



A review of shaped carbon nanomaterials

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Materials made of carbon that can be synthesised and characterised at the nano level have become a mainstay in the nanotechnology arena. These carbon materials can have a remarkable range of morphologies. They can have structures that are either hollow or filled and can take many shapes, as evidenced by the well-documented families of fullerenes and carbon nanotubes. However, these are but two of the shapes that carbon can form at the nano level. In this review we outline the types of shaped carbons that can be produced by simple synthetic procedures, focusing on spheres, tubes or fibres, and helices. Their mechanisms of formation and uses are also described.

Introduction

Carbon is a remarkable element and has been described as ‘the key element of living substances’.¹ It is the ability of carbon to bond to itself to form oligomers and polymers that allows carbon to play this important role in life processes. This property can also be used to produce the myriad of structures that makes carbon such an important commodity element; for example, it is the element that leads to the basis of the Fischer–Tropsch process used by Sasol in South Africa to make fuels and chemicals. But the ability of carbon to form strong bonds to oxygen to generate CO₂ and lead to a carbon sink also reveals the ‘dark side’ of carbon. The control and understanding of the bonding properties of carbon thus becomes crucial if the chemistry of carbon is to be harnessed for the good of the world’s population.

Carbon has four electrons that can be used for bonding and this determines the structural chemistry that is associated with the element. In the classical valence bond model, these four electrons (called sp³ electrons) are used to form four bonds to other atoms. In the simplest case, when the bonds only occur between carbon atoms, C–C bonds are formed and the classical structure of diamond is produced (Figure 1a). However, it is the ability of carbon to form multiple bonds between elements that gives carbon many of its unique features. In this way carbon can also link to another carbon atom to give C=C (as found in graphite, Figure 1b) and C≡C bonds (as found in acetylene, Figure 1c). The chemical and physical properties associated with the C–C, C=C and C≡C interactions are all different and the ability to control the synthesis of structures containing these units has led to an exploitation of the chemistry of carbon.

This ability to make all-carbon containing nanomaterials, in particular those containing networks of C=C double bonds, has been one of the key events that has led to the current nanotechnology revolution. The discovery of fullerene in 1985 (Figure 2a)² and the subsequent studies by Iijima³ on carbon nanotubes in 1991 were key events that have spurred the study of nanostructures in general and nanocarbon structures in particular. Through these discoveries a third allotrope of carbon, following from the graphite (sp² hybridised carbon) and diamond (sp³ hybridised carbon) allotropes, was recognised – this allotrope is based on a bent sp² hybridised carbon. These discoveries coincided with attempts to miniaturise devices (such as cell phones and computers) and the use and development of new characterisation tools (such as scanning probe microscopes and electron microscopes) to visualise these new structures. The outcome has been the emergence of the field of nanotechnology.

The most common form of oligomerised or polymerised carbon is soot (Figure 2b). Soot, produced by burning carbonaceous materials, has an amorphous structure with little long-range order. But, by controlled decomposition of carbon-containing reactants under appropriate conditions, it has been possible to make these carbons with long-range order. Control of the experimental conditions permits morphology control (shape, length, diameter, etc.) of the carbon products at the nano level and this has generated a wide range of variously shaped carbon nanomaterials (SCNMs). The synthetic approach is based on templating and self-assembly principles, similar to the processes used to grow NaCl (salt) crystals from a salt solution, or raindrops in clouds. Some of these SCNMs are shown in Figure 3 and discussed in more detail below. As can be seen in Figure 3, a wide range of structures can be made (tubes, spheres, helices and Y-junctions). Each shape influences the property of the carbon material and it is this carbon shape–property relationship that is the key to the manufacture of new devices. These new properties will also be influenced by the size of the SCNMs.

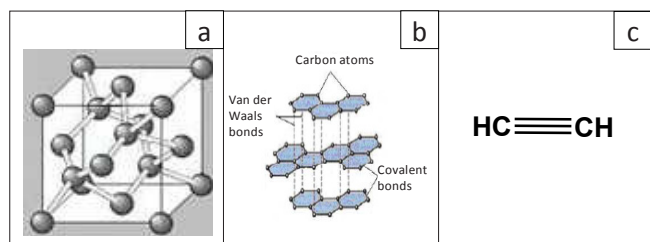


FIGURE 1: Schematic diagrams of different carbon types: (a) diamond, (b) graphite and (c) acetylene.

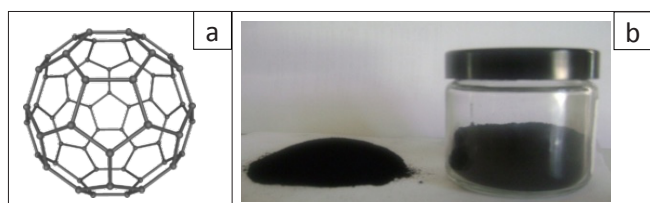


FIGURE 2: (a) A schematic representation of a fullerene model and (b) a photograph of soot.

Nanocarbons have a number of remarkable properties:

1. Carbon is a light element and structures made from carbon tend to be lightweight (carbon is about six times lighter than iron).
2. Carbon in tubular form has been shown to be the strongest material synthesised to date (Young's modulus for a single-walled carbon nanotube (SWCNT) is about 1 TPa).⁴

3. Carbon can act as conductor, semi-conductor or insulator, depending on the carbon-carbon bonding and the carbon structure.
4. Carbon in the form of diamond or SWCNTs is the hardest material known.
5. The optical studies of carbon have shown that SWCNTs have absorbances of 0.98 a.u. – 0.99 a.u. over a wide range of wavelengths, making them a near perfect black body.
6. The thermal conductivity of carbon is variable. In SWCNTs the thermal conductivity along the tube axis is 'ballistic' (10 times that of copper) but when perpendicular to the axis, a SWCNT is an insulator.⁵
7. The surface of carbon materials can be chemically modified (functionalised), leading to a new generation of reagents that can be used in new applications, for example, in composite materials.

Our own involvement in SCNMs dates back to the exploitation of using carbon as a catalyst support i.e. a material used to spread a metal catalyst and increase the number of metal atoms available at the surface for reaction. The finding that gold supported on carbon could be used to catalyse the reaction between ethyne (acetylene) and HCl to give $\text{CH}_2=\text{CHCl}$ (vinyl chloride) as a monomer for polyvinylchloride synthesis⁵ led us to investigate carbon nanotubes as gold supports in the mid-1990s. This required that we develop a programme for the synthesis of carbon

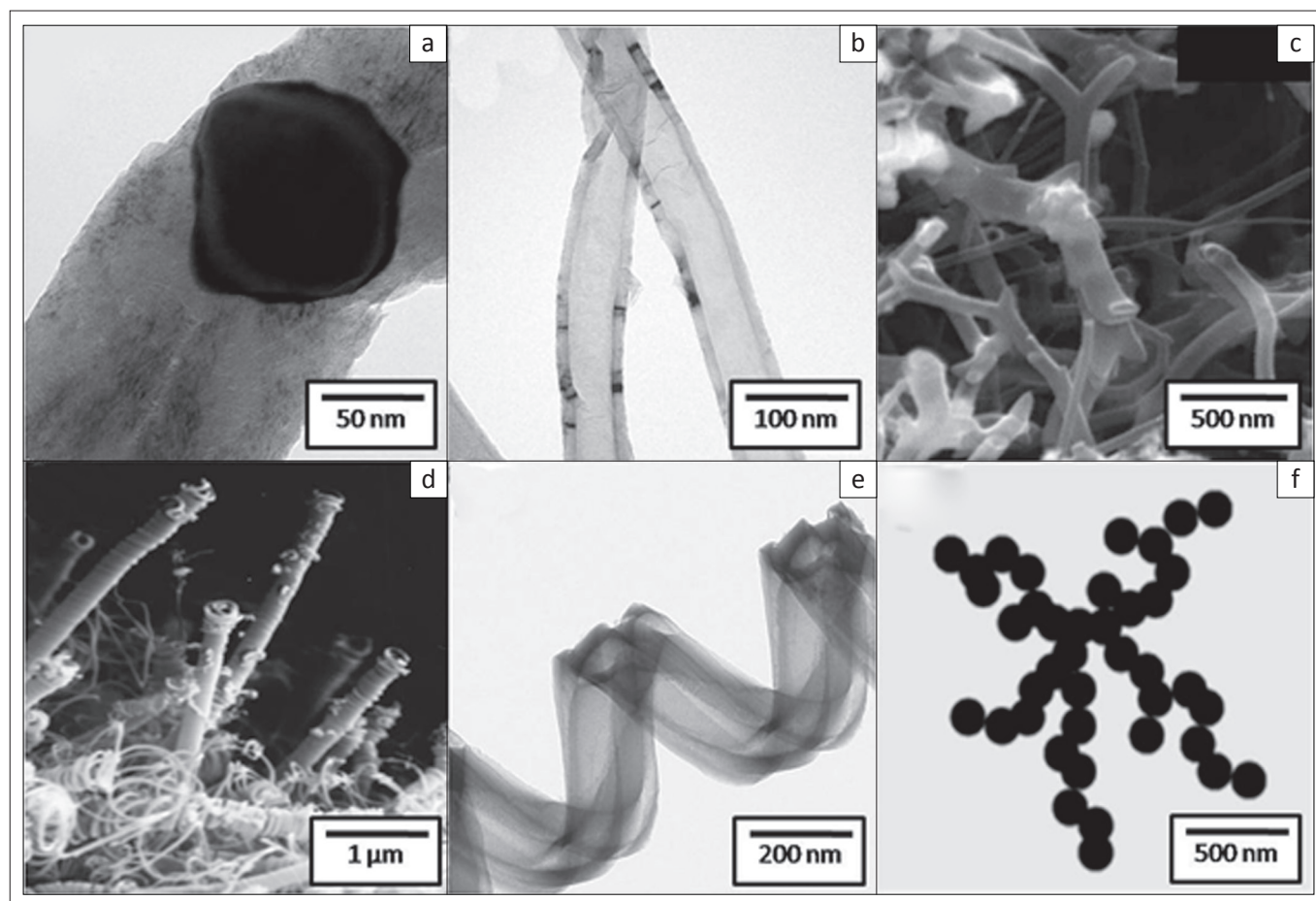


FIGURE 3: A variety of shaped carbon materials: (a) a solid fibre growing from a catalyst particle, (b) a tubular structure with hollow inner, (c) a scanning electron microscopy (SEM) image of branched carbon fibres, (d) a SEM image of coiled carbon fibres, (e) a transmission electron microscopy image of a spring-like fibre and (f) a spherical carbon material.



nanotubes, studies that have since led us to investigate the synthesis of other shaped carbons as generic catalyst support materials.

A consideration of work on carbons in South Africa (and elsewhere in Africa) has revealed little research in this area (with the exception of diamonds) prior to the mid-1990s. In South Africa, the company SA Carbide (operating out of Newcastle), has made carbon spheres for the battery market for decades. The carbon in pulp technology, for concentrating gold, has also been exploited in the mining industry since the 1990s.⁷ More recently, the possibility of making C@U core-shell spheres for a proposed Pebble Bed Modular Reactor to generate nuclear energy in South Africa has also seen an exploitation of the carbon market in the country.⁸

Other than these examples the main development of carbons in South Africa has been in the research arena, with activities focused in academic chemistry and physics departments. For example, our research group, CATOMAT, based in the School of Chemistry at the University of the Witwatersrand, is working on the synthesis of SCNMs and their application as strong materials in sensors, as catalyst supports, and in solar and fuel cells. Other groups at this university are working on new reactor designs for making SCNMs (Chemical Engineering), and studying their physical properties e.g. mechanical and electronic properties (School of Physics) or exploring their use as neuropharmaceuticals (Medical School). Research is also being performed on carbon nanotubes at many other South African universities (such as the University of Johannesburg, Tshwane University of Technology, the University of KwaZulu-Natal at Westville and Vaal University of Technology), as well as at other South African research organisations (the Centre for Nanostructured Materials at the Council for Scientific and Industrial Research, and MINTEK). The programmes range from pure synthesis to studies on the properties of SCNMs.

Research in South Africa in this area is largely funded by the South African Department of Science and Technology while nanotechnology activities in South Africa are coordinated by the South African Nanotechnology Initiative (SANi).

In the sections below we describe some of the new SCNMs that are being studied in our group. The descriptions have been categorised according to the shape of the carbon material (tubes or fibres, spheres, helices and 'other', which includes graphene). Indeed all the SCNMs to be discussed can be viewed as being generated from a single graphene sheet. For example, Figure 4 shows how a fullerene, a carbon nanotube or a graphite (layer or layers) can be made from a graphene sheet.⁹ The review should thus provide an introduction to this new area of solid carbon chemistry.

Carbon nanotubes and carbon nanofibres

Carbon has the ability to form carbon nanotubes (CNTs) and carbon nanofibres (CNFs) in which the diameters are typically 1 nm – 100 nm while the lengths can range from 10 nm to a few centimetres. In addition, although typically represented

as a material showing good alignment, CNTs and CNFs are generally synthesised with an appearance more like 'cooked spaghetti', made of interwoven strands of carbon as shown in Figure 5. It is also possible to make carbon tubes that have Y-junctions and T-junctions (Figure 2d).

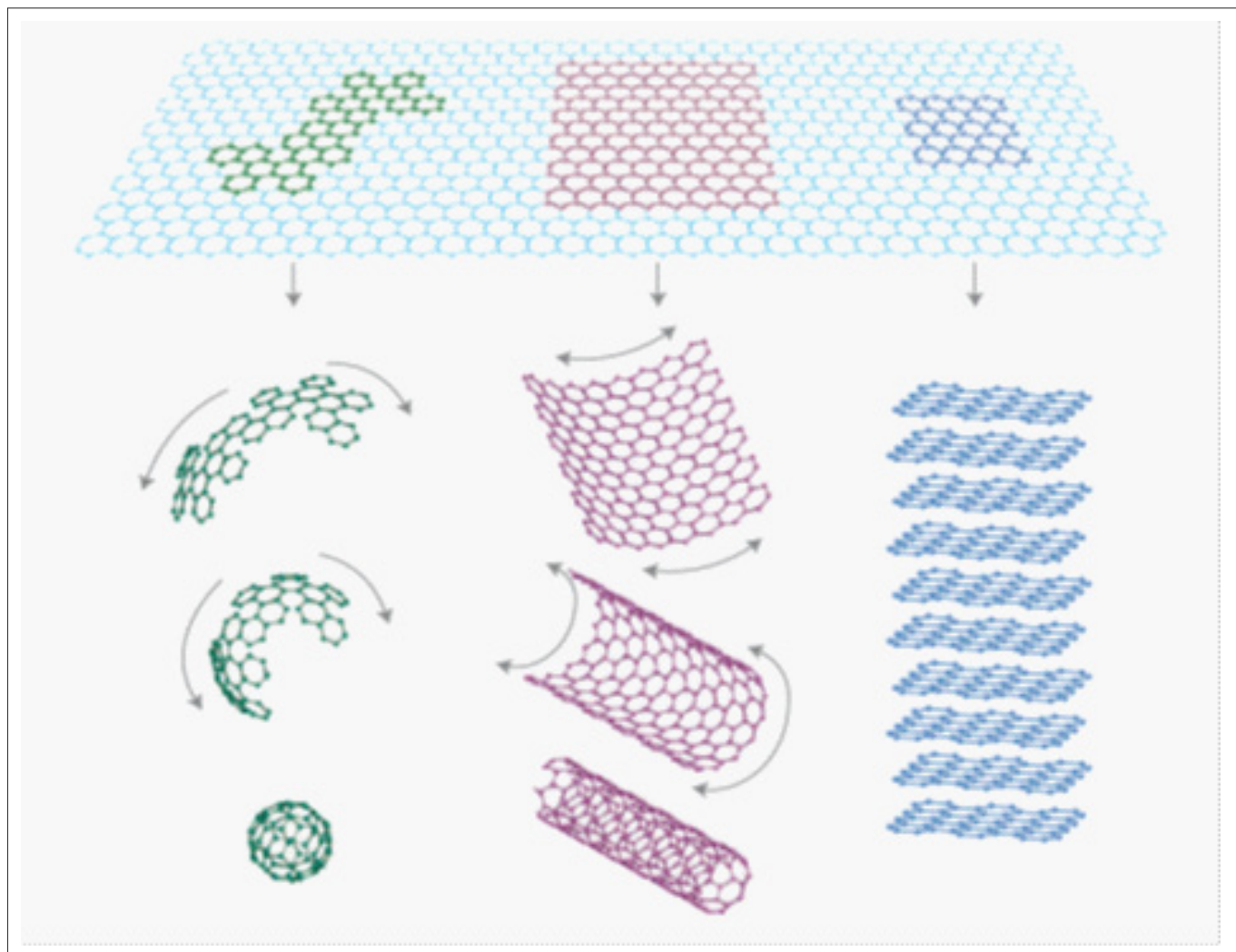
Many variations of both filled and hollow tubes exist. Thus, the carbon tube or fibre can be made of V-shaped cups stacked on top of each other, or of flakes that generate a herringbone structure. Finally, the tubes can be partially layered in the tube hollow, generating a bamboo structure. (Figures 2 and 6). The ability to visualise the structures of carbon at the nano level has permitted the exploration of the synthesis and morphology of nanocarbons. Clearly, variations in the structural morphology must be related to the properties and uses of the tubes or fibres.

CNTs can be described as seamless cylinders of rolled up graphene sheets of carbon atoms.¹⁰ Depending on the number of rolled up graphene sheets, three types of CNTs have been observed: SWCNTs, double-walled CNTs (DWCNTs) and multi-walled CNTs (MWCNTs). On the other hand, CNFs are cylindrical nanostructures (Figure 6c) with graphene layers arranged as stacked cones, cups or plates, as mentioned above. The history of CNFs dates back to 1889¹¹ when CNFs were reported to be grown from carbon-containing gases using a metallic crucible as the catalyst. In contrast, the history of CNTs dates to the 1950s¹² but with the explosive study of these materials only commencing in the 1990s.³ In general, CNFs tend to be wider (> 100 nm) than CNTs (typically having internal diameters of < 50 nm) and can be synthesised at lower temperatures than required for CNT synthesis. Indeed fibres can be formed at temperatures below 250 °C; these CNFs tend to be highly amorphous.

Synthesis of CNTs and CNFs

SCNMs are generally produced from the catalytic decomposition of hydrocarbon gases over selected metal nanoparticles. This process produces black soot, and, when observed under an electron microscope, the tubular structures (tubes or fibres) can readily be detected. Generally, CNFs and CNTs are fabricated using similar synthetic approaches – heating a carbon source in the presence of a catalyst. However, changes in the reaction conditions, for example catalysts and precursors, determine whether CNFs or CNTs are produced. There are three conventional methods used to synthesise CNTs and CNFs: (1) arc-discharge, (2) laser ablation and (3) catalytic chemical vapour deposition (CCVD). The CCVD process is a widely used technique that generates a relatively high yield of pure CNTs. Use of the CCVD method can produce aligned and ordered CNTs that can be grown in a controlled manner, which is not possible using the other conventional methods.

Typically, the CCVD approach requires a catalyst or template and a carbon source to produce SCNMs, in particular CNTs. The reaction is generally performed in a horizontal reactor such as that shown in Figure 7. The reactor can also be arranged in a vertical geometry. The reactor system comprises a quartz tube inserted into a hot



Source: Reprinted from Nature Materials, 6(3), Geim AK, Novoselov KS, The rise of graphene, p. 183-191, Copyright 2010, with permission from Nature Publishing Group.⁹ doi:10.1038/nmat1849

FIGURE 4: Graphene is a two-dimensional building material for carbon materials of all other dimensionalities. It can be wrapped up into zero-dimensional buckyballs, rolled into one-dimensional nanotubes or stacked into three-dimensional graphite.

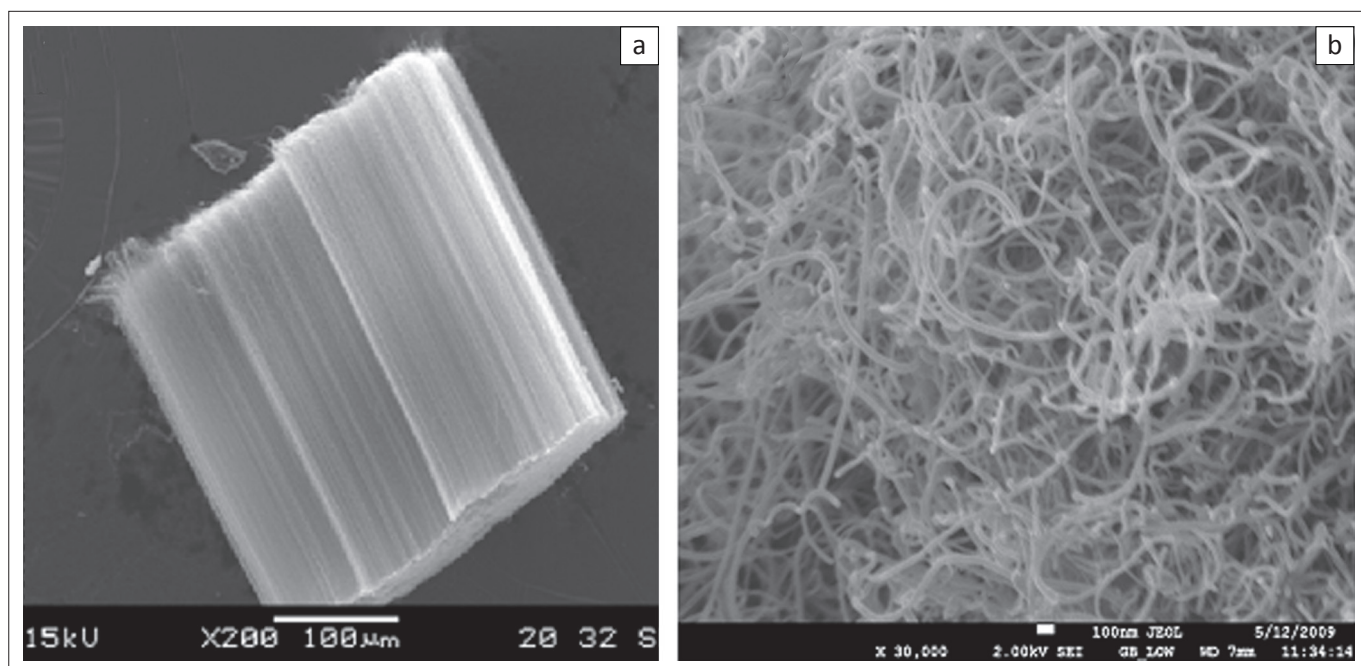


FIGURE 5: Scanning electron microscopy images showing (a) aligned carbon nanofibres and (b) 'cooked spaghetti type' carbon nanofibres.

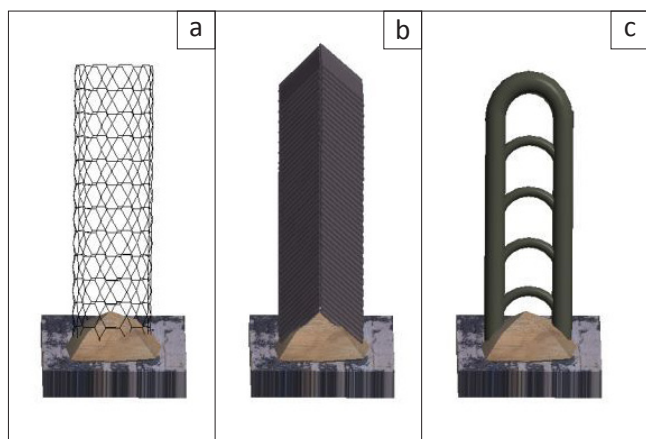
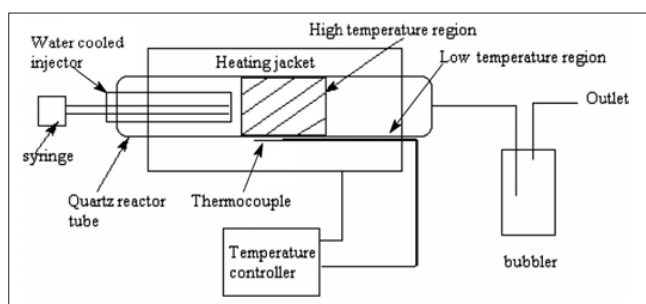


FIGURE 6: Animated representations of: (a) carbon nanotubes, (b) carbon nanofibres and (c) bamboo shapes.



Source: Reprinted from *Organometallics*, 24(5), Mohlala MS, et al., *Organometallic precursors for use as catalysts in carbon nanotube synthesis*, Copyright 2010, with permission from American Chemical Society.¹⁶ doi:10.1021/om049242o

FIGURE 7: A floating catalyst chemical vapour deposition reactor for the synthesis of shaped carbon nanomaterials.

oven. The carbon source is then passed through the quartz tube using an appropriate carrier gas at high temperature (typically 600 °C – 1100 °C), resulting in the decomposition of the reactants and production of the SCNMs. The reaction is usually performed in the presence of a catalyst. The catalyst can either be placed in the reactor (typically supported on an inert carrier to increase surface area)¹³ or passed as a gas through the reactor (as a floating catalyst).¹⁴ While the supported catalyst method involves a catalyst dispersed on a support, the floating catalyst method normally uses volatile organometallic compounds as precursors, with $\text{Fe}(\text{CO})_5$ and ferrocene typically being used in the catalytic synthesis procedure.^{15,16} The floating catalyst method is advantageous because no support removal procedures are required after the reaction and the catalyst can also be introduced into the CCVD reactor as either a liquid or a gas.

Modification of the CNT structure

CNTs are polymers of pure carbon that can be reacted and manipulated using the rich chemistry associated with carbon (sp^2 and sp^3 hybridisation states of carbon). This provides an opportunity to control the carbon nanostructure and also to optimise the solubility and dispersion characteristics of CNTs. In addition, modification can enhance the chemical and physical properties (e.g. electronic and magnetic properties and conductivity). Several strategies have been employed

to modify the structure of the CNT both during and after synthesis. These methods include surface functionalisation and substitutional doping.

Functionalisation of CNTs

Many applications of CNTs require them to be dispersible in solvents (water or polar solvents) and to be compatible with polymer matrices. To achieve this, surface functionalisation, especially of the outer wall of the CNT, is necessary. Functionalisation modifies the physical and chemical properties of the CNTs. CNT functionalisation can be achieved by both covalent and non-covalent interactions and indeed, reviews have summarised functionalisation strategies for CNTs.¹⁷ Most of the methods reported require the synthesis and reactions of carboxylated CNTs, followed by covalent attachment of other functional groups to the CNTs.¹⁸

Dispersion of CNTs can be achieved by sonication. The dispersion produced can be very stable and the CNTs can remain in solution for weeks or months. Functionalisation methods, such as oxidation of the CNTs, can create more active bonding sites on the CNT surface. For biological uses, CNTs can be functionalised by attaching biological molecules such as lipids and proteins to surfaces. The CNT–biomolecule materials can be used to mimic biological processes, such as protein adsorption, the binding of DNA and drug molecules and the fixing of red blood cells. These reactions are very useful in medicine (and pharmaceuticals), in particular in drug-delivery systems.

Doping of CNTs

Doping is the intentional introduction of impurities into a material and the study of the doping of SCNMs with foreign atoms has attracted considerable interest. In the case of CNTs, this entails the inclusion of heteroatoms of nitrogen and boron into the all-carbon lattice. The heteroatom can be introduced into the CNT during the synthesis reaction (by using NH_3), or by adding nitrogen atoms to the carbon source or the catalyst ligand (if a floating catalyst is used).

The incorporation of heteroatoms into a CNT modifies the tube characteristics. Microscopy studies reveal that nitrogen-doped CNTs (N-CNTs) are hollow inside with a likely occurrence of bamboo compartments¹⁹ (Figure 6 and Figure 8). Incorporation of nitrogen atoms favours the formation of pentagons and heptagons and increases the reactivity of the neighbouring carbon atoms resulting in a higher degree of disorder in a N-CNT relative to a 'pure' CNT. Thus, considerable effort has been made to study the fabrication and the growth mechanism of the related carbon nanostructures with nitrogen as the dopant.

Growth mechanisms of CNTs and CNFs

Many studies have reported the catalytic synthesis of CNTs and CNFs, in particular when using metals such as iron and cobalt as catalysts. There are two major mechanisms used to explain the catalytic growth of CNTs or CNFs that depend on the position of the catalyst with respect to the substrate

(Figure 9). These are (1) the tip-growth mechanism (where the catalyst particle is located at the tip of a growing tube) and (2) the root-growth mechanism (where the catalyst particle is found at the bottom of the tube).^{14,20} Thus, if the catalyst-support interaction is strong, the root-growth mechanism results, but, if the interaction is weak, the tip-growth mechanism results. In both processes, the carbon reagent decomposes on the metal particle under the reaction conditions. The carbon deposited on the metal particle either dissolves in the metal and re-precipitates to form a CNT (or CNF) or the carbon migrates over the metal particle to form the tube or fibre. If the catalyst particles are small, SWCNTs are formed and if they are larger, MWCNTs and CNFs are formed.

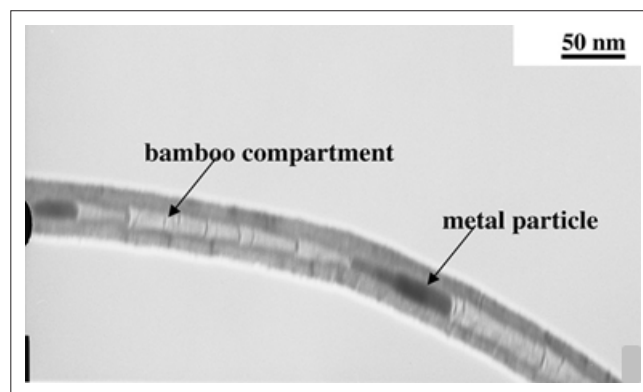
The use of a floating catalyst also generates metal particles leading to CNT or CNF growth similar to that described above. The type of carbon formed will depend on the control of the catalyst particle morphology and catalyst particle size distribution during the reaction. For instance, a low iron to carbon ratio generates more carbon spheres and less amorphous material, while a high iron to carbon ratio produces high yields of CNTs and less amorphous material.²¹ No spheres are formed when the ratio is high, reflecting a strong iron catalyst influence during the growth. Further, large diameter CNTs originate from large catalytic nanoparticles and small diameter CNTs originate from small catalytic species. To complicate mechanistic studies for carbon growth, carbon structures can also be formed without the use of a catalyst, although more typically carbon spheres and amorphous carbon are produced in this instance.

Other types of tubular carbons

A few years after the discovery of straight tubular carbons, the synthesis of branched nanotubes was achieved.²² These branched nanostructures (Figure 3c) form when non-hexagonal carbon rings are incorporated into the nanotube framework of the graphene sheet that builds the carbon nanostructure. Experimental studies on the production of branched MWCNTs, such as Y-branched CNTs (Y-CNTs), were first reported in 1995 using the arc-discharge method. These experiments were carried out under quite specific conditions, using a helium atmosphere at 500 torr pressure and a hollow anode and copper as a catalyst. Most methods used to produce Y-CNTs usually take place at a relatively low growth temperature (typically between 650 °C and 1000 °C, or even at room temperature). In our own studies we have investigated the growth of branched CNTs using copper as a catalyst (in the arc-discharge method) and also observed that reaction conditions significantly affect the product obtained.²³

Properties and uses of tubular carbons

CNTs have been the focus of extensive studies because of their remarkable properties. However, CNFs also possess some of these special properties, including, among others: high electrical conductivity, high tensile strength, high elasticity and high thermal conductivity, as well as a low



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FIGURE 8: A transmission electron microscopy image of a carbon nanotube grown from ferrocene–aniline mixtures. The bamboo compartments and metal catalyst particle trapped in the tube can be seen.

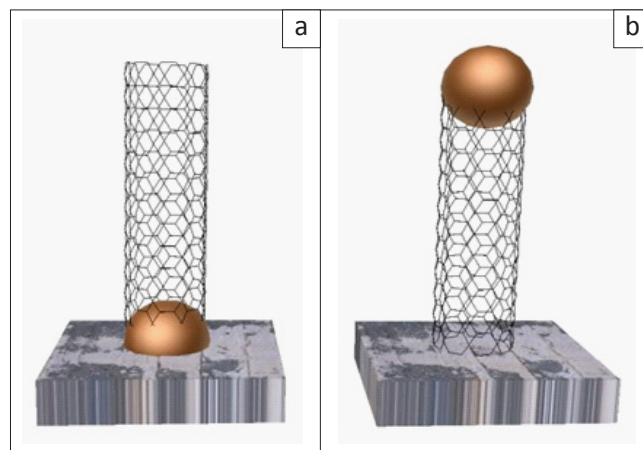


FIGURE 9: Carbon nanotube mechanistic models: (a) root-growth mechanism and (b) tip-growth mechanism.

thermal expansion coefficient, a high aspect ratio and good field emission properties.²⁴ As a result of their extraordinary properties, tubular carbons provide a wide spectrum of applications in industry as well as in scientific research. Examples of these applications are field emission flat panel displays, field emission lamps, polymer fillers, hydrogen storage systems, gas sensors, X-ray sources, composite materials, electronics and gene or drug delivery.²⁵

CNTs and CNFs are also being used as catalyst supports for heterogeneous catalytic reactions. Because of their high surface area and diverse morphologies (sizes and shapes), tubular carbons have been used as supports in various catalytic reactions, for example, in Fischer–Tropsch synthesis.^{26,27} These metal–carbon materials display excellent activity and selectivity when compared to conventional catalyst supports such as alumina or silica. CNTs have high aspect ratios and small tip radii of curvature as well as a two-dimensional array which is suitable for their use in electron field emission.²⁸ Because of their flexibility, SWCNTs are used in the tips of atomic force microscopy (AFM) probes to make the tip sharper, which allows for an increase in the atomic resolution of the surface being studied.²⁹ The high strength of CNFs has promoted their incorporation in polymer nanocomposites and their use as polymer fillers.³⁰



Doping of CNTs with nitrogen or boron induces novel electronic properties into the CNTs, and provides a means for tuning the field emission of CNT emitters. It has also been shown that nitrogen doping can enhance the mechanical, conducting, energy storage and electron transport properties of CNTs.

The branched CNTs have potential applications as building elements in nanoelectronic devices. For example, they can be used in a nanoscale three-terminal device or in other transistor applications.

Spherical carbons

Fullerenes

The discovery of the fullerene molecule, C_{60} , in 1985 is associated with the emergence of the study of nanocarbons and more importantly its discovery gave impetus to the emergence of the nanotechnology field.³¹ The fullerene molecule has a well-known shape, similar to that of a soccer ball. It comprises 60 carbon atoms linked together to form a perfect, one-atom thick, hollow sphere. This requires that the carbons (all sp^2 hybridised) be linked together to form 12 pentagons and 20 hexagons. If the number of pentagons remains constant and the number of hexagons is varied, a family of differently sized and shaped fullerenes (C_{72} , C_{80} , etc.) can be generated. Initially detected in small quantities, a high-yield synthesis of fullerenes was reported in 1990 when Krätschmer et al.³² discovered a simple method to produce isolable quantities of the C_{60} . The number of publications and patents relating to fullerenes has increased ever since.

Synthesis of fullerenes

The fullerene molecule requires that the C-C bonds interact through bent sp^2 hybridised carbon atoms. This leads to a strained structure with good reactivity; for example, a fullerene can act as an electron acceptor. For this reason, many derivatives of fullerenes have been made; one method of making these derivatives is the Prato reaction,³³ which involves the reaction of azomethine ylides generated *in situ* by decarboxylation of ammonium salts derived from the thermal condensation of amino acids and aldehydes (or ketones).

In one of our own studies we have functionalised C_{60} using the Prato reaction and reacted this functionalised C_{60} with thiophene to generate C_{60} -polythiophene composites (via a ring-opening metathesis polymerisation reaction) for possible use in solar cell devices.³⁴

Growth mechanisms of fullerenes

The mechanism for the formation of fullerenes is still not known. A number of proposals have been made in which carbon atoms coalesce to give small structures which then grow into a fullerene by addition of more carbon atoms, dimers, etc. Some possibilities include: (1) a graphene to fullerene transformation (Figure 4), (2) the pentagon road mechanism based on growth from a curved small carbonaceous material such as corranulene, (3) ring stacking

in which rings of carbons build a fullerene and (4) the fullerene road mechanism in which small fullerenes grow into larger fullerenes by addition of mainly C_2 units.³⁵

Uses of fullerenes

Some potential applications of fullerenes include use in optical devices, hardening agents for carbides, chemical sensors, gas separation devices, thermal insulators, batteries, catalysts, hydrogen storage media, polymers and polymer additives, and medical applications (e.g. fullerenes and their derivatives have potential antiviral activity, which has strong implications for the treatment of HIV infection). Various researchers in the United States are manufacturing and developing proprietary fullerene derivatives for use in diagnostics and therapeutics.

Carbon spheres

A carbon sphere (CS) generally refers to a spherical form of carbon that can be either semi-crystalline or crystalline (graphitic) and can have a solid, hollow or core shell morphology (Figure 10). The CS differs from a fullerene in that the outer carbon layer is more than one carbon layer thick. Solid carbon spheres, especially with diameters smaller than 100 nm tend to accrete and form bead- or necklace-like structures (Figure 11). The spherical carbons include carbon black, carbon onions, carbon microbeads and mesoporous carbon microbeads.³⁶

Historically, carbon black is one of the oldest forms of the spherical carbons known. Early documentation reveals that it was used for writing letters on papyrus in ancient Egypt and writing on bamboo strips in ancient China.³⁷ Carbon black is largely produced by the partial combustion and thermal decomposition of hydrocarbons such as oil or natural gas. It is an important chemical commodity used in various applications, from the black pigment of newspaper inks to the electrically conductive agent used in high-technology materials.³⁶

CSs have been categorised in four ways. Firstly, CSs, like all spherical bodies, can be classified as solid, core-shell or hollow (Figure 10).³⁸ Secondly, they can be classified according to whether the spheres are made of concentric, radial or random carbon layers (Figure 12).³⁹ Thirdly, spheres can be categorised in terms of their diameter.⁴⁰ In this method three types are recognised: (1) well-graphitised spheres (2 nm – 20 nm), (2) less graphitised spheres (50 nm – 1000 nm) and carbon beads (> 1000 nm). Fourthly, it is possible to classify spheres in terms of strategies used in their synthesis.³⁶

Synthesis of CSs

Recently, there has been a renewed interest in the synthesis and study of carbon spheres, with many being prepared under non-oxidative conditions. The new synthesis procedures have generated spheres with an enormous range of sizes and surface properties.

CSs are synthesised using procedures similar to those that generate CNTs and CNFs. Thus, CSs can be synthesised using arc discharge, laser ablation and plasma processes,

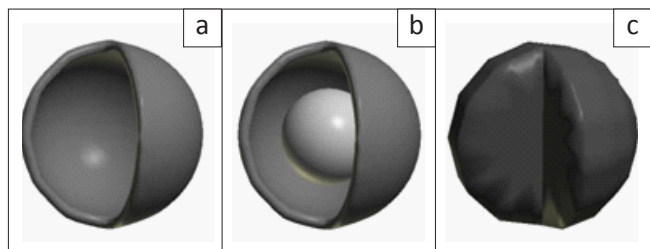


FIGURE 10: A cartoon of (a) hollow, (b) core shell and (c) filled spheres.

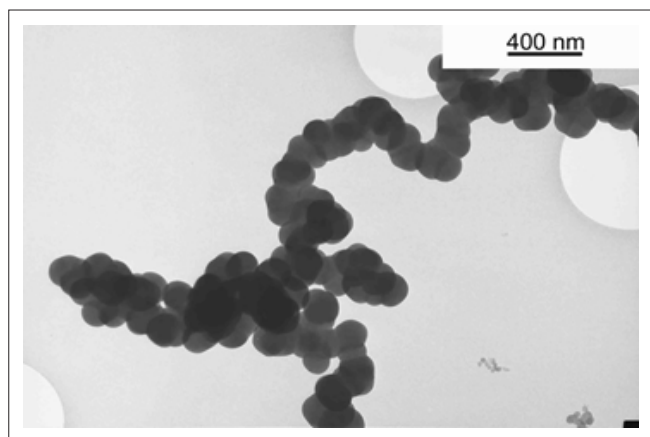
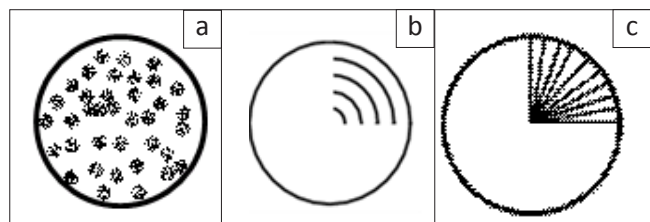


FIGURE 11: A transmission electron microscopy image of accreted filled carbon spheres.



Source: Reprinted from Materials Science and Engineering: R: Reports, 70(1-2), Deshmukh AA, Mhlanga SD, Coville NJ, Carbon spheres, p. 1–28, Copyright 2010, with permission from Elsevier.³⁶ doi:10.1016/j.mser.2010.06.017

FIGURE 12: A cartoon indicating (a) random, (b) concentric and (c) radial layer orientations in carbon spheres.

shock compression techniques, chemical vapour deposition (catalytic and non-catalytic), autoclave processes (catalytic and non-catalytic), and by carbonisation routes.³⁶ Their diameters can range from 10 nm to 10 μm and their surface areas from 2 m^2/g to > 1500 m^2/g . Key issues when making CSs is to ensure monodispersity of size.

The rim of a CS with concentric structure is made up of carbon flakes. These carbon flakes are comprised predominantly of aromatic structures, made up of condensed benzene rings. These flakes can be small (< 10 nm), but after graphitisation at high temperatures these grow in size leading to structures that contain curved graphite planes. The sp^2 carbon atoms at the edge of the flakes will react with other atoms, such as hydrogen and oxygen atoms, to give OH and COOH groups to satisfy valence requirements. The oxygen content typically varies between 1% and 5% for low surface area CSs. CSs like CNTs have curved structures because of the presence of C5 and C7 rings. The CSs once formed can be characterised by particle size, structure and surface chemistry (Figure 13).

Hollow and core-shell spherical CSs

Hollow spherical CSs (carbon nanocages or calabashes) have been extensively investigated in recent years. They can be made by a number of generic approaches, the most popular being a templating process, whereby a spherical material (metal nanoparticle, micelle, silica particle, etc.) is covered by a carbon-containing material that self-assembles on the template. The self-assembly process involves C-C bond formation on the surface of the spherical template to yield a core-shell structure.⁴¹ The components that make up the interior of the sphere can be materials that have properties that may be exploited. For example, if the core is made of a magnetic material then magnetic fields can be used to manipulate the carbon spheres. It is also possible to remove the core, usually thermally, to generate a hollow sphere.⁴¹

Modification of the CS structure

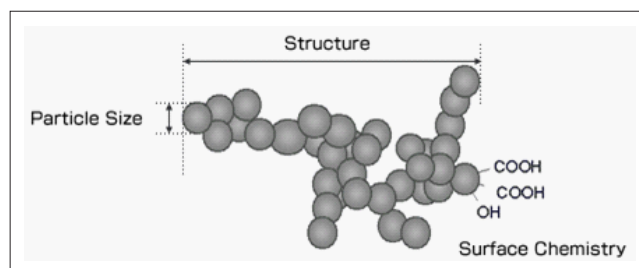
The chemistry of CSs will be different from that of graphite and SWCNTs, which are dominated by reactions at the graphite edges of extended fused ring structures. Much of the reported chemistry of CSs relates to early extensive studies on carbon blacks, dominated by acid and base reactions or oxidation reactions.³⁶

The surface modification of CSs has been shown to increase the reactivity of these materials (e.g. solubility and wettability), thus widening their applications. Many chemical treatments have been performed on CSs such as oxidation with potassium persulphate, severe air oxidation, halogenations and grafting reactions. All the chemical procedures modify the CS surface properties and the structural changes correlate with their reactivity.⁴² It was observed that carbon blacks have different behaviour depending on their mode of preparation but they generally perform similarly, after a given modification procedure.

As with other forms of carbon, such as nanotubes, CSs can be doped with heteroatoms such as nitrogen and boron.^{43,44} As expected, the doping of CSs with a heteroatom modifies their electronic and chemical properties making them suitable for a wide range of applications.

Growth mechanisms of CSs

The growth mechanism for CSs can be influenced by the synthesis process used, i.e. whether the reaction occurs in



Source: Reprinted from Materials Science and Engineering: R: Reports, 70(1-2), Deshmukh AA, Mhlanga SD, Coville NJ, Carbon spheres, p. 1–28, Copyright 2010, with permission from Elsevier.³⁶ doi:10.1016/j.mser.2010.06.017

FIGURE 13: The structure of carbon black showing some functional groups on the surface of the spherical carbon structure.

the presence of a catalyst or template, or not. Consequently, numerous mechanisms have been proposed for the synthesis of CSs; mechanisms that appear to depend on the reaction conditions, carbon source, catalyst, etc. In this review, we give a mechanism proposed by Lahaye et al.⁴⁵, further explored by others, for the non-catalytic growth of CSs. The conversion of a carbon source typically into carbon and hydrogen radicals (and oxygen-containing radicals if oxygen is present), and finally a reaction to give the CSs was found to be the key feature in the growth process. However five factors were considered to be crucial: (1) carbon black precursors and their formation, (2) carbon black particle inception, (3) the agglomeration of nuclei into particles and of particles into aggregates, (4) surface growth and (5) post oxidation of the carbon black.⁴⁵

Wang et al.⁴⁶ proposed that the sphere is nucleated from a pentagonal carbon ring followed by a spiral shell growth (Figure 14). This type of mechanism was also proposed by Kroto and McKay³¹ to explain the formation of large fullerenes.

Properties and uses of spherical carbons

As a result of their high surface area, thermal stability, unique electronic properties, low density and, most importantly, their structure, CSs (e.g. carbon blacks) have been used as catalyst-support materials; as cathode materials for field emission; as strong fillers for composites; in lithium

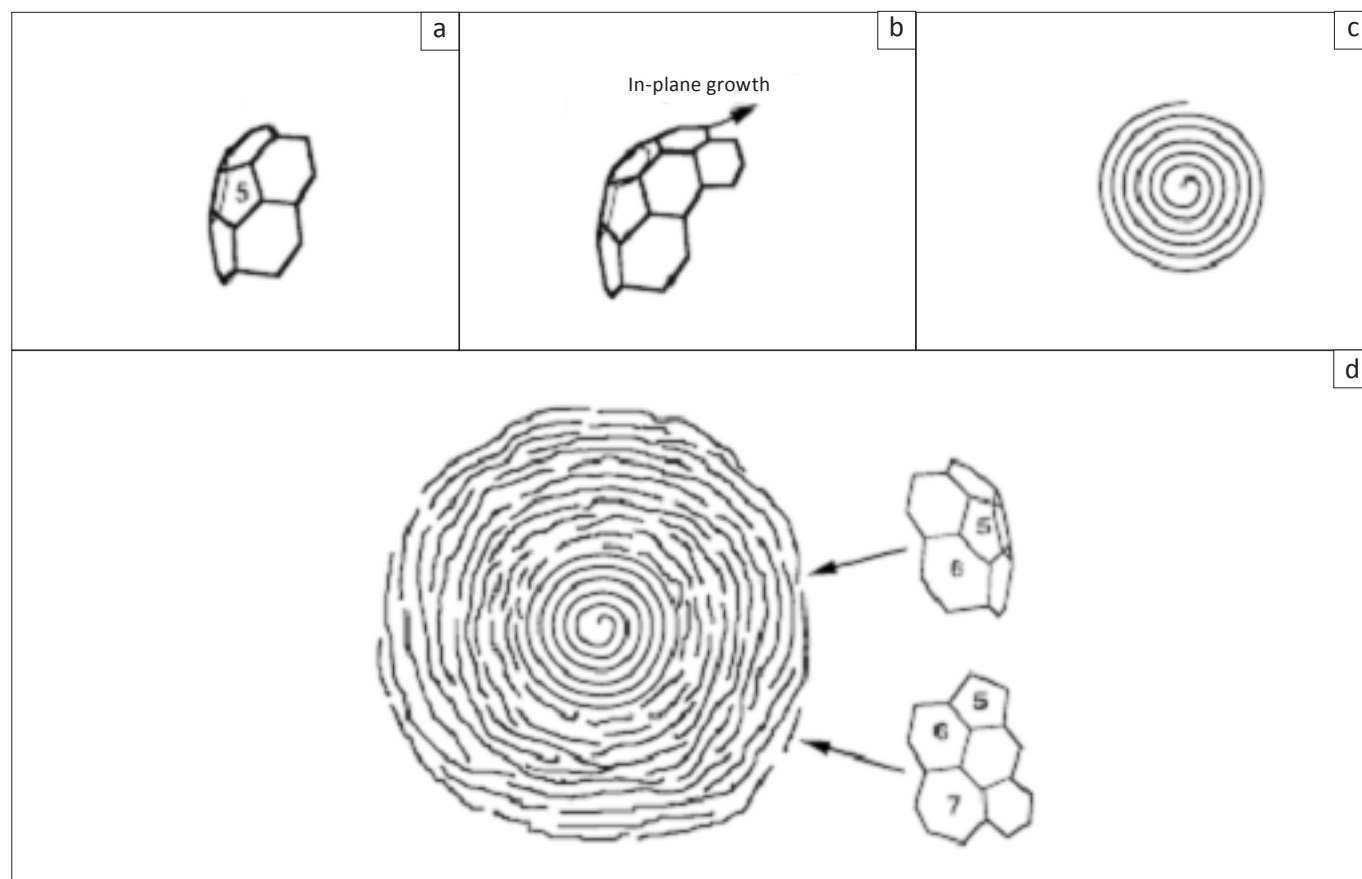
batteries, capacitors and fuel cells; in drug delivery, for the encapsulation of active transition metals; as lubricants; as injectable scaffolds for tissue regeneration; in heterogeneous catalysis; in dye encapsulation; in removal of contaminants from water; in enzyme and protein protection; and for magnetic data storage. Many excellent books and reviews³⁶ are available on the topic.

CSs exhibit properties such as blackness and dispersibility when they are mixed with inks, paints, or resins. Recent studies have shown that 'ultrastrong' spherically shaped materials can be made. Pol et al.⁴⁷ synthesised CSs from polyethylene terephthalate in an autoclave at 700 °C. The 2 mm – 10 mm solid spheres reportedly 'broke one diamond knife and damaged a second' during microtome measurements. The tensile strength of a CS was measured under a compressive load and showed linear behaviour with time until the sphere fractured.^{36,39,47}

Hollow spheres have also been exploited and have been used in rechargeable batteries, in the protection of proteins and enzymes, gene and drug delivery, hydrogen storage, catalysis, sensing, and fuel cell electrodes.⁴⁸

Carbon helices

First observed as an 'unusual form of carbon' by Davis et al.⁴⁹ in 1953, the study and synthesis of carbon helices (CHs) has grown considerably within the past decade. This is in part



Source: Reprinted from the Journal of Physical Chemistry, 100(45), Wang ZL, et al., Pairing of Pentagonal and Heptagonal Carbon Rings in the Growth of Nanosize Carbon Spheres Synthesized by a Mixed-Valent Oxide-Catalytic Carbonization Process, Copyright 2010, with permission from American Chemical Society.⁴⁶ doi:10.1021/jp962762f

FIGURE 14: (a) Nucleation of a pentagon, (b) growth of a quasi-icosahedral shell, (c) formation of a spiral shell carbon particle proposed by Kroto and McKay³¹ and (d) growth of a large carbon sphere.



because of the development of new synthetic methodologies and the unique properties and use of the helical carbons in versatile applications.^{50,51}

Synthesis of CHs

The synthesis of helical materials in the past generally occurred by accidental procedures and reproducibility was often difficult to achieve. In order to fully exploit these helical carbon materials, an understanding of the best ways of mass producing these structures was thus required. In 1990, Kawaguchi et al.⁵² observed that carbon fibres with three-dimensional helical morphology were obtained in high yields by the pyrolytic decomposition of acetylene containing a small amount of sulphur impurity over a transition metal catalyst. Further studies, following their discovery, led researchers to the understanding that the morphology and quality of helical materials depended upon many factors: catalyst, carbon source, reaction temperature and carrier gas.^{53,54,55} Consequently, a wide variety of experimental conditions have been used to synthesise carbon structures with helical morphology. Most notably, it has been shown that the CCVD method is the most efficient method for obtaining helical carbon materials. The effectiveness of the CCVD method is based on the use of low temperatures during synthesis (250 °C – 700 °C), which produces materials with poor crystallinity, but with diverse morphologies.⁵¹ It was also observed that the use of metal promoters such as copper, chromium and tin, as well as alkali metals, aided the synthesis of the helices.^{56,57} How these impact on the preparation conditions, growth mechanisms, structure and properties of helical carbon materials are still under intense investigation.

Several distinct forms of helical carbon can be produced by employing a specific set of reaction conditions. The different individual structures and morphologies (tubular, filamentous, graphitic or amorphous) are shown in transmission electron microscopy (TEM) images (Figure 15) and reflect the morphological diversity of the family of helical carbon materials: spring-like, single, double or triple helices, twisted belts, spirals, etc. The shape and type of materials can be tailored by adjusting the temperature. For example, using an iron–copper catalyst supported on CaCO₃, single helix multi-walled carbon nanocoils (with tubular structure) can be grown at 750 °C (Figure 15a), while twisted ribbons are formed at 650 °C (Figure 15b). Lowering the temperature to 550 °C produces solid fibres with tight spirals (Figure 15c) and if iron is replaced by nickel, branched spirals (non-tubular) can be produced (Figure 15d). The addition of silver to an iron/nickel catalyst produces tightly twisted ribbons (Figure 15e). The current lack of understanding with regard to the mechanism of carbon nanomaterial formation makes it difficult to propose a specific reason as to why certain morphologies are preferred over others.

The dimensions of these materials are typically reported by measuring the pitch and diameter of the helices or coils (Figure 16).⁵¹ Such dimensional analysis is used to determine

the regularity and tightness, as well as the axial and radial diameters, of a helical material. It has also been suggested that a statistical study of these dimensions can be used to indirectly determine whether the formation of helical material correlates to internal or external stresses.⁵⁸

Growth mechanisms of CHs

It has been proposed that the curvature found in helical nanotubes is because of plane buckling and/or the regular insertion of pentagon–heptagon pairs at the coil junctions. The presence of pentagon and heptagon rings (Figure 17a), as well as plane buckling and deformation, can cause curvature of the graphite sheet in SWCNTs. It is unclear whether a similar mechanism would apply to MWCNTs or coiled CNFs.⁵⁹

The morphology of the helical carbons formed should be related to the shape of the catalyst particle used and this can be evaluated from the dimensions of the regularly shaped metal particles found within or at the ends of the helical products.^{52,53,56} In order to investigate the growth mechanism, Qin et al.⁵⁶ carried out the synthesis of helical carbon at low temperature (220 °C) over a copper catalyst; they observed that two helical fibres grew symmetrically from a single catalyst nanoparticle (Figure 18). These helical fibres had opposite helical senses, identical coil pitch and diameter, and the fibre diameters were approximately equal to the size of the nanoparticle.

Qin et al.⁵⁶ concluded that the size of the metal particle played a key role, and that catalyst particles with regular shapes and small sizes (≤ 50 nm) gave helical material. However, Du et al.⁶⁰ prepared copper particles with octahedral geometry, and found no helical material formed, presumably because of the large copper particle sizes (> 100 nm) used. However, helical material several microns in diameter has been synthesised, indicating that metal particle size was not the only factor that determined carbon morphology.^{50,51}

The catalyst particle shape has also been proposed to control the carbon growth. Motojima⁵⁰ showed that different crystal faces of a metal particle could show variable coil growth. From these results it was proposed that coiling could be related to unequal extrusion rates of carbon from different catalyst faces (Figure 17b). We have also investigated the effect of the shape of copper particles on the carbons formed by analysing TEM images of the copper particles at various tilt angles (Figures 18) and observed that there is a relationship between the particle morphology and the type of helical carbon extruded.

Thus both size and shape of the catalyst particles impact upon the type of helical material extruded. The stability of certain particle morphologies is only possible under a certain set of conditions and this is a likely source of the variability in carbon fibre morphology observed. The change in cross-section shape of a coil, as reported by Cheng et al.⁵³, and observations made by Hanson et al.⁶¹ suggest that particle morphology can also be altered by the gas environment.

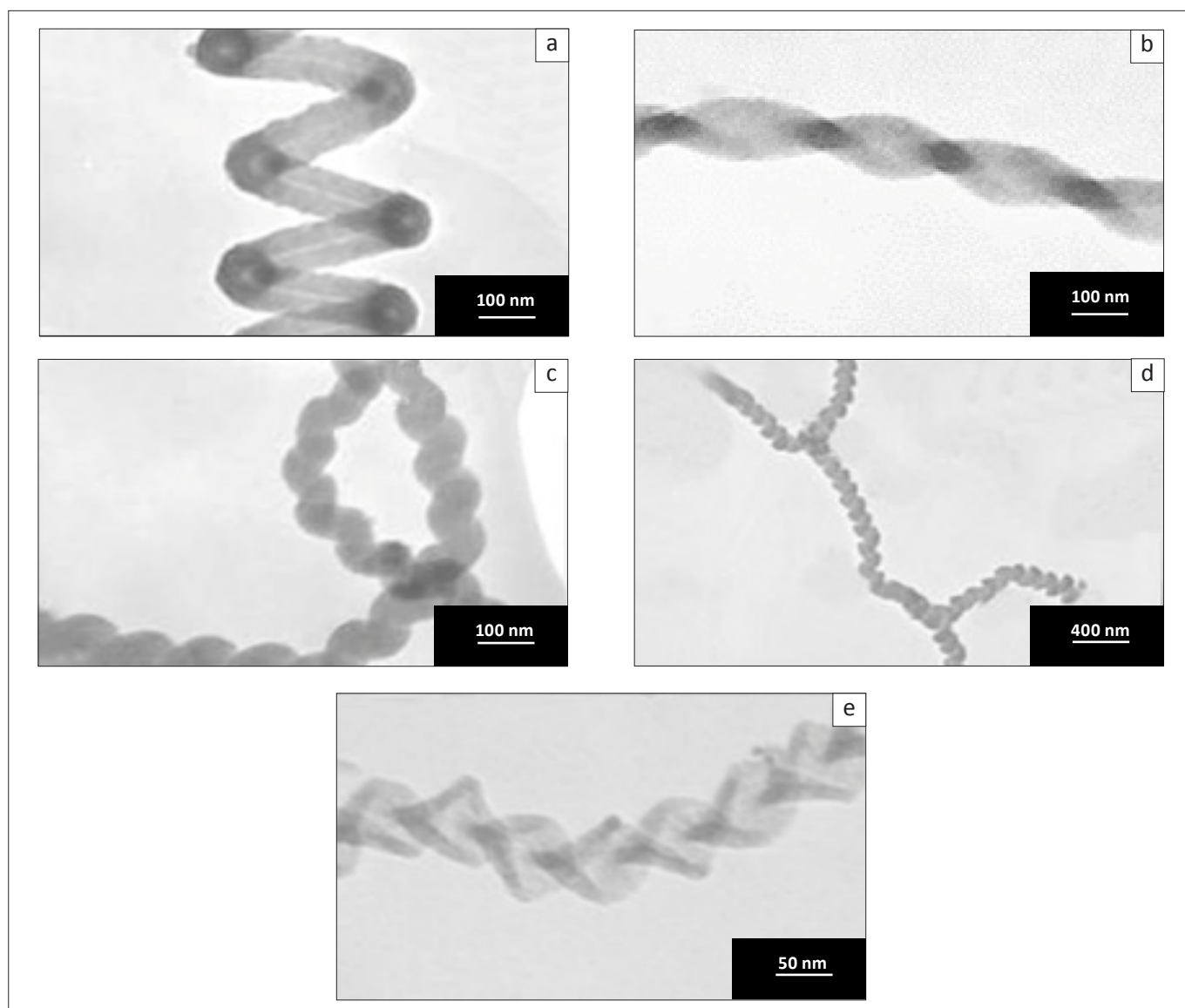


FIGURE 15: Transmission electron microscopy images of helical carbon material: (a) tubular spring-like (formed using Fe/Cu – 750 °C), (b) twisted ribbon (Fe/Cu – 650 °C), (c) spiralled solid fibres (Fe/Cu – 550 °C), (d) branched spirals (Ni/Cu – 750 °C) and (e) tightly twisted ribbon (Fe/Ni/Ag – 650 °C).

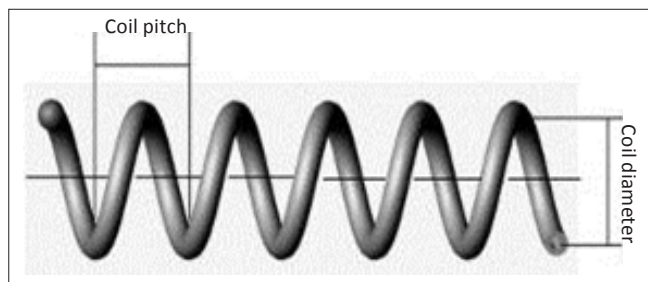
Properties and uses of CHs

Carbon materials with helical morphology have revealed a broad spectrum of applications, from electromagnetic wave absorbers to bio-activators.⁵⁰ Volodin et al.⁶² conducted the first AFM measurements of the mechanical properties of carbon nanocoils. The force modulation measurements agreed with the elasticity theory and showed a Young's modulus of ~ 0.7 TPa. Studies performed by Chen et al.⁶³ showed that as-synthesised carbon coils could be elongated by ~ 42% (Figure 19). Further studies by Motojima⁵⁰ revealed that helical fibres with circular cross section could be expanded to between 4.5 times and 15 times that of the original coil length. By contrast, a coil with flat cross section could only be extended to 1.5 times its original coil length. Motojima showed that the rigidities of circular and flat carbon coils were 22 GPa – 46 GPa and 22 GPa – 32 GPa, respectively.

Given these properties, it has been suggested that helical fibres could increase the fracture toughness of polymer-based nanocomposites. The coiled shape could

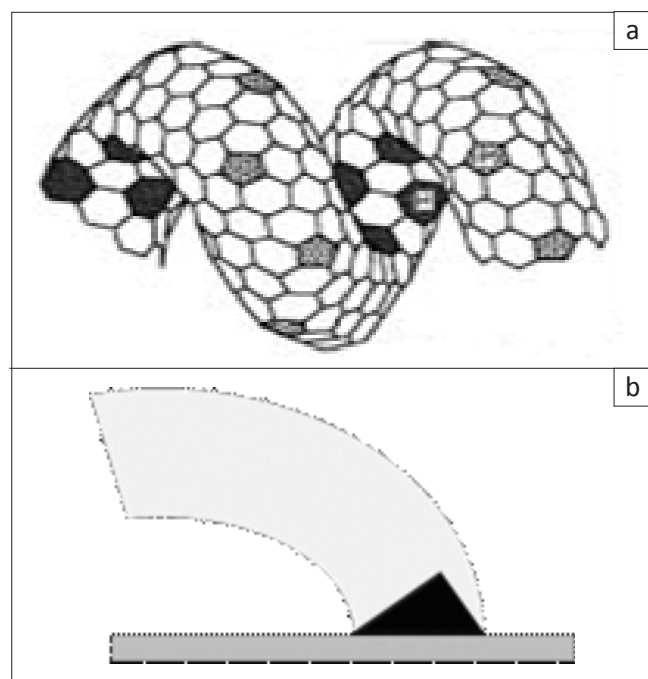
improve the problem of polymer reinforcement that exists with straight carbon nanotubes, thus reducing the possibility of polymer fracture.⁵⁸ They can also be incorporated into nanodevices that require nanosprings as resonating elements. Volodin et al.⁶² reported that, when nanomaterials with helical morphology were excited electrically or acoustically, they were able to detect resonances ranging from 100 MHz to 400 MHz. It has been suggested that such a device could detect mass changes as small as a few attograms.

Given the helical morphology of carbon microcoils (CMCs), Motojima et al.⁶⁴ were able to show that when CMC-polymethylmethacrylate composite beads were prepared and studied, a 1–2 wt.% addition of CMCs resulted in strong electromagnetic wave absorptivity. This absorptivity was attributed in part to the chiral character of the CMCs. More recently, Tang et al.⁶⁵ explored the electric properties of carbon nanocoils by developing nanodevices based on these materials. It was found that the conduction mechanism could be described as three-dimensional electron hopping with



Source: Reprinted from Composites Part B: Engineering, 37(6), Lau KT, Lu M, Hui D, Coiled carbon nanotubes: Synthesis and their potential applications in advanced composite structures, p. 437–448, Copyright 2010, with permission from Elsevier.⁵¹ doi:10.1016/j.compositesb.2006.02.008

FIGURE 16: Schematic representation of dimensions used to describe helical morphology: coil pitch and coil diameter.



Source: (a) Reprinted from Composites Part B: Engineering, 37(6), Lau KT, Lu M, Hui D, Coiled carbon nanotubes: Synthesis and their potential applications in advanced composite structures, p. 437–448, Copyright 2010, with permission from Elsevier.⁵¹ doi:10.1016/j.compositesb.2006.02.008

FIGURE 17: Schematic representations of: (a) a coiled nanotube with insertion of pentagon-heptagon rings and (b) a catalyst particle with different facets, showing curvature in extrusion.

robust Coulomb interaction, with Coulomb gaps ranging from several mega electrons to 20 Me. Helical materials are also considered a promising candidate for making novel catalyst supports. It is expected that bends or junctions in the carbon may be effective in stabilising deposited metal particles that could influence the selectivity of reactants as a result of possible steric interferences.

Other shaped carbon nanomaterials

While the sections above have related to the three most popular and common types of SCNMs made and studied in laboratories throughout the world, including South Africa, carbon can also form other morphologies. These morphologies include nanocones, nanohorns, nanofoam and graphene.

Nanocones and nanohorns

The ability of elemental carbon to form extended two-dimensional sheet structures with extremely strong bonds makes it a stable material to produce isolated objects (graphene). The sheets can also be curved to yield cylindrical geometries (nanotubes) or quasispherical geometries (fullerenes) where pentagonal rings provide the required Gaussian curvature.⁶⁶ In addition, just as a sheet of paper with a wedge removed can be resealed to form a conical hat, a graphene sheet with a wedge removed can be resealed, notionally, to form a cone or horn.⁶⁶ Indeed single-walled carbon nanohorns (SWNHs), can be prepared using a well-characterised high-yield synthesis route and form one class of such conical structures, with a particularly sharp apical angle, and a distinct aggregate microstructure (Figure 20).

Depending on the synthesis conditions (e.g. CO₂ laser ablation of graphite at room temperature,⁶⁶ low-temperature Ar + H₂ + CH₄ plasma-enhanced CVD⁶⁷ or microwave plasma-assisted CVD⁶⁸), carbon nanocones with different opening angles with respect to the apex of the cone can be made. For example, tubular carbon nanocones with single crystal nanotips were synthesised by Shang et al.⁶⁸ by means of microwave plasma-assisted CVD using *in situ* evaporated iron as a catalyst (Figure 21). The nanocones were stable even at high temperatures, making them potential candidates for scanning probes in high temperature, oxygen-containing

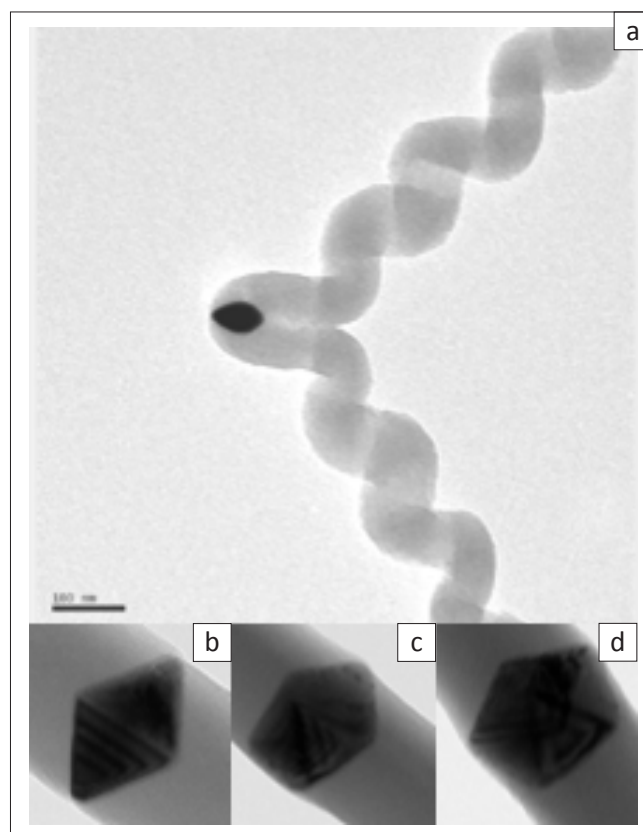
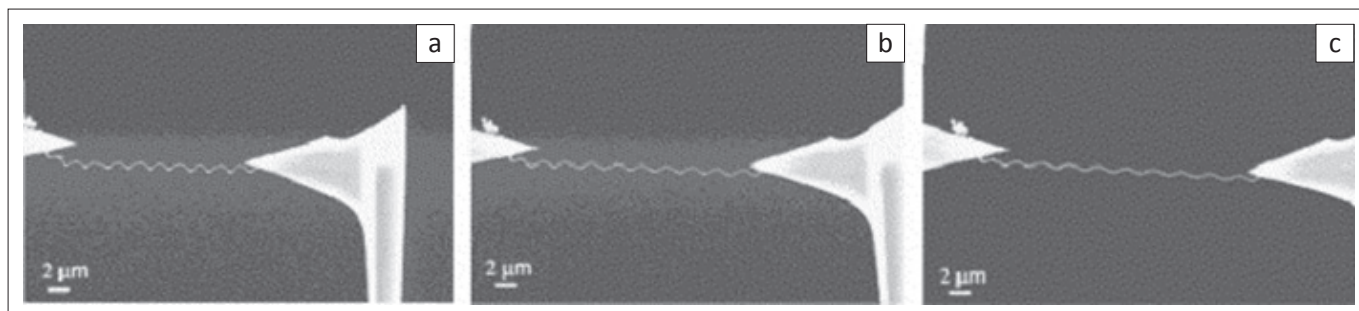
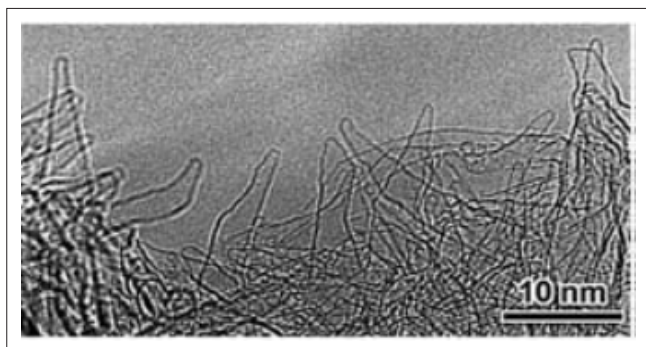


FIGURE 18: (a) Transmission electron microscopy (TEM) image of a spiralled carbon fibre with symmetrical growth from a copper particle and tilted TEM images of a copper particle from different angles: (b) A – 0° and B – 0°, (c) A – 24° and B – 29° and (d) A – 42° and B – 21°.



Source: Reprinted from Nano Letters, 3(9), Chen X, et al., Mechanics of a carbon nanocoil, Copyright 2010, with permission from American Chemical Society.⁶³ doi:10.1021/nl034367o

FIGURE 19: Coiled carbon material at various elongation percentages: (a) 0%, (b) 20% and (c) 33%.



Source: Reprinted from Chemical Physics Letters, 309(3-4), Iijima S, Yudasaka M, Yamada R, Bandow S, Suenaga K, Kokai F, Takahashi K, Nano-aggregates of single-walled graphitic carbon nano-horns, p. 165–170, Copyright 2011, with permission from Elsevier.⁶⁶ doi:10.1016/S0009-2614(99)00642-9

FIGURE 20: Transmission electron microscopy image of single-walled nanohorns.

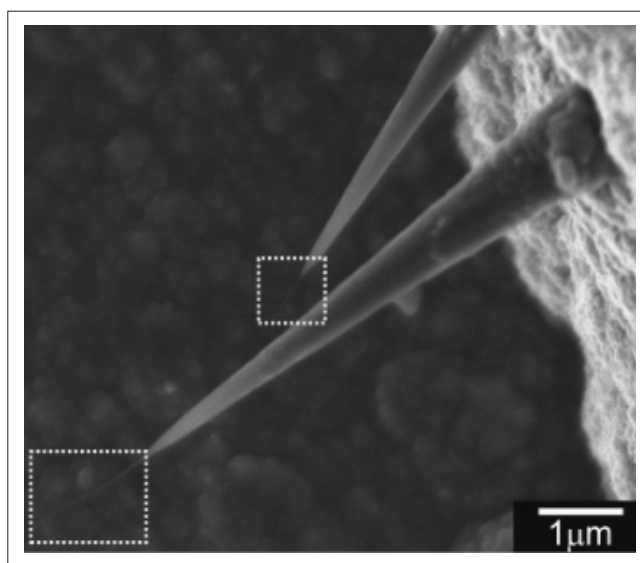
environments. Carbon nanohorns also have potential applications in nanocage applications, such as for gas storage and as drug carriers.⁶⁹

Carbon nanofoam

Recently Rode and co-workers⁷⁰ discovered a new form of carbon called carbon nanofoam. Carbon nanofoam consists of a low-density cluster-assembly of carbon atoms strung together in a loose three-dimensional web. Interestingly, carbon nanofoam can be viewed as an incomplete carbon nanotube and can be produced using similar conditions used to make carbon nanotubes (Figure 22).⁷¹ The unusual property of carbon nanofoam is that it is attracted to magnets; a feature not observed with other forms of carbon (such as carbon nanotubes or spheres). It is believed that clusters of carbon atoms combine to form the spongy nanofoam – a cross between diamond and graphite.

Graphene and other related carbons

Graphene is the basic structural element for many of the graphitic carbons mentioned above (Figure 4).⁹ It is a one-atom-thick planar sheet of sp^2 -bonded carbon atoms that forms a densely packed honeycomb crystal lattice. The extraordinary mechanical, structural, electronic and thermal properties have created a host of potential commercial applications for this material. Such applications include the development of electronic devices (e.g. transistors, integrated circuits and electrodes), sensors for single molecule gas detection and ultra capacitors.^{9,72,73} However, isolation and



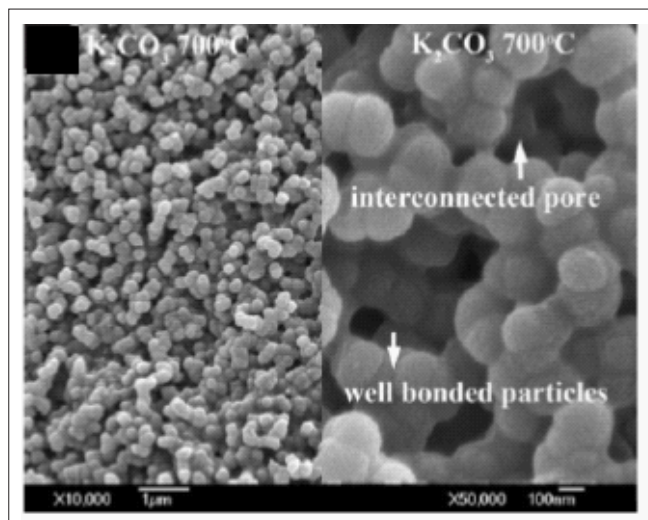
Source: Reprinted from Journal of the American Chemical Society, 129(28), Shang N, et al., Tubular graphite cones with single-crystal nanotips and their antioxygenic properties, Copyright 2010, with permission from American Chemical Society.⁶⁸ doi:10.1021/ja071830g

FIGURE 21: Scanning electron microscopy image of tubular graphite cones grown on silicon substrates.

production of graphene in commercial quantities remains a challenge and is being explored by many researchers all over the world. A number of procedures for producing graphite have been developed including graphite exfoliation, epitaxial methods and CVD procedures. The CVD method is the most widely used method, in which a hydrocarbon gas (usually CH_4) is added over a metal surface like nickel or copper to deposit the graphene layers.

According to Geim and Novoselov⁹, the study of graphene has led to the emergence of a new paradigm of 'relativistic' condensed-matter physics, where quantum relativistic phenomena, some of which are unobservable in high-energy physics, can now be mimicked and tested in tabletop experiments. This is attributed to the unusual electron spectrum of graphene.

More recently, Li and co-workers⁷⁴ discovered a new form of carbon called graphdiyne. This material was synthesised and predicted to be the most stable of the non-natural carbon allotropes. It is a two-dimensional layer with one-atom thickness and a strongly bonded carbon network that shows remarkable chemical stability and electrical conductivity. In



Source: Reprinted from *Advanced Materials*, 2007;19, Zhang Y, Sun X, Synthesis of carbon nanofibres and foam by catalytic chemical vapour deposition using a water-soluble alkali salt catalyst, p. 961–964, Copyright Wiley-VCH Verlag GmbH & Co. KGaA, with permission.⁷¹ doi:10.1002/adma.200602084

FIGURE 22: Scanning electron microscopy images of carbon nanofoam produced at 700 °C. Both straight and helical fibres can be clearly seen from the images. Aggregation of the fibres became significant with increasing deposition temperature. Carbon particles with a relatively uniform particle size, produced at 700 °C, are bonded together, forming an interconnected structure.

the report, a novel methodology was used to generate large area graphdiyne films (3.61 cm²) on the surface of copper via a cross-coupling reaction of hexaethynylbenzene. A device based on graphdiyne films for measurement of electrical property was fabricated and exhibited semi-conducting properties.⁷⁴

Toxicity issues

Working at the nano level raises issues regarding human health. Studies to investigate the toxicity of these new SCNMs are in their infancy, with the impact of the materials on human cells being unknown. Studies are further complicated by the belief that effects will be influenced by the size, shape and agglomeration, as well as the concentration of the SCNMs. Care must thus be exercised by workers in this area of nanotechnology.⁷⁵

Conclusion

Although SCNMs have been known for many years, it is still difficult to understand why different shapes of carbon can be formed under certain conditions. In this review, an overview of the types of shaped carbons that can be produced by simple production techniques was outlined with a focus on tubes or fibres, spheres and helices and with more emphasis on the work carried out in South Africa. The synthesis, properties or applications and mechanisms of formation of the different shaped carbons were also described. In addition, we demonstrated that it is possible to manipulate the morphology or carbon nanostructure of SCNMs by functionalisation and doping, which help enhance the solubility and dispersion characteristics and electronic structures of the new carbons. In the last part of the review,

we discussed briefly the health implications associated with the use of the nanomaterials.

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