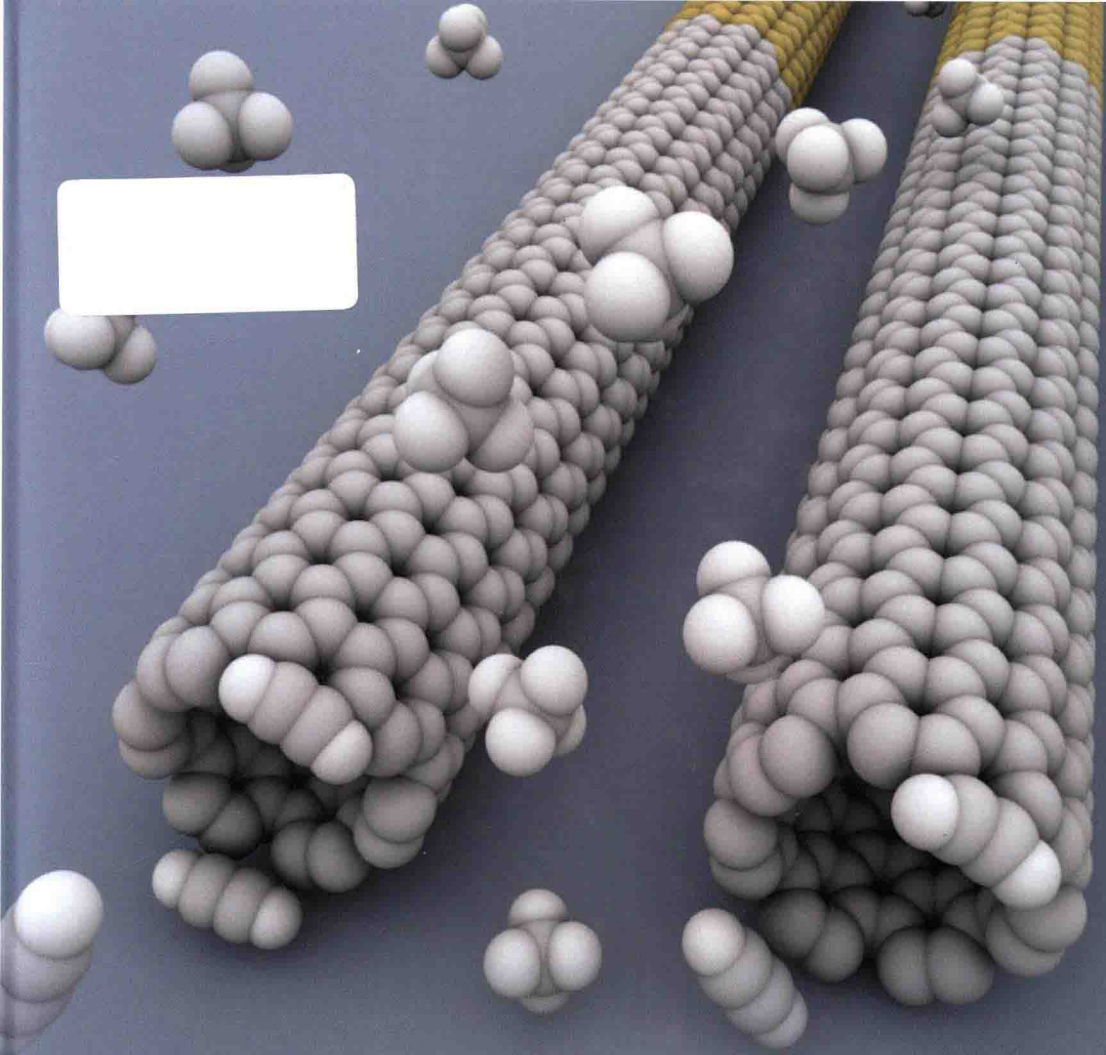

Handbook of Applications of Carbon Nanotubes

Synthesis, Properties and Applications

Prancias Houterberg
Editor

Handbook of
APPLICATIONS OF CARBON NANOTUBES
Synthesis, Properties and Applications

VOLUME 1

Editor
Dr Prancias Houterberg
University of Leoben

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Preface

A Carbon Nanotube is a tube-shaped material, made of carbon, having a diameter measuring on the nanometer scale. A nanometer is one-billionth of a meter, or about one ten-thousandth of the thickness of a human hair. The graphite layer appears somewhat like a rolled-up chicken wire with a continuous unbroken hexagonal mesh and carbon molecules at the apexes of the hexagons. Carbon Nanotubes have many structures, differing in length, thickness, and in the type of helicity and number of layers. Although they are formed from essentially the same graphite sheet, their electrical characteristics differ depending on these variations, acting either as metals or as semiconductors. As a group, Carbon Nanotubes typically have diameters ranging from <1 nm up to 50 nm. Their lengths are typically several microns, but recent advancements have made the nanotubes much longer, and measured in centimetres. Carbon nanotubes are the strongest and stiffest materials yet discovered in terms of tensile strength and elastic modulus respectively. This strength results from the covalent sp^2 bonds formed between the individual carbon atoms. In 2000, a multi-walled carbon nanotube was tested to have a tensile strength of 63 gigapascals (GPa). (For illustration, this translates into the ability to endure tension of a weight equivalent to 6422 kg (14,158 lbs) on a cable with cross-section of 1 mm^2.) Further studies, such as one conducted in 2008, revealed that individual CNT shells have strengths of up to ~100 GPa, which is in agreement with quantum/atomistic models. Since carbon nanotubes have a low density for a solid of 1.3 to 1.4 g/cm^3, its specific strength of up to 48,000 $kN \cdot m \cdot kg^{-1}$ is the best of known materials, compared to high-carbon steel's 154 $kN \cdot m \cdot kg^{-1}$. Under excessive tensile strain, the tubes will undergo plastic deformation, which means the deformation is permanent. This deformation begins at strains of approximately 5% and can increase the maximum strain the tubes undergo before fracture by releasing strain energy.

Although the strength of individual CNT shells is extremely high, weak shear interactions between adjacent shells and tubes leads to significant reductions in the effective strength of multi-walled carbon nanotubes and carbon nanotube bundles down to only a few GPa's. This limitation has been recently addressed by applying high-energy electron irradiation, which crosslinks inner shells and tubes, and effectively increases the strength of these materials to ~60 GPa for multi-walled carbon nanotubes and ~17 GPa for double-walled carbon nanotube bundles. Multi-walled nanotubes are multiple concentric nanotubes precisely nested within one another. These exhibit a striking telescoping property whereby an inner nanotube core may slide, almost without friction, within its outer nanotube shell, thus creating an atomically perfect linear or rotational bearing. This is one of the first true examples of molecular nanotechnology, the precise positioning of atoms to create useful machines. Already, this property has been utilized to create the world's smallest rotational motor. Future applications such as a gigahertz mechanical oscillator are also envisioned. Techniques have been developed to produce nanotubes in sizeable quantities, including arc discharge, laser ablation, high-pressure carbon monoxide disproportionation (HiPco), and chemical vapour deposition (CVD). Most of these processes take place in vacuum or with process gases. CVD growth of CNTs can occur in vacuum or at atmospheric pressure. Large quantities of nanotubes can be synthesized by these methods; advances in catalysis and continuous growth processes are making CNTs more commercially viable.

The present book has been designed to outline the basic and fundamental aspects of this subject to be understood in its right perspective. The book uses straight forward, less-technical jargon and manages to introduce each chapter with a basic concept, which ultimately evolves into a more specific detailed principle.

—Editor

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Chapter 1

Carbon Nanofiber

Carbon nanofibers (CNFs), vapour grown carbon fibers (VGCFs), or vapour grown carbon nanofibers (VGCNFs) are cylindric nanostructures with graphene layers arranged as stacked cones, cups or plates. Carbon nanofibers with graphene layers wrapped into perfect cylinders are called carbon nanotubes. Introduction

Carbon is the building block of a myriad of organic and inorganic matter around us. It is a versatile atom capable of joining to other atoms in *sp*, sp^2, and sp^3 hybridised structures giving rise to millions of stable molecules. In its single element form, it has a number of allotropes (polymorphs) like diamond, graphite, and fullerenes with different properties ranging from extremely hard to very soft scope]]. Carbon can be made to form tubular microstructure called filament or fiber. The unique properties of carbon fibers have expanded the science and technology of composite materials in recent decades.

VGCFs and their smaller size variant, VGCNFs are among short carbon fibers that have drawn lots of attention for their potential thermal, electrical, frequency shielding, and mechanical property enhancements. They are being more and more utilised in different material systems like composites thanks to their exceptional properties and low cost.

Synthesis

Catalytic Chemical Vapour Deposition (CCVD) or simply Chemical Vapour Deposition (CVD) with variants like thermal and plasma-assisted is the dominant commercial technique for the fabrication of VGCF and VGCNF. Here, gas-phase molecules are decomposed at high temperatures and carbon is deposited in the presence of a

transition metal catalyst on a substrate where subsequent growth of the fiber around the catalyst particles is realised. In general, this process involves separate stages such as gas decomposition, carbon deposition, fiber growth, fiber thickening, graphitisation, and purification and results in hollow fibers. The nanofiber diametre depends on the catalyst size. The CVD process for the fabrication of VGCF generally falls into two categories : 1) fixed-catalyst process (batch), and 2) floating-catalyst process (continuous).

In the batch process developed by Tibbetts , a mixture of hydrocarbon/hydrogen/helium was passed over a mullite (crystalline aluminum silicate) with fine iron catalyst particle deposits maintained at 1000p C. The hydrocarbon used was methane in the concentration of 15% by volume. Fiber growth in several centimetres was achieved in just 10 minutes with a gas residence time of 20 seconds. In general, fiber length can be controlled by the gas residence time in the reactor. Gravity and direction of the gas flow typically affects the direction of the fiber growth.

The continuous or floating-catalyst process was patented earlier by Koyama and Endo and was later modified by Hatano and coworkers. This process typically yields VGCF with submicron diametres and lengths of a few to 100 microns, which accords with the definition of carbon nanofibers. They utilised organometallic compounds dissolved in a volatile solvent like benzene that would yield a mixture of ultrafine catalyst particles (5-25 nm in diametre) in hydrocarbon gas as the temperature rose to 1100p C. In the furnace, the fiber growth initiates on the surface of the catalyst particles and continues until catalyst poisoning occurs by impurities in the system. In the fiber growth mechanism described by Baker and coworkers , only the part of catalyst particle exposed to the gas mixture contributes to the fiber growth and the growth stops as soon as the exposed part is covered, i.e. the catalyst is poisoned. The catalyst particle remains buried in the growth tip of the fiber at a final concentration of about a few parts per million. At this stage, fiber thickening takes place.

The most commonly used catalyst is iron, often treated with sulphur, hydrogen sulfide, etc. to lower the melting point and facilitate its penetration into the pores of carbon and hence, to produce more growth sites. Fe/Ni, Ni, Co, Mn, Cu, V, Cr, Mo and Pd are also used as catalyst. Acetylene, ethylene, methane, natural gas, and benzene are the most commonly used carbonaceous gases. Often carbon monoxide (CO) is introduced in the gas flow to increase the carbon yield through reduction of possible iron oxides in the system.

History

One of the first technical records concerning carbon nanofibers is probably a patent dated 1889 on synthesis of filamentous carbon by Hughes and Chambers. They utilised a methane/hydrogen gaseous mixture and grew carbon filaments through gas pyrolysis and subsequent carbon deposition and filament growth. The true appreciation of these fibers, however, came much later when their structure could be analysed by electron microscope. The first electron microscopy observations of carbon nanofibers were performed in the early 1950s by the Soviet scientists Radushkevich and Lukyanovich, who published a paper in the Soviet Journal of Physical Chemistry showing hollow graphitic carbon fibers that are 50 nanometres in diametre.

Early in the 1970s, Japanese researchers Koyama and Endo succeeded in the manufacturing of VGCF with a diametre of 1 μm and length of above 1 mm. Later, in the early 1980s, Tibbetts in the USA and Benissad in France continued to perfect the VGCF fabrication process. In the USA, the deeper studies focusing on synthesis and properties of these materials for advanced applications were led by R. Terry K. Baker and were motivated by the need to inhibit the growth of carbon nanofibers because of the persistent problems caused by accumulation of the material in a variety of commercial processes especially in the particular field of petroleum processing. The first commercialisation of VGCF was attempted by the Japanese company Nikosso in 1991 under the trade name Grasker® , the same year Sumio Iijima published his famous paper introducing the discovery of Carbon Nanotubes (CNTs) to the world. VGCNF is produced through essentially the same manufacturing process as VGCF, only the diametre is typically less than 200 nm. Several companies around the globe are actively involved in the commercial scale production of carbon nanofibers and new engineering applications are being developed for these materials intensively, the latest being a carbon nanofiber bearing porous composite for oil spill remediation.

Carbon Black

Carbon black is a material produced by the incomplete combustion of heavy petroleum products such as FCC tar, coal tar, ethylene cracking tar, and a small amount from vegetable oil. Carbon black is a form of amorphous carbon that has a high surface-area-to-volume ratio, although its surface-area-to-volume ratio is low compared to that of activated carbon. It is dissimilar to soot in its much higher surface-area-to-

volume ratio and significantly lower (negligible and non-bioavailable) PAH (polycyclic aromatic hydrocarbon) content. Carbon black is used as a pigment and reinforcement in rubber and plastic products.

The current International Agency for Research on Cancer (IARC) evaluation is that, "Carbon black is possibly carcinogenic to humans (Group 2B)". Short-term exposure to high concentrations of carbon black dust may produce discomfort to the upper respiratory tract, through mechanical irritation.

Common Uses

Figure: *A small mound of carbon black.*

The most common use (70%) of carbon black is as a pigment and reinforcing phase in automobile tires. Carbon black also helps conduct heat away from the tread and belt area of the tire, reducing thermal damage and increasing tire life. Carbon black particles are also employed in some radar absorbent materials and in photocopier and laser printer toner.

Total production was around 8,100,000 metric tons (8,900,000 short tons) in 2006. About 20% of world production goes into belts, hoses, and other non-tire rubber goods. The balance is mainly used as a pigment in inks, coatings and plastics. For example, it is added to polypropylene because it absorbs ultraviolet radiation, which otherwise causes the material to degrade. Carbon black from vegetable origin is used as a food colouring, in Europe known as additive E153. It is approved for use in Australia and New Zealand but has been banned in the USA.