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Super-elasticity and deformation mechanism of three-dimensional pillared graphene network structures

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ABSTRACT

Covalently bonded graphene/single-walled carbon nanotube (SWCNT) hybrid material can extend the excellent properties of graphene and SWCNT to three dimensions. We perform molecular dynamics simulations to investigate the mechanical properties of pillared vertically aligned carbon nanotube-graphene (VACNT-graphene) structure under uniaxial tensile and compressive loadings. The simulation results demonstrate that VACNT-graphene structures exhibit excellent elasticity with considerable elastic compressive/tensile strain limit. The early small deformation is dominated by the bending of graphene layers. Under larger elastic strain, graphene layers will form a corrugated pattern and shrink laterally in both the compression and tension processes. In the compression process, the failure mode of VACNT-graphene structure with small pillar distance is the bond breaking and reforming on the ridges of corrugated-shaped graphene and junction areas, while the failure mode of the structure with large pillar distance is the structural buckling. The elastic compressive strain limit exhibits a local maxima at the critical point between the two failure modes. In the tensile process, the failure is due to structural damage and elasticity increases with the pillar distance increasing. The essential tendency in our simulated VACNT-graphene structure might be significant to the further design and application of CNT-graphene hybrid materials.

1. Introduction

Carbon nanotubes (CNTs) [1] and graphene [2] possess extraordinary multifunctional properties including excellent mechanical strength [3–7], high thermal conductivity [8–10] and anisotropic electronic properties [11,12], *etc.*, owing to their structural perfection of the hexagonal lattice as well as the strong carbon-carbon bonds at atom scale. Due to the superior intrinsic physical and chemical properties, CNT and graphene have attracted much attention from scientific research community and shown immense potential in material engineering [13]. To solve the conflicts between strength and toughness in structural materials [14], CNT and graphene often serve as important constituents in composite materials to achieve supreme mechanical performances [15] and special applications.

When CNTs and graphene are introduced as fillers in polymer composites, the interfacial resistance is a bottleneck for achieving desired enhancement of properties [16]. To prevent this bottleneck and utilize the superior intrinsic properties of CNT and graphene, many efforts have been made to fabricate highly ordered carbon-based materials by introducing junctions which connect the low-dimensional structures to form a unity. Theoretical studies predicted several kinds of CNT heterojunctions [17–24] and graphene heterojunctions [28], which inherit the high strength and conductivity from one-dimensional CNTs and two-dimensional graphene. These junction structures have also been demonstrated *via* different experimental methods, such as chemical vapor deposition [25], joule heating process [26] and electron beam welding [27].

Recently, CNT-graphene heterojunctions applied in 3D structural materials have drawn much attention. One of such structures with the potential of reducing the interfacial resistance is a vertically aligned CNT-graphene structure (VACNT-graphene), firstly reported by Matsumoto et al. [29]. Duangkamon et al. discussed several possible configurations of the CNT-graphene junction [30] and versatility of this structure makes its applications possible in nanoelectronics [31,34], energy storage [32,33], heat transfer

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equipment [35] and gas separation membranes [36]. Kondo et al. first put forward a chemical vapor deposition method to synthesize the VACNT-graphene structure [37]. Subsequently, other approaches have been developed to synthesize and characterize the VACNT-graphene [38–42]. The obtained material with the facile catalytic growth method exhibited well performance in Li-S batteries [43].

In order to optimize the application of this structure, one needs to understand the mechanical performance of VACNT-graphene subject to different loading conditions, which is difficult to implement *via* experimental methods. Computer simulation has been proved to be a powerful tool for exploring the unknown mechanical properties of VACNT-graphene structure. There are many computational studies on VACNT-graphene structure. Using finite element method, Sihn et al. predicted the effective mechanical stiffness of this structure [44]. And later they identified the failure stress and strain [47]. Xu et al. studied the stiffness and strength of a similar structure by molecular dynamics (MD) simulations [45]. Moradi et al. examined the mechanical behavior of CNT-graphene junctions with tensile load applied along graphene sheets [46]. To our knowledge, an understanding of the elasticity of VACNT-graphene is still lacking, which is essential in applications where violent deformation is common to encounter. In current study, we investigated the mechanical performance of VACNT-graphene under uniaxial tension and compression using MD simulations. Our attentions are paid to the deformation modes and the favorable elasticity of VACNT-graphene. After-elasticity deformation as well as the influence of pillar distance on the elasticity of VACNT-graphene is discussed.

2. Computational details

The elementary building cell of VACNT-graphene structure is constructed by placing armchair (6, 6) CNTs vertically over the holes pre-created on the graphene sheets and connecting them with carbon-carbon covalent bonds. Carbon atoms at the joint of CNT and graphene form axially symmetric heptagonal and hexagonal rings (Fig. 1a). As shown in Fig. 1b (unit cell), CNTs are served as pillars to support and separate graphene sheets. The final structure (see Fig. 1c) is generated by replicating the unit cell along x-, y-, and z-axis with dimensions of $2 \times 2 \times 2$ repeated units. To differentiate these structures, we use the terminology described by Xu et al. [45], in terms of "PD*d*PH*h*", where "PD*d*" refers to the inter-pillar distance (*d* Å), and "PH*h*" refers to the pillar height (*h* Å) (Fig. 1b).

To investigate the mechanical properties of VACNT-graphene architectures, a series of large-scale MD simulations were carried out using the open-source LAMMPS code [48]. The adaptive intermolecular reactive empirical bond order (AIREBO) potential [49] was adopted to describe the interactions among carbon atoms. AIREBO potential can predict the Young's modulus of graphene well and accurately capture bond-breaking and bond-reforming between carbon atoms [50]. The cut-off parameter was set to be 2.0 Å, which is usually used to avoid nonphysical phenomenon near the fracture region [51,52].

In our MD simulations, periodic boundary conditions were imposed on all three directions of the simulation box. A time step of 1 fs was used for the velocity-Verlet integrator. Firstly the system was relaxed to its minimum energy state. Subsequently, the MD simulations were performed in an isothermal-isobaric (*NPT*) ensemble for 200ps to obtain equilibrium configurations, in which the temperature (300 K) and pressure (zero) were controlled by the Nosé-Hoover thermostat and barostat, respectively. Then, we performed deformation-controlled uniaxial tension or compression tests along z-axis which is perpendicular to graphene layers in the structure. Finally, unloading processes were performed by setting the deformation direction to the opposite. The pressure components (P_{zz}) perpendicular to the loading directions were controlled to be zero to simulate the uniaxial loading condition. The temperature was fixed at 300 K. The strain rate was set as 0.001 ps^{-1} [51] and the strain increments were applied every 1000 time steps. During the simulations, the engineering stress was evaluated by the pressure component P_{zz}. The engineering strain was calculated by $\varepsilon = |(L\text{-}L_0)/L_0|$, where L and L_0 denote the instantaneous and initial length of simulation box in the loading direction (z-axis), respectively. The effective Young's modulus was calculated from the stress-strain curve by linear fitting within a range of small strain. The open visualization tool (OVITO) [53] was used to generate atomistic illustrations.

3. Results and discussion

3.1. Compressive properties

In the first series of MD simulations, the compressive properties of VACNT-graphene structures are investigated. The stress-strain curves and instantaneous structural snapshots are traced in the uniaxial compression/release processes to understand the deformation mechanisms. Fig. 2 illustrates a representative compression/release process of the VACNT-graphene PD25PH17 structure ($d = 25$ Å, $h = 17$ Å). As shown in Fig. 2a, we define three stages in the stress-strain curve based on three different deformation modes during the compression/release process. Meanwhile, the transverse lengths of the simulation box, LX and LY, are displayed in Fig. 2b, which can illustrate the lateral deformations of graphene in the

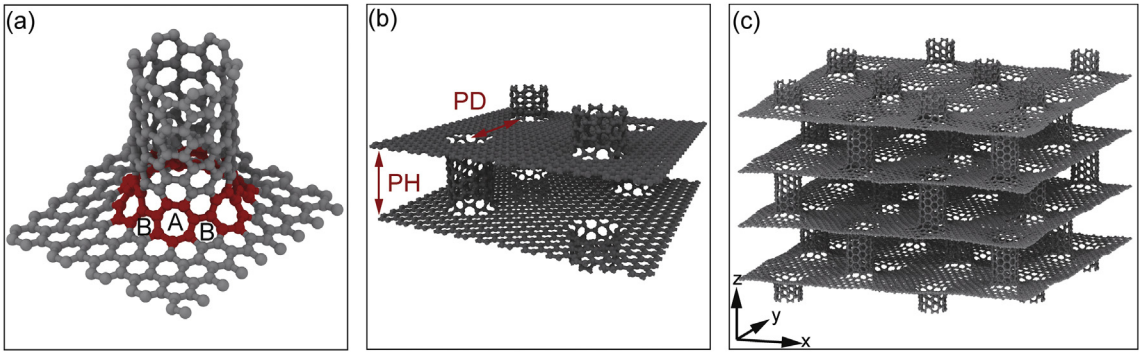

Fig. 1. (a) Junction of (6, 6) CNT and graphene sheet. The red carbon atoms at the joint of CNT and graphene denote the heptagon (A) and hexagon (B) rings. (b) Schematic illustration of unit cell in VACNT-graphene structure. The PD denotes the distance between the center-axis of CNTs. The PH represents the distance between the centers of graphene plane. (c) Typical snapshot of VACNT-graphene consisting of $2 \times 2 \times 2$ building cells. (A colour version of this figure can be viewed online.)