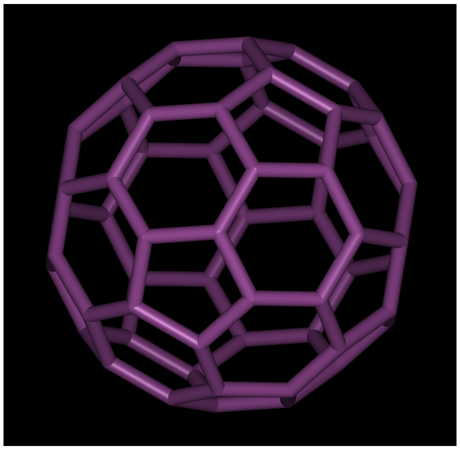
## Introduction to fullerenes



*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

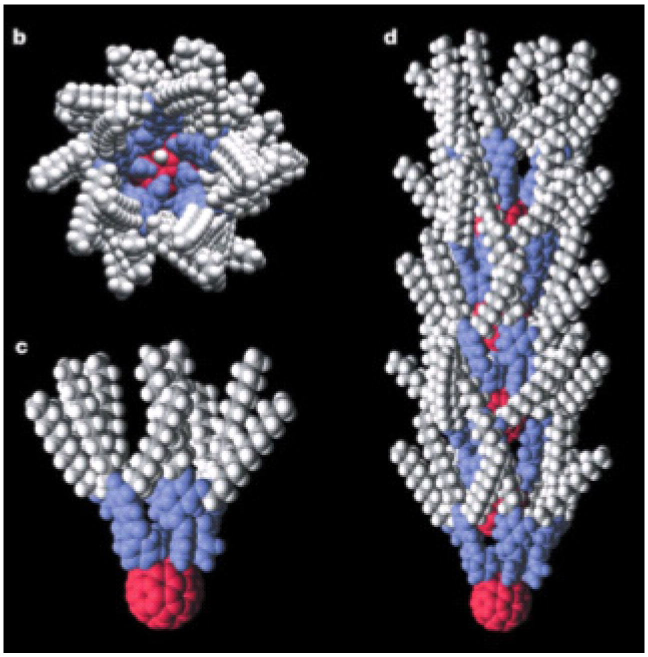
Fullerenes are in fact produced in small amounts naturally, in fires and lightning strikes, and there is some evidence that the massive Permian extinction of 250 million years ago was caused by the impact of an object containing buckyballs. However, they were first produced by man (at least knowingly) 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 $C_{60}$.

A little later, a group at MIT started producing $C_{60}$ 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).

## 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.




*Color code: red, fullerene core; blue, aromatic groups; gray, alkyl chains. The image on the right shows a stack of 5 molecules. Courtesy of Nature Publishing Group (www.nature.com) and the departments of Chemistry, and Chemistry and Biotechnology, The University of Tokyo.*

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 $C_{60}$ 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 $C_{60}$. 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 $C_{60}$. 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.

Corporation set up Fullerene International Corporation with two companies based in Tucson, Arizona: Materials and Electrochemical Research Corporation and Research Corporation Technologies. Then in October 2001, Mitsubishi and Mitsubishi Chemical created Frontier Carbon Corporation. Production is expected to reach 1500 tons a year in 2007, with prices coming down to 100 yen per gram ($0.85) and eventually to 10 yen per gram.

## Bulk materials, layers and coatings

Fullerenes have been investigated as fillers in composite materials, but their cousin, the buckytube, or carbon nanotube, generally attracts more interest. However, there are two important differences when comparing these fillers. The first is that fullerenes are currently a lot cheaper and look set to remain so for some time. The second is that the physical properties are quite different, with carbon nanotubes offering enormous tensile strength but not being that impressive under compressive stress, where fullerenes tend to win out (there is also a directional component to be considered with nanotubes because of their long, thin shape). This does suggest that once prices come down applications such as using fullerenes in car tires, for example, may prove commercially viable. Composites containing carbon nanotubes are already on the market but these are large, multi-walled nanotubes that do not confer any great strength. Their primary attraction is providing conductivity at quite low filler loads (an area in which nanotubes will tend to be better than fullerenes because of their length) and without blackening of the composite that is found with materials such as carbon fibers. Competition will also come in the form of nanoclay composites, which already offer 10-15% increases in strength and could offer up to 25%. These are already being used in various car parts.

Polymers made out of fullerenes tend to be more resilient than other polymers and thus may well find commercial applications, but these will be very limited until the cost of the raw material comes down considerably. In terms of polymer films, composites containing carbon nanotubes may also compete in the future and nanoclay composites are already finding their way into the packaging industry where it is not just their strength that is valuable but also reduced permeability to gases, which comes from the flat, thin shape of the particles. However, it should be noted that fullerene polymers are not composites in which the fullerenes are simply mixed in, but have the fullerenes as part of the basic building blocks of the polymer. No such approach has been found for nanotubes (which cannot anyway be produced in such a uniform way) and this does hold promise of creating pure and well-structured materials that capitalize on the properties of fullerenes. This alone suggests that in years to come fullerenes may give rise to a variety of well-structured materials with desirable physical properties.

## Electrical and (opto)electronic applications

In application areas such as flexible organic solar cells, fullerenes do look promising in comparison with other organic approaches. Some of the most promising research in photovoltaics is around nanoparticles, the size of which can be tuned to respond to different wavelengths of light, allowing, in theory, the harvesting of a wide range of wavelengths and thus efficiencies beyond those of existing silicon-based photovoltaics. Production of materials based upon such particles promises to be very cheap, according to companies such as Nanosys, whose particular line of investigation