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Introductory Chapter: Carbon Nanotubes

Hosam M. Saleh and Martin Koller

1. Background

As a family of rather new nanomaterials, carbon nanotubes (CNTs) are emerging since about two decades. However, their origin dates back almost 70 years ago, when they were observed and described in 1952 for the first time by Radushkevich and Lukyanovich; in 1976, Oberlin and colleagues described the microscopic observation of single- or double-walled carbon nanotubes. In 1991, Iijima demonstrated for the first time a process for preparation of multi-walled carbon nanotubes (MWNTs); this discovery occurred rather fortuitously during testing a new method for arc evaporation to fabricate C_{60} carbon molecules. Soon later, two seminal studies by the groups of Iijima and Bethune provided mechanistic descriptions of the growth process involved in the formation of single-walled carbon nanotubes [1]. Structurally, such single-walled carbon nanotubes (SWNT) can be conceived as one atom-thick sheets of graphite (“graphene”), which are rolled up (wrapped) to form tubes, as illustrated in **Figure 1**.

Since their discovery in 1991, CNTs have experienced considerable investigative efforts, especially regarding potential smart applications. Those structures first reported in 1991 were MWNTs with a broad range of dimensions. These were basically distant relatives of highly defective carbon nanofibers grown via catalytic chemical vapor deposition.

Real molecular nanotubes *sensu stricto* only came up when they were by chance detected while a catalyst (Fe and Co) material was inserted in the anode during electric-arc discharge synthesis. For the first time, it became possible to synthesize molecular fibers exclusively based on carbon; one can imagine that the excitement was tremendous, since many physical properties of such a fiber had already been theoretically predicted [6].

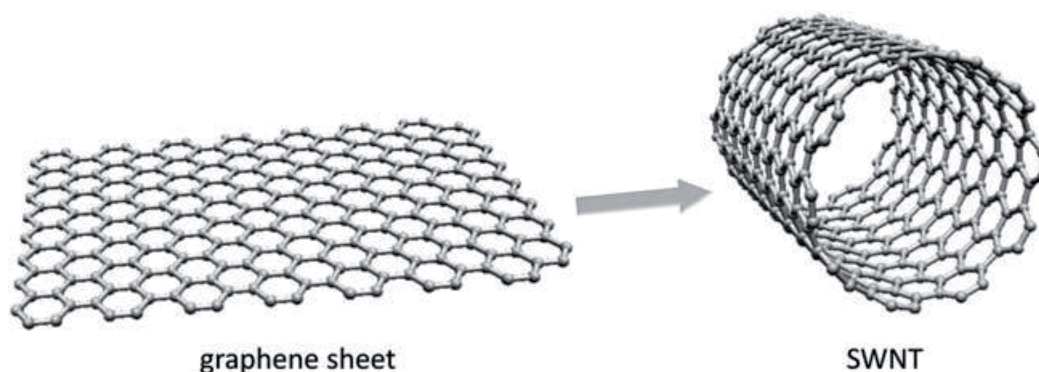


Figure 1.
Wrapping of graphene sheet to form single-walled carbon nanotubes [1].

2. Preparation of carbon nanotubes

High temperature preparation techniques such as arc discharge or laser ablation were the first techniques applied to produce CNTs [1]. In order to examine the properties of nanotubular structures, tubes of well-defined morphology, thickness, length, and a number of concentric shells are needed; however, established carbon-arc synthesis and other established methods generate a range of differently structured tubes [2]. Nowadays, these methods have been substituted by low temperature chemical vapor deposition (CVD) techniques ($<800^{\circ}\text{C}$), which offer the possibility to fine tune orientation, alignment, length and diameter, purity and density of CNTs in a precise way. The most frequently applied methods and some additional non-standard techniques such as liquid pyrolysis and bottom-up organic approaches are introduced below. Most of these techniques need auxiliary gases and *in vacuo* operation, although CNT growth has been already reported also at atmospheric pressure. However, gas-phase methods are volumetric, which makes them suitable for diverse new applications such as development of novel composite materials, which require high amounts of nanotubes and industrial-scale synthesis methods in order to make their production feasible in economic terms. Yet, there are some drawbacks when resorting to gas-phase synthesis methods, namely short catalyst lifetime, low catalyst yields by only a low percentage of catalysts actually forming nanotubes, and low catalyst number density. Independent on which CNT preparation method is applied, CNT production is always accompanied with formation of certain impurities that qualitatively and quantitatively depends on the technique applied. Most of above-mentioned methods generate powders, which contain not only a small fraction of CNTs, but also other carbonaceous particles like nanocrystalline graphite, amorphous carbon, fullerenes, and different heavy metals such as Fe, Co, Mo or Ni, which were needed as catalysts for CNT synthesis. Such contaminations negatively affect the desired properties of CNTs, and cause a serious obstacle for detailed characterization and application of CNTs. Therefore, the development of efficient and convenient purification methods is among the most central challenges in CNT research. Most common purification methods are based on acid treatment of prepared CNTs.

3. Nanotube growth and characterization

Both single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) have turned out as excellent electron emitters due to their large aspect ratio, high chemical stability, and small end radius [3]. However, there has been no successful alignment of single-wall individual or bundle nanotubes reported. Auspiciously, growth of large arrays of well-aligned MWNTs in an area up to the dimension of inches has been accomplished on glass, nickel, and silicon by plasma-enhanced chemical vapor deposition (PECVD), and on silica, porous silicon, and porous aluminum by chemical vapor deposition. Yet, the emission property of these arrays is not acceptable, probably because of the high site density ($>109/\text{cm}^2$), which leads to small electrical enhancement at the tips. In this context, it has been calculated that a site density of about $10^7/\text{cm}^2$ constitutes the adequate number for optimal electron emission characteristics in terms of both emission site and current density. The growth of arrays of well-aligned unconnected MWNTs with sharp tips and controlled dimensions and site spacing has been realized by using PECVD. This technique offers a new strategy to obtain optimal emitter density of CNTs. For aligned MWNTs grown on a uniform Ni layer, a catalyst particle at the tip of each nanotube was detected. Moreover, this metal particle had a preferential orientation

relative to the catalytically active surface, which was explained by a model showing that Ni surfaces except (220) get quickly covered, with the catalytically active (220) surface remaining the only exposed surface.

4. Carbon nanotube metrology

Broad commercialization of CNTs requires bulk material measurements, which are fast, inexpensive, reliable, and traceable to rigorous and quantitative methods. Information such as the volume fraction of semiconducting to metallic bulk material is needed to optimize manufacturing processes, thus enabling successful end-user applications like development of multi-function composites. Chirality and diameter of individual CNTs are crucial for matching species with high-end applications in (micro)electronics and optoelectronics. Metrology at the scale of individual CNTs involves complex optical techniques and imaging, and further launches the fundamental traceability of bulk measurements. Moreover, this introductory chapter describes NIST standards to establish recommended practice guides and reference materials based on industry demand, and shows that collaboration of researchers, stakeholders such as CNT manufacturers, NASA, and other end users is needed for ultimate success of CNTs on the market.

Single-walled carbon nanotubes (SWCNTs) offer multiple opportunities for applications in the fields of electronics, optoelectronics, photonics, or photovoltaics. SWCNTs are definitely almost ideal models of infinite π orbital conjugations, where the sp^2 lattice provides exceptional charge carrier properties. In addition, their real one-dimensional character enables well-defined optical transitions from excitonic states. While their Raman and photoluminescence characteristics have already been comprehensively studied, the basic absorption properties of SWCNT are still scarcely investigated on a quantitative basis, although especially these properties are of major significance for applications. In fact, described absorption measurements on SWCNT assemblies suffer from the problem of sample heterogeneity characteristic for standard synthesis methods.

The huge multiplicity of nanotube chiralities and dimensions, together with the occurrence of impurities from the synthesis process encumber the assessment of the exact SWCNT chirality contributing to an absorption signature [4].

5. Electrochemistry of carbon nanotubes

CNTs have attracted attention because of their exceptional morphology, nanosized dimensions, unique physico-chemical properties, and moreover, their multifarious fields of applications [5]. As illustrated in **Figure 1**, CNTs could be visualized as wrapped graphene sheets (sp^2 carbon arranged in a honeycomb-like grid). As mentioned above, two groups of carbon nanotubes are distinguished, namely multi-walled carbon nanotubes (MWNTs) and single-walled carbon nanotubes (SWNTs). In the case of MWNTs, these can be visualized as concentric and closed graphite tubules with multiple graphene sheet layers defining a hole of typically 2–25 nm, separated by about 0.34 nm. SWNTs consist of a simple single-rolled graphite sheet, forming a cylinder of 1–2 nm diameter. Depending on the structure, mainly on the diameter and helicity, CNTs can behave like metals or semiconductors. Electrically, MWNTs display superconductivity with a relatively high transition temperature. Electron transport in nanotubes is ballistic; hence, the nanotubes' resistance does not depend on its length, because the mean free path λ_m is longer than the length of the nanotube itself. For example, Berger *et al.* reported

the mean free path with $\lambda_m = 30 \text{ } \mu\text{m}$, which was considerably longer than the nanotube used for the study. Recent measurements of the magnetic properties of nanotubes evidence that SWNT might be the heavily desired materials of choice to be used as room-temperature superconductors.

6. Applications of carbon nanotubes

Various potential applications have been proposed in literature for CNTs, encompassing conductive and high-strength composites, sensors, energy storage and energy conversion devices, hydrogen storage media, field emission displays and radiation sources, and nanometer-sized semiconductor devices, probes, and interconnects [6]. Some of these applications were already successfully realized in products, while others were only shown in lab-scale to prototype devices. Cost for nanotube preparation, polydispersity in a given type of nanotubes, and immature processing and assembly methods are still important barriers for some applications, especially in the case of SWNTs [7].

6.1 Potential application of CNTs in vacuum microelectronics

Field emission, a quantum effect, is a smart source to generate electrons in comparison to thermionic emission. When subject to a sufficiently high electric field, electrons near the Fermi level can overcome the energy barrier to get released to the vacuum level. The basic physics of electron emission is already well understood. The emission current from a metal surface is determined by the Fowler–Nordheim equation: $I = aV^2 \exp(-b\phi^3/2/\beta V)$, where I , V , ϕ , β are the current, applied voltage, work function, and field enhancement factor, respectively. Electron field emission materials have been broadly investigated for different technological uses, for example, for flat panel displays, microwave amplifiers, or electron guns in electron microscopes. For technological applications, electron emissive materials should have low threshold emission fields and should be stable at high current density. A current density of $1\text{--}10 \text{ mA/cm}^2$ is required for displays and $>500 \text{ mA/cm}^2$ for a microwave amplifier.

In order to minimize the electron emission threshold field, emitters with a low work function and a large field enhancement factor are favorable. The work function is an intrinsic material property. The field enhancement factor mainly depends on the emitter's geometry, and can be approximated by: $\beta = 1/5r$, where r is the radius of the emitter tip. Various processing techniques to generate different emitter types have been established like Spindt-type emitters, with a sub-micron tip radius. Yet, this process is expensive, and the emitters have only limited lifespan. Malfunction is often caused by ion bombardment from the residual gas species that dull the emission tips.

6.2 Energy storage

CNTs are also considered for energy production and storage. Graphite, carbonaceous materials, and carbon fiber electrodes are used since decades in fuel cells, batteries, and various other electrochemical applications. Nanotubes are unique due to their small dimensions, the smooth surface topology, and perfect surface specificity, which is based on the fact that only the basal graphite planes are exposed in their structure. The electron transfer rate at carbon electrodes finally governs the performance of fuel cells, which depends on different factors, such as arrangement and morphology of the carbon material used in the electrodes. Several experiments

have demonstrated that, compared to traditional carbon electrodes, electron transfer kinetics are fastest on nanotubes, following ideal Nernstian behavior. Nanotube microelectrodes have been built using a binder; such devices have been successfully tested for bioelectrochemical reactions (e.g., oxidation of dopamine). They outperformed the established carbon electrodes in terms of reaction rates and reversibility. Pure MWNTs and MWNTs deposited with noble metal catalysts (Pd, Pt and Ag) have been applied for electro-catalysis of oxygen reduction reactions, which are pivotal for fuel cells. Several studies demonstrate that nanotubes constitute excellent alternatives for traditional carbon-based electrodes. Likewise, the enhanced selectivity of nanotube-based catalysts in heterogeneous catalysis was confirmed. In this context, Ru-supported nanotubes outperformed the same metal on graphite and on other carbon materials in the liquid phase hydrogenation reaction of cinnamaldehyde. The properties of catalytically grown carbon nanofibers (which can principally be conceived as defective nanotubes) turned out to be appropriate for high power electrochemical capacitors.

6.3 Filled composites

The mechanical characteristics of CNTs are stimulating since they are considered the “ultimate” carbon fiber ever produced. Compared with steel, traditional carbon fibers have about 50 times the specific strength (strength/density), and constitute outstanding load-bearing reinforcements when incorporated in composites. Consequently, nanotubes should be the candidates of choice for structural applications. In fact, carbon fibers have successfully been applied as reinforcements in high strength, low density, and high performance composites. They are typically found in a variety of products ranging from expensive tennis rackets to aircraft and spacecraft body parts. In this context, NASA has recently made large investments in developing novel CNTs-based composites to be applied for, for example, the futuristic Mars mission. In addition, carbon nanotubes were also applied as filler materials to fine-tune the mechanical properties of films consisting of biodegradable, microbial bioplastics [8].

6.4 Nanoprobes and sensors

The tiny and constant dimensions of nanotubes pave the way for some highly intriguing applications. With extremely small sizes, high mechanical strength and elasticity, and high conductivity, nanotubes have the potential to ultimately become essential nanoprobes for technological use. Such probes can be conceived as being applied for various applications, such as high resolution imaging, nanoelectrodes, nanolithography, drug delivery systems, sensors, or field emitters. The option of developing nanotube-based field emitting devices has already been discussed above in this chapter. Moreover, also using a single MWNT attached to the end of a scanning probe microscope tip for imaging has already been described. Since MWNT tips are electrically conductive, they can be applied in STM and AFM devices as well as in other scanning probe instruments, such as in electrostatic force microscopes. The benefit of nanotube tips is their thinness and the possibility to image particular structures (such as tiny, deep surface cracks), which are very difficult to probe with larger, blunter-etched Si or metal tips. Compared to conventional STM tips, also large biomolecules, such as DNA or proteins, can be imaged with excellent resolution using nanotube tips. MWNT and SWNT tips were successfully used in a tapping mode to image biomolecules like amyloid- β -protofibrils (related to Alzheimer's disease) with unprecedented resolution. Moreover, based on the high elasticity of the nanotubes, the tips are not damaged by contact with the substrates. Impacts

merely cause buckling of the nanotube, which usually is reversible on retracting the tip from the substrate.

6.5 Templates

Since nanotubes have quite straight and thin channels in their cores, it was discussed from the very beginning that it might be possible to fill different materials into these cavities in order to generate one-dimensional nanowires. Early assumptions proposed that pronounced capillary forces exist in nanotubes, sufficiently strong to hold back gases and liquids inside the cavities. In 1993, this was for the first time proofed experimentally by filling and solidifying molten lead inside MWNT channels. By this technique, wires only 1.2 nm in diameter were successfully manufactured inside nanotubes. Nowadays, a large number of studies dealing with this topic exist, many of them describing the filling of nanotubes with metallic and ceramic materials. Thus, nanotubes constitute proficient templates to create nanowires of different structure and composition.

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