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Carbon Nanotubes – Part I: Introduction, Production, Areas of Application

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Summary

As the basic element of life on Earth, carbon boasts a greater diversity of compounds than any other chemical element. Even elementary carbon occurs in several structural forms, including diamonds, graphite, fullerenes and carbon nanotubes (CNTs). The latter are well known and promising nanomaterials. CNTs have exceptional properties, combining high resistance, tensile strength and electrical conductivity with a very low weight. Carbon nanotubes are produced in numerous industries worldwide, with CVD (chemical vapour deposition) currently being the most relevant processing technology. CNTs are used as additives to various plastics in electronics, car manufacturing and shipbuilding or for the production of sports equipment. In the future, CNTs are expected to be used particularly in environmental and energy engineering, possible applications including enhanced batteries, solar and fuel cells, as well as in the construction industry for high-performance concrete, but also in medicine for drug delivery.

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Introduction

Owing to their unique physical properties, carbon nanotubes (CNTs) are considered one of the most important materials of the 21st century. They consist of graphite-like carbon, have a diameter of ca. 1 to 100 nanometres (nm) and a length of up to several micrometres or even millimetres. Carbon nanotubes can be single-walled (SWCNT) or multi-walled (MWCNT), and their unusual mechanical and electrical properties make them suitable for numerous applications. Because of the high current density achievable in CNTs, researchers are already exploring the next generation of microchips, high-speed and low-loss transistors for highly integrated circuits and new electronic components. Other groups are working on the development of chemical and biological sensors on a CNT basis, on transparent electrodes for solar cells and light-emitting diodes, membranes for fuel cells or CNT applications on circuit boards, to name but a few. CNTs not only raise hopes for innovative applications in a range of fields from technology to medicine, they also harbour the promise of considerable economic benefits. This dossier provides an overview of fundamental facts, production processes and spheres for the application of CNTs.

Carbon and Its Structural Forms

Carbon is the basic element of life on Earth, since every living tissue is composed of organic carbon compounds. As carbon atoms have the ability of combining with other carbon atoms as well as atoms of other elements to form complex molecules, carbon boasts a greater diversity of compounds than any other chemical element. Even elementary carbon exists in various very different structural forms (allotrope modifications, see Fig. 1).

- One well-known form of pure carbon in which the carbon atoms combine to form a crystal structure is **diamond**. Formed in the Earth's crust by high pressure and high temperatures, diamonds are the hardest material found in nature.
- Hypothetically calculated in 1970 by the chemist Eiji Osawa, a new carbon allotrope, the spheroid **fullerene**, was discovered just 15 years later, in 1985. The best known fullerenes, the so-called C60-fullerenes ("Buckyballs"), consist of 60 carbon atoms arranged in a lattice of hexagons and pentagons. While the structure of the C60-fullerenes is reminiscent of a soccer ball, they owe their name to their similarity with the domes designed by the US architect Richard Buckminster Fuller. The discovery of fullerenes earned Robert Curl jr. (USA), Sir Harald Kroto (UK) and Richard Smalley (USA) the 1996 Nobel Prize for Chemistry. The use of fullerenes as lubricants, catalysts or for medical purposes is currently being researched.
- Another form of carbon is **graphite**, which consists of several superimposed layers of carbon with a lattice structure. Rarely found in nature, graphite is used as a sealant or lubricant because of its high temperature resistance. Its most well-known use, however, is for pencil leads.

- A graphite film consisting of only a single-atom-thick lattice-shaped layer of carbon is called **graphene**. Although graphene structures have been known since the 1960s, it was not possible to isolate such a monolayer until a few years ago. The feat was first achieved in 2004 by Andre Geim and Konstantin Novoselov from the University of Manchester (UK), who used adhesive tape to peel thin layers off a graphite crystal[4]. In 2010, Geim and Novoselov were awarded the Nobel Prize in Physics for "groundbreaking experiments regarding the two-dimensional material graphene".
  The methods have meanwhile been technologically refined and allow for producing graphene sheets up to a width of 70 cm. Graphene has astounding properties. It is transparent, 100 times stronger than the strongest steel and has a very high electrical and thermal conductivity. These unique properties make graphene an interesting candidate for a number of applications currently under development, as for instance transparent touch screens, light panels or solar cells. Combined with synthetic materials, graphene opens up new vistas for materials that are both highly resistant and very light-weight, to be used, for instance, in satellite or aircraft construction.

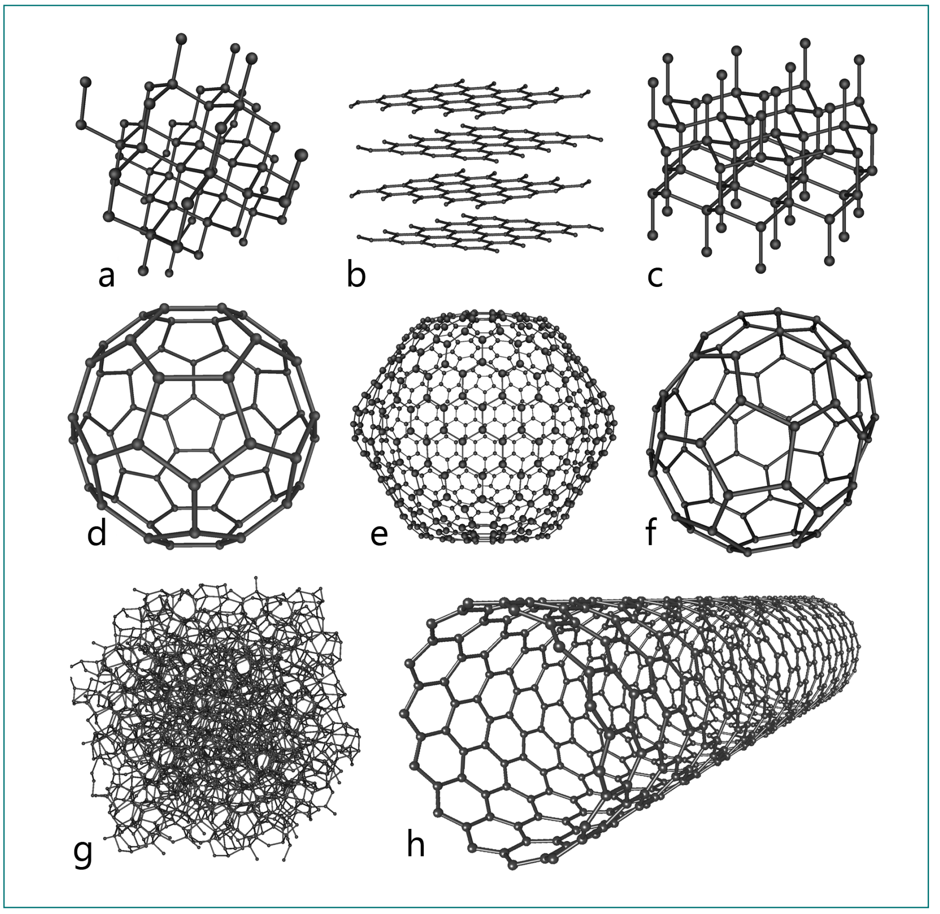

Figure 1: Examples of the various structural forms of carbon. a.) diamond; b.) graphite; c.) Lonsdaleite (hexagonal diamond); d.) Buckminster-Fullerene (C60); e. C540, f. C70; g.) amorphous carbon, h.) Nanotube[2]

Carbon Nanotubes

Whereas diamond has a rigid and unchangeable crystal structure, graphene is flexible and can be bent and even shaped into cylindrical form. (Fig. 2). Such "rolled-up" structures are called carbon nanotubes (CNTs)[5]. One distinguishes single-walled CNTs (SWCNTs), consisting of only one rolled-up layer of graphite with a diameter of up to 3 nm, and multi-walled CNTs (MWCNTs), consisting of several concentrically interlinked graphite tubes[6] with a diameter of up to 100 nm. The rolling-up direction (rolling-up or chiral vector) determines different modifications of the structures which will then have different electrical properties. Depending on the rolling-up vector, SWCNTs can behave like a metal and be electrically conducting, display the properties of a semi-conductor or be non-conducting. MWCNTs will achieve at least the same level of conductivity as metals. CNTs were discovered in 1991 by Sumio Iijima[7]. Like the fullerenes, CNTs occur in nature as by-products of combustion processes. Hence, they are not a human "invention". These materials have even been detected in 10,000 year-old ice core samples[8].

Apart from their electrical properties, CNTs also have special thermal and mechanical properties that make them an interesting option for the development of new materials[5; 6; 9]:

- CNTs are **electrically conducting** (MWCNTs always; SWCNTs as a function of their rolling-up direction)
- their **mechanical tensile strength** can be 400 times that of steel
- CNTs are **very light-weight** – their density is one sixth of that of steel
- their **thermal conductivity** is better than that of diamond – the best thermal conductor known so far
- CNTs have a very **high aspect ratio**, i.e. in relation to their length they are extremely thin

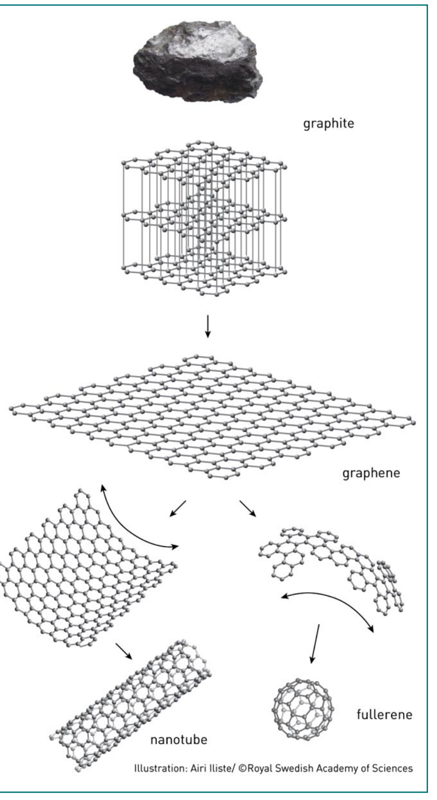

Figure 2: Like fullerenes, carbon nanotubes consist basically of rolled-up layers of graphene[1]

- just like graphite they are **highly chemically stable** and resist virtually any chemical impact unless they are simultaneously exposed to high temperatures and oxygen. Hence, CNTs are extremely resistant to corrosion.
- the **hollow interior** of CNTs can be filled with various nano-scale materials, thus separating and shielding them from the surrounding environment.

Carbon nanotubes must be distinguished from carbon nanofibres (CNFs), even if the terms are often used interchangeably in literature. CNFs are usually several micrometers long and have a diameter of about 200 nm. Carbon fibres have been used for decades to strengthen compound materials (e.g. in boat-building, aeronautics and astronautics, sports equipment, etc.). CNFs do not have the same lattice structure as CNTs, but consist of a combination of several forms of carbon and/or several layers of graphite which are stacked at various angles on amorphous carbon (where atoms do not arrange themselves in ordered structures). CNFs have similar properties as CNTs, but their tensile strength is lower owing to their variable structure and they are not hollow inside.

Production

Three methods are currently available for the production of CNTs: arc discharge, laser ablation of graphite and chemical vapour deposition (CVD). In the first two processes, graphite is combusted electrically or by means of a laser, and the CNTs developing in the gaseous phase are separated. All three methods require the use of metals (e.g. iron, cobalt, nickel) as catalysts. The CVD process currently holds the greatest promise, since it allows the production of larger quantities of CNTs under more easily controllable conditions and at lower cost[3]. During CVD, CNTs form on the surface of a catalyst that is exposed to carbon-containing gas (e.g. carbon monoxide or ethylene) (Fig. 3). First, small secondary catalyst particles of the size of a CNT diameter develop, on which the nanotubes start growing. The catalyst particle is either at the top or at the bottom of the emerging nanotube. Growth will stop if the catalyst particle is deactivated through the development of a carbon envelope. One distinguishes between purely catalytic and plasma-supported CVD. The latter requires slightly lower temperatures (200-500°C) than the catalytic process (up to 750°C) and aims at producing "lawn-like" CNT growth[5; 6]. Structural defects and impurities, such as residues of the metal catalysts, alter the physico-chemical behaviour of CNTs, which is why they need to be cleaned with the help of various methods (e.g. acid treatment or ultrasound) at the end of the production process[3].

Areas of Application

CNTs are credited with the potential to help produce completely new materials and products with properties that were hitherto impossible to realise with available technology. Some even call them a "megatrend" in material technology[10]. A great deal of effort is being invested worldwide in harnessing the special properties of CNTs for new materials and products, and these aspirations have already been fulfilled in several domains. Table 1 provides an overview description and examples of available applications and those currently under research and development. Currently, CNTs are mainly used as additives to synthetics. CNTs are commercially available as a powder, i.e. in a highly tangled-up and agglomerated form (Fig. 4). For CNTs to unfold their particular properties they need to be untangled and spread evenly in the substrate. This major technical challenge is met by special process engineering methods[11]. Another requirement is that CNTs need to be chemically bonded with the substrate, e.g. a plastic material. For that purpose, CNTs are functionalised, i.e. their surface is chemically adapted for optimal incorporation into different materials and for the specific application in question.

Carbon nanotubes can also be spun into fibres[12], which not only promise interesting possibilities for specialty textiles but may also help realise a particularly utopian project – the space elevator[13].

Figure 3: Schematic view of CNT growth on catalyst particles during CVD[3]

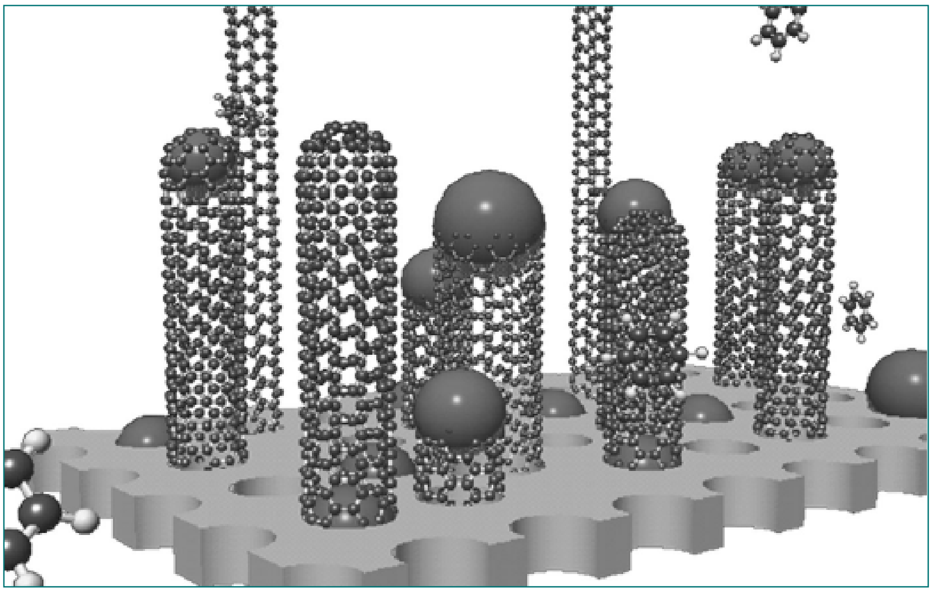

Figure 4: Commercial CNTs (Bayer Baytubes, Bayer AG, Germany)

Table 1: Examples of CNT applications – accomplished and in R&D

Materials and properties[14]:	Areas of application:
Accomplished:	
Plastic masterbatches with CNT additives; improved electrostatic dissipation properties of thermoplastic synthetics; weight reduction; increased corrosion resistance	**Electronics**: Packaging material for integrated-circuit transport and storage (IC trays); test sockets for microchips; transport and storage containers for semi-conductor discs; **Automotive**: fuel system components, mudguards, mirror housings, door handles;
Silicone resins with CNT additives for paints and varnishes; increased fire and scratch resistance; surface treatment of metal, concrete, wood, brick and fibreboard;	**Fire safety**: flame arrester for foam material; coating of cables and wires; **Non-stick coating** for ships to prevent accumulation of marine organisms (such as barnacles)
Epoxy resins (duroplastics) with CNTs; increased wear resistance and breaking strength, antistatic properties; weight reduction	**Sports equipment**: bicycle frames, tennis rackets, hockey sticks, golf clubs, skis, kayaks; sports arrows: **Yachting**: masts and other parts of sailboats; **Aeronautics**: no detailed information available **Energy engineering**: coating of wind-turbine rotor blades **Industrial engineering**: industrial robot arms
Research & Development[15]:	
Electrically conducting inks; improved conductivity and mechanical resistance	**Energy engineering**: solar cells
Bipolar plates and gas diffusion layers	**Energy engineering**: fuel cells
Electrodes made from CNTs	**Energy engineering**: lithium-ion batteries with increased storage capacity
Membranes with CNT; higher energy efficiency and productivity	**Environmental engineering**: seawater desalination, CO_2 separation
Ultra-light **composite materials**	**Aeronautics and astronautics, automotive**
High-strength CNT-based **particle foams**; improved absorption of deformation energy	**Automotive**: improved safety of body parts
Plastic parts and **sealants** on the basis of CNT-elastomers; improved friction, lubrication and wear properties	**Construction industry**
Metals with CNTs	**Automotive**: parts exposed to high mechanical loads
Ultra-high strength CNT-based concrete; improved stability and elasticity	**Construction industry**: e.g. high-rise buildings, bridges
Surface-functionalised, biocompatible CNTs for targeted drug delivery in the human body[16]	**Medicine**: e.g. cancer therapy
CNT-enhanced polymer composite fibres and fabrics; CNT-based fibres; improved resistance; conductivity, hydrophobic and flame retarding properties[17]	**Textiles**: antistatic and electrically conducting textiles ("smart clothes"); bullet-proof vests, water-resistant and flame-retardant textiles
CNT-based transistors: faster and more powerful circuits	**Electronics**: computer chips

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