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Intrinsic strength and failure behaviors of ultra-small single-walled carbon nanotubes

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ABSTRACT

The intrinsic mechanical strength of single-walled carbon nanotubes (SWNTs) within the diameter range of 0.3–0.8 nm has been studied based on *ab initio* density functional theory calculations. In contrast to predicting "smaller is stronger and more elastic" in nanomaterials, the strength of the SWNTs is significantly reduced when decreasing the tube diameter. The results obtained show that the Young's modulus E significantly reduced in the ultra-small SWNTs with the diameter less than 0.4 nm originates from their very large curvature effect, while it is a constant of about 1.0 TPa, and independent of the diameter and chiral index for the large tube. We find that the Poisson's ratio, ideal strength and ideal strain are dependent on the diameter and chiral index. Furthermore, the relations between E and ideal strength indicate that Griffith's estimate of brittle fracture could break down in the smallest (2, 2) nanotube, with the breaking strength of 15% of E. Our results provide important insights into intrinsic mechanical behavior of ultra-small SWNTs under their curvature effect.

1. Introduction

Due to one-dimensional (1D) structures [1], the single-walled carbon nanotubes (SWNTs) are the ideal material for a variety of applications relating to tensile strain. The SWNTs and graphene are known as the strongest materials with ultrahigh axial Young's modulus of about 1.0 TPa and tensile strength approaching 100–130 GPa [3,4,2,5–9]. Both experimental and theoretical studies [5,10,26] showed that the diameter of the large SWNTs does not significantly affect their mechanical properties. However, the physical and mechanical properties of ultra-small SWNTs with the diameters smaller than 0.4 nm expected are different from those larger than that due to their very large curvature effect. Many efforts have been made to synthesize the ultra-small SWNTs in recent years. The smallest stable (2, 2) SWNT with a diameter of 0.3 nm observed by Zhao et al. [11] could be grown inside multi-wall carbon nanotubes (MWNTs). The (2, 2) nanotube investigated by the first principle calculations is tunable between metallic and semiconducting properties by changing the Fermi level [12]. In fact, the ultra-small nanotubes are less stable than the large nanotubes [13,14]. However, if we fabricated nicely in some special geometries, we can measure the values of the ultra-small SWNTs. Although, many studies have focused on synthesis, physical and chemical properties of the small SWNTs [11,12,15–18], their mechanical properties have yet to be clarified. Moreover, the intrinsic mechanical properties such as Young's modulus, Poisson's ratio and ideal strength are key factors relating to the stability and lifetime of devices. For these reasons, studying the mechanical response of small SWNTs under strain should be a necessary task in order to improve the future SWNTs-based devices.

The SWNT structure is unique due to the strong bonding between the carbons (sp^2 hybridization of the atomic orbitals) of the curved graphene sheet, which is stronger than in diamond with sp^3 hybridization because of the difference in C–C bond lengths (0.142 and 0.154 nm for graphene and diamond respectively) [1]. The changes in the C–C bond structure such as defects, grain boundaries, chemical substitutions or curvature effects are the main causes to make changes in mechanical properties of SWNTs and graphene. The results obtained by the density function theory (DFT) and molecular dynamic (MD) calculations showed that the Young's modulus and tensile strength of SWNTs [19–22] and graphene [23] with vacancy-related defects depend on the concentration of defects and defect characteristics. Zhang et al. [24] investigated that the grain boundaries (GBs) are significantly reduced the mechanical strength of graphene. Mortazavi et al. [25] reported that the Young's modulus of a nitrogen doped in a

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graphene is almost independent of nitrogen atom concentration, but the substituted nitrogen atoms are decreased the tensile strength and ductile failure behavior of graphene. For the perfect (5, 5), (6, 3) and (8, 0) SWNTs, the tight binding (TB) and DFT calculations showed that SWNTs can reach the Young's modulus of 1.0 TPa and a maximum tensile strength of 100 GPa with no chiral dependence [26]. However, the critical tensile strain for breaking has a chiral dependence. The experiment [5] has used the optical characterization with a magnetic actuation technique to measure the stiffness of the (17, 12), (17, 10) and (18, 10) SWNTs and found that the Young's modulus is not dependent on the nanotube chiral index, and has an average value of 0.97 ± 0.16 TPa. This mechanical response is also observed in the graphene. Both the experiment and DFT calculation reported the Young's modulus of 1.0 TPa for both the zigzag and the armchair tensile strain directions [3,28]. In 1920, Griffith [31] extrapolated an maximum intrinsic strength σ_I of about $E/9$ for the fracture of brittle material, where E is the Young's modulus of the material under uniaxial tension. This estimate is still valid for the brittle material in nano-scale. Both the experiment and theory showed that σ_I/E is approximately 0.1 for the graphene and nanotubes [3,28,10]. Therefore, it is interesting to investigate that the mechanical response of the large SWNTs and graphene is consistent with the small SWNTs, which are dominated by their very large curvature effect.

In this paper, we present the first-principles to investigate the structural and mechanical properties of the small SWNTs with the diameter in the range from 0.3 to 0.8 nm under uniaxial tension. The paper is organized as follows. Section 2 describes the setup of the DFT calculations and the detailed simulation procedure. Section 3 describes Young's modulus, Poisson's ratio, ideal strength and fracture mechanism of the SWNTs under tensile strain. Finally, Section 4 summarizes the results.

2. Methodology

First-principle (*ab initio*) simulations for tensile strains of small diameter single-walled carbon nanotubes (SWNTs) was performed. We used Quantum-ESPRESSO (QE) package [32] for the first-principle calculations, which is a full density functional theory [33,34] simulation package using a plane-wave basic set with pseudopotentials. The Rabe-Rappe-Kaxiras-Joannopoulos (RRKJ) [35] ultrasoft pseudopotentials was used to calculate the pseudopotential plane-wave with an energy cutoff of 60 Ry for the wave function. The exchange–correlation energy was evaluated by general-gradient approximation (GGA) [36] using the Perdew-Burke-Ernzerhof (PBE) [37] function.

We examined three models of a series of small diameter single-walled carbon nanotubes: the armchair type (2, 2), (3, 3), (4, 4), (5, 5), (6, 6) SWNTs; the zigzag type (3, 0), (4, 0), (5, 0), (6, 0), (7, 0) SWNTs and the chiral type (3, 1), (3, 2), (4, 1), (4, 2), (5, 2) SWNTs, which have the diameters in the range from 0.3 to 0.8 nm. Here, the SWNT structure in our notation is denoted by a set of integers (n, m) which is a shorthand for the chiral vector $\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$, where $\mathbf{a}_1$ and $\mathbf{a}_2$ are the unit vectors of an unrolled graphene sheet [1]. The chiral vector $\mathbf{C}_h$ defines the circumferential direction of the rolled-up graphene into a cylinder, giving the diameter D_0. The crosssectional area of a SWNT layer was calculated using the interlayer distance of a MWNT (0.34 nm) [29] as its thickness. Since a periodic boundary condition was applied for three dimensions in all models, the thickness of the vacuum region was set at 12 Å perpendicular to the tube axis to avoid the undesirable interactions from the neighboring SWNTs. The **k**-point grids in the Brillouin-zone selected according to the Monkhorst–Pack method [38] was $1 \times 1 \times k$, in which k depends on the length of the SWNTs.

To simulate the effect of tensile strain in the SWNTs, first, the models were fully relaxed by using the Broyden-Fretcher-Goldfarb-Shanno (BFGS) minimization method for the atomic positions, and cell dimensions in the z direction. These models were considered equilibrium until all the Hellmann–Feynman forces and the normal component of the stress σ_{zz} less than 5.0×10^{-4} Ry/a.u. and 1.0×10^{-2} GPa, respectively. Then the loading strain was applied to the models by elongating the cell along the z direction with an increment of 0.02. At near the fracture point, the strain was refined with a very small increment of 0.005. After each increment of the strain, the atomic structure was fully relaxed under fixed cell dimensions. Here, the tensile strain is defined as $\varepsilon_{zz} \equiv \Delta L/L_0$, where L_0 is the length of the unit cell at geometry optimization and ΔL is the increment of the length under tension (Fig. 1 (a)). We also investigated the mechanical response of graphene under tensile strain in the zigzag and armchair directions to elucidate curvature effect, as shown in Fig. 1(b).

3. Results and discussions

The scanning of the potential energy surface (PES) is performed for the smallest (2, 2) SWNT to search for the ground state with the length L_0 ranging from 0.24 to 0.27 nm by calculating the total energy per atom with different lengths. Fig. 2(a) shows the observed minimum of the total energy at $L_0 = 0.257$ nm. In Fig. 2(b), we present the illustrations of atomic structures for the (2, 2) SWNT at the ground state, where $L_0 = 0.257$ nm, $D_0 = 0.282$ nm, and $l_1 = l_3 = 0.149$ nm ($l_2 = 0.139$ nm) represent the length, the diameter, and the C–C bond length parallel to (perpendicular to) the tube axis, respectively. The same optimization is performed for the other nanotubes. The equilibrium configurations are listed in Table 1 for all SWNTs in this study. The results show that the C–C bond lengths of the small nanotubes tend to be longer than those of the large nanotubes. In the calculation of the binding energy, we take the energy of an isolated C atom (E_C) as the reference energies, with E_{tot} being the total energy of the system containing n C atoms in the unit cell. The binding energy per C atom, $E_b = E_{tot} - nE_C$, is summarized in Table 1. It is found that the binding energy becomes larger when the diameter of the SWNTs increases. In other words, the large SWNTs are more stable than the small SWNTs.

The most basic mechanical property of the SWNTs is the Young's modulus E, which is defined as

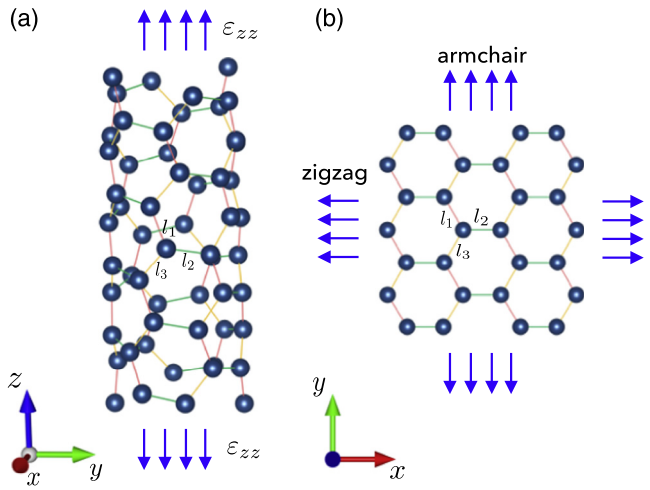

Fig. 1. (a) The simulation model of small nanotubes under tensile strain in z direction. (b) The model of graphene under tensile strain in zigzag and armchair directions. The notations of l_1 to l_3 are three bond lengths around C atomic.