The Structure and Preparation of Carbon Nanotubes

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Contributor: Yukang Zhu , Hongjie Yue , Muhammad Junaid Aslam , Yunxiang Bai , Zhenxing Zhu , Fei Wei

Materials are the basis of the evolution of human civilization. The pursuit of the ultimate properties of materials, such as super strength and super toughness, has strongly promoted the development of human culture. Carbon nanotubes (CNTs) with superior mechanical properties are expected to play a role in the next generation of critical engineering mechanical materials.

carbon nanotubes carbon nanotube fibers tensile strength defect control

1. Introduction

Materials are the basis of the evolution of human civilization. The pursuit of the ultimate properties of materials, such as super strength and super toughness, has strongly promoted the development of human culture. In 1895, Konstantin Tsiokovsky, a Soviet scientist, put forward building a “sky castle” at the top of a giant tower, which later evolved into the concept of “space elevator”. By connecting the earth and the space station with a cable, people can achieve space sightseeing and transport items to the space station [1]. However, the biggest challenge of this concept is finding light and strong cable that can overcome its gravity. A variety of nanostructures can be composed of single carbon elements, such as fullerenes (0D), carbon nanotubes (1D), and graphene (2D). Carbon nanotubes (CNTs) are cylinders rolled from single or multi-layer graphene sheets. Single-walled carbon nanotubes (SWCNTs) are cylinders rolled from a single-layer graphene sheet, while double-walled carbon nanotubes (DWCNTs) and multi-walled carbon nanotubes (MWCNTs) are composed of two and multiple layers of rolled graphene sheets, respectively. As one of the strongest chemical bonds in nature [2][3], the in-plane σ covalent bond of graphene formed by sp^2 hybridization endows CNTs with extremely high axial Young’s modulus (~1.1 TPa) and tensile strength (~120 GPa). Theoretical calculations have shown that CNTs are the most probable material to help mechanical materials achieve a breakthrough and even realize the “space elevator” dream [1]. However, CNTs with extremely excellent mechanical properties are nanoscale solids, and practical applications require macro-scale materials. It is the prerequisite for CNTs to play a significant role in practical applications that they can maintain excellent mechanical properties after being assembled from a single nanoscale unit to a macroscopic aggregate.

In recent years, rapid progress has been made in the preparation and mechanical properties optimization of carbon nanotube fibers (CNTFs). Different spinning methods of CNTFs have been put forward and improved upon, and CNTFs with a tensile strength comparable to carbon fibers (CFs) have been prepared [4][5][6][7]. However, their mechanical properties are still far lower than single CNTs [7], which also shows an unsatisfactory phenomenon of property transfer across scales. Theoretical calculations and experimental results show that the tensile strength of

CNTs with a nanoscale diameter can exceed 100 GPa [8][9]. CNT bundles with a diameter of 10–100 nm can have a tensile strength of up to 80 GPa [10]. CNTFs with a diameter of more than 1 μm, as a representative of macro assemblies of CNTs, have a maximum tensile strength of only 9.6 GPa [4], which is far lower than the intrinsic mechanical strength of CNTs. The reasons for such cross-scale tensile strength transfer are mainly due to defect accumulation and the lack of ideal tube–tube interactions during CNT assembly. Defects can have a fatal effect on the strength of CNTs [11][12]. With the increase in fiber size, defects also accumulate across scales. The improvement of strength for CFs and CNTFs is closely related to the reduction in defect size [13][14]. For CFs, the tensile strength was increased from about 1 GPa to 10 GPa when the defect size was reduced from the micron to the nano scale. For CNTs, due to the fewer defects in structure compared with CFs, less attention was paid to their precise structural control, especially defects, resulting in their tensile strength having long been at a lower level. Until the 2000s, a series of achievements were made in the prepration of defect-free CNTs, which have shown extraodinary tensile strength performance both at the single-tube and bundle levels [9][15]. Therefore, the preparation of ideal solids such as defect-free or defectless CNTs is the basis for preparing CNTFs with high tensile strength. At the same time, many studies have shown that the mechanical properties of CNTFs can be significantly influenced by the tube–tube interactions involving orientation, length, and density. It is of great significance to regulate the tube–tube interactions and precisely control the atomic defects for the improvement of CNTs' mechanical tensile strength [4][16][17][18].

2. The Structure and Preparation of Carbon Nanotubes

2.1. The Structure of Carbon Nanotubes

CNTs can be seen as a graphene sheet curled into a cylinder with a nanoscale diameter [19][20]. Carbon atoms in CNTs are linked by sp^2 hybrid covalent bonds, which is one of the strongest chemical bonds in nature [2][3], providing graphite materials with extremely high in-plane Young's modulus and tensile strength. The special tubular full-atomic-surface (FAS) structure composed of carbon hexagons avoids in-plane hanging bonds, folds, and concentrated local stresses in the tube wall. As a result, CNTs can exhibit excellent mechanical properties far beyond other materials (tensile strength ~120 GPa, Young's modulus ~1.1 TPa, elongation at break ~16%, toughness ~8 GJ/m^3) [8][21][22][23][24]. Similar to other engineering mechanics materials, the existence of defects will destroy the structural perfection of CNTs and affect the mechanical properties. The negative effect is even more pronounced for CNTs. For instance, a single vacancy defect could reduce the tensile strength of CNTs by 26% [25], and a single topological defect could lower that by 50% [12]. Despite that, the formation of topological defects is often accompanied by a high energy barrier, which can effectively protect the sp^2 structure of CNTs. Ding et al. found that the formation energy of the five-membered and seven-membered ring pairs of topological defects was as high as 4.4 eV [26], which could effectively protect the sp^2 structure of CNTs. Such topological protection is an important reason why CNTs are less prone to defects than other materials, such as steel or concrete.

2.2. Controllable Preparation of Carbon Nanotubes

Arc discharge [19][27], laser evaporation [28], and chemical vapor deposition (CVD) [29] are the three main methods for preparing CNTs. Compared with the former two methods, the CVD method has the advantages of low temperature, low energy input, and easy control of parameters and is the primary method in academic research and industrial production. The growth of CNTs by the CVD method can be divided into three stages. (i) The catalyst is in a molten state at a high temperature. (ii) The cracked carbon atoms dissolve on the catalyst, precipitate after supersaturation, and (iii) self-assemble to form CNTs [30]. There are many alternative carbon sources for the preparation of CNTs by the CVD method, such as methane, carbon monoxide, ethylene, acetylene, and ethanol. The type of carbon source has a great influence on the structure and quality of the as-grown CNTs. For example, considering the thermal cracking conditions, people thought that methane is the most appropriate carbon source for producing ultralong CNTs with perfect structure [9][31]. The catalyst is another key factor in regulating the structure and quality of CNTs. The catalysts used for producing CNTs are mainly metal catalysts, including magnetic metal catalysts (iron, cobalt, nickel), noble metal catalysts (copper, gold, silver, platinum), as well as molybdenum and tungsten, etc. Iron-based catalysts are the most commonly used and there are many reports on the preparation of CNTs with ferric chloride or ferrocene as catalysts. Ding et al. [26] also reported the role of iron nanoparticles in defect repair, explaining the high efficiency of iron-based catalysts towards CNT growth from the mechanism level. The macroscopic assembly of CNTs requires a large number of CNTs. Therefore, the large-scale production of CNTs, which can be achieved by the CVD method with relatively low cost and good controllability, is the basis of their subsequent assembly into a fiber structure. Early in 1993, Santiesteban et al. [32] first reported the fabrication of CNTs by the CVD method. The fabrication process of high-purity CNTs in large quantities based on CVD developed rapidly in the first decade [33][34]. Our group combined the traditional chemical fluidized-bed technology with the CVD method to realize the large-scale production of CNTs [35][36][37][38], which dramatically reduced the cost of CNTs. In addition, ultralong CNTs with macro-scale length can be synthesized by carefully regulating the growth kinetics. These ultralong CNTs possess perfect structure without any defects and can be produced at a wafer scale [9][39]. At the same time, these defect-free CNTs provide an ideal system for analyzing mechanical materials and are expected to yield new results in some branches of solid mechanics. Considering the research paradigm of the bottom-up assembly of CNTs into macrostructures as practical engineering materials, individual CNTs are the most basic structural unit. Obviously, if a large number of CNTs with defect-free or defectless structures can be synthesized and assembled into CNTFs, the excellent intrinsic properties of CNTs can be fully exploited. As a result, developing next-generation high-performance engineering materials can be promoted significantly.

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