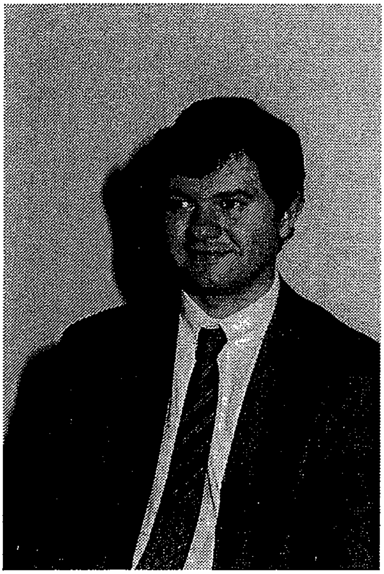
NOVEL GRAPHITIC STRUCTURES: FULLERENES, NANOTUBES AND ONIONS



DR DANIEL MARO UGARTE
INSTITUT DE PHYSIQUE EXPÉRIMENTALE
DÉPARTEMENT DE PHYSIQUE
ECOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE
LAUSANNE, SWITZERLAND

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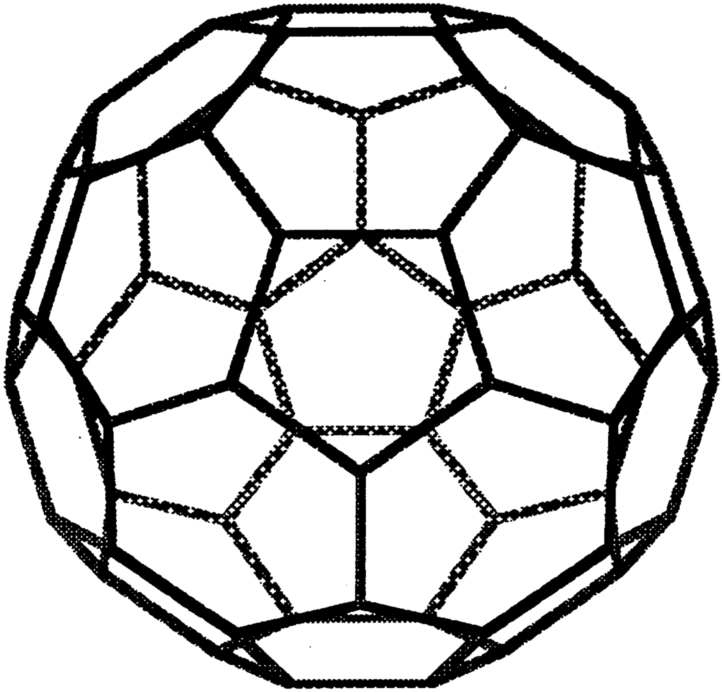
1. Introduction

Carbon is probably the most versatile element from the periodic table, displaying an extremely rich chemical behavior. Alone it accounts for the division of chemistry in organic and inorganic, and forms more compounds than all the other elements all together. The two crystalline forms (allotropes) of pure carbon are well known: Diamond and Graphite. Diamond is probably the hardest known material, a remarkable insulator (5.5 eV gap), and in addition its heat conductivity is 5 times higher than copper. Graphite is a semiconductor with a zero gap energy and is the most stable form of solid carbon at room temperature and pressure. In diamond, each carbon atom has 4 neighbors at the vertices of a tetrahedron (sp^3 hybridization). In graphite, a carbon atom has 3 neighbors within a plane at 120 degrees (sp^2 hybridization), generating a planar hexagonal network. Both forms of carbon have a wide variety of technological applications.

In 1985, astrophysical studies of small carbon molecules led to the finding that the cluster formed by exactly 60 carbon atoms displayed a remarkable stability [1]. Guided by geometric and simple chemical arguments, the authors proposed a structure with the 60 carbon atoms located at the vertices of a truncated icosahedron (see fig. 1). This structure is formed by 20 hexagons and 12 pentagons, constituting the molecular version of a soccer-ball. The authors named this molecule Buckminsterfullerene in honor of the American architect and engineer Buckminster Fuller who had noted the remarkable properties of icosahedral structures and applied them to the

Figure 1: Truncated icosahedral structure of the C60 molecule



construction of geodesic domes. The C_{60} molecule may be considered as a scrolled graphitic sheet because each atom has three neighbors, but as they are lying on curved surface, the electronic structure is intermediate between diamond (sp^3) and graphite (sp^2).

The truncated icosahedral configuration presents several outstanding properties: a) it is a quasi-spherical structure with a central empty space; b) the point group of the molecule is Icosahedral (I_h), which possesses the maximum number of symmetries of the nature; c) in such a molecule all the 60 atoms are in *equivalent* positions. This proposal was taken with some skepticism by a large part of the scientific community, that considered that a mass spectra did not provide enough evidence to confirm the existence of such a revolutionary molecule.

When the mass spectroscopic results showed the enhanced stability of the C_{60} cluster [1], the scientists initially tried to explain these observations by means of the stacking of small planar graphite sheets, but these configurations could not account for the two main magic atomic numbers observed in the experiment (C_{60} and C_{70}). Subsequently, they realized that a curvature could be introduced in the hexagonal network by the incorporation of five-member rings (pentagons). This curvature allows the elimination of the energetic dangling bonds existing at the edge of planar graphitic sheets. The final energy balance favors the formation of a closed graphitic shell, although a certain amount of strain induced by the bending of the graphitic layer.

In 1990, astrophysicists, simulating the formation of carbon soot in red stars, discovered that C_{60} could be produced in gram quantities by a current arc-discharge experiment using graphitic electrodes and run in a low pressure helium atmosphere [2]. The soccer-ball structure of was then confirmed. This cheap and simple experiment was easily repeated all around the world, spurring a burst of interest in the scientific community.

The cage structure is not limited to C_{60} and a wide variety of stable hollow molecules are possible C_{76}, C_{84}, C_{96},... (usually called higher fullerenes). All these cage structures present 12 pentagons and a variable number of hexagons, but in contrast to C_{60} the arrangement is not unique, so many isomers are possible (molecules with equal number of atoms but different structure); this fact introduces an additional difficulty to the study of higher fullerenes. Speculations suggested that even very large hollow molecules containing several hundreds or thousands of atoms could be produced (giant-fullerenes) [3]. Much more complicated structures have been proposed by combining hexagons, pentagons and larger carbon rings (heptagons that induce a negative curvature), e.g. toroidal particles.

Calculations predict the stability of these clusters, nevertheless their existence has not yet been confirmed.

The availability of large quantities of fullerenes, revealed a new crystalline form of pure carbon (allotrope), called "Fullerite", to be added to diamond and graphite [2]. This novel molecular solid is produced by a three dimensional packing of the C_{60} molecules, which occupy the sites of a face centered cubic crystal. Fullerite is a semiconductor, but doped with alkaline metal it becomes superconductor at 33 K [4], so constituting the second better superconductor known to man.

Tantalizing physical and chemical properties of fullerenes were revealed almost daily during the last two years, and were overhelming in number, variety and potential. That an entirely new form of this very well characterized element had been discovered only in 1985 seems unbelievable. The incredulity that such a discovery was possible was at least in part responsible for the skepticism the fullerene hypothesis elicited among many scientists. Beyond the advances in the chemistry and physics of fullerenes themselves, the notion of fullerenes has changed the way scientists are looking at their world. Fullerenes have opened scientists'eyes to a new way of looking how carbon and other atoms bond to each other [5].

At the end of 1991, it was announced that coaxial tubular graphitic structures were produced on the surface of contact between graphitic electrodes used in an electric arc [6]. Typical sizes were 3-10 nm in diameter and several micrometers in length. The electric arc may be optimized to yield up to 70% of the evaporated materials in the form of nanometric graphitic tubules [7]. Theoretical calculations revealed very interesting electronic properties: the nanotubes may be insulators, semiconductors or metallic only by changing their radius and helicity [8]. This is a remarkable case in physics, where the electronic properties of the materials are directly correlated to geometrical parameters. In materials science, a currently employed technique is the doping, this means the change of the electric properties of the material by adding impurity atoms. In the case of nanotubes, no other chemical element is added, and the changes are induced in a material formed by the same element, and in a similar chemical environment (each carbon atom has three neighbors). This is a striking example of novel physical properties that may be found in nanometric objects due to the quantum nature of matter.

Although the discovery of fullerenes and related structures has produced an inestimable development in chemistry and physics, the most intriguing aspect is constituted by the impossibility of synthetizing them by standard chemical techniques, and fundamentally, their formation in the electric arc as a very important percentage of the evaporated material. This last feature raises the natural question of how it is possible to generate such symmetrical, low entropy structures in the random condensation of carbon vapor. To illuminate this issue, it would perhaps be worthwhile contemplating the ease with which these carbon hexagonal networks grow as curved or closed sheets rather than the traditionally planar ones.

In an attempt to understand the formation mechanism of these novel graphitic structures in the extreme conditions of the electric arc, we decided to analyze the behavior of carbon materials when subjected to another extreme situation: bombardment with high energy particles (electrons).

2. Electron irradiation experiments

Intense irradiation in some respects resembles a high temperature regime, allowing an important degree of structural fluidity. Such conditions may be realized in a high resolution electron microscope

(HREM), and consequently the evolution of a sample may be observed, even up to the atomic details under favorable conditions. However, we must remark that electron-beam bombardment may not lead to the same result that thermal heating due to the contribution of the excitation processes.

We have irradiated carbon soot in a 300 kV HREM microscope (Philips EM430 ST) available in the Centre Interdépartemental de Microscopie Electronique (CIME-EPFL). The electron dose used was typically up to 10-20 times higher than under normal operating conditions (10-20 A/cm^2). The original soot, collected in an arc-discharge apparatus, contains mostly nanometric graphitic particles (tubular and polyhedral). After 20 minutes of strong irradiation, the electron annealing led to a sample composed nearly entirely of spherical particles [9]. Detailed examination of the particles shows that they consist of an assembly of concentric spherical graphitic cages, the distance between layers agreeing with bulk graphite (d_{002}= 3.4 Å) (see fig. 2). These particles are usually called onion-like, and constitute a fullerene version of the Russian-doll (see fig. 3). Similar concentric structures were reported in the early eighties, but they displayed a more marked faceting [10].

The transformation from a polyhedral graphitic structure into a quasi-spherical onion, under electron bombardment, can be divided into three main steps: a) elimination of the hollow central space through the collapse of the inner-most shell, and the generation of a rather disordered particle; b) deformation from a cylinder or polyhedron into a sphere, where the particle displays the formation of tiny surface graphitic layers; c) subsequent graphitization follows towards the center by a sort of internal epitaxy [11] (see fig. 4).

Figure 2: HREM image of a quasi-spherical onion-like particle.
Note the remarkable sphericity of the clusters. Graphitic layers are represented by dark lines in the micrograph, and the interlayer distance is 0.34 nm.

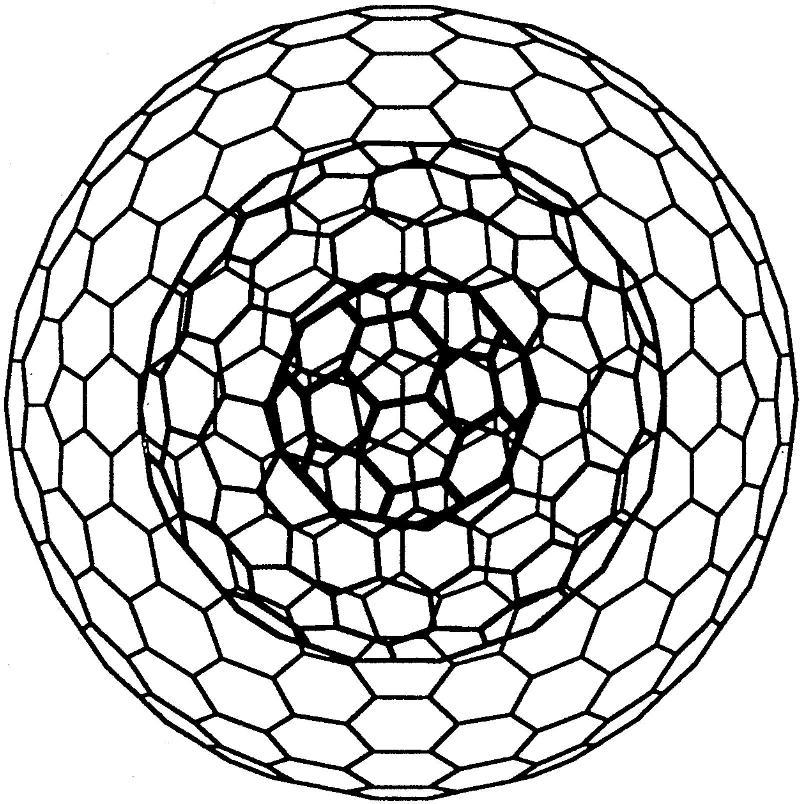


Figure 3: Model particle consisting of a concentric arrangement of three spherical fullerenes (C_{60}, C_{240}, C_{540}).

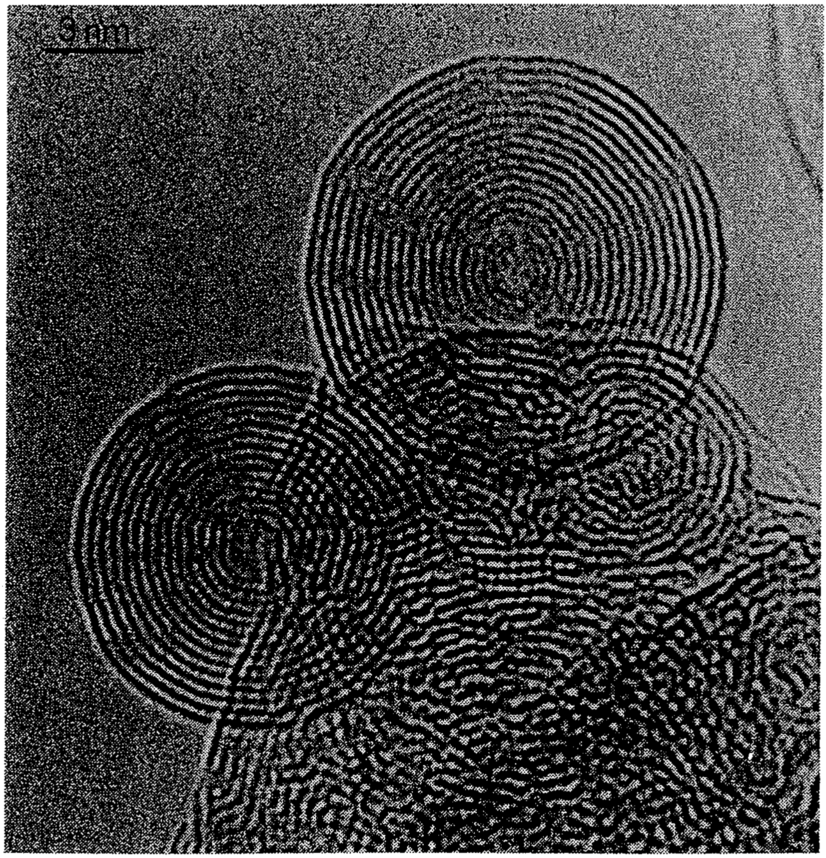
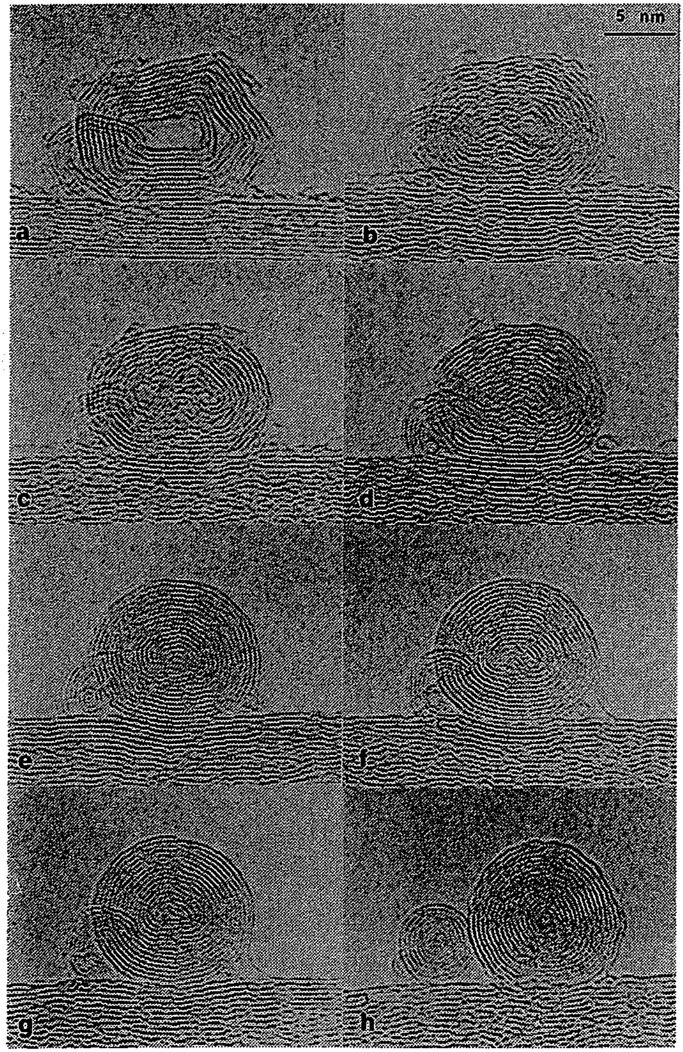


Figure 4: **Polyhedral graphitic particles evolving into a spherical onion-like particle under strong electron irradiation. a) original polyhedral particles; b) ≈ 20" of strong irradiation; c) ≈ 40" ; d) ≈ 70"; e) ≈ 110"; f) ≈ 130"; g) ≈ 150"; h) ≈ 180". Notice the marked disorder in b) and the subsequent formation of the concentric layers from the surface towards the center of the particle.**



3. Fundamental scientific issue

One of the fascinating aspects of fullerene research is the fact that these graphitic structures were found in current and long-time known experiments, and that they were overlooked for so many years. Carbonaceous materials and in particular their transformation in graphite (graphitization process) due to a high temperature treatment (3000° C) has been extensively analyzed. In many studies, the structures were not characterized in detail; this fact is in part due to the lack of equipment and to different interest in the aspects and issues of their research, but also to the basic concept of intrinsic planarity of the honey-comb graphitic network. Some apparently curved structures were analyzed as having been formed by the stacking of tiny planar graphite flakes, the analysis of what happened at the edges of the flakes did not receive enough attention. In contrast, at present the generation of curvature and/or the inclusion of non-six-member-rings is immediately considered and accepted in fullerene-related structure. This phenomenon is not limited to small systems, it may occur in much larger systems, containing up to several millions of atoms. This hypothesis was originated in the molecular domain, but it may apply to the nanotubes or onion-like particles, which may be considered as extremely large molecules.

Small bucky-onions formed by only a few shells (2-4) are very stable under the intense electron bombardment, in contrast with fragility of fullerenes C_{60} and C_{70} in the harsh environment of the electron microscope. Hence, the onion-like particles must represent a remarkable robust form of carbon. On the base of these observations, this structure has been suggested to be the most stable form of carbon clusters [12]. This hypothesis is based on three basic ideas: a) this structure allows the elimination of the energetic dangling bonds; b) the spherical structure distributes to all atoms the strain generated by the bending of graphene sheets; c) optimizes the interaction between concentric shells (van der Waals) that has a stabilizing effect. The quasi-spherical onion hypothesis raises a certain controversy, considering the planar graphite is accepted as the most stable solid form of pure carbon at ambient pressure and temperature [13]. It was expected that a polyhedral particle with planar facets and curvature (and generated strain) concentrated at corners containing pentagons would be the preferred structure. The theoretical determination of the minimal energy structure in carbon nano-system is a difficult task due to the large number of atoms that must be considered: the smaller onion that may be studied is constituted of 300 atoms (C_{60} in C_{240}). This calculation cannot be performed with present computational capabilities. Further theoretical and experimental work is necessary to answer this question, but the controversy is clearly exposed by H. W. Kroto, one of the discoverers of C_{60} [13]: "Nevertheless, the most interesting question is whether, 500 years after Columbus reached the West Indies, flat carbon has gone the way of the flat Earth".

A relevant point of the electron bombardment experiment is constituted by the fact that the irradiation is performed within a high resolution electron microscope. In this case, it is possible to follow the evolution of the sample up to the atomic scale details during the irradiation [11]. This is one of the particularities of the irradiation experiment, a unique and invaluable insight of the formation of graphitic structures. This is a basic piece of information in the general knowledge of the graphitization dynamics in carbonaceous materials.

Fullerenes, as well as their production method, were discovered by astrophysicists, interested in the generation of carbon molecules in the interstellar space [1, 2]. Inspired by this development, materials scientists have continued the discovery of additional graphitic structures [6, 9]. Although, in principle C_{60} was supposed to be abundant in interstellar space, its existence has not been definitively probed. Another fullerene-related structure may play a fundamental role in astrophysics, the onion-like graphitic particle. The composition of interstellar matter may only be inferred from spectroscopic optical data; in particular a ubiquitous remarkably large absorption peak in the ultraviolet region of the spectrum (220 nm) is the basic piece of information about the nature of interstellar grains [14]. Since its discovery in the 60s, the peak has been attributed to hypothetical spherical graphitic particles [15]. This hypothesis is the most logical assumption considering that the graphite is the most stable form of carbon in interstellar conditions, but also from the point of view of the cosmological abundance of chemical elements [14]. Preliminary measurement on spheroidal onion-like graphitic particles display remarkable resemblance to interstellar data [16]. Then, it is possible that this kind of particles are a substantial component of interstellar matter.

4. Conclusions and perspectives

The quasi-spherical onion-like particles have clear implications for the old way of looking to carbon materials: the drive to eliminate dangling bonds is not confined to small fragments of graphite chicken wire (leading to fullerenes), it is common also to larger scale structures (10^6-10^7 atoms). These particles represent *pure* carbon materials, which have no dangling bonds, and a uniform distribution of the strain due to the out-of-plane geometry. They have been suggested to be the most stable form of carbon in limited size systems.

As for the solid allotropes of carbon, Krätschmer et al.[2] synthesized a new, third form, of solid carbon (called fullerite), which is a three dimensional packing of bucky-balls and is distinct from the two traditional crystalline carbon forms: graphite and diamond. Considering the observed tendency of graphite to form shelled spheres (bucky-onions), of which fullerenes, being composed of a single shell are only the first members, we speculate that fullerite is the first member of a family of new solid forms of carbon that could be formed by the packing of these onion-like graphitic spheres, interacting through van der Waals forces.

A purification method for these particles is still lacking, but further experimental work would allow the preparation of monodispersed quasi-spherical graphitic onion samples, and possibly a new generation of nanostructured carbon solids as discussed above. The onion solid would be a semiconductor and the electronic properties could be tuned by selecting onions with a different number of shells or with metallic clusters at its center. The onion-like particles may find an important industrial application in the field of dry lubricants, considering their sphericity and enhanced resistance to compression.

As for the old and very important astrophysical problem concerning the composition of interstellar dust, our laboratory measurements have shown that the carbon onions represent very strong candidates to constitute the main carrier of the 220 nm interstellar dust absorption peak.

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