

CHAPTER 1.

Carbon Materials

Carbon materials are found in variety forms such as graphite, diamond, carbon fibers, fullerenes, and carbon nanotubes. The reason why carbon assumes many structural forms is that a carbon atom can form several distinct types of valence bonds, where the chemical bonds refer to the *hybridization* of orbitals by physicists. This chapter introduces the history of carbon materials and describes the atomic nature of carbon.

1.1 History

We provide here a brief review of the history of carbon fibers, which are the macroscopic analog of carbon nanotubes. The early history of carbon fibers was stimulated by needs for materials with special properties, both in the 19th century and more recently after World War II. The first carbon fiber was prepared by Thomas A. Edison to provide a filament for an early model of an electric light bulb. Specially selected Japanese Kyoto bamboo filaments were used to wind a spiral coil that was then pyrolyzed to produce a coiled carbon resistor, which could be heated ohmically to provide a satisfactory filament for use in an early model of an incandescent light bulb [1]. Following this initial pioneering work by Edison, further research on carbon filaments proceeded more slowly, since carbon filaments were soon replaced by a more sturdy tungsten filament in the electric light bulb. Nevertheless research on carbon fibers and filaments proceeded steadily over a long time frame, through the work of Schützenberger and Schützenberger (1890) [2], Pelabon [3], and others. Their efforts were mostly directed toward the study of vapor grown carbon filaments, showing filament growth from the thermal decomposition of hydrocarbons.

The second applications-driven stimulus to carbon fiber research came in

the 1950's from the needs of the space and aircraft industry for strong, stiff light-weight fibers that could be used for building lightweight composite materials with superior mechanical properties. This stimulation led to great advances in the preparation of continuous carbon fibers based on polymer precursors, including rayon, polyacrylonitrile (PAN) and later mesophase pitch. The late 1950's and 1960's was a period of intense activity at the Union Carbide Corporation, the Aerospace Corporation and many other laboratories worldwide. This stimulation also led to the growth of a carbon whisker [4], which has become a benchmark for the discussion of the mechanical and elastic properties of carbon fibers. The growth of carbon whiskers was also inspired by the successful growth of single crystal whisker filaments at that time for many metals such as iron, non-metals such as Si, and oxides such as Al_2O_3 , and by theoretical studies [5], showing superior mechanical properties for whisker structures [6]. Parallel efforts to develop new bulk synthetic carbon materials with properties approaching single crystal graphite led to the development of highly oriented pyrolytic graphite (HOPG) in 1962 by Ubbelohde and co-workers [7, 8], and HOPG has since been used as one of the benchmarks for the characterization of carbon fibers.

While intense effort continued toward perfecting synthetic filamentary carbon materials, and great progress was indeed made in the early 60's, it was soon realized that long term effort would be needed to reduce fiber defects and to enhance structures resistive to crack propagation. New research directions were introduced because of the difficulty in improving the structure and microstructure of polymer-based carbon fibers for high strength and high modulus applications, and in developing graphitizable carbons for ultra-high modulus fibers. Because of the desire to synthesize more crystalline filamentous carbons under more controlled conditions, synthesis of carbon fibers by a catalytic chemical vapor deposition (CVD) process proceeded, laying the scientific basis for the mechanism and thermodynamics for the vapor phase growth of carbon fibers in the 1960's and early 1970's.[9] In parallel to these scientific studies, other research studies focused on control of the process for the synthesis of vapor grown carbon fibers,[10]-[13] leading to current commercialization of vapor grown carbon fibers in the 1990's for various applications. Concurrently, polymer-based carbon fiber research has continued worldwide, mostly in industry, with emphasis on greater control of processing steps to achieve carbon fibers with ever-increasing modulus and strength, fibers with special characteristics, while decreasing costs

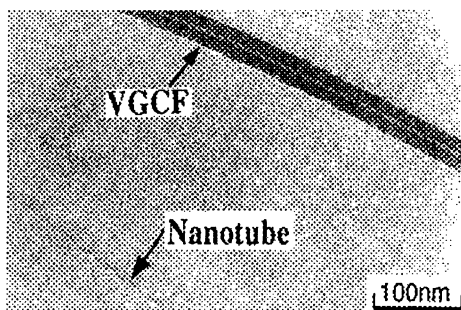


Fig. 1.1: High resolution TEM micrograph showing carbon nanotubes with diameters less than 10 nm [14–17].

of the commercial products.

As research on vapor grown carbon fibers on the micrometer scale proceeded, the growth of very small diameter filaments, such as shown in Fig. 1.1, was occasionally observed and reported [14, 15], but no detailed systematic studies of such thin filaments were carried out. In studies of filamentous carbon fibers, the growth of the initial hollow tube and the subsequent thickening process were reported.[16, 17] An example of a very thin vapor grown tubules ($< 100 \text{ \AA}$) is shown in the bright field TEM image of Fig. 1.1 [14–17].

Reports of such thin filaments inspired Kubo [18] to ask whether there was a minimum dimension for such filaments. Early work [14, 15] on vapor grown carbon fibers, obtained by thickening filaments such as the fiber denoted by VGCF (vapor grown carbon fiber) in Fig. 1.1, showed very sharp lattice fringe images for the inner-most cylinders corresponding to a vapor grown carbon fiber (diameter $< 100 \text{ \AA}$). Whereas the outermost layers of the fiber have properties associated with vapor grown carbon fibers, there may be a continuum of behavior of the tree rings as a function of diameter, with the innermost tree rings perhaps behaving like carbon nanotubes.

Direct stimulus to study carbon filaments of very small diameters more systematically [19] came from the discovery of fullerenes by Kroto and Smalley [20]. In December 1990 at a carbon-carbon composites workshop, papers were given on the status of fullerene research by Smalley [21], the discovery of a new synthesis method for the efficient production of fullerenes by Huffman [22], and a review of carbon fiber research by M.S. Dresselhaus [23]. Discussions at the workshop stimulated Smalley to speculate about the existence of carbon nanotubes of dimensions comparable to C_{60} . These conjectures were later followed

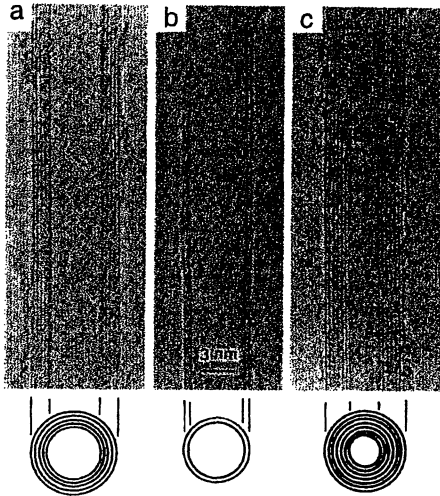


Fig. 1.2: The observation by TEM of multi-wall coaxial nanotubes with various inner and outer diameters, d_i and d_o , and numbers of cylindrical shells N : reported by Iijima using TEM: (a) $N = 5$, $d_o = 67 \text{ \AA}$, (b) $N = 2$, $d_o = 55 \text{ \AA}$, and (c) $N = 7$, $d_i = 23 \text{ \AA}$, $d_o = 65 \text{ \AA}$ [19].

up in August 1991 by an oral presentation at a fullerene workshop in Philadelphia by Dresselhaus [24] on the symmetry proposed for carbon nanotubes capped at either end by fullerene hemispheres, with suggestions on how zone folding could be used to examine the electron and phonon dispersion relations of such structures. However, the real breakthrough on carbon nanotube research came with Iijima's report of experimental observation of carbon nanotubes using transmission electron microscopy (see Fig. 1.2) [19]. It was this work which bridged the gap between experimental observation and the theoretical framework of carbon nanotubes in relation to fullerenes and as theoretical examples of 1D systems. Since the pioneering work of Iijima [19], the study of carbon nanotubes has progressed rapidly.

1.2 Hybridization in A Carbon Atom

Carbon-based materials, clusters, and molecules are unique in many ways. One distinction relates to the many possible configurations of the electronic states of a carbon atom, which is known as the hybridization of atomic orbitals. In this section we introduce the hybridization in a carbon atom and consider the family of carbon materials.

Carbon is the sixth element of the periodic table and is listed at the top