

The logo for 'científica' features the word in a white, lowercase, sans-serif font. A small, stylized graphic of a yellow and orange flame or spark is positioned above the letter 'i'.

Fullerenes

Technology White Papers

nr. 7

The background of the cover is a dark, almost black, field filled with numerous small, out-of-focus, multi-colored spots. These spots, in shades of purple, blue, green, yellow, and red, are arranged in a way that suggests a large number of particles or molecules, possibly representing the structure of fullerenes. The overall effect is a vibrant, abstract pattern against the dark background.

Paul Holister
Cristina Román Vas
Tim Harper

FULLERENES

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Authors

Paul Holister
Cristina Román
Tim Harper

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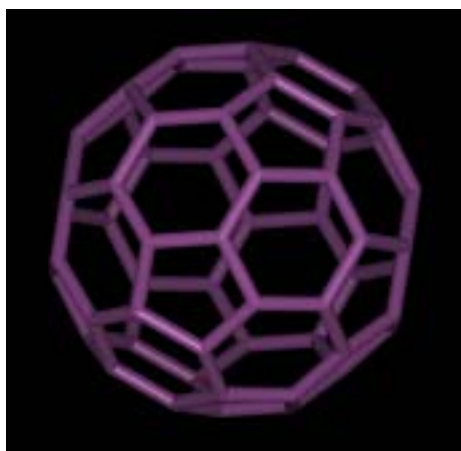
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Origin of content

The free reports in this series are extracted from the technology reports that make up the Nanotechnology Opportunity Report collection and are designed to offer an introduction to the variety of technologies that fall under the nanotechnology umbrella. The full reports also include 'opportunities' sections, covering the various applications of the technology and their effects on markets, and a list describing the companies involved in the technology.

Introduction to fullerenes



*Buckyball. Courtesy of the
Center for Nanoscale Science &
Technology, Rice University*

The first fullerene discovered was the buckyball. Also known as buckminsterfullerene, after the architect Buckminster Fuller, whose geodesic dome it resembles, it was discovered in 1985 at Rice University in Houston by Richard Smalley, Robert Curl and Harry Kroto, who shared a Nobel Prize in 1996 for the discovery. Buckminsterfullerene, or buckyball, molecules are roughly spherical cages of 60 carbon atoms (C_{60}) arranged in interlocking hexagons and pentagons, like the patches on a soccer ball.

Other fullerenes were discovered shortly afterwards with more and fewer carbon atoms, ranging from 28 up into the hundreds, though C_{60} remains the easiest to produce, and cheapest, with prices rising rapidly for the larger fullerenes. The word 'fullerene' covers this collection of hollow carbon molecules made of a cage of interlocking pentagons and hexagons. Carbon nanotubes, made of graphite sheets of hexagonal arrays of carbon rolled into tubes, are close cousins in terms of production methods and some of their properties, and can be included in the fullerene family if their ends are closed, in which case they are like a buckyball extended into a tube by the insertion of carbons along its midriff. For the purposes of this report, the term fullerenes should not generally be taken to include carbon nanotubes.

Production methods

Fullerenes are in fact produced in small amounts naturally, in fires and lightning strikes, and there is some evidence that the massive Permian extinction of 250 million years ago was caused by the impact of an object containing buckyballs. However, they were first produced by man (at least knowingly) in the soot resulting from vaporizing graphite with a laser.

The earliest bulk production process is the arc discharge (or Krätschmer-Huffman) method, using graphite electrodes, developed in 1990. This produces predominantly C_{60} and C_{70} but can be made to produce higher fullerenes, for instance by having more

porous electrodes. Separation with solvents such as toluene can achieve near 100% purity for C₆₀.

A little later, a group at MIT started producing C₆₀ in a benzene flame. And pyrolysis (transformation of a compound by heat, without burning) of a variety of aromatic compounds has also been used to produce fullerenes (aromatic compounds have benzene-derived ring structures. A typical attribute of aromatics is that they have bonding electrons free to move around, so-called delocalized electrons. Fullerenes themselves are aromatic).

Methods such as sputtering and electron beam evaporation (with a graphite precursor) have been shown to preferentially produce higher fullerenes, such as C₇₀, C₇₆, C₇₈, and C₈₄. UCLA has patents on these approaches.

Properties of fullerenes

Physically, buckyballs are extremely strong molecules, able to resist great pressure—they will bounce back to their original shape after being subjected to over 3,000 atmospheres. Their physical strength does seem to offer potential in materials. However, like nanotubes, they do not bond to each other chemically, sticking together instead through much weaker forces—van der Waals—the same forces that hold layers of graphite together. This gives buckyballs, like graphite, potential as a lubricant, though the molecules tend to be too small for many applications, getting stuck in crevices. Buckyballs with shells around them, known as nano-onions, or bucky-onions, are larger and potentially better as a lubricant. A technique for creating these with quite high purity using an underwater arc approach was demonstrated in December 2001 by a group from the University of Cambridge in the UK and the Himeji Institute of Technology in Japan.

Although buckyballs do not stick together well, this does not mean they do not have applications in solids. When incorporated in relatively low amounts in a polymer matrix they can be held in place and impart some of their strength and low density to the material. Companies such as BuckyUSA are working with the tire industry to establish whether C₇₀ would be a superior additive to carbon black.

Research has been done on making buckyballs less slippery. Shortly before the aforementioned production of nano-onions, Lars Hultman and colleagues, of the University of Linköping in Sweden, replaced some of the carbon atoms in buckyballs with nitrogen atoms, allowing them to bond, producing a material that is hard but elastic. These modified buckyballs also formed shells and were also called nano-onions.

Fullerenes and related substances have shown considerable potential as catalysts (basically, substances that enhance a reaction without being consumed themselves). A team at the Fritz Haber Institute in Berlin has used bucky-onions to convert ethylbenzene into styrene, one of the ten most important industrial chemical processes. Existing approaches are limited to a maximum yield of 50% but the researchers achieved styrene yields of 62% in preliminary experiments, and expect further improvement. The bucky-onions seem, however, to be a precursor to the catalyst as they were converted in the reaction into a material that had lost the regular,

concentric-layer structure of bucky-onions, and looked more or less disordered, but was an effective catalyst (*Angewandte Chemie International Edition*, **41**, 1885–1888).

SRI International have also been looking at the catalytic properties of fullerenes and related materials, including the soot produced alongside the fullerenes using arc or combustion methods. This soot contains a variety of carbon forms that can be partially like fullerenes (composed of hexagons and pentagons) but probably with open areas that serve as catalytic sites. The soot can be used for hydrogenation/dehydrogenation of aromatics, for upgrading of heavy oils, and for conversion of methane into higher hydrocarbons by pyrolytic or reforming processes.

Fullerenes have interesting electrical properties, which have led to suggestions of use in a number of electronics-related areas, from data storage devices to solar cells. Researchers at Virginia Tech have used ultra-thin layers of fullerenes as electron acceptors in flexible organic solar cells. Currently the efficiency is about a fifth of conventional silicon photovoltaics (so about 3-4%, compared to 15-20% for mass market silicon solar cells) but the researchers expect to be able, through better control of the nanostructure, to equal or exceed the efficiency of current silicon-based devices.

The same properties also offer potential use in photodetectors for X-rays. Work by Siemens on this is discussed later.

Another use of the electrical properties of fullerenes is in fuel cells. Sony has used them to replace large polymer molecules in the electrolytic membrane of direct methanol fuel cells (with personal electronics being the intended application). The result is a fuel cell capable of operating at lower temperatures than those with polymer-only membranes, and Sony believes the fullerene-based membranes might even work out cheaper. Sony have also been using fullerenes in work on hydrogen-based fuel cells, exploiting their ability to help move protons around (proton exchange membranes are the basis of such fuel cells).

Fullerenes have been inserted into nanotubes, the result sometimes being referred to as 'peapods'. The earliest work on this was done early in 2002 in South Korea (Seoul National University) and the US (University of Pennsylvania in Philadelphia), using C_{82} and C_{60} respectively. The fullerenes alter the electrical behavior of the nanotubes, creating regions of varying semiconducting properties, effectively producing a series of tiny transistors within a nanotube. The properties can be modified by moving the location of the enclosed fullerenes and researchers at Michigan State University have even suggested using this to create memory devices. Such work is still at the very early research stage and applications should not be expected any time soon, if ever (there are many competing approaches to nanoelectronics and memory).



Computer simulation of nanotube-based memory element. The nanotube holds a C_{60} molecule inside. The C_{60} carries a net charge because it contains an alkali atom in the hollow cage. The C_{60} can be shifted from one end to the other by applying an electric field between the ends of the capsule. The two energy minima of this system, with the C_{60} bonded to either end of the capsule, can be associated with bit 0 and bit 1. Courtesy of David Tomanek, Michigan State University, <http://www.pa.msu.edu/~tomanek>.

Fullerene-based materials may have important photonic device applications (photonics being essentially the equivalent of electronics but using light instead of electricity). Fullerenes exhibit a very large non-linear optical response (i.e. their optical properties change with exposure to light) and may well be suitable for a range of telecommunications applications. The non-linear optical properties may be enhanced by the addition of one or more metal atoms externally to the fullerene cage as well as within the cage itself.

Fullerenes are also effective at mopping up free radicals, which damage living tissue. This has led to the suggestion that they might protect the skin in cosmetics, or help hinder neural damage caused by radicals in certain diseases, research on which in rats has already shown promise.

The size of C_{60} is similar to many biologically active molecules, including drugs, such as Prozac, and steroid hormones. This gives it potential as a foundation for creating a variety of biologically active variants. Buckyballs have a high physical and chemical affinity for the active site on an important enzyme for HIV, called HIV protease, and block the action of the enzyme. HIV protease is the target of existing AIDS drugs but resistance has developed to a set of these drugs since they all have similar actions. Buckyballs target HIV protease differently so their effect should not be subject to resistance already developed.

As previously mentioned, the neuroprotective potential of C_{60} has already been demonstrated, and vesicles made out of them could be used to deliver drugs. Applications for buckyballs with other atoms trapped inside them, referred to as endohedral fullerenes, are mentioned later.

Considerable interest was generated in the second half of 2001 by research at Lucent's Bell Labs that showed that buckyballs could be made superconducting at above the temperature of liquid nitrogen, a very important find because liquid nitrogen is relatively cheap to produce but lower temperatures are much harder to maintain. However, some work on molecular electronics by the same researcher, Hendrik Schön, was called into question because of identical graphs being used in different papers to represent different results. Later the buckyball work was similarly questioned and indeed his results have not been duplicated by other researchers.

Fullerenes and their derivatives have indeed been shown to be superconducting, but only at very low temperatures (a few tens of degrees centigrade above absolute zero).

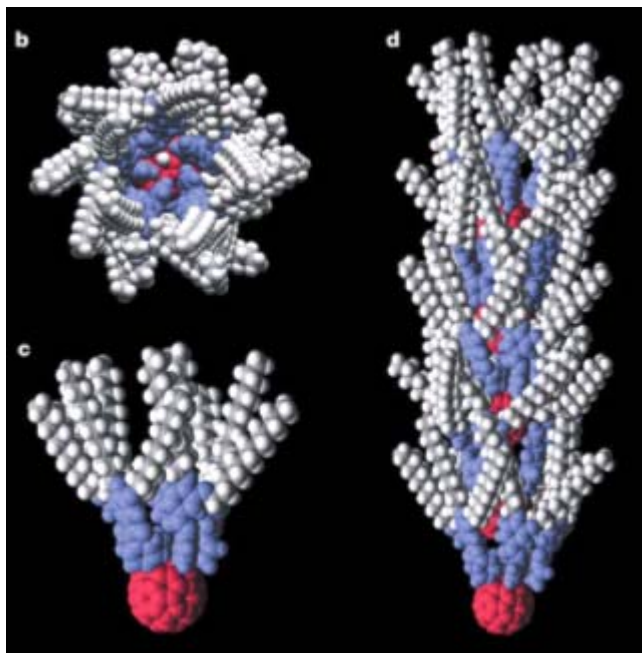
Around the same time there was also a claim that a polymer had been created out of buckyballs that was magnetic at room temperature, making the first non-metallic magnetic material. Though no wrong-doing has been suggested in this case, these results also have not been reproduced. Besides which, in terms of potential value, this result was trumped shortly afterwards by the creation of a polymer (without buckyballs) that was also shown to be magnetic at room temperature, and considerably more so.

Fullerenes can also be used as precursors for other materials, such as diamond coatings or nanotubes (Sony, for example, creates nanotubes by heating fullerenes and platinum).

On the esoteric side, fullerenes have been used in fundamental research in quantum mechanics, being the largest particles in which the wave/particle duality of matter has been demonstrated, by getting a C_{60} molecule to appear to pass through two different slits simultaneously, a famous experiment normally performed with electrons, photons or single atoms.

Functionalization

Chemical groups can be attached to a fullerene's carbon atoms, a process called functionalization, modifying their properties. The number of carbon atoms available to do this has led to the epithet "molecular pincushion", especially within the context of medical applications such as those being developed by the company C Sixty.



Research on functionalization of fullerenes has been particularly active in recent years, with aims varying from the creation of polymers to biologically active variants.

A nice illustration of the lengths to which functionalization can be taken comes from a group at the University of Tokyo in Japan and their creation of molecular 'shuttlecocks' (see picture). These have potential in liquid crystal applications, which goes beyond liquid-crystal displays as there is growing interest in their use in areas such as nonlinear optics, photonics and molecular electronics (*Nature* **419**, 702–705).

The University of Tokyo has also done some interesting work on creating hybrids of ferrocenes and fullerenes. Ferrocenes are compounds containing iron and organic groups that have attracted much interest in the decades since their discovery. The hybrids might create vesicles for drug delivery or be the basis of nanostructures with useful electronic or photonic properties. Vesicles have also been created at the university using the potassium salt of pentaphenylfullerene, each composed of about 13,000 modified C₆₀ molecules.

Rice University, in collaboration with the Russian Academy of Science's Institute for High-pressure Physics, has been working on the fluorination of polyfullerenes, polymer chains and sheets of C₆₀. Polyfullerenes are much more stable than organic polymers like polyethylene, polypropylene or nylon, and the addition of fluorine to the polyfullerenes could make it easier for chemists to use them in subsequent chemical reactions.

Researchers at SRI International have also done work on creating fullerene-based polymers, starting with attaching amines to C₆₀. The result was a variety of highly cross-linked polymers suitable for spray-, dip-, or spin-coating that are very hard and show high thermal stability.

Endohedral fullerenes

An area of research that has been at least as active as functionalization of fullerenes is that of putting atoms inside them. The results are called endohedral fullerenes, which are described with the notation X@C₆₀, where X is the trapped atom (or atoms) and C₆₀ could be any fullerene. Reactive elements can be stabilized inside the fullerene cage. The contained element can also change the electronic and magnetic properties of the fullerene (the caged atom can contribute electrons to the fullerene molecule). The creation of endohedral fullerenes has proved challenging. Simple approaches involve creating the fullerenes in the presence of the element to be encapsulated, but this produces a low yield, typically less than 1%. However, some researchers, such as Lothar Dunsch of the Leibniz Institute for Solid State & Materials Research, have claimed that it is possible, by adjusting reaction conditions, to get certain endohedral fullerenes as the main product of a reaction.

Alternatively, fullerenes can be mixed with the substance to be encapsulated and subjected to high temperatures and pressures, or a chemical approach can be taken to open up the fullerene to let the other substance in. Researchers at UCLA have managed to open quite large holes, although closing them again remains elusive.

A huge number of elements have been encapsulated in fullerenes, including the noble gases, which have no desire to bond with the surrounding carbon atoms but can be used in applications such as magnetic resonance imaging (MRI).

Using endohedral fullerenes for medical imaging applications requires them to be water soluble. The higher fullerenes (above C₆₀) have derivatives that are generally more soluble, but they are more expensive to produce. C₆₀ endohedral fullerenes are generally less soluble and air-sensitive, but relatively cheap to produce. Functionalization has managed to improve solubility and also stability in air.

Additionally, C_{60} derivatives appear to be efficiently excreted while higher fullerenes, such as C_{82} , have shown a tendency to accumulate in the lung, liver and bone.

The relatively high tolerance of biological systems to carbon is one of the reasons for the potential of buckyballs in medical applications, from delivery of radioisotopes to cancer cells, to MRI. Anything included in the buckyball is effectively shielded from the body. Importantly, buckyballs are small enough to pass through the kidneys and be excreted. Biological systems can be sensitized to buckyballs, however, as has been demonstrated by the development of antibodies to them (useful for monitoring the presence of buckyballs in tissue and biological fluids).

Researchers at Rice University have designed C_{60} and other fullerene molecules with an atom of gadolinium inside and with chemical appendages that make them water-soluble. In typical MRI contrast agents, the metal gadolinium is linked to a non-fullerene molecule, which is normally excreted quickly from the body. Fullerene-encapsulated gadolinium might allow the contrast agent to remain in the body longer.

Meanwhile, researchers at Virginia Tech are putting four atoms, three metal atoms and a nitrogen atom, inside C_{80} fullerene cages to create multiple-use contrast agents—two of the metal atoms could be chosen for use in MRI imaging, and one for X-rays, for example. The Virginia Tech work is licensed to Luna Nanomaterials, which calls the product trimetaspheres. The company claims the contrast agents are 50 times better than the most commonly used contrast agent, Magnevist (the patent on which, interestingly, is about to expire). Luna puts the size of the market for MRI contrast agents at a billion dollars.

Virginia Tech has also created (in early 2002) an organic derivative of a metallofullerene that makes it more soluble, facilitating biological applications. The aim is to attach water-soluble groups such as peptides or hydrophilic chains.

Fullerene-related structures

It is important to realize when considering the potential of fullerenes that they represent a variety of new carbon structures, and that there are also related structures of interest, such as carbon nanotubes (if one considers them separately from the roughly spherical fullerenes), or various materials in fullerene soot. As mentioned earlier, these have potential as catalysts.

Additionally, if one considers possible geometries, adding rings with more than 6 atoms (heptagons and octagons, for example) produces curvature in the opposite direction to that created by the pentagons found in fullerenes. Forms of carbon based on such negative curvature had been hypothesized for some time, and dubbed schwartzites, and were created in late 2002 (*Applied Physics Letters* **81**, 3359–3361). These highly porous materials have potential in catalysis, fuel storage and biomaterials and thus share potential applications with fullerenes.

Other materials that should be kept in mind as part of the application landscape of fullerenes are those with similar structures but made out of other materials. The company Applied Nanomaterials specializes in inorganic equivalents of nanotubes and fullerenes. They claim these materials are easier to make and have applications in the electronics (they are semiconducting), composites and lubricants markets.