New carbon nanostructures

Fullerenes and Nanotubes

ANDRZEJ HUCZKO
Department of Chemistry, Warsaw University,
Commission for Low-Temperature Plasma Chemistry,
Lublin Branch of the Polish Academy of Sciences
ahuczko@chem.uw.edu.pl

Dr. Andrzej Huczko, a chemist, has since 1993 been directing the Laboratory of the Physics and Chemistry of Nanomaterials at Warsaw University's Department of Chemistry and studying the physical chemistry of plasma and nanomaterials

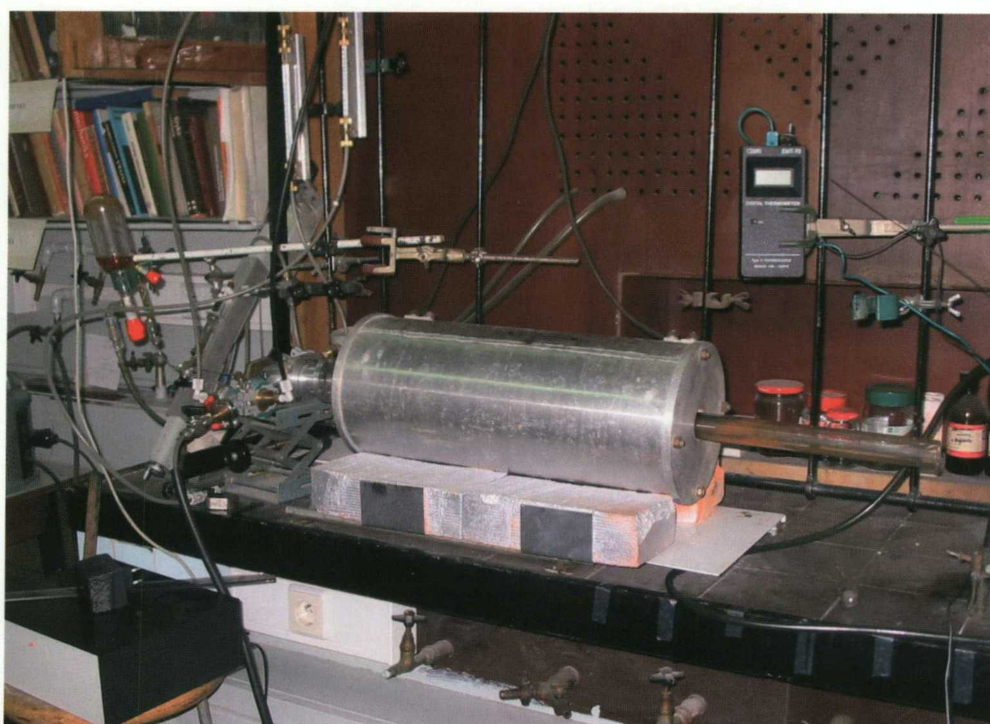
Nanotechnology is now rising to the fore of the most rapidly-developing fields of research. Nanomaterials frequently manifest new properties that differ from those characteristic for the morphology of bulk solids. Moreover, nanomaterials demonstrate certain micro-scale phenomena that are unknown for microcrystal objects

The term *nanotechnology* refers to materials, techniques, and devices that function on the "nano" level (derived from the Greek root *nannos* meaning "dwarf"). A nanometer (nm) constitutes one billionth of a meter, or 10^{-9}m, and objects below the size of 100 nm are conventionally considered to form part of the "nano" world.

Nanostructures are three-dimensional (3D) systems where at least one of the dimensions is below 100 nm. If we reduce two of the dimensions of "macro-scale" matter to the nanometer scale, we can obtain one-dimensional (1D) objects: *nanowires* or *nanotubes*. Such structures may be of macroscopic length in the micron domain (10^{-6}m), but remain nano-objects in the two remaining dimensions. Also possible are zero-dimensional (0D) objects, such as so-called *quantum dots*.

Materials on the "nano" level may also demonstrate special physical and chemical properties, e.g. the melting temperature of nanoparticles may be significantly lower than the same material's melting point in its solid phase. The electron structure of nanoparticles likewise depends on their size; hence the great current interest in quantum dots.

A considerable portion of current world nanotechnology research focuses on carbon,



Prof. H. Lange

Chemical vapor deposition (CVD) is one of the basic techniques for generating carbon dimers, which initiate the growth of carbon nanotubes

especially two recently-discovered nanostructure forms of carbon: *fullerenes* and *carbon nanotubes*.

New carbon nanostructures

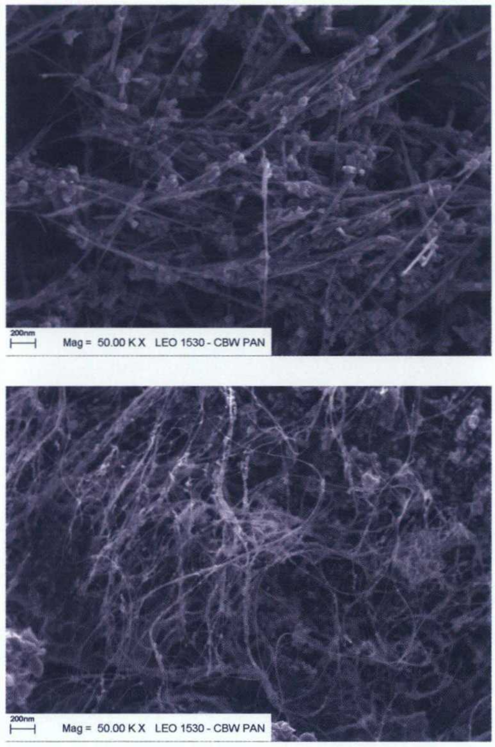
Carbon and carbon compounds are some of the best-understood chemical substances. Indeed, for decades it seemed that we already knew all there was to know about them. Yet in mid-1985, Prof. Harold Kroto (whose family roots stretch back to the village of Bojanowo in Poland's Wielkopolska province) from Sussex University in the UK spent several days at the laboratory of Richard Smalley (Rice University, US) conducting experiments which would earn them a Nobel Prize in chemistry 10 years later (1996), and which moreover revolutionized our awareness of carbon's myriad morphological forms.

Sir Kroto's detection of fullerenes represents an interesting-albeit-rare case when a significant discovery was motivated not just by scientific curiosity, but also inspired by the fields of art and architecture. Kroto was fascinated by the graphic and spatial arts in addition to the hard sciences, although professionally he specialized in spectroscopy - the technique of recognizing various chemical substances by their emission or absorption of radiation. One of Kroto's research aims was to identify the source of the so-called diffuse interstellar bands (DIBs). One theory ascribed their origin to the presence of carbon microparticles (interstellar dust).

Fullerenes

With Smalley's assistance, Kroto produced a generation of carbon clusters that simulated the carbon gas occurring in space, and the spectra he obtained proved to be dominated by a peak corresponding to clusters comprised of 60 atoms. These intriguing experimental results touched off a brainstorm among the researchers: what structure should be ascribed to this C_{60} cluster, whose existence and stability were beyond the slightest doubt? After all, 60 carbon atoms can be joined together in as many as 12,688 different configurations! What they proposed in the end was a kind of "nano-football" (or "nano-soccer-ball") structure consisting of 20 hexagonal rings, plus 12 isolated pentagonal ones that allowed

Adam Presz



Microscope images of carbon nanotubes obtained using the electric arc method (above) and the catalytic method (below)

the surface to curve. This symmetrical solid also has 60 vertices. From the mathematical point of view, the solid is a truncated regular icosahedron (i.e. a 20-sided polyhedron). This as-yet unknown carbon structure was therefore dubbed a *fullerene*, after the architect Buckminster Fuller who designed geodesic domes in the 1960s. The first experiments already pointed to the existence of an entire family of fullerenes, including C_{70} molecules and even larger ones.

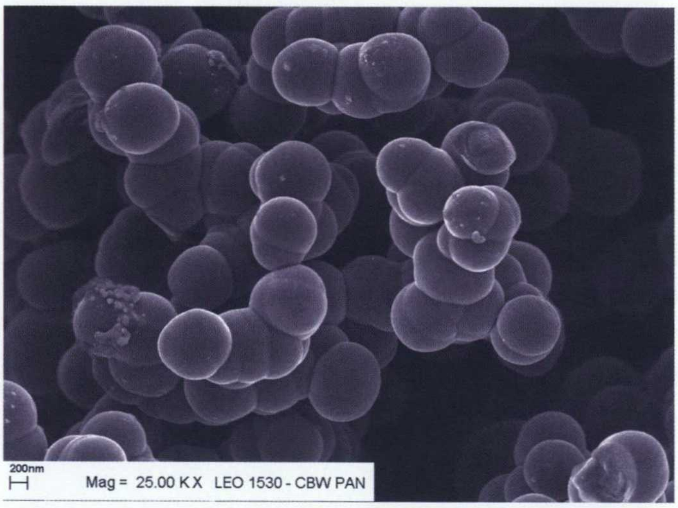
The unique physical and chemical properties of fullerenes give rise to a range of potential applications, in fields such as biomedicine (medical chemistry and therapy), optics (composite polymers with a C_{60} admixture, optical filters), electronics and electrics (transistors, diodes, hetero-junctions, photovoltaic devices, photo-resistors), electrochemistry (hydrogen storage, reversible and irreversible fuel cells), materials science (diamond synthesis, thin film deposition promoters, catalysts, mono-layers, new chemical reagents) and elsewhere (sensors, tribology, membranes, electron microscope sensor tip coverings, etc.)

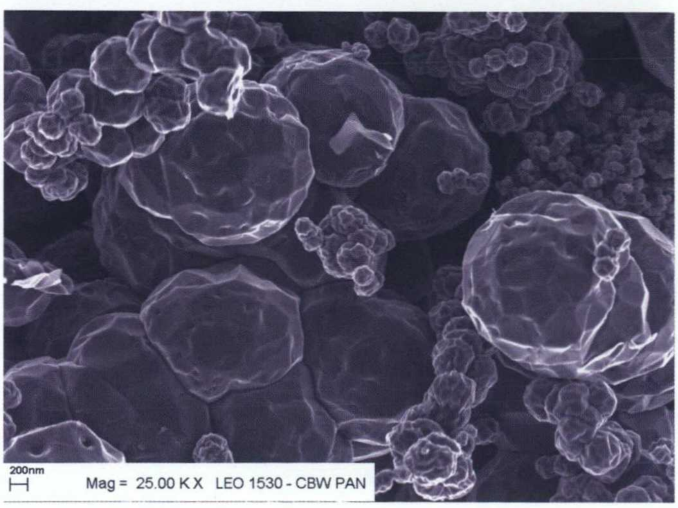
Fullerenes are now being used in the production of such diverse products as tennis and badminton rackets, polymer photocells, automotive air conditioning systems, eyeglass frames, golf clubs, microelectronic systems, snowboard wax, semiconductor boards, bowling balls, and cosmetic creams.

Fullerenes also have a "younger sibling": carbon nanotubes, graphene surfaces which form a cylinder with a diameter ranging from a fraction of a nanometer up into the tens of nanometers, yet have a length of even as much as many microns. Multi-walled nanotubes were discovered in 1991 by the Japanese researcher Iijima. The following year, researchers successfully achieved the catalytic synthesis of single-walled nanotubes.

Carbon nanotubes are characterized by great diversity. Unlike fullerenes, producing pure carbon nanotubes is no easy task. Moreover, the reaction that produces them yields many other outputs as well: amorphous coal, graphite, carbon "bulbs," the catalyst and its compounds, and carbon nanocapsules. The removal of each of these impurities often requires separate procedures.

Microscope images of carbon nanospheres, obtained via the pyrolysis of hydrocarbons (above) and subjected to graphitization (below)





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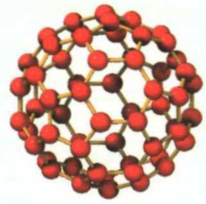
The basic properties of nanotubes which are of fundamental significance for their potential technological application include their new and changeable electron properties (ballistic electron transport and high field emission), a very high longitudinal flexibility factor (a Young module similar to that of diamonds), a high mechanical resistance to stretching (several hundred times greater than the most resilient steel), the highest heat conductivity of all known materials, a special morphology (a very high length-to-diameter ratio), great suitability for storage applications (such as in storing lithium), and a large proper surface area.

Other areas where nanotubes may find potential application include: electron technology (the next generation of computer technology), telecommunications (cellular telephony), multifunction composite materials, rechargeable lithium batteries, materials engineering for medical purposes, imaging equipment, and much more.

Experimental research on new carbon nanostructures in Poland was initiated in the 1990s by Przemysław Byszewski from the PAN Institute of Physics. For years now, the formation of carbon nanostructures and methods of obtaining them using the electric arc method have been leading research topics at the Laboratory of Nanomaterial Physics and Chemistry at Warsaw University's Department of Chemistry. This involves optimization work aimed at understanding how process parameters affect synthesis efficiency, as well as fundamental research aimed at studying the reaction environment in which fullerenes and carbon nanotubes are formed so as to attempt to explain the mechanism (or mechanisms?) involved. Such work employs spectral emission diagnostics, making it possible to identify the temperature fields and spatial distribution of carbon species within the arc discharge zone.

Obtaining fullerenes and nanotubes

A range of parameters have an impact on the electric arc method of fullerene synthesis, including the nature, purity, and pressure of the "buffer" gas, the distance between the electrodes, the nature of the reaction system, the size of the reactor, the way in which the



reaction products are cooled, the configuration and characteristics of the electrodes, and the intensity of the arc current. The efficiency of C_{60} production can range up to 15%, and the fullerenes are then separated out of the soot via an extraction method.

Being a new type of material, carbon nanostructures have in recent years been the subject of research concerning hypothetical health threats - especially those potentially posed by carbon nanotubes, which have a morphology similar to asbestos fibers. Our research has not identified them to have allergic or irritant effects on human skin. As concerns the impact of nanotubes on the respiratory system of living organisms, however, research using guinea pigs carried out in cooperation with Prof. Grubek from the Medical University of Warsaw has shown that high concentrations can be expected to cause inflammatory conditions, hence the need to employ protective measures (masks, gloves) when working with these materials.

Our experiments on methods of obtaining carbon nanotubes are performed in an electric arc reactor, in a gas atmosphere or in deionized water. We also obtain nanotubes from hydrocarbons using a catalytic method (CVD).

Obtaining other carbon nanostructures

Condensing carbon gas can also give rise to other "exotic" nanostructures, known as *nanocapsules*. When carbon is coevaporated with magnetic materials or ferrous metals using an electric arc, the graphene planes that emerge in the cooling and coalescence stage curve and become "sealed up," forming a nanocapsule of carbon that encloses a different element or compound. These are interesting arrangements, chiefly because of their potential for application in fields such as materials engineering or biomedicine. The encapsulated element fully maintains its own physicochemical properties, while being isolated from its environment by an exceptionally strong carbon "encasement."

The rapid pyrolysis of aromatic hydrocarbons could also be a source of other new carbon nanostructures. For example, one of the stable condensation products resulting from the thermal decomposition of styrene vapors at several hundred degrees Celsius using a reducing atmosphere in a tube furnace consists of carbon nanospheres tens or hundreds of nanometers in diameter. Research is currently underway to study the catalytic and electrochemical properties of these nanocarbons in terms of their potential applications.

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Fullerenes are now being used in the production of tennis and badminton rackets and many other products familiar from everyday life

The discove-ry of fullerenes and then carbon nanotubes has undoubtedly propelled the development of nanotechnology research over the past decade. Although these nanostructures have been used in numerous spectacular applications on a smaller scale, they are not yet being put to mass technological use, and research on other potential applications is still underway. Nevertheless, we can already safely say that the above-mentioned discoveries have given a very strong impetus to the development of a new field: the physical chemistry and nanotechnology of new forms of carbon, which are consistently opening up new discoveries. ■

Further reading:

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