

NANOTECHNOLOGY

Nanotubes on the market

Tiny carbon parts are already on sale for universities and companies

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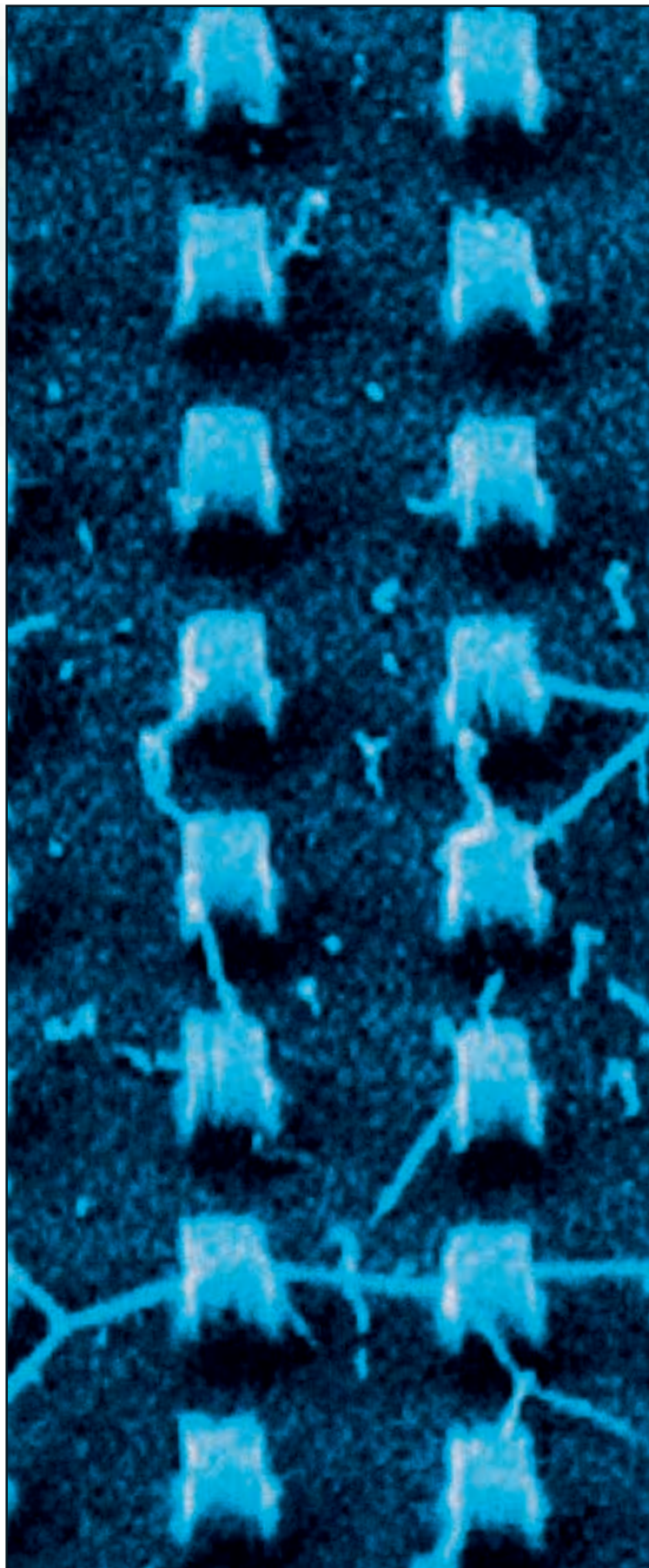


Carbon nanotubes are as yet not in the supermarkets nor in specialist shops, but it is now possible to buy them in Brazil, and with national technology. These miniscule parts can only be seen using powerful electronic microscopes. They measure from 1 to 3 nanometers (nm) in diameter and up to 1,000 nm in length, measurements

comparable to a fine hair divided 50,000 times in a longitudinal manner. The carbon nanotubes are one of the major technological conquests born in the decade of the 1990s and today are being produced in the laboratories of the Federal University of Minas Gerais (UFMG) and commercialized by the Research and Development Foundation of the same institution.

Among other qualities the nanotubes possess excellent electrical conductivity and a mechanical resistance one hundred times greater than that of steel, and at the same time, they have flexibility and elasticity. These are characteristics that give them the credentials for an infinity of important applications in science and technology. They could, for example, interlink silicon nanochips in the electronics industry, make up polymers to make them more resistant or to make cloth impermeable or ceramics stronger. In the medicine they are also welcome because they are biocompatible and could, for example, liberate, in a safer and more gradual manner, a medicine into a specific point of the human body or carry molecules to the interior of cells and be a basic component in the architecture of biological nanomachines.

These extremely small tubes have already become merchandise in various parts of the world. Only a few companies produce the material as yet in a large part for experiments and the



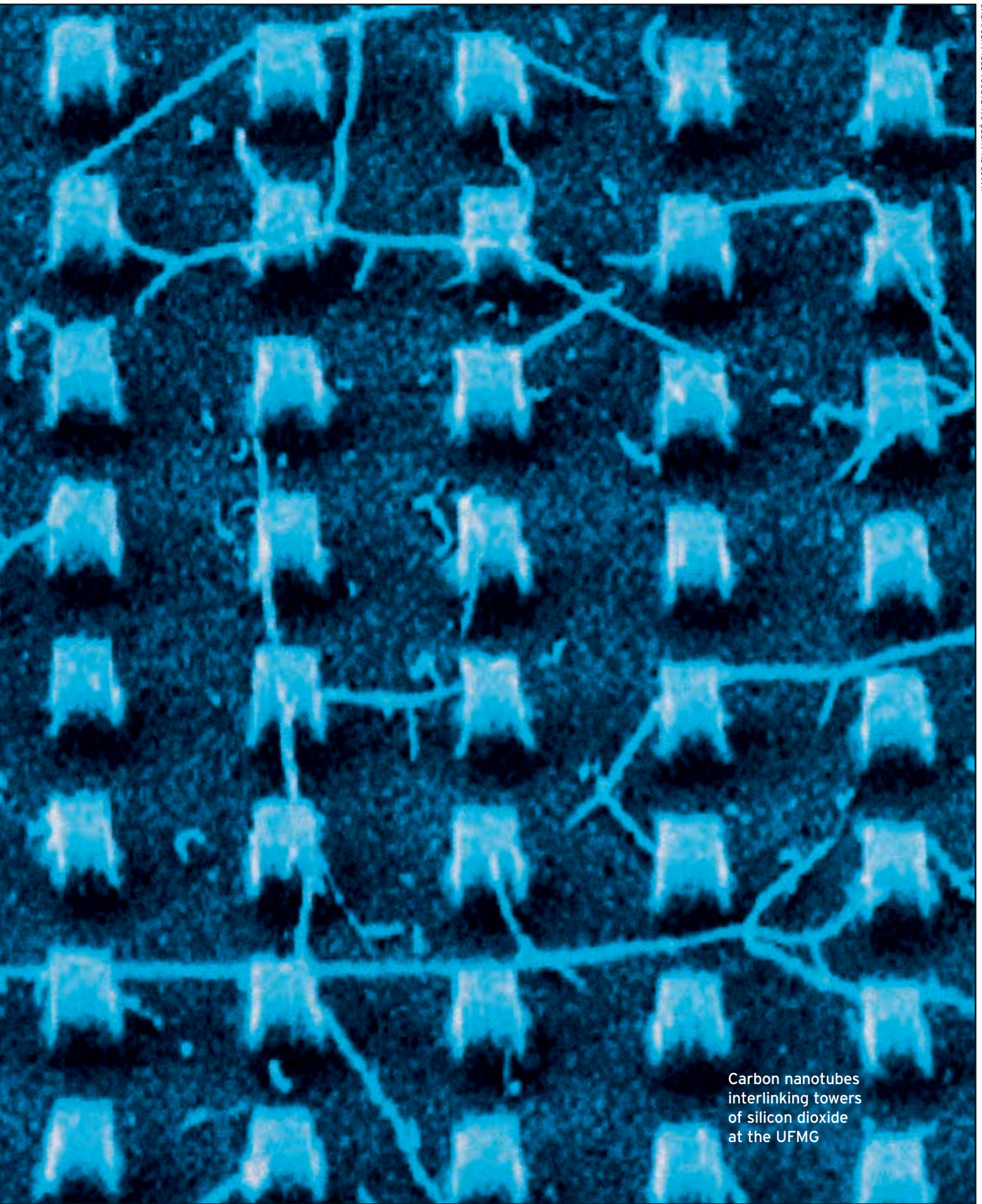


IMAGE BY ANDRÉ SANTAROSA FERLAUTO/UFMG

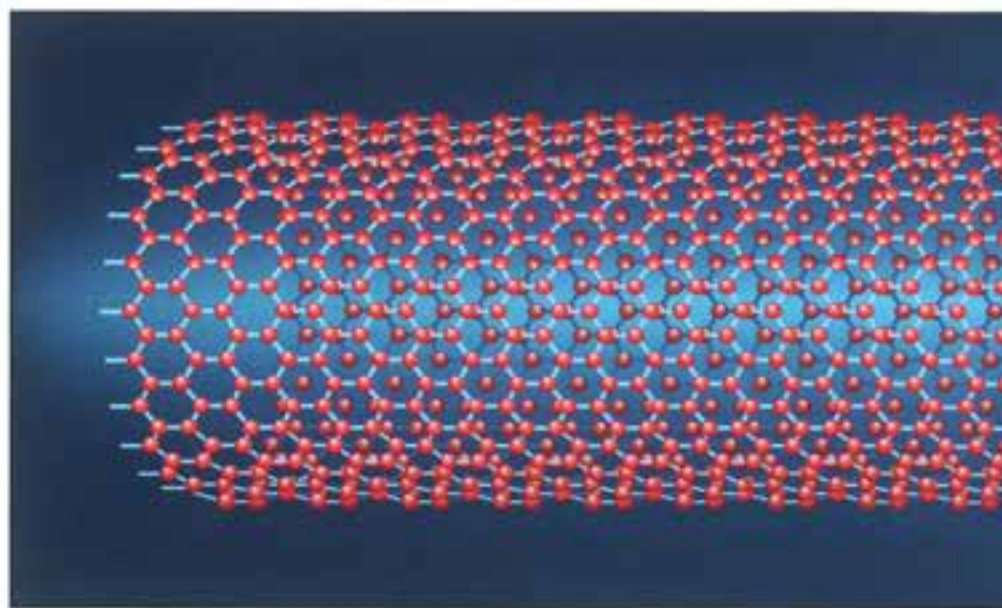
Carbon nanotubes interlinking towers of silicon dioxide at the UFMG

development of high technology products in Japan, China and the United States. An example is a bulletproof vest manufactured with nanotubes that makes it much lighter, malleable and resistant than the conventional ones. Perhaps for this and also for a possible use in nuclear energy and in the production of armaments and bombs, it is the reason why the United States has vetoed the export of this product claiming strategic interests. The ban was confirmed by Brazilian researchers who received negatives from American companies for importing this material.



The production of nanotubes at the UFMG, as well as demonstrating national scientific capacity and forming researchers in this area, is also creating technological independence for the country.

This story began to be detailed out in 1999 at the Nanomaterials Laboratory of the Physics Department, under the leadership of professor Luiz Orlando Ladeira. "Our innovations in the synthesis of carbon nanotubes were in the process and the equipment used for producing them on a large scale", says Ladeira. With the advance in our studies, it was perceived that it was the time to make this material available for a greater number of researchers. The idea was to make nanotubes available to other universities, research institutes or Brazilian companies that would have easier access to the material, without the need to import it. Thus, with the sales that started at the beginning of September of this year, the Fundep has already sold carbon nanotubes to a university and a Brazilian company. Up until the start of November, there were 60 grams (g) of nanotubes sold at a price of US\$ 30 per gram, totaling US\$ 1,800, which will be divided among the researchers, one third, and the UFMG, two thirds, after discounting the 5% due to the Fundep. On the international market the price ranges from US\$ 60 to US\$ 200 per gram, depending on the degree of purity. Thus the national product, which is of high quality and offers manipulati-



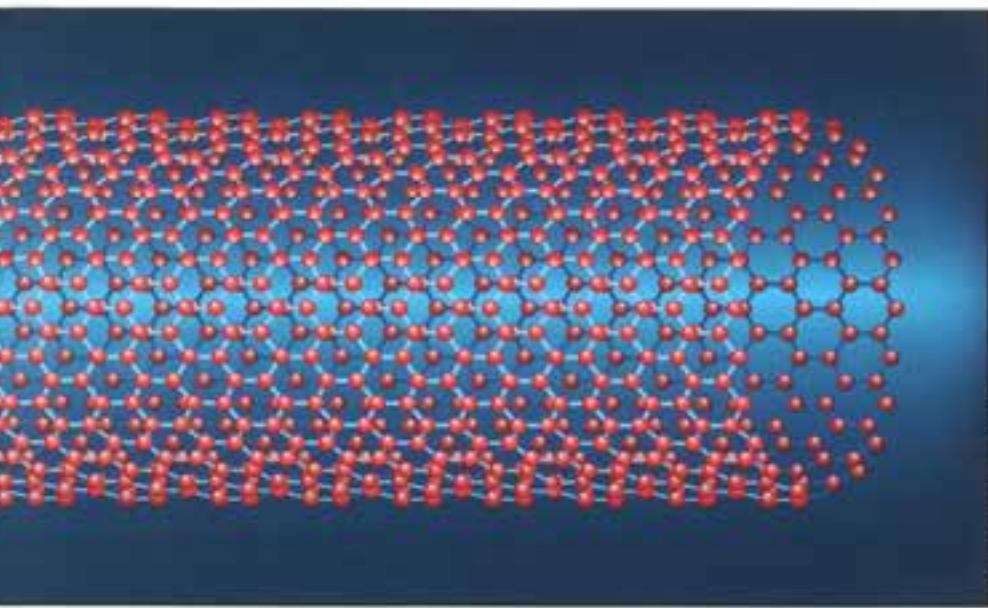
on options in various areas, has a competitive price.

The first Brazilian sales were to the Chemistry Institute of São Carlos (IQSC) of the University of São Paulo (USP) and to a São Paulo company whose name the researchers prefer not to disclose. "We're negotiating with three other major companies whose names we can't reveal due to a confidentiality clause in the contract", says Francisco Eduardo Ferreira da Cunha, the technology transfer analyst at Fundep, responsible for the product's commercialization.

The initial incentive for the development of nanotubes at UFMG came from professor Marcos Pimenta, from the same Physics Department, who, in 1997, during a sabbatical year, worked at the Massachusetts Institute of Technology (MIT), in the United States. "I worked with nanotubes there and when I returned I encouraged professor Luiz Ladeira to develop them because my area's the optical spectroscopy and he already had experience in studying carbon", the professor tells. "I'd already been working with special

Quick History

In 1991, the carbon nanotubes were discovered by the Japanese physicist Sumio Iijima, a researcher with the company NEC of Japan. Using a scanning electron microscope, he found nanotubes and nanoparticles upon an electrode when he had been studying the synthesis of fullerenes, which are carbon arrangements in the form of soccer balls that possess hexagonal sections in the inter-atomic linkages. In 1985 the fullerenes were discovered by the Americans Robert Curl and Richard Smalley (who died last October 28th), from Rice University, and by the Englishman Harold Kroto, from Sussex University. This was the first stable configuration of a molecule essentially made of carbon, after the well-known examples of graphite and diamond, found in nature. This result bestowed upon the three of them the Nobel Prize for Chemistry in 1996. The nanotube became the fourth form of a molecule made up exclusively of carbon atoms.



Nanotube structure: a rolled up leaf of carbon atoms available in a hexagonal form

carbons since 1996 and from there I started to attempt to make nanotubes", adds Ladeira.

In the manufacture of the first examples there was no lack of creativity and even an original recycling method of scientific instruments. "I'd been thinking about how to make nanotubes when I remembered an obsolete piece of equipment for growing crystals that had been doing nothing in my laboratory", says Ladeira. "Then I transformed it into a machine that would make carbon nanotubes." How much did this

adaptation cost? "Practically nothing. One couldn't even add up a bill."

Continuous process - Using the adapted machine, the researchers managed to produce the first nanotube in 2001. "This was a semi-continuous process in which, during the production, it was necessary to open the chamber in which they were being produced various times. Afterwards we found a way of producing in a continuous form for a long time", reveals Ladeira. "At this moment we're developing a new process of con-

tinuous synthesis that could reach a production rate of 20 to 25g per day."

An availability of nanotubes for the scientific and innovation research system in Brazil is of extreme importance at the moment in which these carbon parts are candidates for a number of scientific experiments and industrial use. The very acquisition of USP's IQSC shows the diversity and the possibilities that open up with carbon nanotubes. Sérgio Spinola Machado and his master's degree student Cláudia Razzino have acquired 20g of Fundep's product in the form of a black powder similar to the mineral of its origin, namely graphite, within a small glass receptacle. They are going to use these nanotubes in the formation of biosensors capable of identifying the contamination by pesticides in foods or in river water. "We're using the nanotubes to immobilize an enzyme, the acetylcholinesterase, which has its action inhibited by pesticides during the analytical process", assures Machado. "Thus we're going to solve a problem of electrodes (for the passage of an electric current during the analysis) made of vitreous carbon that has a

Initially researcher Iijima, who today is a professor at Meijo University, in Japan, discovered nanotubes formed with diverse sheets. In 1993 he and the researcher from IBM, Don Bethune, formed the nanotube from only one sheet of carbon. From there onwards various forms of production and perfecting of these parts have taken place throughout the world. As well as all of the qualities and utilities attributed to nanotubes, there are as well those who would suggest it for making direct connections with the International Space Station, which today orbits around the Earth. This would be a connection between the earth ground and the station, capable of taking supplies to the station. One idea as yet not taken seriously, but which shows the depth of imagination surrounding the carbon nanotubes.

Another aspect, this indeed taken seriously, is the possible interferences of these minuscule parts in the natural environment or in the human body, such as

the cases of transporting anti-cancer drugs to a tumor. "This nanotube would probably stay in the organism for the rest of the individual's lifetime", says Luiz Ladeira from UFMG. "The probability is that nothing would happen because they're made of carbon, as is the major part of our organism, but we need to know this for certain". For Marcos Pimenta, also from UFMG, "cardiac valves are made of carbon and, if the risks exist, they would be very small like, for example, in the case that they would perforate some cell". Also possible environmental possibilities are in this discussion such as: what would happen if nanotubes fell into a river? These are questions that are beginning to be analyzed in various parts of the world and in Brazil. "We initiated a project with the Biological Sciences Institute of UFMG to study the bio-distribution of carbon nanotubes in human beings", says Ladeira.

ILLUSTRATION BY SERGIO J. B. CAMARGO

smooth surface and serves as support for the enzyme. This molecule's 3-dimensional structure adapts itself better in the pores of the nanotube that are fixed in the electrode." Stuck only on the smooth surface, the enzyme remains established as if it were flattened and its activity diminished. Thus, with the nanotubes, the analysis process of pesticides should be more precise and efficient.

The nanotubes that the UFMG have available are of the single wall type, in which only one sheet of carbon atoms gains the format of a tube. Another form exists and that is multiple walls, in which various sheets of carbon are rolled together into the form of a tube. This type of nanotube is also one of the objects of the UFMG study group, which during the period between 2004 and 2005, for example, published four scientific papers in the journal *Physical Review Letters*.

The nanotube with the single wall is a potential candidate for two expected technological revolutions for this century in the electro-electronic industry and medicine. In the latter, researchers all over the world are searching for ways to send the nanotubes, full of antibodies and cytotoxins, to a cancerous tumor, with

the objective of annihilating the sick cells. "One of our dreams here at the UFMG is to produce these intelligent nano-missiles for cancer treatment", explains Ladeira.

In the electro-electronic industry the single wall carbon nanotube is pointed to as the ideal link for future nanochips, totally substituting the sili-

con chips used today. In this case the nanotubes will make the linkage between the transistors and diodes of an electronic circuit, in a situation that will improve the components' performance and that of the whole system. Similar connections, between silicon dioxide posts, with nanotubes have already

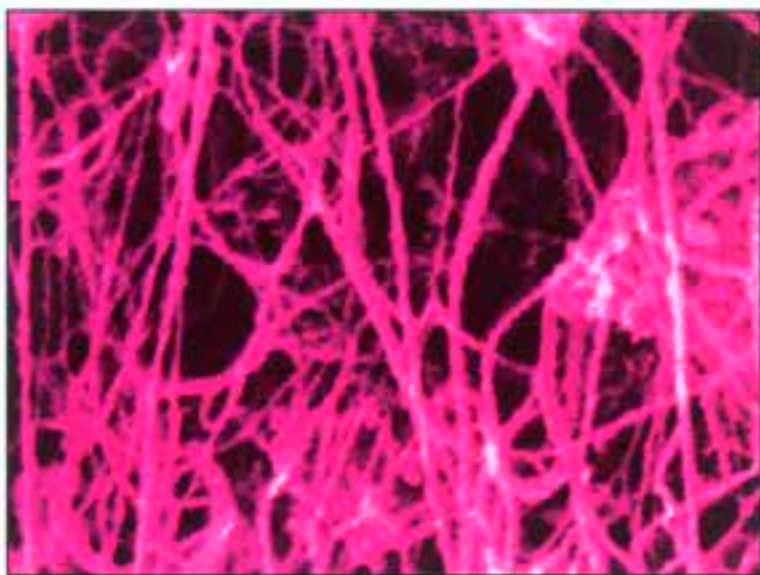


IMAGE BY UFMG LABORATORY

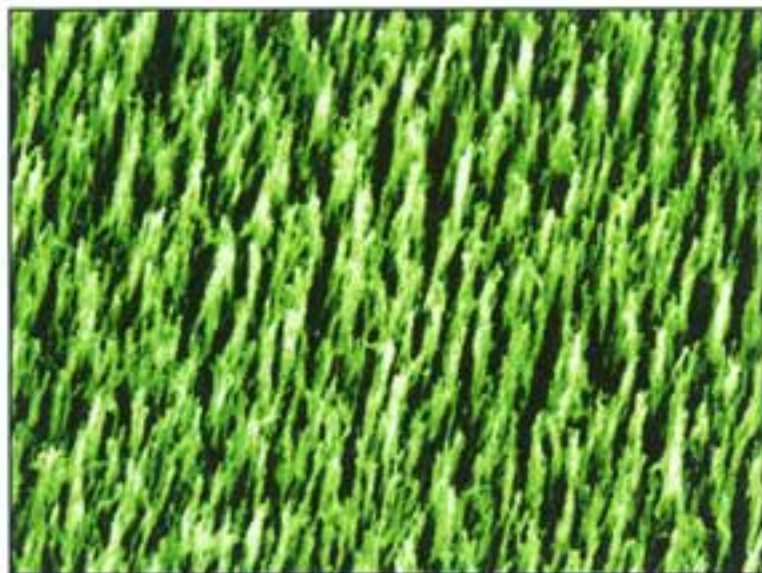
Spaghetti: single wall nanotubes produced on a large scale

Manufacturing nanotubes

Carbon possesses a property which is its self-organization. When inside a chamber under special conditions of temperature, pressure and other parameters, the carbon atoms spontaneously group themselves into the form of a tube. "It's natural for carbon to form itself in this manner", says the physicist Marcos Pimenta, from UFMG. The researchers' work is to provide the necessary conditions for the formation of these extremely small tubes. "Within the chamber we need to control temperature, pressure and other parameters in a very precise manner", says Ladeira. The initial technique used at UFMG was the discharge of an electric arc, where the nanotubes grew together with metallic nanoparticles that catalyzed their formation reaction. "We vaporized carbon in a chamber with helium gas, together with metals such as nickel, at temperatures

between 3,700°C and 4,000°C. Inside the chamber there are two electrodes that established an electric current, leading the material to transform itself into a gaseous mixture of nickel and carbon. When this vapor is cooled, the nickel no longer manages to support the quantity of carbon dissolved in its interior and thus it expels the carbon, leading to the formation of nanotubes." The result is a tangle of fine threads that remind one of a plate of spaghetti.

Another technique that is being used by the researchers throughout the world is the technique called Chemical Vapor Deposition (CVD). In this case the nanotubes are produced in a thermal decomposition reaction in a hydrocarbon gas, such as methane, within a chamber at a temperature between 600°C and 1,000°C, which also contains a ceramic powder with metallic nanoparticles. In this process, the carbon nanotubes are formed upon this ceramic material. The CVD technology is cheaper and currently more in use. "The Nanomaterials Laboratory at UFMG has two sets of CVD apparatus. One of them we imported and the other we made here", says Ladeira.



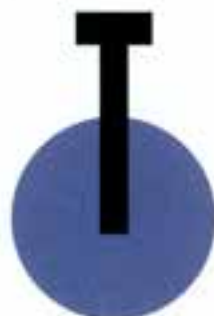
Forest: carbon nanotubes of multiple walls

been tested at UFMG and proven through scanning electron microscope images. Some research groups in the world, such as the pioneering group at Harvard University in the United States, in 1998 had experimentally produced transistors and diodes using carbon nanotubes. The American company, Nantero, in Woburn, Massachusetts, for example, developed a system for the manufacture of Complementary Metal Oxide Semiconductor (CMOS), and is now planning a memory system for computers based on nanotubes that will be offered to the market as a substitute for the current RAM memory, Random Access Memory.

The first steps in electronics have already allows researchers to imagine that the nanotubes are candidates to be installed within computers and in any other type of electronic devices over the next few years. "Today all of the semiconductor research community is interested in carbon nanotubes", says Pimenta. Many problems have yet to be resolved in the production of these parts for electronic ends and to establish the linkages between the elements of an electronic circuit, for example. "The research is still at a stage distant from commercial application."

A characteristic of the nanotubes that favors its inclusion in the electro-

nic world, although carbon is not a conducting element par excellence, is the capacity for electrical conductivity that it possesses. The secret lies in the form of rolling the graphite sheet, the material can then behave with distinct electronic properties, like a semiconductor or a metal", explains Ladeira.



The electronic properties are obtained by the form with which the hexagonal atomic carbon structures are orientated in relation to the axis of the tube (a phenomenon called chirality). "In the extremely small thread of the nanotube, the electrons are confined and move in only one direction in a unidimensional form. They move without colliding with the nuclei of carbon, which endows them with an electrical conductivity much better than that of copper", says Ladeira.

With a long wall of one atom in thickness, flexible and highly resistant, the carbon nanotubes are also good absorbers and accumulators of gases. One of the forecast uses for nanotubes is in the transport and storage of hydrogen in fuel cell systems, the equipment that transforms this gas and oxygen into water and electrical energy. "Their characteristics permit the accumulation of gases between and within the tubes placed

side by side like two soft drink straws, as well as fixing gaseous molecules on their surfaces for some type of analysis such as an electronic nose, for example", suggests Pimenta. This project is one of the lines of study of the recently established National Research Network into Carbon Nanotubes, funded by the National Council of Scientific and Technological Development (CNPq). "We've brought together 15 universities, such as USP, the State University of Campinas (Unicamp), and the federal universities of Rio de Janeiro (UFRJ), Fluminense (UFF), of Paraná (UFPR), of Maranhão (UFMA), of Pará (UFPA), of Santa Maria (UFSM), in Rio Grande do Sul, and of Juiz de Fora (UFJF) and Lavras (UFLA), in Minas Gerais State", advised professor Pimenta, the network's coordinator.

Technological transference - The applications looked upon within the projects, now united into a network, are varied such as the mixing of nanotubes with polymers or resins in such a manner as to increase the mechanical and thermal properties of the coating on aircraft, gaining more resistance and lightness in relation to steel (six times lighter).

"A fundamental aspect of the network is to have nanotubes available on a large scale for the work groups without their preoccupation of having to produce them", says Pimenta. There again comes in the importance of the production by Luiz Ladeira's group. The UFMG has already been passing nanotubes for free to the research projects in which the university's research group had been involved. This is happening with Unicamp, the Federal University of Ceará and the Nuclear Technology Development Center of the National Nuclear Energy Commission. With a growing demand and the university not being truly a location for parts production of a scientific and technical nature on a large scale, the researchers are already imagining the formation of a company for the manufacture of nanotubes. "This is going to depend on the market", says Ladeira. Another possibility is the transfer of technology to a company that invests in the production, paying royalties to the researchers and university. •