Nanotubes and Nanoparticles: The Newest Forms of Carbon

Jeremy J. Way Literature Seminar September 16, 1993

The discovery of buckminsterfullerene by Smalley in 1985 caused a flurry of studies of all-carbon molecules [1]. The proposition that nanotubes may exist prompted Iijima to review his former work on graphitic carbon [2]. Under reaction conditions similar to Smalley's, Iijima successfully isolated a new species of carbon - the carbon nanotube, also known as buckytubes. Ebbesen [3], in attempts to improve the yield of this new carbon species, recovered a deposit from a negative graphite electrode in a plasma-arc apparatus that consisted of a hard outer layer and a softer inner layer. About 25% of the softer inner layer was found to consist of nanotubes.

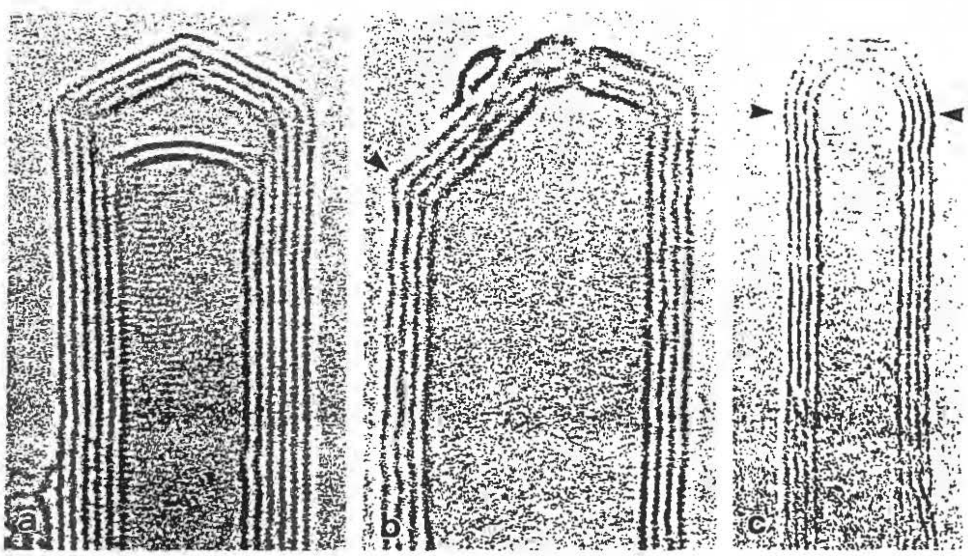

Figure 1: HRTEM micrographs of carbon nanotubes (buckytubes) [4]
(a) symmetric polyhedral capping with 5 pentagons
(b) asymmetric capping with 5 pentagons
(c) symmetric capping with 4 pentagons

There have been many transmission electron microscopy (TEM) [5-7], scanning electron microscopy (SEM) [8], and high-resolution electron microscopy (HREM) [3] studies of nanotubes. These microscopy images (Figs. 1, 2) have revealed that many morphologies may be assumed by these tubes, including bill-like [9], conical [10], polyhedral [10], and toroidal [10]. It has not yet been determined whether the tubes grow via an open- or closed-end mechanism [11]. However, the evidence is pointing to open-end growth, which would support the proposition that the formation of many different morphologies occurs due to the introduction of pentagons and heptagons into the helical hexagonal lattice that makes up the walls of the nanotubes [9]. A pentagon is formed when a single carbon species binds to the growing tube, while a heptagon forms when a three-carbon species binds. Current research is trying to determine what physical or chemical phenomena keep the tube tips open for further growth. It appears that the extremely high electric field can maintain openness of the tube [11].

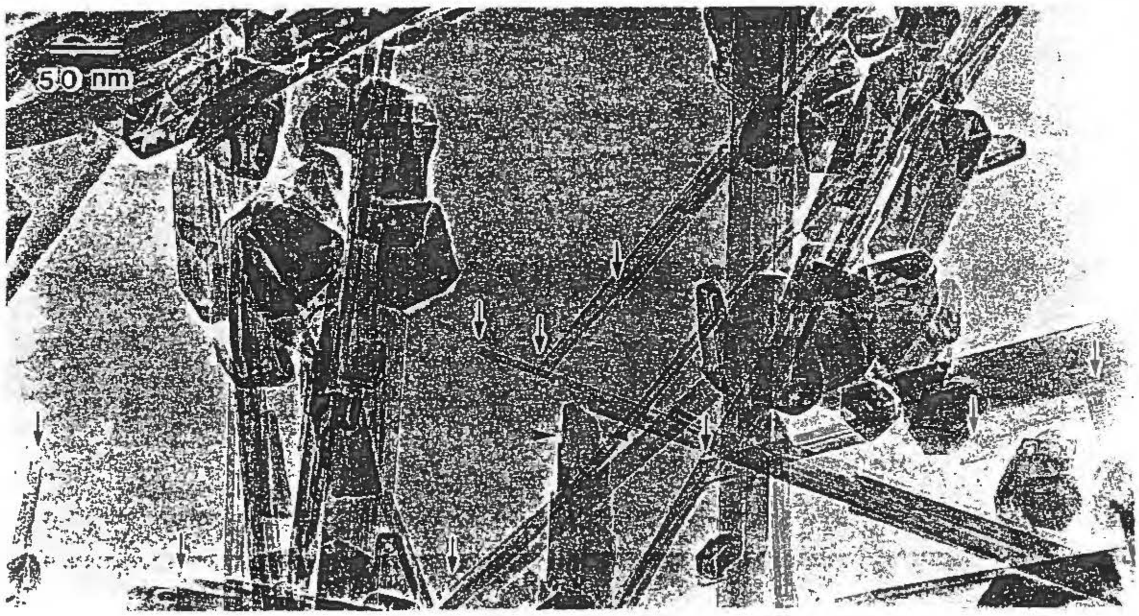

Figure 2: TEM micrograph of a mixture of nanotubes and nanoparticles [6]

The electronic absorption spectrum [8] of nanotubes and nanoparticles shows a broad feature at about 202nm which tails into the visible and infrared regions. The exact shape of this peak is sample dependent due to the nonuniformity of the tubes. Raman spectroscopy studies [12] show that nanotubes and nanoparticles are structurally similar to highly oriented pyrolytic carbon (HOPG), a perfectly crystalline form of carbon. There is a 6 cm^{-1} shift in the Raman band from that of HOPG which may be attributable to the curvature of the nanotubes. Thermogravimetric analyses [13] have determined that carbon nanotubes are more oxidatively stable than graphite and show no weight loss in air up to 700°C. The conductivity of bulk samples of carbon nanotubes has been estimated to be 100 ohm^{-1} cm^{-1} [3].

It may be possible to improve the conductivity of nanotubes if they can be filled with a conducting metal species. Ajayan and Iijima have successfully opened nanotubes in the presence of lead [14]. The filling efficiency is dictated by the reaction conditions under which the opening is carried out. The most effective filling has been found to occur when the metal is vaporized in the presence of tubes in air. It is also possible to remove the outer layers of multi-layer tubes by treating them with CO_2 [15] or oxygen [6].

Single-layer tubes have recently been prepared by vaporizing graphite in the presence of cobalt [16] and iron [17] catalysts. The growth of these single-layer tubes has confirmed the proposed helical growth mechanism. The cobalt-catalyzed product consists of a rubbery web-like deposit in the fullerene-containing soot. The uniformity and single-layer structure of these tubes will be useful for comparing their properties with theoretical predictions [16].

It has been found that interaction with electron beams or heat causes nanotubes to become nanoparticles, or carbon onions [20, 21]. (Figs. 2, 3) In the presence of metals such as lanthanum [22, 23], onions will encapsulate single metal crystals. Limited exposure to electron beams causes the tubes to become buckminsterfullerene [24].

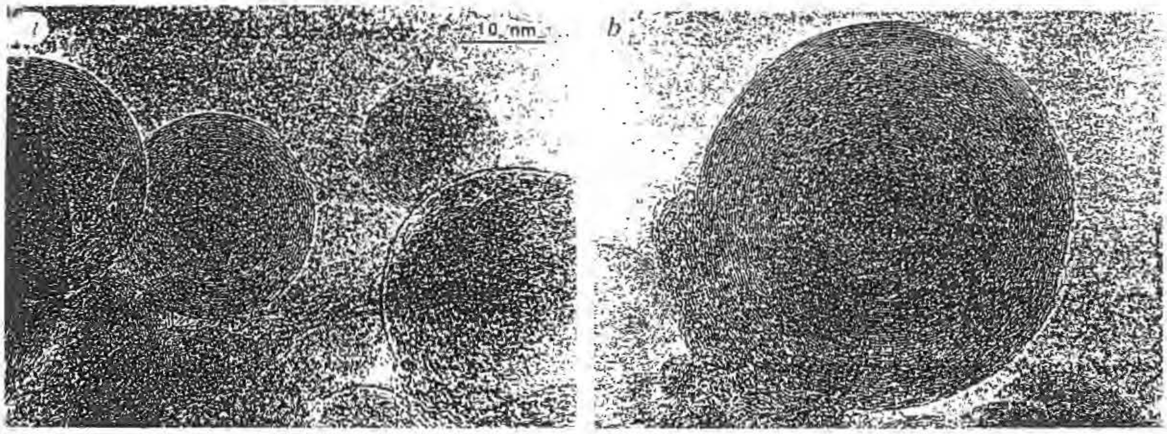

Figure 3: Spherical carbon nanoparticles (onions) [20]

Current electronics research is progressing toward nano-scale technology. This new form of carbon has only been studied for a short time, but there are numerous possibilities for its use in nanoelectronics technology. Controlled filling of nanotubes may lead to their use in the production of nanowires [18]. Their small, confining diameters may also make them useful as waveguides [19]. This group of compounds may lead to the efficient fabrication of nanowires and nanoelectronics and in turn, superconducting materials.

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