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Effect of geometrical defects on the tensile properties of graphene

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ABSTRACT

The tensile properties of graphene with the Stone-Wales (S–W) defect are investigated by first principle calculations. It is found that the defect will not affect the elastic modulus and Poisson's ratio of graphene but causes the pre-stress of graphene, which makes the graphene to be anisotropic: the deformation along one direction is much easier than that along another direction. The pre-stress field causes only about 10% decrease of the intrinsic stress of graphene but causes more than 50% decrease of the maximum failure strain, which is significantly different with the results calculated by the empirical potential. The main reason is that the pre-stress field created by the S–W defect predicted by first principle calculations is different than that calculated from molecular mechanics simulations. In addition, it is also found that the theoretical solution (on the basis of the continuum disclination dipoles model) of the pre-stress field created by the S–W defect is also different with that determined from MM simulations, which is different from the results of the aligned 7-5 defects of graphene.

1. Introduction

Graphene has attracted extensive research investigations because of its particular electrical, thermal, chemical and mechanical properties [1–7]. The basic building blocks of graphene are the hexagonal rings (6-rings) of the sp^2-bonded carbon atoms located in the same plane. However, in real manufacturing, graphene always includes geometrical defects, such as vacancy [8–10], five- and seven-membered ring pairs (7–5 rings or 7-5 defect) [11,12], Stone-Wales (S–W) defect [13–15], 7-5-5-7 defect [16–18], 5-8-5 defect [16,19], and so on. In addition to the isolated defects, grain boundary (GB) is commonly found in large-area polycrystalline graphene [20,21], which is mainly formed by the connected 7-5 defects [22–24].

Pristine graphene is one of the strongest materials ever measured: having an ultrahigh elastic modulus of ~1 TPa and an intrinsic strength of ~130 GPa [6]. The mechanical properties of polycrystalline graphene have been studied and the highly inconsistent results were reported. Lee et al. [21] reported that the elastic stiffness of polycrystalline is identical to that of pristine graphene and the strength is slightly reduced due to the presence of GBs; whereas Huang et al. [25] and Ruiz-Vargas et al. [26] shown that GBs severely waken the mechanical strength of graphene. Rassol et al. [27] recently found that GB strength is highly sensitive to its mismatch angle in polycrystalline graphene: GBs with a large angle have a comparable strength with single-crystal graphene, whereas GB strength rapidly decreases with the angle.

In addition to experimental works, theoretical and numerical works have also developed to show the GB effect on the strength of polycrystalline graphene [12,13,15,28–39]. Based on molecular dynamics (MD) simulations of bicrystalline graphene, GB strength was firstly considered to be a function of mismatch angle [28,29,38]: GBs with large mismatch angle (with a higher density of 7-5 defects) are much stronger than those with low angle (with a lower density of 7-5 defects), whereas the abnormal cases for armchair-type graphene were then reported [28,29]. It was shown that the distribution/arrangement of defects also affects GB strength due to the coupling effect of stress field created by 7-5 defects, which can be partially canceled with each other for uniformly distributed defects but not for those non-uniformly distributed. Actually, for both uniformly and non-uniformly distributed defects, the GB strength is not directly related to the mismatch angle of GB but depends on the strength of the bond (belongs to one 7-5 defect) with the highest pre-tensile stress component along the loading direction (created by the other 7-5 defects) [28]. Moreover, Grantab et al. [29] reported that the GB strength depends on the initial C–C bond stretching ratio created by 7-5 defects: the higher the bond is per-stretched, the lower the

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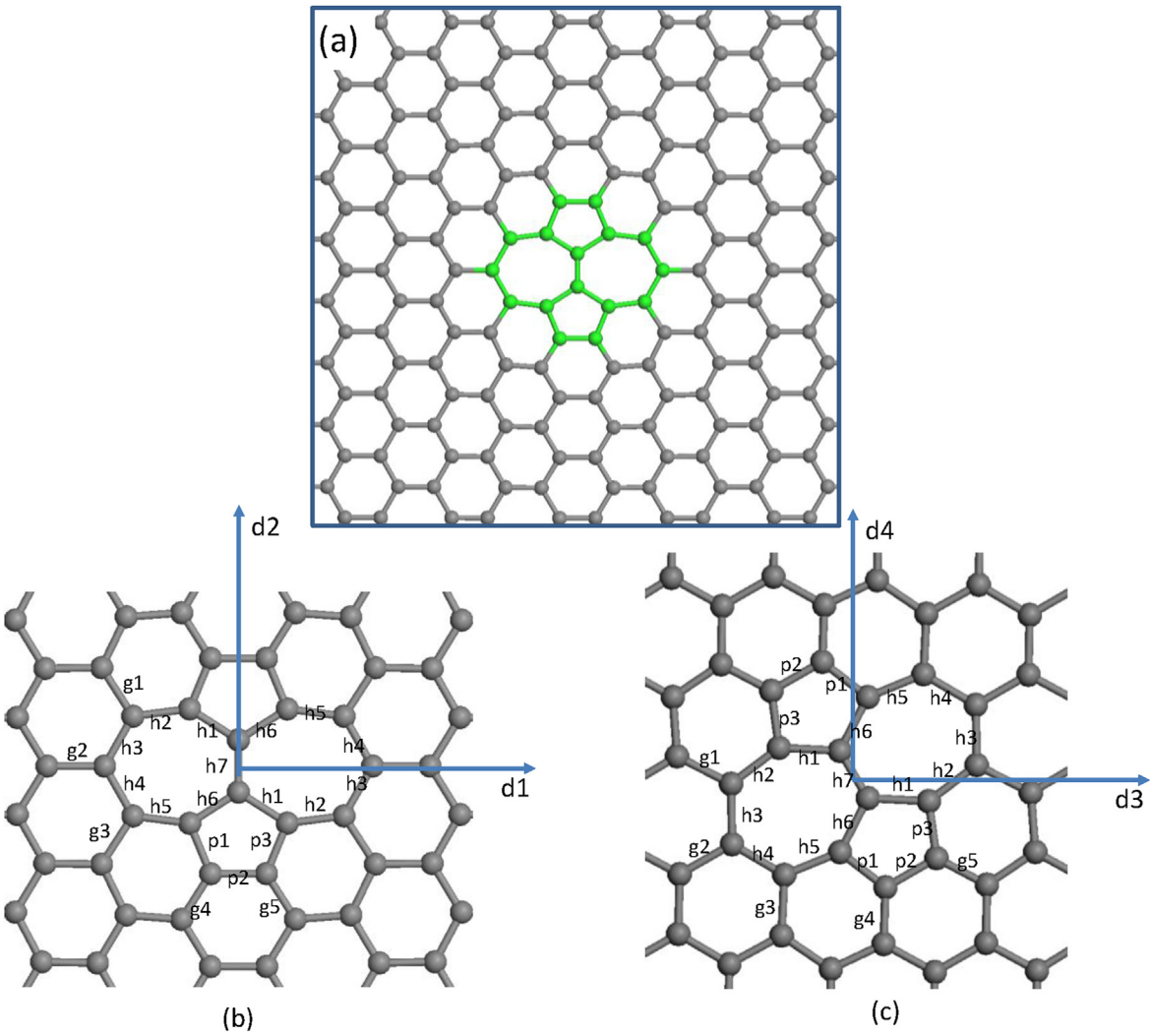

Fig. 1. The computational model of graphene with a S–W defect in DFT calculations. (a) computational cell; (b) *x*-, *y*-axis along d_1, d_2 direction, respectively; (c) *x*-, *y*-axis along d_3, d_4 direction, respectively. The 7-ring includes h1–h7 C–C bonds; the 5-ring includes p1–p3, h1 and h6 bonds. Bonds g1–g5 are in the 6-rings close to the defect. (A colour version of this figure can be viewed online.)

strength.

Most of the aforementioned computational works are based on classic molecular dynamics (MD) simulations, in which the adaptive intermolecular reactive empirical bond-order (AIREBO) potential is used to simulate the mechanical failure of polycrystalline graphene under tension. However, the assumptions taken by the empirical potential might not accurately show the effect of defect on the failure behavior of graphene. For example, it is reported that the empirical potential gives the different values of the elastic modulus and Poisson's ratio of prefect graphene [13,40] as well as its geometrical response under a large tensile load [41,42]. Therefore, a comprehensive study based on first principle calculations is highly necessary to investigate the effect of geometrical defect on the tensile strength and failure strain of graphene, which can provide a useful guideline to understand the GB strength. To the best of our knowledge, this might be the first study to investigate the effect of geometrical defect on the tensile properties (including elastic modulus, intrinsic strength and failure strain) of graphene monolayer by using first principle calculations.

2. Computational methods

In the present study, we investigated the effect of geometrical defects on the tensile strength and failure strain of graphene under the uniaxial/biaxial tension by density functional theory (DFT) calculations, which is performed using the Vienna Ab Initio Simulation Package (VASP) [43,44]. Since the number of atoms in the computational cell calculated by DFT is very low, the boundary effect will strongly affect the effectiveness of the simulation results. In order to use the periodical boundary condition to remove the boundary effect in DFT calculations, a pair of 7-5 defects with the opposite direction connected with each other (also called the S–W defect) are considered in the present work, which are introduced into the computational cell by a S–W bond rotation, as shown in Fig. 1. Fig. 1(b) and (c) show the defect structures obtained from the armchair (ac) and zigzag (zz) graphene, respectively, where d_1 and d_4 are along ac direction, d_2 and d_3 are along zz direction. The uniaxial/biaxial strain tension is applied by increasing the computational cell size along the loading direction. It has been verified that a larger computational cell size produces only a negligible change of the defect formation energy.

The exchange-correlation terms are calculated by the Perdew-Burke-Ernzerh (PBE) generalized gradient approximation (GGA). The computational cell size is 2.4692 × 2.1384 × 1.5 nm, which includes 200 carbon atoms. A Monkhorst-Pack *k*-point mesh grid 2 × 2 × 1 is selected, and the plane wave energy cut-off is set at