

A study led by Alexandra Porter from the University of Cambridge shows that CNTs can enter human cells and accumulate in the cytoplasm, causing cell death.

Results of rodent studies collectively show that regardless of the process by which CNTs were synthesized and the types and amounts of metals they contained, CNTs were capable of producing inflammation, epithelioid granulomas (microscopic nodules), fibrosis, and biochemical/toxicological changes in the lungs. Comparative toxicity studies in which mice were given equal weights of test materials showed that SWCNTs were more toxic than quartz, which is considered a serious occupational health hazard when chronically inhaled. As a control, ultrafine carbon black was shown to produce minimal lung responses.

The needle-like fibre shape of CNTs is similar to asbestos fibres. This raises the idea that widespread use of carbon nanotubes may lead to pleural mesothelioma, a cancer of the lining of the lungs or peritoneal mesothelioma, a cancer of the lining of the abdomen (both caused by exposure to asbestos). A recently published pilot study supports this prediction. Scientists exposed the mesothelial lining of the body cavity of mice to long multiwalled carbon nanotubes and observed asbestos-like, length-dependent, pathogenic behaviour that included inflammation and formation of lesions known as granulomas. Authors of the study conclude: This is of considerable importance, because research and business communities continue to invest heavily in carbon nanotubes for a wide range of products under the assumption that they are no more hazardous than graphite. Our results suggest the need for further research and great caution before introducing such products into the market if long-term harm is to be avoided.

According to co-author Dr. Andrew Maynard: This study is exactly the kind of strategic, highly focused research needed to ensure the safe and responsible development of nanotechnology.

It looks at a specific nanoscale material expected to have widespread commercial applications and asks specific questions about a specific health hazard. Even though scientists have been raising concerns about the safety of long, thin carbon nanotubes for over a decade, none of the research needs in the current U.S. federal nanotechnology environment, health and safety risk research strategy address this question.

Although further research is required, the available data suggests that under certain conditions, especially those involving chronic exposure, carbon nanotubes can pose a serious risk to human health.

Synthesis

Techniques have been developed to produce nanotubes in sizeable quantities, including arc discharge, laser ablation, high-pressure carbon monoxide (HiPco), and chemical vapour deposition (CVD). Most of these processes take place in vacuum or with process gases. CVD growth of CNTs can occur in vacuum or at atmospheric pressure. Large quantities of nanotubes can be synthesized by these methods; advances in catalysis and continuous growth processes are making CNTs more commercially viable.

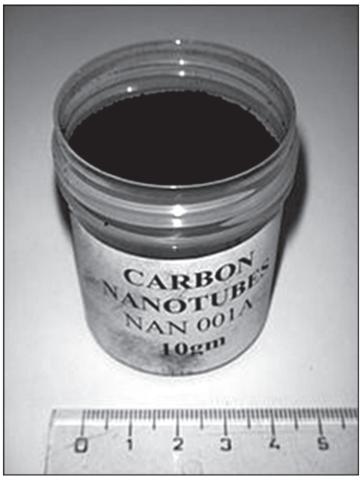


Figure : Powder of Carbon Nanotubes.

Arc Discharge

Nanotubes were observed in 1991 in the carbon soot of graphite electrodes during an arc discharge, by using a current of 100 amps, that was intended to produce fullerenes. However the first macroscopic production of carbon nanotubes was made in 1992 by two researchers at NEC's Fundamental Research Laboratory.

The method used was the same as in 1991. During this process, the carbon contained in the negative electrode sublimates because of the high-discharge temperatures. Because nanotubes were initially discovered using this technique, it has been the most widely used method of nanotube synthesis.

The yield for this method is up to 30% by weight and it produces both single- and multi-walled nanotubes with lengths of up to 50 micrometers with few structural defects.

Laser Ablation

In the laser ablation process, a pulsed laser vapourizes a graphite target in a high-temperature reactor while an inert gas is bled into the chamber. Nanotubes develop on the cooler surfaces of the reactor as the vaporized carbon condenses. A water-cooled surface may be included in the system to collect the nanotubes.

This process was developed by Dr. Richard Smalley and co-workers at Rice University, who at the time of the discovery of carbon nanotubes, were blasting metals with a laser to produce various metal molecules. When they heard of the existence of nanotubes they replaced the metals with graphite to create multi-walled carbon nanotubes. Later that year the team used a composite of graphite and metal catalyst particles (the best yield was from a cobalt and nickel mixture) to synthesize single-walled carbon nanotubes.

The laser ablation method yields around 70% and produces primarily single-walled carbon nanotubes with a controllable diameter determined by the reaction temperature. However, it is more expensive than either arc discharge or chemical vapour deposition.

Chemical Vapour Deposition (CVD)

The catalytic vapour phase deposition of carbon was reported in 1952 and 1959, but it was not until 1993 that carbon nanotubes were formed by this process. In 2007, researchers at the University of Cincinnati (UC) developed a process to grow aligned carbon nanotube arrays of 18 mm length on a FirstNano ET3000 carbon nanotube growth system.

During CVD, a substrate is prepared with a layer of metal catalyst particles, most commonly nickel, cobalt, iron, or a combination. The metal nanoparticles can also be produced by other ways, including reduction of oxides or oxides solid solutions. The diameters of the nanotubes that are to be grown are related to the size of the metal particles.

This can be controlled by patterned (or masked) deposition of the metal, annealing, or by plasma etching of a metal layer. The substrate is heated to approximately 700°C. To initiate the growth of nanotubes, two gases are bled into the reactor: a process gas (such as ammonia, nitrogen or hydrogen) and a carbon-containing gas (such as acetylene, ethylene, ethanol or methane).

Nanotubes grow at the sites of the metal catalyst; the carbon-containing gas is broken apart at the surface of the catalyst particle, and the carbon is transported to the edges of the particle, where it forms the nanotubes. This mechanism is still being studied.

The catalyst particles can stay at the tips of the growing nanotube during the growth process, or remain at the nanotube base, depending on the adhesion between the catalyst particle and the substrate. Thermal catalytic decomposition of hydrocarbon has become an active area of research and can be a promising route for the bulk production of CNTs. Fluidised bed reactor is the most widely used reactor for CNT preparation. Scale-up of the reactor is the major challenge.

Figure: Nanotubes being grown by Plasma Enhanced Chemical Vapour Deposition

CVD is a common method for the commercial production of carbon nanotubes. For this purpose, the metal nanoparticles are mixed with a catalyst support such as MgO or Al_2O_3 to increase the surface area for higher yield of the catalytic reaction of the carbon feedstock with the metal particles. One issue in this synthesis route is the removal of the catalyst support via an acid treatment, which sometimes could destroy the original structure of the carbon nanotubes. However, alternative catalyst supports that are soluble in water have proven effective for nanotube growth.

If a plasma is generated by the application of a strong electric field during the growth process (plasma enhanced chemical vapour deposition), then the nanotube growth will follow the direction of the electric field. By adjusting the geometry of the reactor it is possible to synthesize vertically aligned carbon nanotubes (*i.e.*, perpendicular to the substrate), a morphology that has been of interest to researchers interested in the electron emission from nanotubes. Without the plasma, the resulting nanotubes are often randomly oriented. Under certain reaction conditions, even in the absence of a plasma, closely spaced nanotubes will maintain a vertical growth direction resulting in a dense array of tubes resembling a carpet or forest.

Of the various means for nanotube synthesis, CVD shows the most promise for industrial-scale deposition, because of its price/unit ratio, and because CVD is capable of growing nanotubes directly on a desired substrate, whereas the nanotubes must be collected in the other growth techniques. The growth sites are controllable by careful deposition of the catalyst. In 2007, a team from Meijo University demonstrated a high-efficiency CVD technique for growing carbon nanotubes from camphor. Researchers at Rice University, until recently led by the late Richard Smalley, have concentrated upon finding methods to produce large, pure amounts of particular types of nanotubes. Their approach grows long fibres from many small seeds cut from a single nanotube; all of the resulting fibres were found to be of the same diameter as the original nanotube and are expected to be of the same type as the original nanotube.

Super-growth CVD

Super-growth CVD (water-assisted chemical vapour deposition) process was developed by Kenji Hata, Sumio Iijima and co-workers at AIST, Japan. In this process, the activity and lifetime of the catalyst are enhanced by addition of water into the CVD reactor. Dense millimetre-tall nanotube "forests", aligned normal to the substrate, were produced. The forests growth rate could be expressed, as

$$H(t) = \beta\tau_0\left(1 - e^{-t/\tau_0}\right).$$

In this equation, β is the initial growth rate and τ_0 is the characteristic catalyst lifetime.

Their specific surface exceeds 1,000 m^2/g (capped) or 2,200 m^2/g (uncapped), surpassing the value of 400–1,000 m^2/g for HiPco samples. The synthesis efficiency is about 100 times higher than for the laser ablation method. The time required to make SWNT forests of the height of 2.5 mm by this method was 10 minutes in 2004. Those SWNT forests can be easily separated from the catalyst, yielding clean SWNT material (purity >99.98%) without further purification. For comparison, the as-grown HiPco CNTs contain about 5–35% of metal impurities; it is therefore purified through dispersion and centrifugation that damages the nanotubes. The super-growth process avoids this problem. Patterned highly organized single-walled nanotube structures were successfully fabricated using the super-growth technique.

The mass density of super-growth CNTs is about 0.037 g/cm^3. It is much lower than that of conventional CNT powders (~1.34 g/cm^3), probably because the latter contain metals and amorphous carbon.

The super-growth method is basically a variation of CVD. Therefore, it is possible to grow material containing SWNT, DWNTs and MWNTs, and to alter their ratios by tuning the growth conditions. Their ratios change by the thinness of the catalyst. Many MWNTs are included so that the diameter of the tube is wide.

The vertically aligned nanotube forests originate from a “zipping effect” when they are immersed in a solvent and dried. The zipping effect is caused by the surface tension of the solvent and the van der Waals forces between the carbon nanotubes. It aligns the nanotubes into a dense material, which can be formed in various shapes, such as sheets and bars, by applying weak compression during the process. Densification increases the Vickers hardness by about 70 times and density is 0.55 g/cm^3. The packed carbon nanotubes are more than 1 mm long and have a carbon purity of 99.9% or higher; they also retain the desirable alignment properties of the nanotubes forest.

Natural, Incidental and Controlled Flame Environments

Fullerenes and carbon nanotubes are not necessarily products of high-tech laboratories; they are commonly formed in such mundane places as ordinary flames, produced by burning methane, ethylene, and benzene, and they have been found in soot from both indoor and outdoor air. However, these naturally occurring varieties can be highly irregular in size and quality because the environment in which they are produced is often highly uncontrolled. Thus, although they can be used in some applications, they can lack in the high degree of uniformity necessary to satisfy the many needs of both research and industry. Recent efforts have focused on producing more uniform carbon nanotubes in controlled flame environments. Such methods have promise for large-scale, low-cost nanotube synthesis, though they must compete with rapidly developing large scale CVD production.

Application-related Issues

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 colours. Moreover, SWNTs can be separated by the column chromatography method. Yield is 95% in semiconductor type SWNT and 90% in metallic type SWNT.

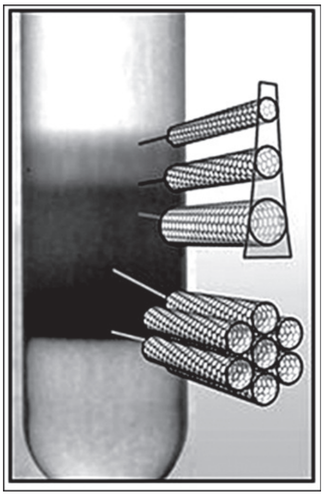


Figure: Centrifuge Tube with a Solution of Carbon Nanotubes, which were Sorted by Diameter using Density-gradient Ultracentrifugation.

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.

Current Applications

Current use and application of nanotubes has mostly been limited to the use of bulk nanotubes, which is a mass of rather unorganized fragments of nanotubes. Bulk nanotube materials may never achieve a tensile strength similar to that of individual tubes, but such composites may, nevertheless, yield strengths sufficient for many applications. Bulk carbon nanotubes have already been used as composite fibres in polymers to improve the mechanical, thermal and electrical properties of the bulk product.

- Easton-Bell Sports, Inc. have been in partnership with Zyvex Performance Materials, using CNT technology in a number of their bicycle components—including flat and riser handlebars, cranks, forks, seatposts, stems and aero bars.
- Zyvex Technologies has also built a 54' maritime vessel, the Piranha Unmanned Surface Vessel, as a technology demonstrator for what is possible using CNT technology. CNTs help improve the structural performance of the vessel, resulting in a lightweight 8,000 lb boat that can carry a payload of 15,000 lb over a range of 2,500 miles.
- Amroy Europe Oy manufactures Hybtonite carbon nanoepoxy resins where carbon nanotubes have been chemically activated to bond to epoxy, resulting in a composite material that is 20% to 30% stronger than other composite materials. It has been used for wind turbines, marine paints and variety of sports gear such as skis, ice hockey sticks, baseball bats, hunting arrows, and surfboards.

Other current applications include:

- Tips for atomic force microscope probes
- In tissue engineering, carbon nanotubes can act as scaffolding for bone growth.

Potential Applications

The strength and flexibility of carbon nanotubes makes them of potential use in controlling other nanoscale structures, which suggests they will have an important role in nanotechnology engineering. The highest tensile strength of an individual multi-walled carbon nanotube has been tested to be is 63 GPa. Carbon nanotubes were found in Damascus steel from the 17th century, possibly helping to account for the legendary strength of the swords made of it.

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 vapour 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 towards 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 (CNTFETs), 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. 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

One of the promising applications of single-walled carbon nanotubes (SWNTs) is their use in solar panels, due to their strong UV/Vis-NIR absorption characteristics. Research has shown that they can provide a sizeable increase in efficiency, even at their current unoptimized state.

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, but 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.

Additional research has been conducted on creating SWNT hybrid solar panels to increase the efficiency further. These hybrids are created by combining SWNT's with photexcitable electron donors to increase the number of electrons generated.

It has been found that the interaction between the photoexcited porphrin and SWNT generates electro-hole pairs at the SWNT surfaces. This phenomenon has been observed experimentally, and contributes practically to an increase in efficiency up to 8.5%.

Hydrogen Storage

In addition to being able to store electrical energy, there has been some research in using carbon nanotubes to store hydrogen to be used as a fuel source. By taking advantage of the capillary effects of the small carbon nanotubes, it is possible to condense gasses in high density inside single-walled nanotubes.

This allows for gasses, most notably hydrogen (H_2), to be stored at high densities without being condensed into a liquid. Potentially, this storage method could be used on vehicles in place of gas fuel tanks for a hydrogen-powered car. A current issue regarding hydrogen-powered vehicles is the onboard storage of the fuel.

Current storage methods involve cooling and condensing the H_2 gas to a liquid state for storage which causes a loss of potential energy (25–45%) when compared to the energy associated with the gaseous state.

Storage using SWNTs would allow one to keep the H2 in its gaseous state, thereby increasing the storage efficiency. This method allows for a volume to energy ratio slightly smaller to that of current gas powered vehicles, allowing for a slightly lower but comparable range.

An area of controversy and frequent experimentation regarding the storage of hydrogen by adsorption in carbon nanotubes is the efficiency by which this process occurs.

The effectiveness of hydrogen storage is integral to its use as a primary fuel source since hydrogen only contains about one fourth the energy per unit volume as gasoline.

Experimental Capacity

One experiment sought to determine the amount of hydrogen stored in CNTs by utilizing elastic recoil detection analysis (ERDA).

CNTs (primarily SWNTs) were synthesized via chemical vapour disposition (CVD) and subjected to a two-stage purification process including air oxidation and acid treatment, then formed into flat, uniform discs and exposed to pure, pressurized hydrogen at various temperatures.

When the data was analysed, it was found that the ability of CNTs to store hydrogen decreased as temperature increased. Moreover, the highest hydrogen concentration measured was ~0.18%; significantly lower than commercially viable hydrogen storage needs to be.

In another experiment, CNTs were synthesized via CVD and their structure was characterized using Raman spectroscopy. Utilizing microwave digestion, the samples were exposed to different acid concentrations and different temperatures for various amounts of time in an attempt to find the optimum purification method for SWNTs of the diameter determined earlier.

The purified samples were then exposed to hydrogen gas at various high pressures, and their adsorption by weight percent was plotted. The data showed that hydrogen adsorption levels of up to 3.7% are possible with a very pure sample and under the proper conditions. It is thought that microwave digestion helps improve the hydrogen adsorption capacity of the CNTs by opening up the ends, allowing access to the inner cavities of the nanotubes.

Limitations on Efficient Hydrogen Adsorption

The biggest obstacle to efficient hydrogen storage using CNTs is the purity of the nanotubes. To achieve maximum hydrogen adsorption, there must be minimum graphene, amorphous carbon, and metallic deposits in the nanotube sample. Current methods of CNT synthesis require a purification step. However, even with pure nanotubes, the adsorption capacity is only maximized under high pressures, which are undesirable in commercial fuel tanks.

Ultracapacitors

MIT Laboratory for Electromagnetic and Electronic Systems uses nanotubes to improve ultracapacitors. The activated charcoal used in conventional ultracapacitors has many small hollow spaces of various size, which create together a large surface to store electric charge.

But as charge is quantized into elementary charges, *i.e.* electrons, and each such elementary charge needs a minimum space, a significant fraction of the electrode surface is not available for storage because the hollow spaces are not compatible with the charge's requirements. With a nanotube electrode the spaces may be tailored to size—few too large or too small—and consequently the capacity should be increased considerably.

Radar Absorption

Radars work in the microwave frequency range, which can be absorbed by MWNTs. Applying the MWNTs to the aircraft would cause the radar to be absorbed and therefore seem to have a smaller signature. One such application could be to paint the nanotubes onto the plane. Recently there has been some work done at the University of Michigan regarding carbon nanotubes usefulness as stealth technology on aircraft.

It has been found that in addition to the radar absorbing properties, the nanotubes neither reflect nor scatter visible light, making it essentially invisible at night, much like painting current stealth aircraft black except much more effective.

Current limitations in manufacturing, however, mean that current production of nanotube-coated aircraft is not possible. One theory to overcome these current limitations is to cover small particles with the nanotubes and suspend the nanotube-covered particles in a medium such as paint, which can then be applied to a surface, like a stealth aircraft.

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.

Other Applications

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

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.

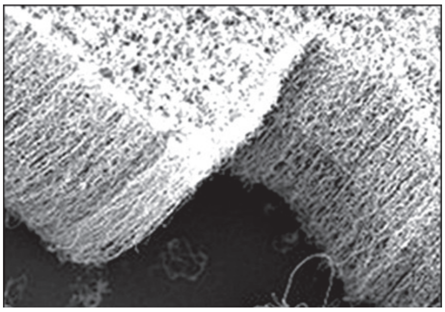


Figure : Aligned Nanotubes are Preferred for Many Applications.

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.

Carbon nanotubes provide a certain potential for metal-free catalysis of inorganic and organic reactions. For instance, oxygen groups attached to the surface of carbon nanotubes have the potential to catalyse oxidative dehydrogenations or selective oxidations. 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. Here, the nanotubes have the added benefit of not being subject to carbon monoxide poisoning.

Discovery

A 2006 editorial written by Marc Monthioux and Vladimir Kuznetsov in the journal *Carbon* described the interesting and often-misstated origin of the carbon nanotube. A large percentage of academic and popular literature attributes the discovery of hollow, nanometre-size tubes composed of graphitic carbon to Sumio Iijima of NEC in 1991.

In 1952 L.V. Radushkevich and V.M. Lukyanovich published clear images of 50 nanometre diameter tubes made of carbon in the Soviet *Journal of Physical Chemistry*. This discovery was largely unnoticed, as the article was published in the Russian language, and Western scientists' access to Soviet press was limited during the Cold War. It is likely that carbon nanotubes were produced before this date, but the invention of the transmission electron microscope (TEM) allowed direct visualization of these structures.

Carbon nanotubes have been produced and observed under a variety of conditions prior to 1991. A paper by Oberlin, Endo, and Koyama published in 1976 clearly showed hollow carbon fibres with nanometre-scale diameters using a vapour-growth technique. Additionally, the authors show a TEM image of a nanotube consisting of a single wall of graphene. Later, Endo has referred to this image as a single-walled nanotube. In 1979, John Abrahamson presented evidence of carbon nanotubes at the 14th Biennial Conference of Carbon at Pennsylvania State University. The conference paper described carbon nanotubes as carbon fibres that were produced on carbon anodes during arc discharge. A characterization of these fibres was given as well as hypotheses for their growth in a nitrogen atmosphere at low pressures.

In 1981, a group of Soviet scientists published the results of chemical and structural characterization of carbon nanoparticles produced by a thermocatalytical disproportionation of carbon monoxide. Using TEM images and XRD patterns, the authors suggested that their "carbon multi-layer tubular crystals" were formed by rolling graphene layers into cylinders. They speculated that by rolling graphene layers into a cylinder, many different arrangements of graphene hexagonal nets are possible. They suggested two possibilities of such arrangements: circular arrangement (armchair nanotube) and a spiral, helical arrangement (chiral tube).

In 1987, Howard G. Tennett of Hyperion Catalysis was issued a U.S. patent for the production of "cylindrical discrete carbon fibrils" with a "constant diameter between about 3.5 and about 70 nanometres..., length 10^2 times the diameter, and an outer region of multiple essentially continuous layers of ordered carbon atoms and a distinct inner core...."

Iijima's discovery of multi-walled carbon nanotubes in the insoluble material of arc-burned graphite rods in 1991 and Mintmire, Dunlap, and White's independent prediction that if single-walled carbon nanotubes could be made, then they would exhibit remarkable conducting properties helped create the initial buzz that is now associated with carbon nanotubes. Nanotube research accelerated greatly following the independent discoveries by Bethune at IBM and Iijima at NEC of *single-walled* carbon nanotubes and methods to specifically produce them by adding transition-metal catalysts to the carbon in an arc discharge. The arc discharge technique was well-known to produce the famed Buckminster fullerene on a preparative scale, and these results appeared to extend the run of accidental discoveries relating to fullerenes. The original observation of fullerenes in mass spectrometry was not anticipated, and the first mass-production technique by Krätschmer and Huffman was used for several years before realizing that it produced fullerenes. The discovery of nanotubes remains a contentious issue. Many believe that Iijima's report in 1991 is of particular importance because it brought carbon nanotubes into the awareness of the scientific community as a whole.

Carbon Credits

Essentially, the types of carbon credits can be split into two forms, those within the voluntary market and those within the compliance market. Each type of carbon credit adheres to a particular standard or certification.

Certified Emission Reduction (CER) Units

The most common type of compliance credit is a CER (Certified Emission Reduction unit) which originates from projects in developing counties. Certification and overall approval of these abatement projects and their credits is known as the Clean Development Mechanism (CDM).

Emission Reduction Unit (ERU)

Like CER in developing nations, within developed nations, a mechanism known as Joint Implementation or JI, produces compliance credits referred to as Emission Reduction Units or ERUs.

New South Wales Greenhouse Gas Abatement Certificate (NGAC)

The New South Wales Greenhouse Abatement Certificate (NGAC) certification process is comprehensive. It includes Kyoto Protocol measures, but goes beyond these. In summary the NGAC certification process ensures the following:

- That each NGAC represents one tonne of carbon dioxide stored for at least 100 years.
- That the trees have been planted since 1990.

- That the trees weren't planted on old growth forest cleared land (the land must have been clear prior to 1990).
- That should the tree from which your carbon credit came come to any harm within 100 years of your purchase *e.g.*, Fire, disease, logging; that carbon credit will be replaced immediately from another source.

Voluntary Carbon Credits

More information on the voluntary market can be found here. The credit types below are just a sample of the most commonly used products in Australia and globally. Many more types exist overseas and if you want more information on these, please contact us.

Voluntary Carbon Unit (VCU) or Voluntary Carbon Standard (VCS) Credit

The VCS Programme provides a robust, global standard for approval of credible voluntary carbon credits.

VCS credits or Voluntary Carbon Units (VCU) must be real, the abatement must have occurred, they must be additional by going beyond business-as-usual activities, be measurable, permanent, not temporarily displace emissions, the findings need to be independently verified and unique so they cannot be used more than once to offset emissions.

The VCS is the most widely known and chosen standards in the voluntary market due to it's Kyoto compatibility as well as it's ability to manage a wide range of project types and methodologies.

Verified (or Voluntary) Emissions Reduction (VER) and Gold Standard VER

The most popular type of carbon credit used to offset emissions around the world voluntarily is a VER, a Verified or Voluntary Emission Reduction unit and there are many different types. Before CDM or JI projects deliver credits used for Compliance purposes such as CERs and ERUs they can produce VERs.

These credits can be verified to a number of specific standards, including the Gold Standard. Not all projects go on to register within the CDM or JI, often due to the size of the project and the inhibitive costs associated with compliance registration, so their choice of one or more of these voluntary standards is made based on it's overall viability and compatibility to them.

Renewable Energy Certificate (REC)

A REC is not a carbon credit that represents one tonne of CO_2e emissions but rather a unit that relates to how much CO_2e is saved by the adoption of renewable energy and how efficiently one mega watt hour (MWh) of electricity can be produced.

This can vary from as little as a 500 kilos of CO_2e, to as much as almost two tonnes from older, less efficient power stations.

Like carbon credits, in an attempt to faze out and replace traditional, emission intensive activities, RECs provide financial subsidies for the power sector to help renewable energy projects become more viable around the world.

New technology and innovations to existing technology are rapidly being realised in areas such as; solar Photo Voltaic (PV) cells, wind farms, subterranean geothermal power plants, wave collection technology, hydroelectric, tidal power, renewable biomass and more. Depending on their location, these projects can produce RECs but as they also displace CO_2e they can often be a more viable project if a choice was made in favour of producing carbon credits instead, for example VCUs, VERs or CERs.

Allotropes of Carbon Nanotubes

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. Nanotubes have been constructed with length-to-diameter ratio of up to 132,000,000:1, significantly larger than for any other material. These cylindrical carbon molecules have unusual properties, which are valuable for nanotechnology, electronics, optics and other fields of materials science and technology. In particular, owing to their extraordinary thermal conductivity and mechanical and electrical properties, carbon nanotubes find applications as additives to various structural materials. For instance, nanotubes form only a tiny portion of the material(s) in (primarily carbon fibre) baseball bats, golf clubs, or car parts.

Nanotubes are members of the fullerene structural family, which also includes the spherical buckyballs, and the ends of a nanotube may be capped with a hemisphere of the buckyball structure. Their name is derived from their long, hollow structure with the walls formed by one-atom-thick sheets of carbon, called graphene. These sheets are rolled at specific and discrete ("chiral") angles, and the combination of the rolling angle and radius decides the nanotube properties; for example, whether the individual nanotube shell is a metal or semiconductor. Nanotubes are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). Individual nanotubes naturally align themselves into “ropes” held together by van der Waals forces, more specifically, pi-stacking.

Applied quantum chemistry, specifically, orbital hybridization best describes chemical bonding in nanotubes. The chemical bonding of nanotubes is composed entirely of sp^2 bonds, similar to those of graphite. These bonds, which are stronger than the sp^3 bonds found in alkanes and diamond, provide nanotubes with their unique strength.

Carbon Nanotube Material

A Carbon Nanotube is a tube-shaped material, made of carbon, having a diameter measuring on the nanometre scale. A nanometre is one-billionth of a meter, or about one ten-thousandth of the thickness of a human hair. The graphite layer appears somewhat like a rolled-up chicken wire with a continuous unbroken hexagonal mesh and carbon molecules at the apexes of the hexagons.

Carbon Nanotubes have many structures, differing in length, thickness, and in the type of helicity and number of layers. Although they are formed from essentially the same graphite sheet, their electrical characteristics differ depending on these variations, acting either as metals or as semiconductors.

As a group, Carbon Nanotubes typically have diameters ranging from <1 nm up to 50 nm. Their lengths are typically several microns, but recent advancements have made the nanotubes much longer, and measured in centimeters.

Properties of a Carbon Nanotube

The intrinsic mechanical and transport properties of Carbon Nanotubes make them the ultimate carbon fibres. The following tables compare these properties to other engineering materials. Overall, Carbon Nanotubes show a unique combination of stiffness, strength, and tenacity compared to other fibre materials which usually lack one or more of these properties. Thermal and electrical conductivity are also very high, and comparable to other conductive materials.

Table : Mechanical Properties of Engineering Fibres

Fibre Material	*Specific Density*	*E (TPa)*	*Strength (GPa)*	*Strain at Break (%)*
Carbon Nanotube	1.3 - 2	1	10 - 60	10
HS Steel	7.8	0.2	4.1	< 10
Carbon Fibre - PAN	1.7 - 2	0.2 - 0.6	1.7 - 5	0.3 - 2.4
Carbon Fibre - Pitch	2 - 2.2	0.4 - 0.96	2.2 - 3.3	0.27 - 0.6
E/S - glass	2.5	0.07/0.08	2.4/4.5	4.8
Kevlar* 49	1.4	0.13	3.6 - 4.1	2.8

Kevlar is a registered trademark of DuPont.

Table : Transport Properties of Conductive Materials

Material	*Thermal Conductivity (W/m.k)*	*Electrical Conductivity*
Carbon Nanotubes	> 3000	106 - 107
Copper	400	6 x 107
Carbon Fibre - Pitch	1000	2 - 8.5 x 106
Carbon Fibre - PAN	8 - 105	6.5 - 14 x 106

Potential Applications for Carbon Nanotubes

Carbon Nanotube Technology can be used for a wide range of new and existing applications:

- Conductive plastics
- Structural composite materials
- Flat-panel displays
- Gas storage
- Antifouling paint
- Micro- and nano-electronics

- Radar-absorbing coating
- Technical textiles
- Ultra-capacitors
- Atomic Force Microscope (AFM) tips
- Batteries with improved lifetime
- Biosensors for harmful gases
- Extra strong fibres.

Nanocyl Produce Carbon Nanotubes

Nanocyl uses the "Catalytic Carbon Vapour Deposition" method for producing Carbon Nanotube Technologies. This proven industrial process is well known for its reliability and scalability. It involves growing nanotubes on substrates, thus enabling uniform, large-scale production of the highest-quality carbon nanotubes worldwide.

Types of Carbon Nanotubes and Related Structures

Terminology of Carbon Nanotubes

There is no consensus on some terms describing carbon nanotubes in scientific literature: both "-wall" and "-walled" are being used in combination with "single", "double", "triple" or "multi", and the letter C is often omitted in the abbreviation; for example, multi-walled carbon nanotube (MWNT).

Single-walled

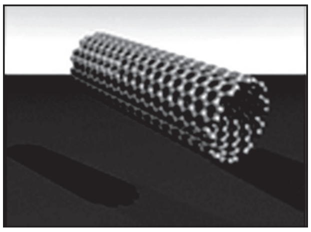


Figure : Armchair (n,n)

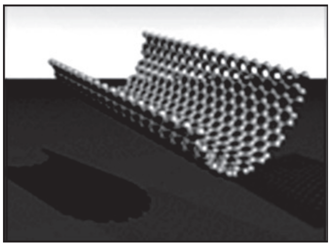


Figure : The Translation Vector is Bent, while the Chiral Vector Stays Straight

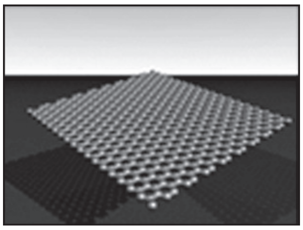


Figure : Graphene Nanoribbon

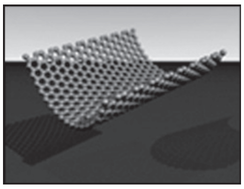


Figure : The Chiral Vector is Bent, while the Translation Vector Stays Straight

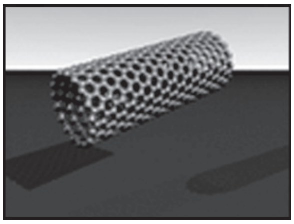


Figure : Zigzag (n,0)

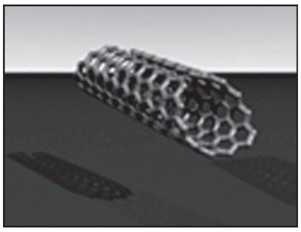


Figure : Chiral (n,m)

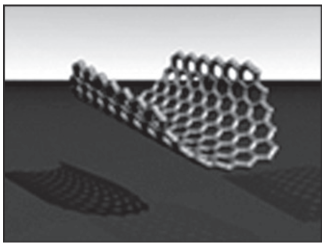


Figure : n and m can be Counted at the end of the Tube

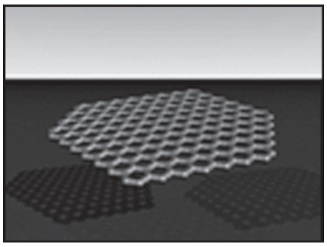


Figure : Graphene Nanoribbon.

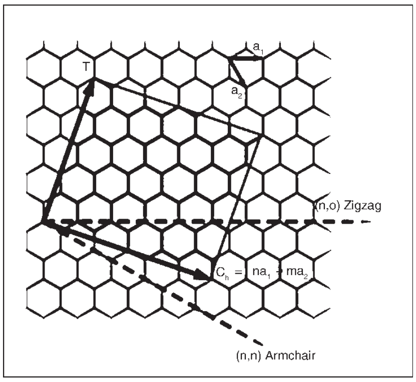


Figure : The (*n*,*m*) Nanotube Naming Scheme can be thought of as a Vector (C_h) in an Infinite Graphene Sheet that Describes how to "Roll Up" the Graphene Sheet to make the Nanotube. T Denotes the Tube Axis, and a_1 and a_2 are the Unit Vectors of Graphene in Real Space.

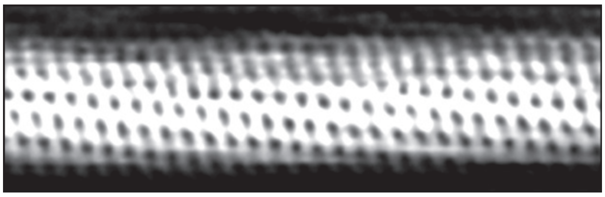


Figure : A Scanning Tunnelling Microscopy Image of Single-walled Carbon Nanotube

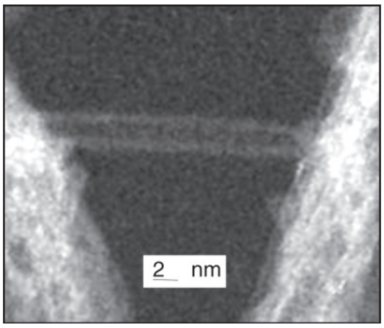


Figure : A Transmission Electron Microscopy Image of a Single-walled Carbon Nanotube

Most single-walled nanotubes (SWNT) have a diameter of close to 1 nanometre, with a tube length that can be many millions of times longer. The structure of a SWNT can be conceptualized by wrapping a one-atom-thick layer of graphite called graphene into a seamless cylinder. The way the graphene sheet is wrapped is represented by a pair of indices (n,m). The integers n and m denote the number of unit vectors along two directions in the honeycomb crystal lattice of graphene. If $m = 0$, the nanotubes are called zigzag nanotubes, and if $n = m$, the nanotubes are called armchair nanotubes. Otherwise, they are called chiral. The diameter of an ideal nanotube can be calculated from its (n,m) indices as follows

$$d = \frac{a}{\pi}\sqrt{\left(n^2 + nm + m^2\right)}.$$

where $a = 0.246$ nm.

SWNTs are an important variety of carbon nanotube because most of their properties change significantly with the (n,m) values, and this dependence is non-monotonic. In particular, their band gap can vary from zero to about 2 eV and their electrical conductivity can show metallic or semiconducting behaviour. Single-walled nanotubes are likely candidates for miniaturizing electronics.

The most basic building block of these systems is the electric wire, and SWNTs with diameters of an order of a nanometre can be excellent conductors. One useful application of SWNTs is in the development of the first intermolecular field-effect transistors (FET). The first intermolecular logic gate using SWCNT FETs was made in 2001. A logic gate requires both a p-FET and an n-FET.

Because SWNTs are p-FETs when exposed to oxygen and n-FETs otherwise, it is possible to protect half of an SWNT from oxygen exposure, while exposing the other half to oxygen. This results in a single SWNT that acts as a NOT logic gate with both p and n-type FETs within the same molecule.

Single-walled nanotubes are dropping precipitously in price, from around $1500 per gram as of 2000 to retail prices of around $50 per gram of as-produced 40–60% by weight SWNTs as of March 2010.

Multi-walled

Multi-walled nanotubes (MWNT) consist of multiple rolled layers (concentric tubes) of graphene. There are two models that can be used to describe the structures of multi-walled nanotubes.

In the *Russian Doll* model, sheets of graphite are arranged in concentric cylinders, *e.g.*, a (0,8) single-walled nanotube (SWNT) within a larger (0,17) single-walled nanotube. In the *Parchment* model, a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled newspaper. The interlayer distance in multi-walled nanotubes is close to the distance between graphene layers in graphite, approximately 3.4 Å. The Russian Doll structure is observed more commonly.

Its individual shells can be described as SWNTs, which can be metallic or semiconducting. Because of statistical probability and restrictions on the relative diameters of the individual tubes, one of the shells, and thus the whole MWNT, is usually a zero-gap metal.

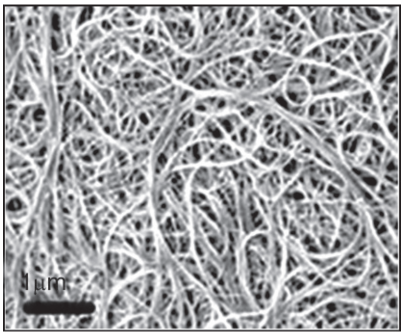


Figure : A Scanning Electron Microscopy Image of Carbon Nanotubes Bundles

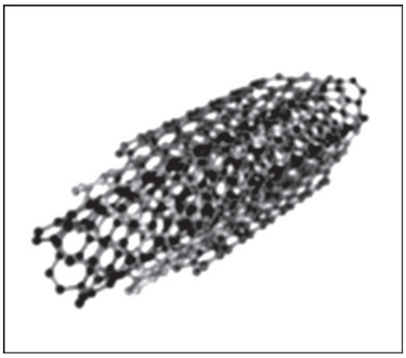


Figure : Triple-walled Armchair Carbon Nanotube

Double-walled carbon nanotubes (DWNT) form a special class of nanotubes because their morphology and properties are similar to those of SWNT but their resistance to chemicals is significantly improved. This is especially important when functionalization is required (this means grafting of chemical functions at the surface of the nanotubes) to add new properties to the CNT. In the case of SWNT, covalent functionalization will break some C=C double bonds, leaving "holes" in the structure on the nanotube and, thus, modifying both its mechanical and electrical properties. In the case of DWNT, only the outer wall is modified. DWNT synthesis on the gram-scale was first proposed in 2003 by the CCVD technique, from the selective reduction of oxide solutions in methane and hydrogen. The telescopic motion ability of inner shells and their unique mechanical properties permit to use multi-walled nanotubes as main movable arms in coming nanomechanical devices. Retraction force that occurs to telescopic motion caused by the Lennard-Jones interaction between shells and its value is about 1.5 nN.

Torus

In theory, a nanotorus is a carbon nanotube bent into a torus (doughnut shape). Nanotori are predicted to have many unique properties, such as magnetic moments 1000 times larger than previously expected for certain specific radii. Properties such as magnetic moment, thermal stability, etc. vary widely depending on radius of the torus and radius of the tube.

Figure: A Stable Nanobud Structure

Nanobud

Carbon nanobuds are a newly created material combining two previously discovered allotropes of carbon: carbon nanotubes and fullerenes. In this new material, fullerene-like “buds” are covalently bonded to the outer sidewalls of the underlying carbon nanotube. This hybrid material has useful properties of both fullerenes and carbon nanotubes. In particular, they have been found to be exceptionally good field emitters. In composite materials, the attached fullerene molecules may function as molecular anchors preventing slipping of the nanotubes, thus improving the composite's mechanical properties.

Graphenated Carbon Nanotubes (g-CNTs)

Graphenated CNTs are a relatively new hybrid that combines graphitic foliates grown along the sidewalls of multiwalled or bamboo style CNTs. Yu *et al.* reported on "chemically bonded graphene leaves" growing along the sidewalls of CNTs. Stoner *et al.* described these structures as "graphenated CNTs" and reported in their use for enhanced supercapacitor performance. Hsu *et al.* further reported on similar structures formed on carbon fibre paper, also for use in supercapacitor applications.

The foliate density can vary as a function of deposition conditions (*e.g.* temperature and time) with their structure ranging from few layers of graphene (< 10) to thicker, more graphite-like. The fundamental advantage of an integrated graphene-CNT structure is the high surface area three-dimensional framework of the CNTs coupled with the high edge density of graphene.

Graphene edges provide significantly higher charge density and reactivity than the basal plane, but they are difficult to arrange in a three-dimensional, high volume-density geometry. CNTs are readily aligned in a high density geometry (*i.e.*, a vertically aligned forest) but lack high charge density surfaces—the sidewalls of the CNTs are similar to the basal plane of graphene and exhibit low charge density except where edge defects exist. Depositing a high density of graphene foliates along the length of aligned CNTs can significantly increase the total charge capacity per unit of nominal area as compared to other carbon nanostructures.

Carbon Peapod

Carbon peapod is a novel hybrid carbon material which traps fullerene inside a carbon nanotube. It can possess interesting magnetic properties with heating and irradiating. It can also be applied as an oscillator during theoretical investigations and predictions.

Cup-stacked Carbon Nanotubes

Cup-stacked carbon nanotubes (CSCNTs) differ from other quasi-1D carbon structures, which normally behave as quasi-metallic conductors of electrons. CSCNTs exhibit semiconducting behaviours due to the stacking microstructure of graphene layers.

4

Nanomaterials

The history of nanomaterials began immediately after the big bang when Nanostructures were formed in the early meteorites. Nature later evolved many other Nanostructures like seashells, skeletons etc. Nanoscaled smoke particles were formed during the use of fire by early humans.

The scientific story of nanomaterials however began much later. One of the first scientific report is the colloidal gold particles synthesised by Michael Faraday as early as 1857. Nanostructured catalysts have also been investigated for over 70 years. By the early 1940's, precipitated and fumed silica nanoparticles were being manufactured and sold in USA and Germany as substitutes for ultrafine carbon black for rubber reinforcements. Nanosized amorphous silica particles have found large-scale applications in many everyday consumer products, ranging from non-diary coffee creamer to automobile tires, optical fibres and catalyst supports. In the

1960s and 1970s metallic nanopowders for magnetic recording tapes were developed. In 1976, for the first time, nanocrystals produced by the now popular inert-gas evaporation technique was published by Granqvist and Buhrman. Recently it has been found that the Maya blue paint is a nanostructured hybrid material. The origin of its colour and its resistance to acids and biocorrosion are still not understood but studies of authentic samples from Jaina Island show that the material is made of needle-shaped palygorskite (a clay) crystals that form a superlattice with a period of 1.4 nm, with intercalcates of amorphous silicate substrate containing inclusions of metal (Mg) nanoparticles. The beautiful tone of the blue colour is obtained only when both these nanoparticles and the superlattice are present, as has been shown by the fabrication of synthetic samples. Probably most celebrated historical comment on the advancement of nanomaterials was the public speculation by physicist Richard Feynman in 1959 at a meeting of the American Physical Society about the effects of manipulating minuscule bits of condensed matter in his famous talk “There’s plenty of room at the bottom”.

Today nanophase engineering expands in a rapidly growing number of structural and functional materials, both inorganic and organic, allowing tomanipulate mechanical, catalytic, electric, magnetic, optical and electronic functions. The production of nanophase or cluster-assembled materials, is usually based upon the creation of separated small clusters which then are fused into a bulk-like material or on their embedding into compact liquid or solid matrix materials. E.g. nanophase silicon, which differs from normal silicon in physical and electronic properties, could be applied to macroscopic semiconductor processes to create new devices.

For instance, when ordinary glass is doped with quantized semiconductor "colloids," it becomes a high performance optical medium with potential applications in optical computing.

Importance of Nanomaterials

These materials have created a high interest in recent years by virtue of their unusual mechanical, electrical, optical and magnetic properties. Some examples are given below:

- Nanophase ceramics are of particular interest because they are more ductile at elevated temperatures as compared to the coarse-grained ceramics.
- Nanostructured semiconductors are known to show various non-linear optical properties. Semiconductor Q-particles also show quantum confinement effects which may lead to special properties, like the luminescence in silicon powders and silicon germanium quantum dots as infrared optoelectronic devices. Nanostructured semiconductors are used as window layers in solar cells.
- Nanosized metallic powders have been used for the production of gas tight materials, dense parts and porous coatings. Cold welding properties combined with the ductility make them suitable for metal-metal bonding especially in the electronic industry.
- Single nanosized magnetic particles are mono-domains and one expects that also in magnetic nanophase materials the grains correspond with

domains, while boundaries on the contrary to disordered walls. Very small particles have special atomic structures with discrete electronic states, which give rise to special properties in addition to the superparamagnetism behaviour. Magnetic nanocomposites have been used for mechanical force transfer (ferrofluids), for high density information storage and magnetic refrigeration.

- Nanostructured metal clusters and colloids of mono- or plurimetallic composition have a special impact in catalytic applications. They may serve as precursors for new type of heterogeneous catalysts (Cortex-catalysts) and have been shown to offer substantial advantages concerning activity, selectivity and lifetime in chemical transformations and electrocatalysis (fuel cells). Enantioselective catalysis was also achieved using chiral modifiers on the surface of nanoscale metal particles.
- Nanostructured metal-oxide thin films are receiving a growing attention for the realization of gas sensors (NOx, CO, CO_2, CH_4 and aromatic hydrocarbons) with enhanced sensitivity and selectivity. Nanostructured metal-oxide (MnO_2) finds application for rechargeable batteries for cars or consumer goods. Nanocrystalline silicon films for highly transparent contacts in thin film solar cell and nano-structured titanium oxide porous films for its high transmission and significant surface area enhancement leading to strong absorption in dye sensitized solar cells.

- Polymer based composites with a high content of inorganic particles leading to a high dielectric constant are interesting materials for photonic band gap structure.

Nanomaterials Establishment

Some nanomaterials occur naturally, but of particular interest are engineered nanomaterials (EN), which are designed for, and already being used in many commercial products and processes. They can be found in such things as sunscreens, cosmetics, sporting goods, stain-resistant clothing, tires, electronics, as well as many other everyday items, and are used in medicine for purposes of diagnosis, imaging and drug delivery. Engineered nanomaterials are resources designed at the molecular (nanometre) level to take advantage of their small size and novel properties which are generally not seen in their conventional, bulk counterparts. The two main reasons why materials at the nano scale can have different properties are increased relative surface area and new quantum effects. Nanomaterials have a much greater surface area to volume ratio than their conventional forms, which can lead to greater chemical reactivity and affect their strength. Also at the nano scale, quantum effects can become much more important in determining the materials properties and characteristics, leading to novel optical, electrical and magnetic behaviours.

Nanomaterials are already in commercial use, with some having been available for several years or decades. The range of commercial products available today is very broad, including stain-resistant and wrinkle-free textiles, cosmetics, sunscreens, electronics, paints and varnishes. Nanocoatings and nanocomposites are finding uses in Book title 1.3 diverse consumer products, such as windows, sports equipment, bicycles and automobiles. There are novel UV-blocking coatings on glass bottles which protect beverages from damage by sunlight, and longer-lasting tennis balls using butylrubber/nano-clay composites. Nanoscale titanium dioxide, for instance, is finding applications in cosmetics, sun-block creams and self-cleaning windows, and nanoscale silica is being used as filler in a range of products, including cosmetics and dental fillings.

Advances in Nanomaterials

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Classification of Nanomaterials

Nanomaterials have extremely small size which having at least one dimension 100 nm or less. Nanomaterials can be nanoscale in one dimension (*e.g.* surface films), two dimensions (*e.g.* strands or fibres), or three dimensions (*e.g.* particles). They can exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and irregular shapes. Common types of nanomaterials include nanotubes, dendrimers, quantum dots and fullerenes. Nanomaterials have applications in the field of nano technology, and displays different physical chemical characteristics from normal chemicals (*i.e.*, silver nano, carbon nanotube, fullerene, photocatalyst, carbon nano, silica).

Classification

Materials referred to as “nanomaterials” generally fall into two categories: fullerenes, and inorganic nanoparticles.

Fullerenes

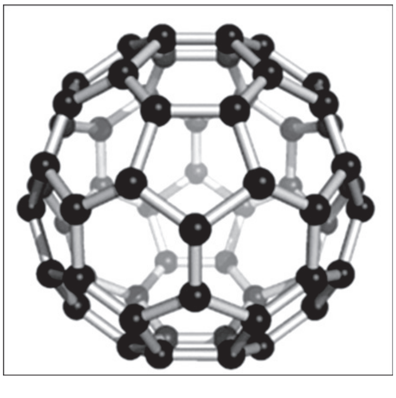


Figure: Rotating View of Buckminsterfullerene C_{60}

The fullerenes are a class of allotropes of carbon which conceptually are graphene sheets rolled into tubes or spheres. These include the carbon nanotubes (or silicon nanotubes) which are of interest both because of their mechanical strength and also because of their electrical properties.

For the past decade, the chemical and physical properties of fullerenes have been a hot topic in the field of research and development, and are likely to continue to be for a long time. In April 2003, fullerenes were under study for potential medicinal use: binding specific antibiotics to the structure of resistant bacteria and even target certain types of cancer cells such as melanoma. The October 2005 issue of Chemistry and Biology contains an article describing the use of fullerenes as light-activated antimicrobial agents. In the field of nanotechnology, heat resistance and superconductivity are among the properties attracting intense research. A common method used to produce fullerenes is to send a large current between two nearby graphite electrodes in an inert atmosphere. The resulting carbon plasma arc between the electrodes cools into sooty residue from which many fullerenes can be isolated. There are many calculations that have been done using ab-initio Quantum Methods applied to fullerenes. By DFT and TDDFT methods one can obtain IR, Raman and UV spectra. Results of such calculations can be compared with experimental results.

Nanoparticles

Nanoparticles or nanocrystals made of metals, semiconductors, or oxides are of particular interest for their mechanical, electrical, magnetic, optical, chemical and other properties. Nanoparticles have been used as quantum dots and as chemical catalysts such as nanomaterial-based catalysts. Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale this is often not the case. Size-dependent properties are observed such as quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and superparamagnetism in magnetic materials.

Nanoparticles exhibit a number of special properties relative to bulk material. For example, the bending of bulk copper (wire, ribbon, etc.) occurs with movement of copper atoms/clusters at about the 50 nm scale. Copper nanoparticles smaller than 50 nm are considered super hard materials that do not exhibit the same malleability and ductility as bulk copper. The change in properties is not always desirable. Ferroelectric materials smaller than 10 nm can switch their magnetisation direction using room temperature thermal energy, thus making them useless for memory storage. Suspensions of nanoparticles are possible because the interaction of the particle surface with the solvent is strong enough to overcome differences in density, which usually result in a material either sinking or floating in a liquid. Nanoparticles often have unexpected visual properties because they are small enough to confine their electrons and produce quantum effects. For example gold nanoparticles appear deep red to black in solution. The often very high surface area to volume ratio of nanoparticles provides a tremendous driving force for diffusion, especially at elevated temperatures. Sintering is possible at lower temperatures and over shorter durations than for larger particles. This theoretically does not affect the density of the final product, though flow difficulties and the tendency of nanoparticles to agglomerate do complicate matters. The surface effects of nanoparticles also reduces the incipient melting temperature.

Sol-gel

The sol-gel process is a wet-chemical technique commonly used to synthesise a wide variety of nanomaterials.

Characterization

The first observations and size measurements of nanoparticles were made during the first decade of the 20th century. They are mostly associated with the name of Zsigmondy who made detailed studies of gold sols and other nanomaterials with sizes down to 10 nm and less. He published a book in 1914. He used an ultramicroscope that employs a *dark field* method for seeing particles with sizes much less than light wavelength.

There are traditional techniques developed during 20th century in Interface and Colloid Science for characterizing nanomaterials. These are widely used for *first generation* passive nanomaterials.

These methods include several different techniques for characterizing particle size distribution. This characterization is imperative because many materials that are expected to be nano-sized are actually aggregated in solutions. Some of methods are based on light scattering. Other apply ultrasound, such as ultrasound attenuation spectroscopy for testing concentrated nano-dispersions and microemulsions.

There is also a group of traditional techniques for characterizing surface charge or zeta potential of nanoparticles in solutions. This information is required for proper system stabilzation, preventing its aggregation or flocculation. These methods include microelectrophoresis, electrophoretic light scattering and electroacoustics. The last one, for instance colloid vibration current method is suitable for characterizing concentrated systems.

Safety

Nanomaterials behave differently than other similarly-sized particles. It is therefore necessary to develop specialized approaches to testing and monitoring their effects on human health and on the environment. The OECD Chemicals Committee has established the Working Party on Manufactured Nanomaterials to address this issue and to study the practices of OECD member countries in regards to nanomaterial safety.

While nanomaterials and nanotechnologies are expected to yield numerous health and health care advances, such as more targeted methods of delivering drugs, new cancer therapies, and methods of early detection of diseases, they also may have unwanted effects. Increased rate of absorption is the main concern associated with manufactured nanoparticles.

When materials are made into nanoparticles, their surface area to volume ratio increases. The greater specific surface area (surface area per unit weight) may lead to increased rate of absorption through the skin, lungs, or digestive tract and may cause unwanted effects to the lungs as well as other organs. However, the particles must be absorbed in sufficient quantities in order to pose health risks.

As the use of nanomaterials increases worldwide, concerns for worker and user safety are mounting. To address such concerns, the Swedish Karolinska Institute conducted a study in which various nanoparticles were introduced to human lung epithelial cells. The results, released in 2008, showed that iron oxide nanoparticles caused little DNA damage and were nontoxic. Zinc oxide nanoparticles were slightly worse. Titanium dioxide caused only DNA damage. Carbon nanotubes caused DNA damage at low levels. Copper oxide was found to be the worst offender, and was the only nanomaterial identified by the researchers as a clear health risk.

Future for the Nanomaterials Sector

Three years of negotiations to update the EU Novel Foods regulations fell apart last week when a last-ditch attempt to reach a compromise between the EU Parliament, the European Commission and the EU Council of Ministers failed. While the talks fell down on the use of cloned animals and their descendants, their failure to reach a compromise will have wider ramifications, with the disagreement meaning that there will be no updates on legislation around nanotechnology. What is this likely to mean for the burgeoning sector? Petah Marian reports.

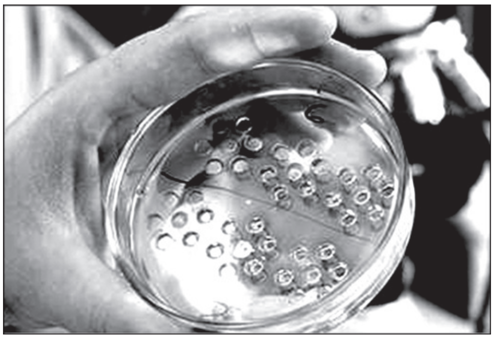


Figure: Scientists are Currently Assesing the Risk Around Nanomaterials

Nanomaterials, products that are less than one millionth of one millimetre, are set to become an important channel for innovation in the food sector. This technology has the potential to offer benefits around product reformulation and functional foods, longer food shelf life, and improved levels of food safety. While the channel is one that is still very nascent, and not currently being used commercially in food products, a UK government report from March last year valued nanotechnology in food and agriculture as being worth US$3.2bn by 2015, up from $265m in 2007.

Current applications are focused around antimicrobial packaging, with nano silver included in food containers to prevent bacteria from sticking to food, as well as the ability to improve the shelf life of products by making packaging less permeable. For example, there are beer bottles that contain nano silica, which Leatherhead microscopy consultant Kathy Groves says, makes it more difficult for oxygen to get through the polymer of the plastic, which would make the beer go off.

A Food Standards Agency (FSA) spokesperson told just-food today that the European Food Services Authority (EFSA) recently provided a “positive opinion” on the use of titanium nitride nanoparticles in the manufacture of polyethylene bottles. It said that this will be reflected in EU legislation from 1 May. Dr. Barry Park from NanoKTN, a knowledge transfer network for the nanotechnology sector, also highlighted the potential for nanotechnology to be used in product reformulation, with nano-sized salt particles set to become available that will allow manufacturers to use less salt, while still maintaining the salty flavour.

He also said that there is work being done in reducing the amount of fat, and sugar in products using nanotechnology, saying that research is underway to reduce the droplet size of fat in emulsions, using water in oil in water emulsions. While nanoparticles are the same as traditional ingredients, only smaller, there are concerns that nanoparticles can penetrate into parts of the body where larger particles can not go.

Park said the FSA is currently investigating what happens when nanomaterials pass through the gut wall and where they end up. "Some of those studies have been done, and there are a lot of studies yet to be completed," he said. "Many of the studies have found that they don't pass through and they don't reside in the gut, which means they don't play any part in issues we should be concerned about," he added.

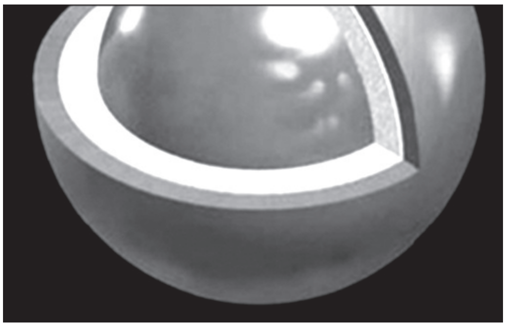
The current Novel Foods regulation dates back to May 1997 and regulates food and ingredients that have not been significantly used for human consumption in the EU before 15 May 1997. Talks to update the regulation fell down last week when the European Parliament and European Council of Ministers could not come to an agreement on regulations around cloned meat and that of their offspring.

Last year, the European Parliament called for nano-ingredients to be subject to Novel Food regulations. It also called for a moratorium on their use until a specifically designed risk assessment of nanotechnology processes or nano-ingredients can prove them to be safe, expressing concerns that nanotechnology is already being used in food and food packaging. However, the FSA confirmed to just-food that no engineered nanomaterials have been approved for marketing as foods or ingredients in the EU. “We are also not aware of any food additive that is specifically engineered to consist of nano-sized particles,” the spokesperson said.

Groves said that some people believe there is no need for new regulations on nanotechnology. “The novel food regulations will address any ‘novel’ properties of ingredients, say for instance nano,” she said. “And I’ve got lots of sympathy for that, I think that it’s true.” Park echoed Groves’ position, saying that the lack of a change in the regulation gives the industry a sense of certainty, as some companies would have been waiting to understand what the changes will mean.

According to Park, the lack of change means that “clarity [in legislation], at least for the moment” will mean that companies have a “clearer sense of what they can do, based on what they’ve done in the past”. He added that any change may have meant that companies would have “held fire” on their nanotechnology strategies until they understood what the changes in legislation would have meant in practice.

While the industry feels that current Novel Foods regulations cover the sector well, Groves said that it is important to get a clear definition of what is considered “nano”, particularly in terms of labelling. She suggested that under many definitions products like icing sugar and boiled eggs would be considered nanomaterials due to the size of the natural ‘nano’ particles in the products. The new regulations, had they gone ahead, would have meant a legal definition of the term nanomaterials. A European Commission spokesperson told just-food that would have triggered a pre-market approval under Novel Foods Regulation and a mandatory labelling requirement on the ingredients list with the word 'nano' after the name of the ingredient. Groves said she has been involved in discussions with the FSA on the labelling of nanomaterials and said that her personal position is that it is "not worthwhile". However, she said that in the FSA's consumer study of nanomaterials, which is set to be released next week, found that "many people favour simple labelling". She said the study found that people can understand the need for nanomaterials in packaging, but can not really understand the need for nanomaterials in their food.



"Even in the beginning, they weren't sure if they wanted technology to tell them if products were fresh or not, but they were asked to keep a diary of the food they bought and the food they threw away and when they came back they were all quite different, and said they were now aware of how much food they do waste and do throw away. So I think it's just about getting people to think about the benefits," says Groves. She says that the argument is that if you put an 'N' or something simple on the product, people can then go away and look it up. However, Groves emphasised that putting an 'N' or a 'nano' on the label is not going to help consumers without more education into the way that science and technology feeds into the food sector. "We do need to educate people more about their food. And they need to take responsibility about learning about it."

While studies into the viability and safety of nanomaterials continue, food companies may face an uphill battle in swinging consumer perception in their favour, with concerns that a lack of education may mean that this technology goes the way of cloned meat and GM. Groves said that the industry needs to be more open, as there is a "climate of fear around the word nanotechnology". A House of Lords report into nanotechnology and food found that food companies' failure to publish details of their research into nanotechnology was "unhelpful" and that the industry's attempts to be "secretive" about its research "is the type of behaviour which may bring about the public reaction it is trying to avert". While it seems as though there is still a some way to go before nanomaterials and technologies make their way into our food, industry may have even further to go before it is able to convince consumers to eat it.

5

Semiconductor Lasers

Although silicon is not inherently a very good material for building semiconductor lasers, there is still interest in silicon lasers because they could be integrated on the same chip with silicon microelectronics, not only potentially reducing cost of the overall system but providing such niceties as fast optical internal links for silicon microchips. For the moment, silicon lasers remain lab toys. The earliest had to be activated by a second laser, which made them of minimal usefulness, but improved devices have appeared that can be electrically driven to generate a laser beam. These devices manage to get around the limits of silicon by employing the "Raman effect", a shift in wavelength that occurs when a photon interacts with an atom in a transparent material. Free electrons in silicon tend to damp laser action, but the experimental devices use a matrix of electrodes that pull electrons out of the lasing channel.

Applications

One of the important applications of the laser in aerospace applications is in the form of the "optical gyroscope" or "laser gyroscope", used as the core element of an "inertial navigation system (INS)". An INS is carried by an aircraft or other vehicle to give its position relative to a point of origin. In modern times, navigation is primarily performed using the GPS navigation satellite system, but since GPS can be jammed, a GPS navigation system usually has an INS backup.

Early INS units developed in the 1950s used mechanical gyroscopes to determine changes in direction. Although such technology was highly refined, ultimately featuring mechanical gyros spinning on a film of gas to reduce friction that could throw off their accuracy, there was no way to eliminate friction entirely, limiting the accuracy of the INS.

The development of the laser led to a new approach, the optical gyroscope, in which a rotating loop of light was used to determine changes in direction. The optical gyroscope was not affected by friction. The basic principle was not new, going back to a paper published by the French physicist Georges Sagnac before the First World War, but the concept wasn't practical until the introduction of the laser.

An optical gyroscope is a type of optical interferometer, in which two laser beams travel in opposite directions, or "counterpropagate", over a closed path, or "optical cavity", inside the gyroscope. The two beams optically interfere with each other, and the effects of motion on the interference can be used to determine the rate and direction of rotation of the system. The first optical gyroscope, the "ring laser gyro (RLG)", was developed in 1962 by Warren Macek of Sperry

Corporation, and the device was quickly incorporated into the guidance systems of missiles and other vehicles. The classic RLG is built out of a flat triangular block of “Zerodur”, a type of glass that resists changes in dimensions with temperature, with a channel fabricated into it not only to act as a resonant path for the gyro’s laser beam, but also to generate the laser beam itself. This is why the classic RLG is sometimes called an “active optical resonator”.

The channel is filled with a lasing gas mix, usually helium-neon. Three highly reflective mirrors are placed at the squared-off corners of the triangular block. Anodes are placed on two sides of the block and a cathode is place on the third to provide laser stimulation. One of the corner mirrors is semi-transparent, to allow reading the laser light into a detector. In effect, a classic RLG is a helium-neon laser bent into a loop.

Consider the effect of rotation on the length of the path the light beams traverse in the resonant cavity. If the tube rotates in one direction, the light beam propagating in that direction sees a longer path length, while the one propagating in the other direction sees a shorter path length. This is the “Sagnac effect”.

The frequency of laser light is dependent on two factors: the spontaneous light emission frequency of the lasing material, and to a lesser extent the cavity length. Lasing only occurs if there are an integral number of wavelengths of light in a cavity, and so changing this length can shift the laser’s frequency from the center frequency of the lasing medium, at least up to the point where the cavity becomes an integer multiple of that center frequency again.

Under rotation, the Sagnac effect changes the path lengths seen by the counterpropagating light beams, resulting in raising the frequency of the beam moving against the rotation and lowering the frequency of the beam moving with the rotation. This frequency difference results in optical interference effects that can be measured by the output detector.

*A practical RLG incorporates a number of refinements to compensate for potential errors. The lasing system includes polarizes to ensure that the laser emits linearly polarized light, eliminating errors that might arise if the RLG were subjected to a magnetic field, which can rotate the polarization of light.

The laser medium is excited by a DC current, which can lead to gas flows that throw off the lasing center frequency through Doppler shifts. This is why the RLG has two anodes: they set up flows in opposite directions, and their effects cancel.

The RLG also is subject to a troublesome problem known as “frequency lock-in”. At low rotation rates, a small amount of “backscatter” from the reflective lasing mirrors interacts with the lasing medium and causes the counter propagating beams to stay locked together, and the output does not change until the rotation increases beyond a certain threshold, resulting in a “dead band” in the output range. The simplest technique for reducing the dead band is “mechanical dithering”, in which the RLG is vibrated over a small arc at a typical frequency of 400 hertz. Dithering tends to lead to unstable output if the rates of rotation are high, as they often are in high-speed aircraft or spacecraft. Some researchers have experimented with RLGs using pulsed lasers as a potential solution. Frequency lock-in won't occur if the laser beam is sourced outside the ring cavity, and experiments have been performed with RLGs using an external laser source. Such devices were generally relatively bulky, complicated, and expensive, and their advantages were not sufficient to replace the classic RLG.

The accuracy of radar ranging is a function of the wavelength and pulse length, with accuracy improving as both get shorter. However, sensitivity of radar is a function of total pulse power, which increases with pulse width. Lasers could provide very short pulses with short wavelengths and high power, offering the best of both worlds. Laser rangefinders were in use in military applications by the 1970s; since a laser rangefinder required a laser detector system, some aircraft used laser rangefinders that also provided a laser spot tracker capability.

Modern infantry laser target designators may include a laser range finding capability. The latest laser rangefinders/ designators may also have a GPS receiver and a communications interface, allowing them to determine the location of a target and then relay its coordinates to a "strike platform" for attack by a GPS-guided weapon.

Laser rangefinders have scientific applications as well. The US Mars Global Surveyor spacecraft used a precision laser altimeter to obtain a highly accurate map of Martian ground levels. Earth-based laser rangefinders have been used to target reflector units left on the Moon by the Apollo manned Moon missions to determine the rate at which the Moon is receding from the Earth and the rates of continental drift.

Experimental imaging laser radar systems have been developed. They provide very high resolution compared to microwave imaging radar systems, but are limited in range by dust or fog. Yet another application of laser ranging is in laser 3D scanners, in which a laser beam is precisely scanned over an object to digitize it into a set of three-dimensional digital coordinates, possibly for generating 3D computer graphics imagery.

Lasers have become extremely important for high-speed digital communications. The amount of information that can be crammed into a communications channel is in principle proportional to the frequency, and the high frequencies/ short wavelengths of light mean that a data link using light can carry much more information than a data link using longer wavelength radio waves.

The biggest problem with using light for data transmission is of course the fact that it is easily blocked by rain or dust in the air, but the introduction of fiber-optic communications cables in the 1970s provided an uninsured long-distance path. LEDs were used for optical data links at first, but semiconductor lasers could generate shorter and cleaner pulses, permitting higher data transmission rates, and they now predominate.

Since there's little in space to interfere with a laser beam, optical communications links are being considered for spacecraft. Such "free space" optical links would allow spacecraft observing Mars or other planets to send large volumes of data back to Earth, to be picked up by satellites with telescopic optical receivers. Some researchers interested in searching for extra-terrestial (ET) civilizations have considered the possibility that ETs are using powerful lasers to communicate over interstellar distances and are searching for such laser emissions.

More practically, blue-green lasers, which can penetrate seawater to a substantial depth, have been used to communicate with underwater submarines, and incidentally as elements of sensor systems used to hunt naval mines.

Laser Energy Weapons and Fusion Power

Of course, the original vision of a laser as an offensive weapon, a "death ray", has not died out, and in fact seems not too far away. As a first step, lasers are now being used in directed infrared countermeasures (DIRCM)" systems carried by aircraft to dazzle heat-seeking missiles and cause them to go astray. There was some talk of using lasers to blind enemy troops as well, but the public reaction to such concepts has been loud and negative.

The next step is to use a laser to destroy the missiles, not simply dazzle them. The US military has developed prototype diode-pumped battlefield lasers to intercept small rockets and even artillery shells. Such systems are not ready for fielding yet, but progress is rapid at this time, and attack laser systems for aircraft or armored vehicles are expected to be available in the 2010:2020 timeframe.

The Air Force is now developing a very high power chemical laser that will be shot out of a modified Boeing 747 jumbo jet to intercept missiles just after they are launched. The Airborne Laser (ABL)" uses a "combustive oxygen and iodine laser (COIL)" system based on light emission in the burning of oxygen and iodine; earlier exercises along this line used hydrogen fluoride lasers, based on the combustion of ethylene

(C2H4) and nitrogen trifluoride (NF3), the fluorine analogue of methane. The Air Force is also interested in developing a satellite platform with a high energy laser to shoot down missiles.

During the "Strategic Defence Initiative (SDI)" or "Star Wars" effort of the 1980s, work was done on an X-ray laser system that, it was hoped, could shoot down missiles as well. A coherent X-ray beam would be very energetic and implementing shielding against it would be very difficult. The concept involved a laser system that was pumped by the detonation of a small nuclear weapon, generating the beam in the instant before the weapon destroyed itself. However, demonstration tests of the scheme did not produce useful results and it was abandoned.

In an inverse application, lasers have been used to experimentally produce nuclear reactions, if on a small scale. As mentioned earlier, high-power laser systems have been used to perform fusion in deuterium/ tritium fuel pellets as a means of performing controlled fusion. Initially, physicists were very optimistic about laser fusion, believing that it would only take modest laser power to do the job. Unfortunately, the plasma formed around the pellet during the process had instabilities that required laser power an order of magnitude greater than expected. It didn't turn out to be so simple after all. The technology is not remotely close to producing a practical fusion reactor, but the lasers used in the experiments have been impressive. The Nova laser, at Lawrence Livermore National Laboratories is one of the world's biggest, a neodymium-glass apparatus with ten arms that covers an area about the size of an athletic field and can focus a 100 terawatt pulse onto a strip of selenium, which produces an X-ray beam that is focused on a capsule of deuterium.

The French Atomic Energy Commission, in hopes of demonstrating the feasibility of inertial confinement fusion, is now underway on the National Ignition Facility (NIF) at Lawrence Livermore Labs, and the Laser Megajoule (LMJ) facility near Bordeaux, building development. The NIF laser system will be 60 times more powerful than the Nova laser system.

A small group of advocates has been promoting a less brute-force scheme, known as “fast ignition”, which uses two relatively low-power lasers instead of one big laser system. In fast ignition fusion, one laser keeps the fuel pellet confined, while the second laser is focused into the pellet through a gold cone to drive fusion. Even the advocates admit that fast ignition is highly theoretical at this time and needs a lot of proving.

6

Nano Process in Chromatography

Introduction

Chromatography is a process which can be used to isolate the various components of a mixture. There are a number of different types of chromatography in use, including gas, liquid, paper, and gel permeation chromatography, and this process can get quite involved, especially with complex mixtures. It is also an extremely useful addition to a variety of fields, including pure and applied sciences, forensics, and athletics, among many others.

The process relies on the fact that different molecules will behave in different ways when they are dissolved in a solvent and moved across an absorbent medium. In a very simple example, one could take ink and make a mark on a piece of paper. The paper could be dipped into water, and the capillary action of the water would pull the ink through the paper. As the ink moved, its ingredients would separate out, revealing a distinctive pattern which could be used to determine the components of the ink.

In preparative chromatography, researchers separate individual components of a compound for use in the lab or in research. This process can get extremely precise: using a preparative chromatography technique, for example, a scientists can isolate two strands of DNA which differ by only a few pieces of information. In analytical chromatography, the goal is to figure out what is in a sample. Drug testing relies on analytical chromatography to isolate illicit substances in urine and blood samples, for instance.

In the example above with a dot of ink and a piece of paper, the basic concepts behind the process are illustrated, although most chromatography machines are a bit more sophisticated. It is important to choose the right solvent or carrier fluid to dissolve the sample in, and to select an appropriate solid medium to pass the sample through. Poor choices can result in confusing or inaccurate results, and the chromatography procedure requires substantial skills on the part of the operator to ensure that it returns useful data.

All sample preparation methods basically ensure the transfer of the analytes of interest from their original surroundings (sample matrix) into a form more suitable for introduction into the analytical instrument. This can be achieved by many different techniques which all have their strengths for specific analyte/matrix combinations. Most often, the sample is placed in direct contact with the extraction phase (extractant) to accomplish transfer of the analytes into the extractant. Subsequently, the extractant can be further processed or in some cases it can be directly introduced into the analytical device. Several basic concepts in sample preparation are described as follows:

Static Sampling

Static sampling techniques bring the entire amount of extractant in contact with the entire amount of sample at the start of the method; the same amount of extractant is continuously kept in contact with the same portion of sample. This means that in static techniques neither the sample nor the extractant is renewed. Static techniques rely on the diffusion of sample analytes into the extractant with the ultimate goal of reaching equilibrium between both phases. Usually, selection of the extractant phase is based on the so-called 'like-like' principle.

A substance will always have the highest affinity for a phase with similar properties as itself. This means that if an apolar compound is to be extracted from a polar matrix, an apolar extractant should be used. It has to be noted that mixing procedures such as stirring, shaking or sonnication are often applied to speed up diffusion of analytes from the sample into the extractant. This, however, only has an influence on the required time for equilibration but does not affect the equilibrium itself or other properties of the static process.

Static sampling often is an easy, reliable and straightforward technique. However, since it relies on the equilibrium distribution of compounds rather than on complete extraction, care should be taken that the distribution constant (K) is equal in all experiments, including calibration and actual samples. Though this seems to be a simple requirement on first sight, in practice this is often not the case. In chemical equilibria, temperature has a dominant effect on equilibrium and distribution constants. Therefore, careful control of the temperature, often within 0.5°C is necessary. In the laboratory this requirement can easily be met, but in field sampling applications, this can be problematic. As was already pointed, a distinction between adsorption and sorption extraction phases has to be made. Sorption phases (including all organic solvents, water, ideal gases and polymeric materials at a temperature above their glass transition point) retain solutes purely with a dissolution mechanism. The analytes partition into the bulk of these phases where they can freely diffuse through the entire amount of sorbent.

Therefore they experience the bulk properties of the sorbent and as long as the total amount of sorbed compounds is less than 1%, these bulk properties do not chance significantly with concentration. This kind of “high” concentration levels are, however, only seldom found in practice and therefore static sorptive extraction is a very reliable approach.

Dynamic Sampling

The opposite of static sampling is dynamic sampling where the entire amount of extractant is not immediately brought into contact with the entire amount of the sample. Whereas in static sampling mixing, stirring and other dynamic processes are only a means for faster equilibration, dynamic sampling procedures essentially require these basic dynamic processes to ensure complete extraction. Many of the dynamic techniques resemble chromatography in that they are also based on the use of a stationary phase (often the extractant) and a moving, mobile phase (often the sample). In the case of gaseous or liquid samples, the sample is most often pumped through the extractant that can, for example, typically be a packed bed.

The analytes will be retained in the bed and consequently the concentration of analyte in the sample will decrease through the bed. Initially the concentration of analyte in the outgoing sample phase will be zero. Usually sampling is stopped when the first analyte of interest starts to elute from the trap. This is called "breakthrough sampling" which will be discussed in this section. However, it is also possible to continue sampling beyond the breakthrough point until all analytes are in equilibrium with the extractant

Applications

Liquid Chromatography

Liquid chromatography has been used in an extremely wide range of analytical methods and it is impossible to give a comprehensive set of examples that would illustrate its wide applicability. The following are a few LC analyses that may indicate the scope of the technique and give the reader some idea of its importance and versatility.

An example of the use of reversed phase chromatography (employing a C8 column) for the separation of some benzodiazepines. The column used was 25 cm long, 4.6 mm in diameter packed with silica based, C8 reverse phase packing particle size 5 m. The mobile phase consisted of 26.5% v/v of methanol, 16.5%v/v acetonitrile and 57.05v/v of 0.1M ammonium acetate adjusted to a pH of 6.0 with glacial acetic acid and the flow-rate was 2 ml/min. The column efficiency available at the optimum velocity would be about

15,000 theoretical plates. The retention time of the last peak is about 12 minutes (*i.e.*, a retention volume of 24 ml). At a flow rate of 2 ml/min., the mobile phase velocity will be well above the optimum and so the maximum efficiency has not been realised. The general technique used when there are more theoretical plates available than required is to increase the flow rate until the separation required is just realised. A mixture of methanol and acetonitrile is employed, the acetonitrile being used to increase the dispersive interactions in the mobile phase.

The reason for the particular solvent mixture is not clear and it would appear that the separation might be achieved equally well by using a stronger solution of methanol alone or a more dilute solution acetonitrile alone. There is no particular advantage to one solvent mixture over another except for the fact that 'waste' acetonitrile produces greater solvent disposal problems than methanol. Another example of the use of reversed phase chromatography for the separation of mixture of growth regulators.

The selectivity was achieved using a complex mixture of ionic and dispersive interactions between the solutes and the stationary phase and ionic, polar and dispersive forces between the solutes and the mobile phase. The initial solvent in the gradient programme was a 1% acetic acid and 1 mM tetrabutyl ammonium phosphate buffered to a pH of 2.8. The tetrabutyl ammonium salt would be adsorbed strongly on the reverse phase and thus acted as an adsorbed ion exchanger. During the programme, acetonitrile was added to the solvent and initially this increased the dispersive interactions between the solute and the mobile phase.

As the acetonitrile concentration became higher, however, the tetrabutyl ammonium salt would be desorbed from the reverse phase reducing the ionic interactions of the solutes with the stationary phase. At even higher concentrations of acetonitrile, the tetrabutyl ammonium salt would be completely desorbed and the interactions of the solutes with the stationary phase would become almost exclusively dispersive. This is an example where a complex phase system was necessary because there was limited column efficiency available. It is likely that a column with intrinsically more efficiency might achieve the separation with a much simpler solvent system and a more straightforward solvent programme.

An example of the use of native silica is given by for the analysis of Darvocet and its generic equivalent formulation. Darvocet is an acetaminophen product in which the active ingredient (and other material in the medicine) are weakly polar and, consequently, lend themselves to separation on a strongly polar stationary phase such as silica gel. The analysis is completed in less than 4 minutes using a short column 3.3 cm long and 4.6 mm in diameter. The silica packing had a particle size of 3 m providing a maximum efficiency of about 5,500 theoretical plates. In order to identify the impurities, the column had to be significantly overloaded. Despite this, the impurities were well separated from the main component and a substance was shown to be present in the generic formulation that was not in the Darvocet. The mobile phase was 98.5% dichloromethane with 1.5% v/v of methanol containing 3.3% ammonium hydroxide. The ammoniacal methanol deactivated the silica gel but the interaction of the solutes with the stationary phase would still be polar in nature.

Ion chromatography

Ion Chromatography can be used in a number of novel ways and employing the appropriate conditions can even be used to separate mixtures where the components are not ionic or do not normally produce interactive ions in aqueous solution. An example of this type of separation is the analysis of saccharide mixtures using ion exchange interactions. An illustration of such a separation is given. The saccharine are reacted with a borate with which saccharides readily forms complex anions. The procedure for making the complex is simply and is achieve by merely including a borate buffer in the mobile phase.

The column packing was a strong anion exchange resin designated as TSKgel Sugar AXG. It had a particle diameter of 10 m and contained quaternary ammonium ions as the ion exchange moiety. The column was 15 cm long, 4.6 mm in diameter and had a potential efficiency of about 7,500 theoretical plates. The mobile phase consisted of three borate buffer solutions which were used in a stepwise gradient. The first buffer solution was a 0.5 M borate buffer (pH 7.7), the second a 0.7 M borate buffer (pH 7.3) and the last a 0.7 M borate buffer (pH 8.7) and the flow rate was 4 ml/min.

The last example clearly broaches an decidedly different approach to the sample separation. It is just as feasible for the solutes to be modified to suit a particular phase system as it is to choose or modify a phase system to suit the solutes. This emphasizes the wide range of variables and alternative approaches that liquid chromatography provides for the analyst. Before ending an example needs to be include that utilizes Micro-reticulated polystyrene gels as a stationary phase. Micro-reticulated polystyrene gels, as already discussed, are formed from cross-linked styrene-divinyl benzene polymers and can be manufactured with a wide range of different pore sizes.

Due to their method of manufacture, the pore volume of the micro-reticulated polystyrene gels may be significantly lower than that of silica gel. Consequently, some gels may have neither the peak capacity nor the loading capacity normally experienced with silica. However, this is generally not a problem in analytical LC.

The column was 30 cm long and 7.8 mm diameter. In exclusion chromatography, a large diameter column is necessary to provide adequate peak capacity. The particle diameter of the packing was 6 mm and thus, at the optimum velocity, an efficiency of about 25000 theoretical plates should be produced. It is seen that the dead volume time is about 19 minutes and a flow-rate of 1.0 ml/min this would be equivalent to a dead volume of 19.5 ml.

Gas chromatography

Gas chromatography has an entirely different field of applications to that of liquid chromatography. In general, gas chromatography is used for the separation of volatile materials and liquid chromatography for the separation of involatile liquids and solids.

There are certain compounds, however, that can be separated with either techniques, and more importantly, many involatile substances such as amino acids, steroids and high molecular eight fatty acids can be derivatized to form volatile substances that can beseparated by GC. The derivatization must be highly reproducible and usually proceed to completion in order to maintain adequate accuracy.

The capillary columns in GC can have much higher efficiencies than their LC counterpart and thus GC can more easily handle multicomponent mixtures such as essential oils. On the other hand, only LC can separate the peptides, polypeptides, proteins and other large biopolymers that are important in biotechnology.

High Temperature GC Stationary Phases

The major limitation of gas chromatography is the stability of the stationary phase at high temperatures. The higher the polarity and the higher the molecular weight of the solutes, the higher the temperature necessary to provide adequate solute partial vapour pressure to allow a gas chromatographic separation to be realised.

Similarly, the stability of the solutes at high temperature can also become a problem. The solute must be thermally stable so that the partial pressure is sufficiently high to allow elution in a reasonable time. Nothing can be done with respect to the solute stability as this is determined by the nature of the sample.

There are certain materials hat can be used as stationary phases at remarkably high temperatures. These materials are based on the polymerization of carborane substituted siloxanes.

Hydrocarbon Analysis

Due to the perceived toxicity and carcinogenic character of the aromatic hydrocarbons, the presence of these materials is carefully monitored in all areas where they might enter the human food chain. The analysis of water for aromatic hydrocarbons, particularly surface water in those areas where contamination might take place, is a common assay made by the public analyst. It is essential to be able to measure concentrations in the ppb levels, and thus GC method employing a high sensitive detector is essential.

Nevertheless, even if a high sensitivity detector is employed, some sample concentration will be necessary to measure contaminants at such low levels. One method is the purge and trap procedure, using a solid adsorbent to remove the hydrocarbon vapours. A diagram of the purge and trap system. A 5 ml sample of spiked water was placed in a small vial through which a stream of helium was passed at a flow rate of 40 ml/min.

The purge was carried out at room temperature for 11 min. After bubbling through the sample, the helium passed through a stainless steel adsorption tube, 1/8 in. diameter having a 7 cm length packed with Carbopack C and a 1.2 cm length packed with Carbopack B. Carbopack C is 20/40 mesh, graphitized carbon, having a surface area of 10 m^2/g and the short length of Carbopack B packing had a surface area of about 100 m^2/g.

Essential Oils

Without the use of gas chromatography the analysis of essential oils would be extremely difficult. Prior to the technique being developed, only the major components of the oils could be separated, achieved by distillation with high efficiency columns. Even so, such columns rarely contained more than 100 theoretical plates (distillation plates), were very slow in operation, and took many days to complete an analysis. Due to the limited separation efficiency of the distillation column, even the major components were contaminated with traces of materials, many of which had strong olfactory intensity and thus confused the olfactory character of the major component.

The gas chromatograph had a startling impact on the essential oil industry. Not only was the complex nature of the raw materials disclosed for the first time, but the character of each pure individual components could be accurately ascertained by olfactory assessment of the eluted peaks (using a non destructive detector such as the katherometer, and smelling them).

The first separations of essential oils were carried out on packed columns that provided limited efficiency but, nevertheless represented a tremendous advance on distillation. The introduction of the technique of temperature programming improved the separation even more.

However, it was not until the capillary column, with its many thousands of theoretical plates, became commercially available that the true complex nature of many of the essential oils was revealed. The chemical structure of the individual components of many of the oils, elucidated by the GC/MS tandem systems, provided the knowledge necessary to synthesize a number of commercially important synthetic flavours. For example, the synthetic flavours that closely imitate those of the peach, melon and other fruits that are presently available to the contemporary food chemist are a direct result of the separating capabilities of gas chromatography.