

The nano-forms of carbon†

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Since the discovery of C₆₀ fullerene, carbon-based nanostructures have become one of the hottest research topics in science. During the past decade research efforts have mainly been devoted to the investigation of C₆₀ and carbon nanotubes, although the ability of carbon to exist in different allotropic forms has provided a variety of nanoscale size shapes with fascinating properties. In this article we highlight some of the most representative examples that document the scientific progress accomplished in this field which, surprisingly, started with a serendipitous discovery.

1. Introduction

Carbon is considered a singular element because of its rather unique ability to form long chains whose central core is constituted exclusively by carbon atoms, thus giving rise to molecules able to create new materials or even life through Mother Nature.¹ Over twenty years ago, the classical allotropes of carbon—diamond and graphite—were enriched with the discovery of fullerenes in 1985,² which were referred to as the third allotropic form of this natural element. Soon afterwards, carbon nanotubes (CNTs) were also discovered and, since then, a huge amount of studies have been dedicated to these new and intriguing forms of carbon.³

Interestingly, fullerenes and CNTs are only the tip of the iceberg (Fig. 1) and, more recently, a wide variety of new carbon nanostructures such as endohedral fullerenes, cup-stacked nanotubes, nanohorns, nanotori, nanobuds, nano-onions, and graphenes, have emerged as new and fascinating forms of carbon whose chemical and physical properties are currently being unravelled.

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The aim of this review article is to present the variety of different forms in which carbon is appearing and to show the most recent advances in their chemical modification in order to achieve their solubility or functionalization for further practical applications. Because of the broad scope of the topic, the goal of this work is not to achieve a detailed and comprehensive

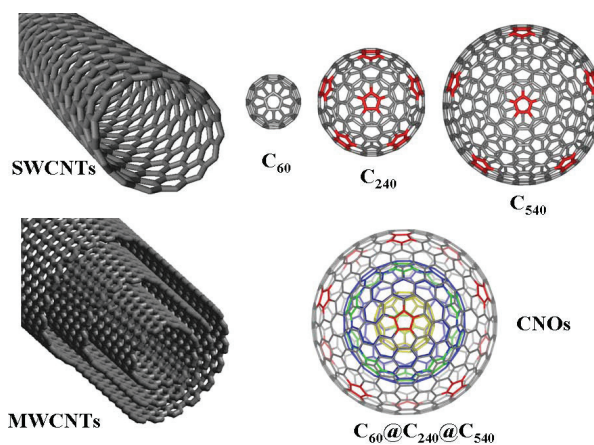


Fig. 1 Different carbon nanostructures: single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), fullerenes (C₆₀, C₂₄₀ and C₅₄₀) and a carbon nano-onion (CNO) (figure courtesy of Amit Palkar).



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presentation of the different carbon nanostructures, but to show their basic and relevant aspects for a general account. In this regard, the reader will be referred to some outstanding previously published review papers on those forms of carbon that, like fullerenes and carbon nanotubes, have been extensively studied during the past years.⁴

In retrospect, it is interesting to know that C₆₀ fullerene, probably the most investigated molecule in chemistry in the past years, was serendipitously⁵ discovered when the conditions under which carbon nucleates in the atmosphere of red giant stars were simulated.⁶ In 1991, Iijima found that when using the electric arc discharge evaporation method of Krätschmer and Huffman,⁷ some special form of “needle like species” was produced on one of the electrodes. Electron microscopy studies revealed that each needle was built up of coaxial tubes of graphitic sheets, ranging in number from 2 up to about 50. These species are nowadays known as multi-walled carbon nanotubes (MWCNTs).⁸ This unexpected revelation was followed two years later by the production of tubes of only one graphitic sheet, known as single-walled carbon nanotubes (SWCNTs), by Iijima and Ichihashi⁹ and Bethune *et al.*,¹⁰ who independently found that by doping one of the electrodes, in the production method of MWCNTs, with some elements such as Fe and Co only SWCNTs were obtained. About a year before that, Ugarte found, when studying fullerenes and increasing the current in the electron microscope, that a new type of structure was produced in the form of Russian dolls known as carbon nano-onions.¹¹

2. Fullerenes: twelve years after the Nobel Prize

Fullerenes, with a distinctive symmetrical carbon cage structure, have been the object of intense research since their discovery more than two decades ago. The large amount of research articles and books published about fullerenes' reactivity, as well as their properties and applications in research areas such as materials science or biomedicine, evidenced the important progress made in the knowledge of these characteristic three-dimensional structures.⁴ However, it is still possible to discover new reactions on the fullerene surface,¹² which could provide a better understanding of the chemical reactivity that new carbon allotropes present and will help in predicting the properties expected for these new carbonaceous structures in different disciplines. The most recent advances made in the preparation and investigation of the chemical reactivity and the properties of fullerenes are presented below.

2.1. Endohedral fullerenes

Since the beginning of fullerene investigations and discovery, people have speculated about the possibility of inserting atoms and molecules into the carbon cages and wondered about the modification effect on the chemical and physical properties of the empty cages. Even though mass spectrometry evidence of the existence of endohedral fullerenes was already mentioned in the first paper reporting the discovery of C₆₀ fullerene in 1985,² there was a big controversy about the location of the metal, since fullerenes with exohedral metals were also observed. In 1991, Smalley and coworkers unequivocally showed that

a lanthanum atom was encapsulated in a C₈₂ fullerene shell, thus ending the discussion.¹³ Since then, many analogous species have been isolated incorporating metals, noble gases and other atoms.^{14,15}

Unfortunately, investigation of the properties and the exohedral derivatization of endohedral fullerenes has advanced slowly due to the considerable effort required to obtain samples of adequate purity and in macroscopic amounts. Only recently, important advances have been carried out for the production of endohedral fullerenes by following the two approaches considered in the next paragraphs.

2.1.1. Endohedral metallofullerenes. The chemistry of endohedral metallofullerenes—fullerenes that encapsulate metal atom(s) within the fullerene interior space—has been rapidly developed during the past years, driven by the remarkable chemical and physical features that some of these structures present.¹⁶ Endohedral metallofullerenes are usually stable under ambient conditions, even when their empty fullerene cages might not be stable, or when the metallic clusters incarcerated in their interior might not exist outside the fullerene cage. The electronic structure of these metallofullerenes is very different from the corresponding empty cages and some of these species, after metal incorporation, exhibit interesting magnetic or nuclear properties that could provide very important applications in nanomaterials and biomedical sciences.¹⁷ As an example, Bolskar, Wilson and coworkers carried out the preparation of the first soluble Gd@C₆₀ molecular species, Gd@C₆₀[(C(COOH)₂)₁₀] (Fig. 2), by following a non-chromatographic procedure.^{17a} Gd-containing metallofullerenes are currently being pursued as a new generation of magnetic resonance imaging (MRI) contrast agents because of their high relaxivities and complete lack of Gd³⁺ ion release under metabolic processes. The Gd@C₆₀[(C(COOH)₂)₁₀] derivative exhibits one of the largest outer sphere proton relaxivities ever recorded for a Gd³⁺-based MRI contrast agent and its high solubility in water makes it cross cell membranes, suggesting its application as an intracellular MRI agent as well as a pH-responsive one.^{17b}

An important breakthrough in endohedral metallofullerene chemistry occurred in 1999, when Dorn and coworkers reported the family of encapsulated trimetallic nitride clusters inside fullerenes.¹⁸ Their trimetallic nitride template (TNT) method to produce endohedral metallofullerenes has afforded macroscopic

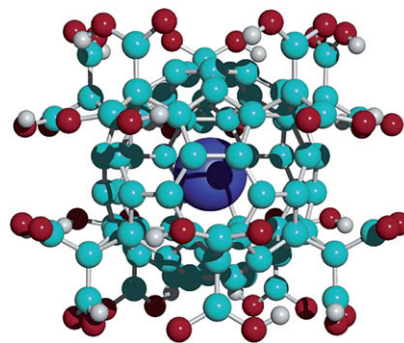


Fig. 2 Molecular model for the Gd@C₆₀[(C(COOH)₂)₁₀] structure [reprinted with permission from ref. 17a. Copyright (2003) American Chemical Society].

quantities of materials such as $\text{Sc}_3\text{N}@\text{C}_{80}$, with yields that exceed those of the third most abundant (next to C_{60} and C_{70}) empty cage C_{84} , produced under normal conditions.⁷ The TNT method, with subsequent modifications,¹⁹ has resulted in the preparation of many other members of this interesting family of compounds.²⁰

Isolation of $\text{Sc}_3\text{N}@\text{C}_{80}$ in macroscopic quantities has facilitated the study of its physical structure.²¹ There are seven possible constitutional isomers for C_{80} satisfying the isolated pentagon rule (IPR), yet only the most stable empty cages with D_2 and D_{5h} symmetry have been isolated. In contrast, the two least stable empty isomers with I_h and D_{5h} symmetries are the ones that predominate when they are filled with metallic nitride cluster, the I_h isomer certainly being the most abundant.²² When considering the electronic structure of $I_h\text{-C}_{80}$ it is possible to rationalize this observation. It is characterized by the presence of an energetically low-lying 4-fold degenerate LUMO, which enables this fullerene to accept up to six electrons. This is corroborated by an electron affinity of 3.75 eV. After the TNT inclusion, the electron affinity of the new molecule decreases to 2.99 eV for $\text{Sc}_3\text{N}@\text{C}_{80}$.

The interactions present within the TNT metallofullerenes consist of four components, as Fig. 3 represents. First of all, we should consider the covalent C–C bonds that form the cage itself. This cage then mechanically entraps the TNT unit. In addition to these two interactions, there is a strong ionic component to the bonding in the endohedral complex. The $\text{M}_3\text{N}@\text{C}_{80}$ molecule ($M = \text{Sc}, \text{Y}, \text{La}, \text{Gd}$) can be thought in formal terms to consist of three concentric rings of charge starting with the core nitride (N^{3-}), which is surrounded by three Sc^{3+} ions, which are then encapsulated by the $(\text{C}_{80})^{6-}$ cage.²³ In fact, photoemission and X-ray absorption spectroscopy experiments determined an effective transfer of 6.3 electrons for the $\text{Sc}_3\text{N}@\text{C}_{80}$ structure.²⁴ For this reason, the $I_h\text{-Sc}_3\text{N}@\text{C}_{80}$ metallofullerene has a relatively large HOMO–LUMO gap and higher stability than the other isomers of C_{80} .

Considering all these peculiar characteristics of endohedral metallofullerenes, it is clear that their chemical reactivity is not just routine. In fact, when the first exohedral derivative of an endohedral metallofullerene was reported, $\text{La}@\text{C}_{82}(\text{Mes}_2\text{Si})_2\text{CH}_2$,²⁵ all results seemed to indicate that metallofullerenes were very reactive towards organic functionalization, giving rise to multiple adducts or regioisomers of the monoadducts.²⁶ However, remarkable selectivities for the formation of specific regioisomeric monoadducts have been observed several times. In most of the cases, regioselectivity has been observed in Diels–Alder cycloadditions,²⁷ Bingel-type reactions (cyclopropanation)²⁸ or 1,3-dipolar cycloadditions²⁹ carried out with $\text{M}_3\text{N}@\text{C}_{80}$ structures (where $M = \text{Sc}, \text{Y}$ or Er) (see Fig. 4 for representative examples).

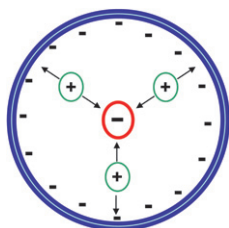


Fig. 3 Charge distribution in TNT metallofullerenes.

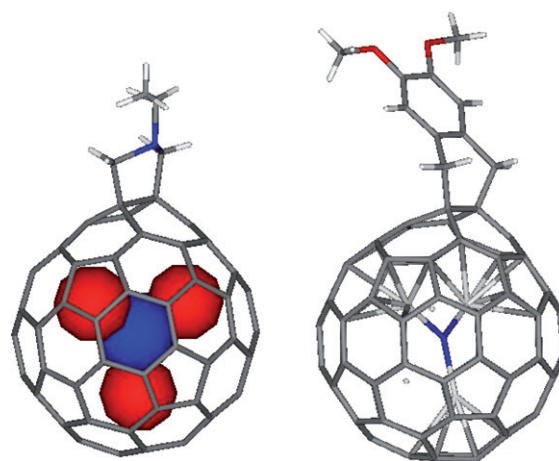


Fig. 4 DS Viewer representation of the *N*-ethyl endohedral fulleropyrrolidine of $\text{Sc}_3\text{N}@\text{C}_{80}$ (left) and the crystal structure of its Diels–Alder derivative (right). The location of the Sc_3N cluster in the fulleropyrrolidine adduct is only shown as an illustration [modified with permission from ref. 29a. Copyright (2005) American Chemical Society].

More recently, new reactions that do not resemble the ones observed in C_{60} have been discovered in endohedral metallofullerenes.^{28,29} These are isomerization reactions between different regioisomeric monoadducts,³⁰ or exohedral functionalization reactions that allow control of the geometry of the metal encapsulated.^{29d} All these observations evidenced that the chemistry of endohedral metallofullerenes is a research area still in its infancy, where important still open questions about reactivity, properties and applications should be addressed in the next years.

2.1.2. Molecular surgery in fullerenes. Another important challenge that bothered fullerene chemists for a long time was the idea of opening the fullerene cage in a controlled way, in order to introduce atoms or small molecules inside. The original fullerene structure is subsequently recovered by closing the cage. In a first step, in the paper entitled “*There is a hole on my bucky*” Wudl and coworkers pioneered an efficient route to open an 11-membered ring orifice on the surface of C_{60} .³¹ However, even a small atom such as helium, was found to be difficult to pass through this orifice. Nevertheless, synthetic chemists devoted an important effort to the preparation of other open fullerene structures and, in 1999, Rubin and coworkers coined the term “molecular surgery” to report the synthesis of a cobalt(III) complex, whose cobalt atom was ideally located above a 15-membered ring orifice.³² The same research group prepared a bis-lactamic derivative of C_{60} with a 14-membered ring orifice, which allowed the insertion of He (1.5%) and H_2 (5%) for the first time.³³

Three years ago, as the final process of molecular surgery, the challenge was finally accomplished by Komatsu and coworkers.³⁴ They synthesized a C_{60} derivative with a 13-membered ring orifice by thermal reaction of C_{60} with a 1,2,4-triazine derivative (Fig. 5)³⁵ and incorporated molecular hydrogen with a 100% yield. After the H_2 insertion, the complete closure of the orifice was carried out in a four-step process that afforded an entirely new endohedral fullerene, $\text{H}_2@\text{C}_{60}$, in an amount of more than 100 mg.³⁴

This new molecule, $\text{H}_2@\text{C}_{60}$, is formally a hydrocarbon according to its constitution in which, however, no covalent

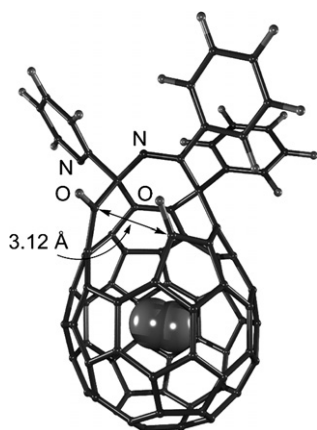


Fig. 5 Optimized structure of the C_{60} derivative with a 13-membered ring that incorporates H_2 in a 100% yield [reprinted with permission from ref. 35. Copyright (2006) American Chemical Society].

bond between carbon and hydrogen is present. Therefore, endohedral fullerenes open new avenues in chemistry with a variety of aspects about their structure and properties which will define their potential future applications.

3. Carbon nanotubes

Carbon nanotubes display intriguing electronic and mechanical properties that have attracted the attention of many scientists all around the world.³⁶ The first observation of their formation in substantial quantities was described by Iijima *et al.* seventeen years ago,⁸ although preparation of similar structures was reported as early as 1953.³⁷

A great variety of CNT derivatives have been obtained by different synthetic methodologies. CNTs can be chemically modified mainly by the following strategies: (a) functionalization of the defects located on the sidewall and the rims; (b) non-covalent interactions; (c) sidewall covalent functionalization and (d) endohedral inclusion.

3.1. Defect functionalization

Smalley and coworkers³⁸ reported a purification method of CNTs, consisting of the treatment of a raw nanotube material with a mixture $H_2SO_4 : HNO_3$ (3 : 1). By means of this methodology the original CNTs with closed tips are transformed into shorter nanotubes with opened ends, that display carboxylic groups in the regions where the oxidative damage takes place (sidewall and opened ends).

This carboxylic functionality made possible the development of an elegant and simple strategy to functionalize CNTs. Generation of the acyl chloride followed by simple esterification or amidation reactions offers the possibility of attaching many organic fragments and synthesizing a great variety of CNT derivatives. Based on this approach, Haddon and coworkers³⁹ reported the functionalization of SWCNTs, with octadecylamine (ODA) to produce the corresponding SWCNT-ODA amide. The introduction of long hydrocarbon chains increases the solubility of the SWCNT-ODA in organic solvents, assisting its characterization and facilitating the obtention of highly purified SWCNT materials that are suitable for physical properties measurements.

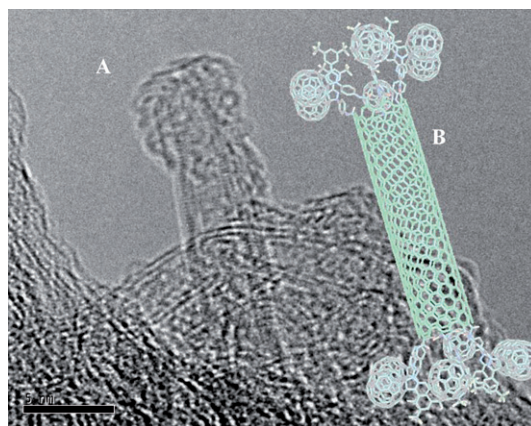


Fig. 6 (A) HRTEM image of covalently linked nanohybrid material SWCNT-[60]fullerene (bar = 5 nm) (reprinted from ref. 41 with permission from Elsevier). (B) Computer generated image of the hybrid.

The above general and useful chemical functionalization under very strong oxidizing conditions afforded a wide variety of functionalized CNTs which have been collected in a variety of outstanding review papers.⁴⁰

In the following, we will mention some remarkable recent examples based on this functionalization approach. For instance, Langa and coworkers⁴¹ have recently described the synthesis of hybrid conjugated SWCNT-[60]fullerene materials (Fig. 6). The authors decorated the SWCNTs with fragments of *N*-anilino-pyrazolino[60]fullerene, by an amidation reaction with the SWCNT-acyl chloride. Vibrational spectroscopy and high resolution transmission electron microscopy (HRTEM) evidenced the existence of [60]fullerene units located at the rims of the SWCNTs. The presence of attached fullerenes in the SWCNT material could improve the mechanical properties of the CNTs and tune the electronic and optical properties of the fullerene derivative, a subject of great interest for many optoelectronic applications.

By following a similar strategy, Martín, Prato, Guldi *et al.*⁴² described an efficient way to functionalize SWCNTs with the strong electron donor tetrathiafulvalene (TTF) or its π -extended analogs (exTTF) (Fig. 7). The procedure implies the reaction of SWCNT-containing carboxylic acid groups with TTF or exTTF derivatives, through esterification or amidation reactions. This work depicts the preparation of the first TTF-SWCNT

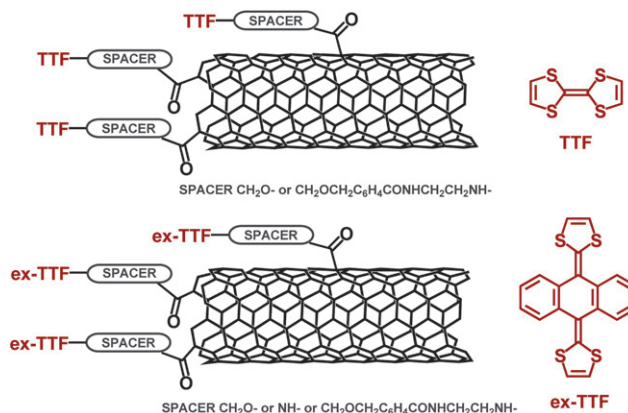


Fig. 7 TTF-SWCNT and exTTF-SWCNT derivatives.

donor–acceptor systems, to evaluate the possible use of CNTs in solar energy conversion applications. The analysis of these compounds by different analytical, spectroscopic and microscopic techniques confirmed the presence of TTF or exTTF units connected to the SWCNTs. Photophysical analysis by time resolved spectroscopy revealed the presence of radical species ($\text{TTF}^{\bullet+}$, $\text{exTTF}^{\bullet+}$ and $\text{SWCNT}^{\bullet-}$) indicating the existence of an efficient photoinduced electron transfer, a critical point for photovoltaic devices.

3.2. Non-covalent functionalization

Non-covalent interactions provide a way to functionalize CNTs, without causing any damage to the electronic structure of the parent CNT. These strategies have been used to prepare CNT derivatives with surfactants (SDS), DNA, proteins, polymers and pyrene.⁴⁰

Guldi, Maggini, Paolucci, Prato *et al.*⁴³ reported recently an attractive example of non-covalent modification of CNTs based



Fig. 8 Computer generated image of the first supramolecular hybrid [60]fullerene–pyrene–SWCNT.

on π – π pyrene–SWCNT interactions. The authors prepared a [60]fullerene-bisadduct bearing a pyrene unit, that was capable of solubilizing the CNTs thanks to non-covalent interactions between the pyrene moiety and the sidewall of the SWCNTs (Fig. 8). The compound was investigated by cyclic voltammetry, transmission electron microscopy, and photophysical experiments and the results confirmed the existence of π – π interactions, revealing therefore the formation of the first supramolecular hybrids of [60]fullerene and SWCNTs.

By following the pyrene strategy, a variety of organic addends, including photo- and electro-active moieties have been supramolecularly connected to CNTs. As recent examples, porphyrins⁴⁴ and exTTF⁴⁵ have afforded the respective radical ion species upon photoexcitation.

3.3. Covalent functionalization

The curved morphology of CNTs plays an important role in their reactivity. The sidewall is built of a graphene sheet rolled on itself, which implies that the sp^2 carbon atoms present a certain degree of pyramidalization, which makes the convex surface susceptible to addition reactions. This pyramidalization character is stronger for small diameter tubes which, consequently are more reactive.

A great variety of CNTs compounds have been synthesized by sidewall covalent modification,⁴⁰ following different approaches like halogenation and hydrogenation reactions, and radical or nucleophilic additions.

Cycloaddition reactions have been extensively used in order to prepare new CNTs derivatives. In fact, many organic moieties have been covalently linked to the CNTs by carbene and nitrene insertion, nitrilimine and nitrile oxide cycloaddition, as well as azomethyne ylides cycloaddition. The methodology developed by Prato and coworkers⁴⁶ is one of the most useful protocols for preparing CNT derivatives. Thermal generation of azomethyne ylides by condensation between α -aminoacids and aldehydes, provides an efficient and simple way to link many organic fragments to the CNTs (Fig. 9).⁴⁷ Since this method

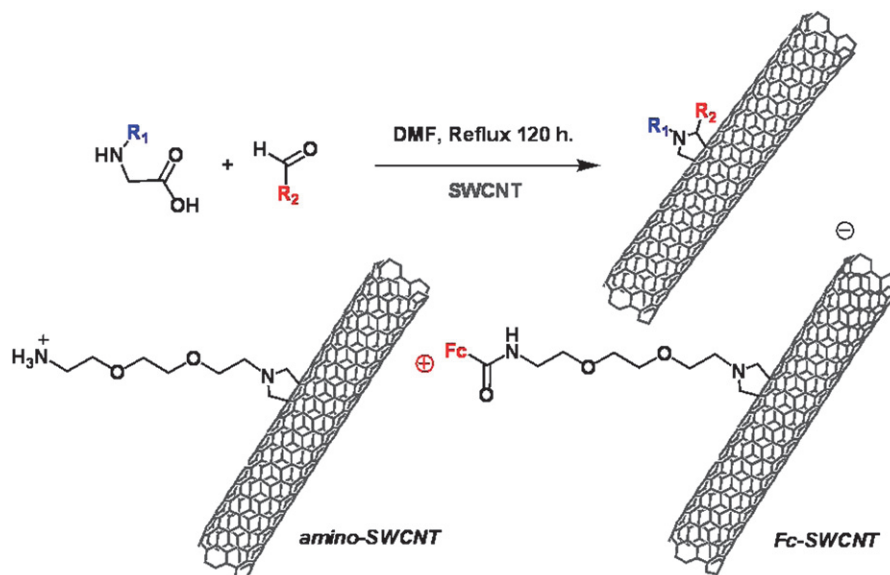


Fig. 9 1,3-dipolar cycloaddition of azomethyne ylides.

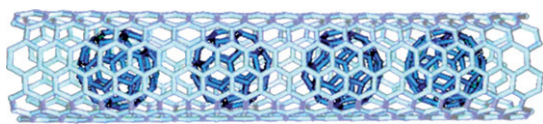


Fig. 10 Computer generated image of a SWCNT filled with [60]fullerene units.

was reported, extensive applications have been carried out to prepare, among others, CNTs bearing pendant amino groups ($\text{NH}_2\text{-SWCNT}$) that were particularly suitable to attach to amino acids, peptides, nucleic acids or electron donors like ferrocene (Fc-SWCNT).⁴⁸

Photophysical analysis of Fc-SWCNT revealed the existence of a photoinduced electron transfer process and an effective generation of charges, evidencing the great potential applications of these SWCNT-based compounds to prepare photovoltaic devices.

3.4. Endohedral functionalization

The fascinating geometry of CNTs provides the possibility to decorate them by different exohedral approaches as well as by endohedral filling of their inner cavities. Pure elements like gold and silver; small molecules like metallic halides and metal oxides; small proteins like lactamase; fullerenes and endohedral fullerenes have been successfully inserted into the cavity of CNTs (Fig. 10).⁴⁹

In the past years, many approaches to incorporate fullerenes inside CNTs have been described. Heating open ended CNTs under vacuum at 400–600 °C in the presence of [60]fullerene provided a high yield of inclusion that was clearly evidenced by electron microscopy. Treatment of this material at a higher temperature (1200 °C) produced the coalescence of the [60]fullerene units located inside the tubes, obtaining double-walled CNTs starting from SWCNTs.⁴⁹ Intertube distance was found to be about 0.36 nm.

Nakamura and coworkers⁵⁰ have recently reported the introduction of various *ortho*-carborane-based molecules into SWCNTs. Analysis of these materials by TEM provided clear images of the organic molecule either at rest or translating inside a SWCNT, proving the utility of TEM for single-molecule chemical analysis.

4. Other forms of carbon nanotube

In the current times, where molecules can be imaged at near-atomic resolution by techniques such as transmission electron microscopy (TEM) or atomic force microscopy (AFM) and powerful strategies in chemistry have been developed, it is possible to access an almost unlimited number of surprising carbon nanostructures. In this sense, an amplified growth process of SWCNTs from individual short SWCNTs seeds, tethered with Fe salts at its ends, has been demonstrated by AFM.⁵¹ TEM images have also provided direct evidence of the iodine doping effect at the intratubular position of C_{60} peapods which assists the coalescence of C_{60} molecules inside SWCNTs, forming a double-walled carbon nanotube (DWCNT).⁵²

The procedure used for the generation of carbon nanotubes, for example, subjected to minute modifications, has led to new

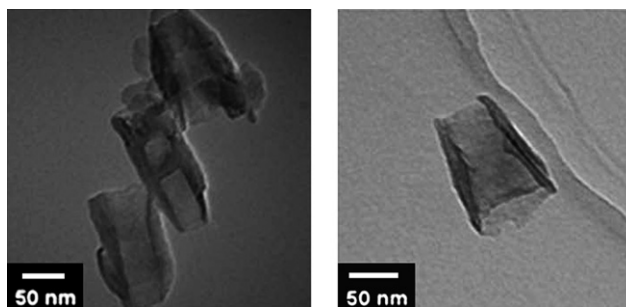


Fig. 11 TEM images of reduced CSCNTs [reprinted with permission from ref. 54a. Copyright (2007) American Chemical Society].

structures with fascinating geometries, such as those mentioned in the following paragraphs.

4.1. Cup-stacked carbon nanotubes

Cup-stacked carbon nanotubes (CSCNTs) consist of truncated conical graphene layers with diameters ranging from 50 to 150 nm and lengths up to 200 μm (Fig. 11),⁵³ in contrast to conventional carbon nanotubes made of multiseamless cylinders in a hexagonal carbon network. In addition, the edges on the outer and inner surface of cup-shaped carbons seem to be more accessible to a possible chemical functionalization that other types of carbon nanotubes.

Recent photophysical investigations demonstrated how highly dispersible nanocarbon materials, with uniform size in solution, can be prepared by photoinduced electron transfer reduction of CSCNTs with a mild organic electron donor.⁵⁴

4.2. Carbon nanohorns

Nanostructured carbon nanohorns (CNHs) are observed by TEM with a typical dahlia-flowerlike morphology (aggregated in spherical superstructures), typically ranging between 50 and 100 nm (Fig. 12).⁵⁵ When compared with carbon nanotubes, they are obtained with higher purity, due to the absence of any metal nanoparticles during their production. They present a heterogeneous surface structure due to their highly strained

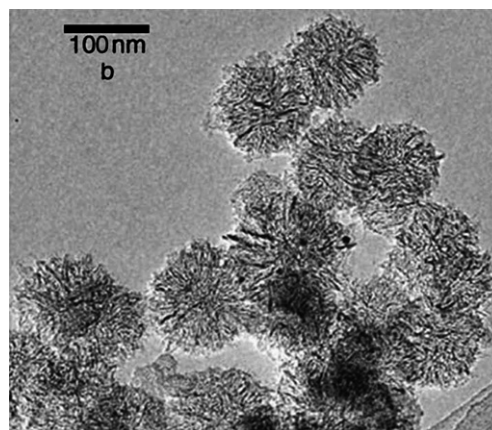


Fig. 12 High-resolution transmission electron microscopy (HRTEM) micrographs of soluble functionalized CNHs (reprinted from ref. 56a with permission from Wiley-VCH).

conical ends, which gives rise to better dispersions of CNHs in different organic solvents.

The chemical functionalization of CNHs has been explored in recent years considering several covalent and non-covalent approaches.⁵⁶ The properties observed in the nano-ensembles formed are similar to those of carbon nanotubes, although the obtained materials are easily dispersible and processable.

4.3. Carbon nanotori

Toroidal carbon nanotubes also named toroidal “crop circles” were experimentally observed by Smalley and coworkers⁵⁷ while examining laser-grown SWCNT materials. These intriguing molecules consist of a circular carbon nanotube with no beginning or end, with a tube diameter of approximately 10–12 Å and a ring diameter of approximately 3000–5000 Å (Fig. 13). Carbon nanotori can be theoretically formed following two different approaches: (i) connecting small sliced parts of the CNT through pairs of pentagons and heptagons rings that provide the curvature to the final structure; (ii) by means of bending a CNT and connecting its two ends together without introducing the pairs of pentagons and heptagons.

Many theoretical and experimental studies have revealed that these curious molecules display interesting properties such as: conducting behaviour, magnetic response, and persistent current. Further research is needed in order to find out how factors like hybridization, curvature, defects or chirality can influence all these properties.

4.4. Carbon nanobuds

A new hybrid carbon material has been recently described by Nasibulin, Kauppinen and coworkers⁵⁸. This new material consists of fullerene units covalently attached to SWCNTs, which have been prepared by using particles grown *in situ* via ferrocene vapour decomposition or by using premade iron-catalyst particles produced by a hot wire generator. Careful investigation of this material by TEM revealed the presence of C₄₂ and C₆₀ fullerene units covalently bonded to the outer surface of the SWCNTs. This new carbon nanomaterial presents many potential applications. Thus, for instance, due to the higher and well-known reactivity of fullerenes, this new hybrid nanomaterial could open new strategies to chemically modify CNTs (Fig. 14).

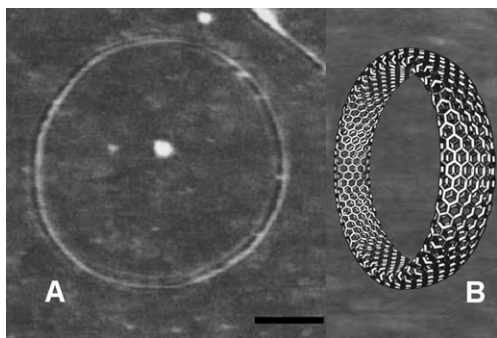


Fig. 13 (A) Scanning probe micrograph of a carbon nanotorus (reproduced from ref. 57 with permission from the Nature publishing group). (B) Computer generated image of a carbon nanotorus built without introducing the pairs of pentagons and heptagons.

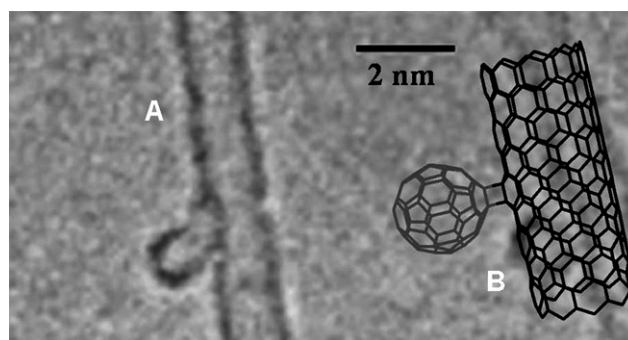


Fig. 14 (A) TEM observation of a nanobud structure, with a fullerene linked to the SWCNT (reproduced from ref. 58 with permission from the Nature publishing group). (B) Computer generated image of [60]fullerene linked to the outer surface of the SWCNT by [2 + 2] cycloaddition.

5. Carbon nano-onions

Although multi-shelled fullerenes or carbon nano-onions (CNOs) were discovered almost simultaneously with carbon nanotubes,⁹ these molecules have not received much attention yet.

Since Ugarte first observed CNOs under the microscope,¹¹ two main preparative methods have been described in the literature: (i) Kuznetsov *et al.* reported the production of extremely pure CNOs in high yields by annealing carbon nanodiamond particles at temperatures above 1200 °C;⁵⁹ and (ii) more recently, Sano *et al.* described a method of producing CNOs that involves arcing between two graphite electrodes under water.⁶⁰ The carbon nano-onions obtained by both methodologies are rather different. The annealing of the ultradispersed nanodiamond particles (5 nm average) under vacuum produces mainly small CNOs (N-CNOs) with 6–8 shells (5 nm). The arcing of graphite under water, however, leads to the formation of large CNOs (A-CNOs) with diameters in the range of 15–25 nm (20–30 shells) (Fig. 15).

The majority of the investigations about the chemical functionalization of CNOs have been carried out only with large CNOs, which were produced by the arc-discharge method^{61a,62} and, due to their huge dimensions, exhibit poor solubilities in most organic solvents and a chemical reactivity similar to graphite. However, Echegoyen's group recently succeeded in the isolation, separation and purification of CNOs of diverse dimensions, as well as the chemical functionalization of the smaller species by using 1,3-dipolar cycloaddition reactions.⁶¹

CNOs have even attracted the attention of NASA researchers, who are interested in their tribological properties as additives for aerospace applications. These carbon particles have demonstrated superior lubrication properties to other conventional lubricants,⁶³ and a very promising future is expected for these new forms of carbon.

6. Graphenes

Graphenes are two-dimensional structures that consist of hexagonal rings constructed from sp²-hybridized carbon atoms. Two different methods have been applied in order to obtain these two-dimensional compounds. A large variety of graphenes, also named polycyclic aromatic hydrocarbons (PAHs) have been obtained by chemical synthesis;⁶⁴ hexa-*peri* and hexa-*cata*-hexabenzocoronene derivatives, as well as other larger-size

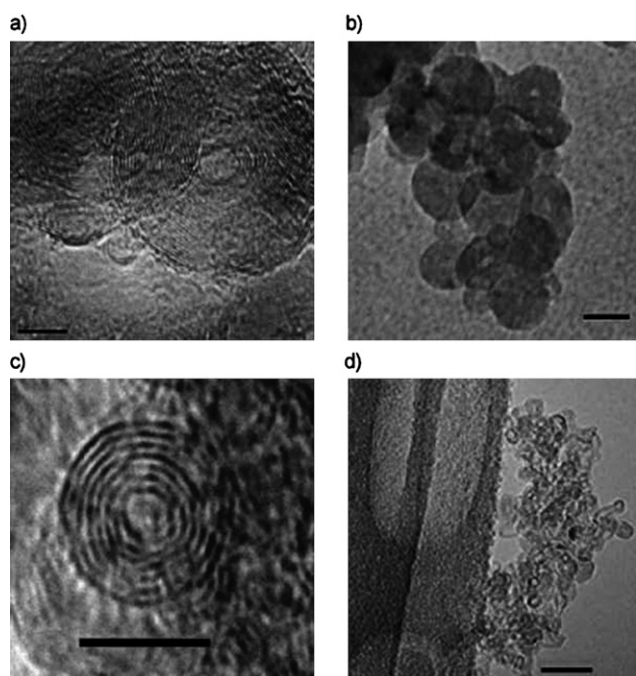


Fig. 15 (a) High- and (b) low-resolution TEM images of CNOs obtained by arcing under water. (c) High- and (d) low-resolution TEM images of CNOs obtained from nanodiamonds. Scale bars represent 20 nm and 5 nm in the low and high-resolution images, respectively (reprinted from ref. 61c with permission from Wiley-VCH).

graphenes have been obtained by different chemical methodologies. The use of these methodologies usually implies tedious experimental procedures and a low yield of graphene obtention.

A number of studies have demonstrated that graphenes display excellent electron transport properties; although obtention of graphene sheets starting from graphite is severely limited by the high cohesive energy of graphite, to overcome this problem two strategies have been applied: (i) graphene or chemically modified graphene sheets have been obtained by mechanical treatment⁶⁵ (repeated peeling) of highly oriented pyrolytic graphite or, (ii) chemical modification of monocrystalline graphite.

Haddon and coworkers⁶⁶ have recently reported an effective way to obtain graphene sheets functionalized with long hydrocarbon chains (G-ODA) (Fig. 16). Oxidative treatment of

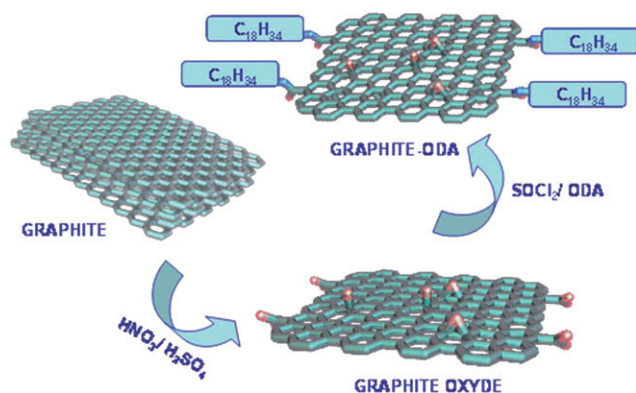


Fig. 16 Synthetic methodology developed by Haddon and coworkers.⁶⁶

microcrystalline graphite with nitric and sulfuric acid produce oxidized graphite, decorated with acidic groups at the edges. The presence of these acidic functionalities provides a way to introduce long hydrocarbon chains by treatment of graphite-oxide with SOCl_2 and octadecylamine. Thanks to the ODA chains, G-ODA is soluble in polar solvents, which is important to improve graphite processability as well as its possible use in the fabrication of electronic devices.

7. Summary and outlook

Only a few years ago, it was impossible to predict the impressive progress experienced in the knowledge of carbon allotropes' chemistry, from the well-known fullerenes and carbon nanotubes, to the less-known or scarce new allotropes examined among these pages. It is clear that the incorporation of these systems in practical applications requires the development of larger-scale production methods, already implemented for carbon nanotubes.

Although fullerenes and in particular C_{60} , have been an important landmark in establishing the basic principles of the chemical reactivity of these species and their expected properties, the singular geometric and electronic distribution of some of these carbonaceous materials will certainly provide unanticipated and surprising chemical structures with outstanding properties, as is already occurring with endohedral metallofullerenes.

Carbon is the closest chemical element to the human being. It was essential for the appearance of life in our planet and it is present in a large extent in our body. In the current nanoscience and nanotechnology revolution that we are watching, carbon also has a prominent role, through the new nanostructures discussed in this article. By force, they will play an essential role in the coming future.

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