

Carbon Nanofibers

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Carbon nanofibers are sp^2 -based linear, non-continuous filaments that are different from continuous, several micrometer diameter carbon fibers. This chapter gives a review on the growth, structural properties and practical applications of carbon nanofibers as compared with those of conventional carbon fibers. Carbon nanofibers could be produced via the catalytic chemical vapor deposition (CVD) as well as the combination of electrospinning of organic polymer and thermal treatment. The commercially available carbon nanofiber around the world is ca. 500 t/y. Carbon nanofibers exhibit high specific area, flexibility, and super strength due to their nanosized diameter that allow them to be used in the electrode materials of energy storage devices, hybrid-type filler in carbon fiber reinforced plastics and bone tissue scaffold. It is envisaged that carbon nanofibers will be key materials of green science and technology through close collaborations with carbon fibers and carbon nanotubes.

7.1 Similarity and Difference Between Carbon Fibers and Carbon Nanofibers	2
7.1.1 Basic Concepts	2

7.1.2 Synthesis and Properties of Carbon Fibers	3
7.1.3 Vapor-Grown Carbon Fibers	4
7.2 Growth and Structural Modifications of Carbon Nanofibers	6
7.2.1 Catalytically Grown Cup-Stacked-Type	6
7.2.2 Catalytically Grown Platelet-Type	9
7.2.3 Electrospun-Based Carbon Nanofibers	12
7.2.4 Electrospun-Based Porous Carbon Nanofibers	17
7.3 Applications of Carbon Nanofibers	19
7.3.1 Electrode Material in Lithium Ion Secondary Battery	19
7.3.2 Electrode Material for Supercapacitors	21
7.3.3 Supporting Material for Metal Nanoparticles	24
7.3.4 Bone Tissue Scaffold	25
7.4 Concluding Remarks	25
References	27

Carbon nanofibers could be defined as sp^2 -based linear filaments with diameter of ca. 100 nm that are characterized by flexibility and their aspect ratio (above 100). Materials in a form of fiber are of great practical and scientific importance. The combination of high specific area, flexibility, and high mechanical strength allow nanofibers to be used in our daily life as well as in fabricating tough composites for vehicles and aerospace. However, they should be distinguished from conventional carbon fibers [7.1–3] and vapor-grown carbon fibers (VGCFs) [7.4–10] in their small diameter (Fig. 7.1). Conventional carbon

fibers and VGCFs have several micrometer-sized diameters (Fig. 7.1c, d). In addition, they are different from well-known carbon nanotubes [7.5, 11–14]. Carbon nanofibers could be grown by passing carbon feedstock over nanosized metal particles at high temperature [7.4–10], which is very similar to the growth condition of carbon nanotubes. However, their geometry is different from concentric carbon nanotubes containing an entire hollow core, because they can be visualized as regularly stacked truncated conical or planar layers along the filament length [7.15–18]. Such a unique structure renders them to show semi-

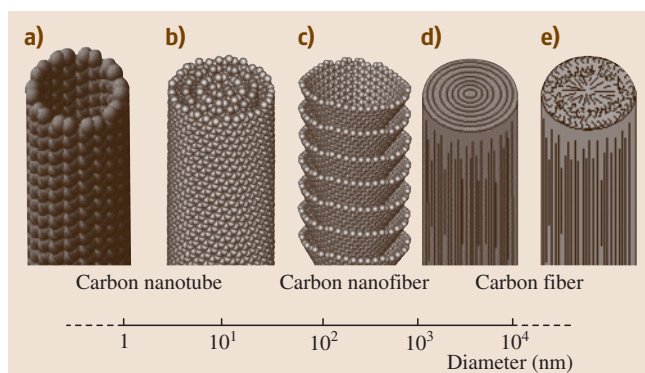


Fig. 7.1 Schematic comparison of the diameter dimensions on a log scale for various types of fibrous carbons

conducting behavior [7.19] and to have chemically active end planes on both the inner and outer surfaces of the nanofibers, thereby making them useful as supporting materials for catalysts [7.20], reinforcing fillers in polymeric composites [7.21], hybrid-type filler in carbon fiber reinforced plastics [7.22–

24], and photocurrent generators in photochemical cells [7.25, 26].

Alternatively, carbon nanofibers could be fabricated by the right combination of electrospinning of organic polymers and thermal treatment in an inert atmosphere. The electro-spinning technique has been considered to be one of the advanced fiber formation techniques from polymer solution by using electrostatic forces [7.27–30]. Electrospun-based nanofibers exhibited noticeable properties, such as nanosized diameter, high surface area and thin web morphology, which make them applicable to the fabrication of high-performance nanocomposites, tissue scaffolds and energy storage devices [7.31–37].

Within these contexts, intensive studies on the synthesis, characterization, possible application of carbon nanofibers have been carried out for the last decade. In this chapter, we have reviewed the synthesis techniques, their interesting textural properties, and, furthermore, the promising usages of carbon nanofibers that have been developed over the past 10 years.

7.1 Similarity and Difference Between Carbon Fibers and Carbon Nanofibers

Since carbon nanofibers could be considered as the 1-D form of carbon, their structure and properties are closely related to those of other forms of carbon, especially to crystalline three-dimensional graphite, turbostratic carbons, and to their constituent 2-D layers. Therefore, several forms of conventional carbon materials should be mentioned in terms of their similarities and differences relative to a carbon nanofiber. Especially, a direct comparison should be made between fibrous carbon materials, because the carbon fiber acts as a bridge between carbon nanofibers and conventional bulky carbon materials. In this section, the structures of carbon fibers as well as VGCFs are described with a strong emphasis on the similarities and differences of these 1-D carbon materials.

7.1.1 Basic Concepts

Carbon fibers represent an important class of graphite-related materials that are closely related to carbon nanofibers, with regard to structure and properties. Carbon fibers have been studied scientifically since the late 1950s and fabricated industrially since 1963.

They are now becoming a technologically and commercially important material in the aerospace, construction, sports, electronic device and automobile industries. The global carbon fiber market has now grown to about 12 500 t/y of product, after 40 years of continuous R&D work [7.1–3]. Carbon fibers are defined as a filamentary form of carbon with an aspect ratio (length/diameter) greater than 100. Probably, the earliest documented carbon fibers are the bamboo-char filaments made by Edison for use in the first incandescent light bulb in 1880. With time, carbon fibers were replaced by the more robust tungsten filaments in light bulb applications, and consequently carbon fiber R&D vanished at that early time. But in the late 1950s, carbon fibers once again became important because of the aggressive demand from aerospace technology for the fabrication of lightweight, strong composite materials, in which carbon fibers are used as a reinforcement agent in conjunction with plastics, metals, ceramics, and bulk carbons. The specific strength (strength/weight) and specific modulus (stiffness/weight) of carbon fiber-reinforced composites demonstrate their importance as engineering mater-

ials, due to the high performance of their carbon fiber constituents.

Since the temperature and pressure necessary to prepare a carbon fiber from the liquid phase is at the triple point ($T = 4100\text{ K}$, $p = 123\text{ kbar}$), it would be almost impossible to prepare carbon fibers from the melt under industrial processing conditions. Carbon fibers are therefore prepared from organic precursors. This preparation is generally done in three steps, including stabilization of a precursor fiber in air (at $\approx 300^\circ\text{C}$), carbonization at $\approx 1100^\circ\text{C}$, and subsequent graphitization ($> 2500^\circ\text{C}$). Fibers undergoing only the first two steps are commonly called *carbon fibers*, while fibers undergoing all three steps are called *graphite fibers*. Carbon fibers are generally used for their high strength, while graphite fibers are used for their high modulus. Historically, Bacon's graphite whisker (Fig. 7.2) has demonstrated the highest mechanical properties of a carbon fiber (with regard to both strength and modulus), comparable to the ideal value for a graphite network [7.38]. Graphitic whiskers were grown under conditions near the triple point of graphite. Then, the structural model was proposed, in which the layers consisting of graphene sheets are wound around the axis like as in rolling up a carpet. These whiskers were used as the performance target in the early stages of carbon fiber technology, even though they have never been produced on a large-scale.

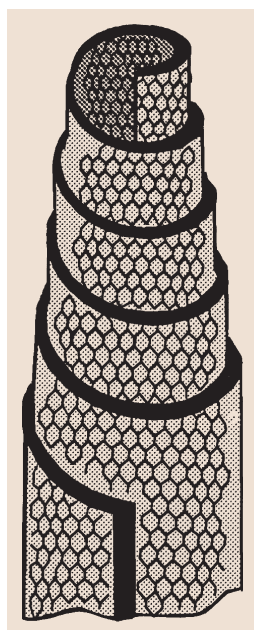


Fig. 7.2 Model for graphite whiskers grown by the direct current (DC) arc-discharge of graphite electrodes. Whiskers were reported to have the carpet-rolling structure of graphite sheets and to have high mechanical strength and modulus along the fiber axis, similar to the ideal values of a graphene sheet

7.1.2 Synthesis and Properties of Carbon Fibers

SEM photographs together with schematic structural models are shown in Fig. 7.3 for typical carbon fibers: a high-strength polyacrylonitrile (PAN)-based fiber (Fig. 7.3a), a high-modulus PAN-based fiber (Fig. 7.3b) and a mesophase pitch-based carbon fiber (MPCF) (Fig. 7.3c) [7.38, 39]. The PAN-based fibers consist of small sp^2 -carbon structural units preferentially aligned with the carbon hexagonal segments parallel to the fiber axis. This orientation is responsible for the high tensile strength of PAN-based carbon fibers [7.40]. By varying the processing conditions (e.g., oxidation conditions, choice of precursor material, and especially by increasing the heat treatment temperature) of PAN fibers, a better alignment of the graphene layers can be achieved (structural model of Fig. 7.3b), thus leading to stiffer, higher-modulus PAN fibers, but with lower strength [7.39]. PAN-based fibers are one of the typical hard carbons. MPCFs consist of well-aligned graphitic layers arranged nearly parallel to the fiber axis, and this high degree of preferred orientation is responsible for their high modulus or stiffness as well as their relatively high graphitizability. The structures described above give rise to different physical properties, although each type of fiber features carbon hexagonal networks, possessing the strongest covalent bonds in nature (C–C bonds). These strong interatomic bonds lie in sheets essentially parallel to the fiber axis, and are responsible for the high mechanical performance of these carbon fibers.

Referring to Fig. 7.4a we see that PAN-based fibers have high strength and MPCFs have high modulus, while VGCFs provide mainly ultra-high modulus materials [7.4, 41]. In this figure we also observe isotropic pitch-based (general grade) fibers, exhibiting much lower modulus and strength, but widely used in composites with cement matrix for construction due to their low cost and chemical stability. Figure 7.4b demonstrates a direct indication of the differences in the mechanical properties of various carbon fibers, from low modulus – high strength to high modulus – low strength fibers from the lower left to the upper right in the photograph, where a yarn containing 500 fibers was initially placed in a horizontal position. These fibers are combined with other materials in order to design suitable mechanical properties and the fibers are used as a filler for various advanced composite materials. In order to get high performance in carbon and graphite fibers, it is very important

mesophase pitch-based fiber
 fiber structure!schematic diagram
 carbon fiber!vapor-grown
 tubular filament
 sp²-carbon

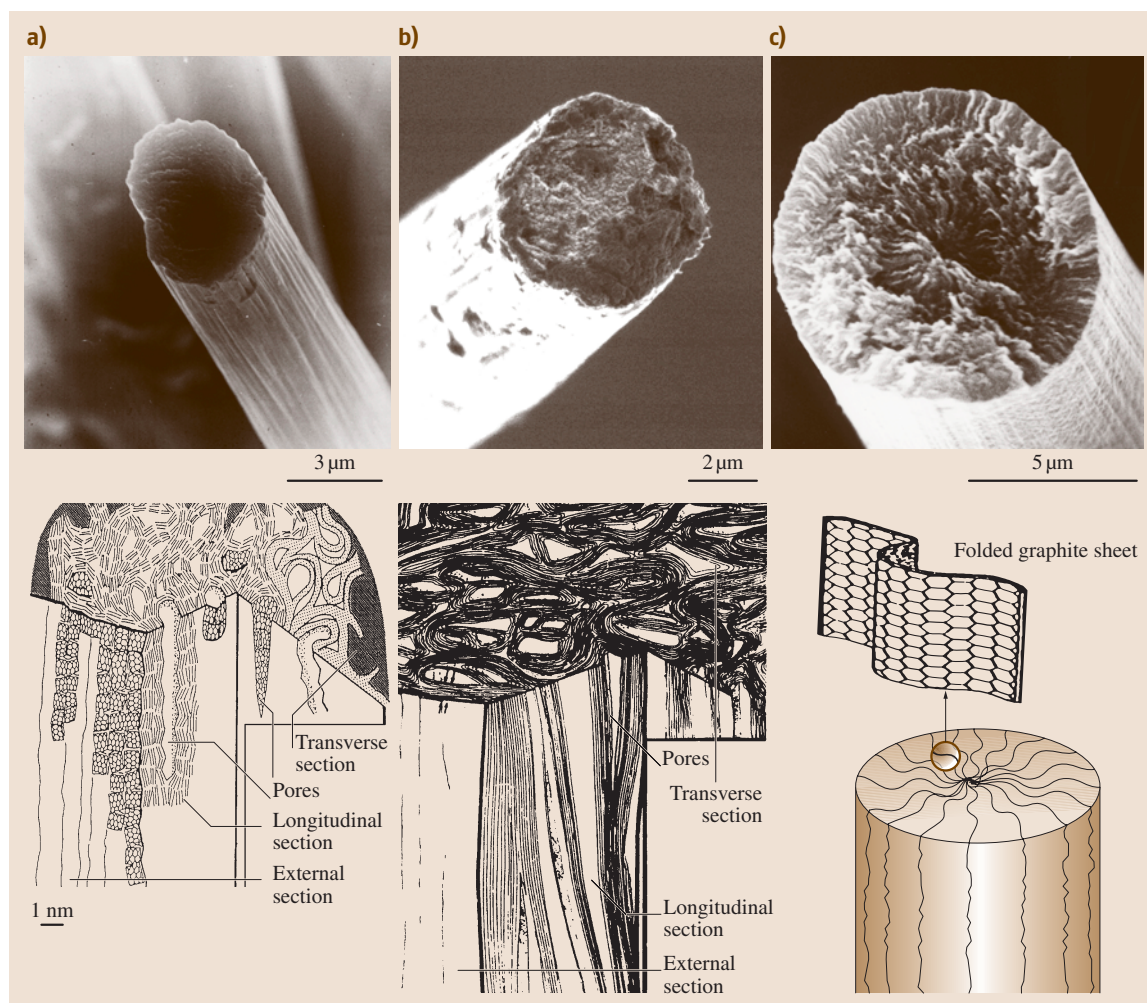


Fig. 7.3a–c SEM micrographs of three types of carbon fibers and their corresponding structural models. **(a)** High-strength PAN-based fiber, **(b)** High-modulus PAN-based fiber, and **(c)** a mesophase pitch-based fiber. In the *second row* of each fiber type, a schematic diagram of the fiber structure is shown

to control the microstructure by selecting the appropriate organic precursor as well as the processing conditions.

7.1.3 Vapor-Grown Carbon Fibers

VGCFs have a very special structure like annular-rings (Fig. 7.5a) and are synthesized by a somewhat different formation process than that used to produce PAN-based and MPCFs. In particular, VGCFs are not prepared from a fibrous precursor, but rather from hydrocarbon gas, using a catalytic growth process outlined in Fig. 7.5b [7.5–10]. Ultrafine transition metal particles,

such as iron particles with diameter less than 10 nm, are dispersed on a ceramic substrate, and a hydrocarbon, such as benzene diluted with hydrogen gas, is introduced at temperatures of about 1100 °C. Hydrocarbon decomposition takes place on the catalytic particle, leading to a continuous carbon uptake by the catalytic particle and a continuous output by the particle of well-organized tubular filaments of hexagonal sp²-carbon. The rapid growth rate of several tens of μm/min, which is 106 times faster than that observed for the growth of common metal whiskers [7.37], allows the production of commercially viable quantities of VGCFs. Evidence in support of this growth model

carbon!mechanical property
graphite fiber!mechanical property
vapor-grown carbon fiber
carbon fiber!vapor-grown
growth mechanism
catalytic metal particle
elongation growth
pyrolytic deposition

Index entries on this page

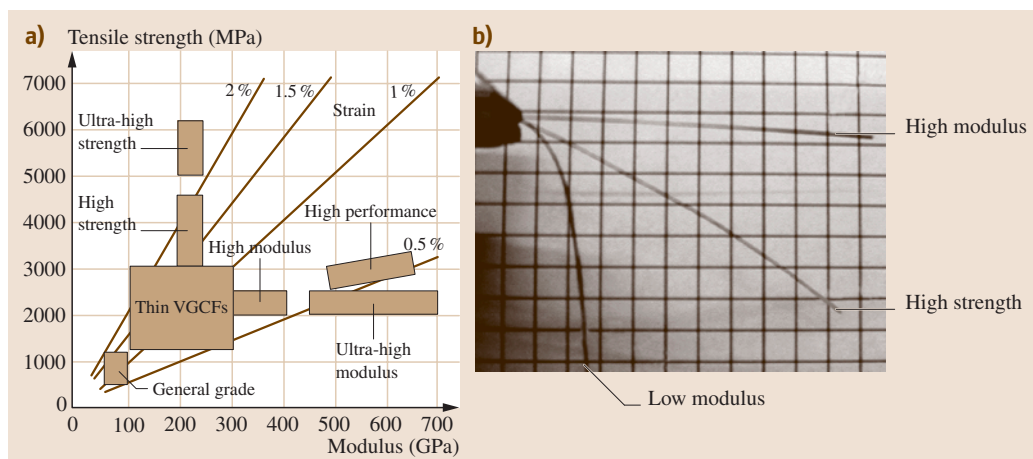


Fig. 7.4 (a) The mechanical properties of various kinds of carbon and graphite fibers and (b) a direct comparison of the mechanical properties for high strength and high modulus fibers. Low modulus fiber droops under its own weight, but the high modulus fibers does not

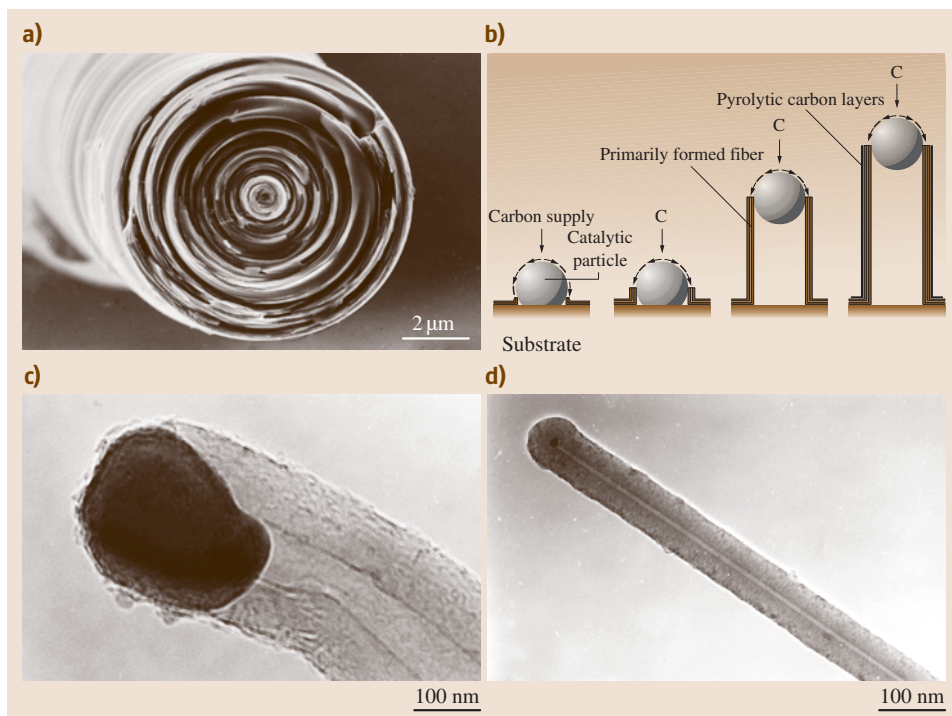


Fig. 7.5 (a) SEM image of vapor-grown carbon fibers, (b) suggested growth mechanism of VGCFs using ultra-fine catalytic metal particles, (c) very early stage of tubule growth in which the catalytic-particle is still active for promoting elongation growth. The primary tubule thus formed acts as a core for vapor grown fibers. (d) The fiber is obtained through a thickening process, such as the pyrolytic deposition of carbon layers on the primary tubule. The encapsulated catalytic particle can be seen at the tip of the hollow core

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