Unraveling the influence of grain boundaries on the mechanical properties of polycrystalline carbon nanotubes

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A B S T R A C T

The ability to produce homogeneous defect-free carbon nanotubes (CNTs) represents a major challenge in terms of utility and cost. Specifically, the existence of grain boundaries (GBs) are ubiquitous in large diameter CNTs obtained by various large-scale growth methods and their effects on the mechanical properties of CNTs are not fully explored. Understanding the influence of the grain size and the GB orientation upon the mechanical behavior of CNTs is crucial for their functional and structural applications. The significance and novelty of the current work lies in its ability to establish the mechanical properties and the fracture behavior of CNTs containing grain boundaries of varied size, orientation and structure to an applied uniaxial load using comprehensive molecular dynamics simulations. A specially developed program, using Voronoi tessellation method and Delaunay triangulation, was implemented to generate the atomistic descriptions of the considered polycrystalline CNTs with a variety of GB morphology. Our results reveal that the mechanical performance of CNTs is significantly affected by the orientations of the GBs, diameter and temperature. In terms of the fracture strength, the resulting failure patterns indicate that the polycrystalline CNTs fail in a brittle fashion and that pentagon-heptagon defects along the GBs serve as crack nucleation sites.

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1. Introduction

In view of their extraordinary mechanical, thermal, optical, and electronic properties [1,2], CNTs have attracted intensive interest in many fields such as aerospace, automotive, and bio-nano engineering [3]. While each of these fields exploits a different key property of CNTs, they all implicitly depend on their remarkable mechanical properties for structural reliability and/or sensory characteristics. Due to the inherent limitations of fabrication and purification processes, CNTs typically contain a variety of crystallographic orientations and defects [4]. The common domain interface, grain boundaries (GB), can be regarded as a one-dimensional array of dislocations [5]; some experimental studies also provide evidence of the existence of GBs in CNTs [6–9]. Under certain circumstances, GBs are deliberately introduced for the purpose of tailoring the electronic properties of CNTs to suit the requirements of a particular application. For example, Yao et al. [10] introduced a pentagon and a heptagon into the hexagonal carbon lattice to fuse together two nanotube segments with different atomic and electronic structures to create intramolecular metal-metal, metal-semiconductor, or semiconductor-semiconductor junctions. In another study by Yao et al. [11], well-controlled temperature-mediated growth of intramolecular junctions in CNTs was achieved by changing the temperature during growth. That particular study outlined a potential approach for growing intramolecular junctions in CNTs of different sizes and orientations at desired locations. This is important for tailoring CNT-based electronic circuits. Zhang et al. [12] studied the mechanical properties of 20 representative graphene grains using density functional theory and molecular dynamics (MD). They found that the intrinsic tensile strength of the inflected GBs generally decrease with increasing inflection angle and identified Stone Wales transformation as the major failure mechanism of graphene with GBs at high temperature: whereas the initial fracture site found can be on the boundary line or inside the domain. Electronic properties of polycrystalline CNTs were investigated by Wang et al. [13] using density-functional theory considering parallel and perpendicular GBs to the tube axis. That study reported that the CNTs with parallel GBs have a narrow or zero band gap (<0.16 eV) which is

independent of the misorientation angle and the diameter of the CNTs. On the other hand, CNTs with perpendicular GBs show a slightly large band gap (up to 0.6 eV). Zhang et al. [14] carried out MD simulations to determine the mechanical strength and fracture behavior of GBs. Their study revealed that the intrinsic strength, the critical failure strain and the failure mechanism of graphene with GBs mainly rely on the temperature and inflection angle, whereas Young's modulus does not vary significantly with temperature or boundary configuration. More recently, quantum transport and thermoelectric properties were reported by Lehmann et al. [5] for graphene sheets, graphene nanoribbons, and CNTs with a variety of GB types in a wide temperature range. Their study demonstrated that GBs are a viable tool to tailor the thermal properties of carbon-based nanomaterials, paving the way for the design of new thermoelectric nano devices. Several studies also reported that by controlling the GBs and creating pores, the band gap in graphene sheets can be tuned, and thus the electronic structure can be controlled via strain engineering [15—17]. The effect of GBs on the mechanical properties of polycrystalline graphene was also investigated using experimental and numerical techniques; see, e.g., Refs. [18—21]. On the contrary, the effects of relatively simple defects such as atom vacancies, doping, substitutional impurities, Thrower-Stone-Wales (TSW) and hybridization, on the thermomechanical properties of CNTs were studied in Refs. [22—24].

Intrinsic topological existence of GBs in polycrystalline CNTs are expected to markedly alter their mechanical properties and failure behavior. It is well-established that the mechanical properties of polycrystalline solids are strongly influenced by their grainy structure. CNTs have been produced in a much controlled environment and as such are less susceptible to large extrinsic defects [25]. Therefore, it is natural to expect the variations in their mechanical properties to arise from intrinsic GBs. These GBs will influence the stress state and may act as a precursor to crack initiation within the CNTs. However, the mechanical properties of CNTs with GBs have not yet been fully explored and investigated. As a result, we lack comprehensive understanding of the influence of these GBs which may limit the remarkable exploitation of the properties of polycrystalline CNTs. Indeed, this has motivated our interest in the current study. Specifically, the focus of our highly original study is to determine the influence of grain size orientation, and atomic structure upon the mechanical properties of polycrystalline CNTs using MD simulations. Additionally, we widen the scope of our research beyond the mechanical properties by investigating the failure behavior and the associated failure mechanisms of polycrystalline CNTs. The outcome of this work should lead to a greater insight into the mechanical behavior and fracture strength of polycrystalline CNTs thus allowing the community to explore the essence of their remarkable multifunctional properties.

2. Voronoi tessellation and polycrystalline CNTs

In this work, we created polycrystalline CNTs by rolling graphene sheets containing GBs. The atomic structures of the graphene sheets with randomly distributed grain sizes and shapes were created by using Voronoi tessellation technique [26,27]. First, based on the required average grain size, a specific number of points were randomly placed inside a square. Second, Delaunay triangulation was performed to obtain a set of spatial coordinates that forms a minimum distance with each nucleus from the randomly created grain nuclei. The circumcenter of neighbouring triangles that was generated in the last step was connected to create GBs and form a particular grain for each nucleus in our simulation cell. Although the grain nuclei were placed randomly, the distribution of the grain sizes (grain area) can be fitted following a gamma distribution [28]. This method has been widely used to model the grain structures in polycrystalline graphene sheets [29,30]. Fig. 1 demonstrates three typical grain size distributions in polycrystalline graphene sheets generated from the Voronoi construction. Fig. 2 shows the systematic steps involved in creating the graphene sheet with randomly distributed GBs, which was then rolled to create a polycrystalline CNT. We generated a collection of polygons separated by planar cell walls perpendicular to lines connecting neighbouring nucleation sites, as shown in Fig. 2(a). A polycrystalline graphene sheet was constructed by filling each cell with randomly oriented graphene domains, where the atoms adjacent to the planar cell walls represent the GBs. The initial C—C bond length in the graphene sheets was set to 1.41 Å, which has been confirmed experimentally [3]. Several polycrystalline graphene sheets with dimensions of 30 nm × 30 nm and an average grain size ranging from 5 nm to 10 nm were constructed [see Fig. 2(b)]. Several regions at different locations inside the polycrystalline graphene with dimensions of 80 Å × 80 Å were selected and extracted to create the basic structure that is rolled to form CNTs, as shown in Fig. 2(c). Pentagons and heptagons were created at the boundaries of the grains in each extracted region and then the energy of a graphene system was minimized using the conjugate gradient method to obtain its optimized structure (see Fig. 3). The obtained structure was then annealed by equilibrating it at room temperature in the constant temperature and volume canonical (NVT) ensemble over 100 ps with 0.5 fs time step using the velocity Verlet algorithm. The annealing process allows the rearrangement of C—C atomic positions at the GBs [31]. The annealed structures were further equilibrated using the isothermal—isobaric (NPT) ensemble over another 100 ps at 300 K and 1 atm to reach the atmospheric pressure.

In polycrystalline graphene, the GBs have 1D interface between two domains of a material with different crystallographic orientations. The structure of the grain is defined by its orientation angle θ_i, where θ_i is the angle between the zigzag direction $(n, 0)$ and the horizontal axis (see Fig. 3). We can also define the tilt angle φ_i of a GB as the joint between two mismatched angles (θ_L and θ_R) of adjacent grains, as shown in Fig. 3.

Accordingly, the chiral vectors for the left (n_L, m_L) and the right (n_R, m_R) grains along the GB can be defined as follows [15]:

$$\sin(\theta) = \frac{\sqrt{3}m}{2\sqrt{n^2 + nm + m^2}}, \text{ and} \tag{1}$$

$$\cos(\theta) = \frac{2n + m}{2\sqrt{n^2 + nm + m^2}} \tag{2}$$

These equations can be bridged to obtain the tilt angle (φ), such that [32]:

$$\varphi = \tan^{-1}\left[\frac{\sqrt{3}m_L}{m_L + 2n_L}\right] + \tan^{-1}\left[\frac{\sqrt{3}m_R}{m_R + 2n_R}\right] \tag{3}$$

In principle, different arrangements can develop along the GB. Formation of pentagon and heptagon defects along the GB can develop and defects such as quadrilaterals, octagons, and nonagons can also form due to higher formation energy, and are rarely observed in experiments [33]. Therefore, we consider pentagon and heptagon defects in this work and ruled out all other types of defects. These kinds of GB structures in graphene have also been modeled in several studies [18,21,34,35]. To study the effect of grain shape, size and structure on the mechanical properties of polycrystalline CNTs, four types of CNTs were considered, (see Fig. 4). These are: CNT with (i) random GBs, (ii) helical GBs to the CNT axis, (iii) parallel GB to the CNT axis, and (iv) transverse GB to the CNT