Effect of atomic adsorption of catalytic metals on mechanical properties of graphene

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Abstract. The effect of the adsorption of catalytic metal atoms on tensile strength and structural deformation of graphene is examined using the density functional theory. In the case when a line of Ni atoms is adsorbed at hollow sites aligned along zigzag direction of the honeycomb structure, the tensile strength against the uniaxial strain in armchair direction is calculated to be 82.64 GPa, which is 21% smaller than that of the pristine graphene. The reduction of the tensile strength monotonically depends on the line density of Ni. It is predicted that if the stress reaches the tensile strength, the system will undergo a stress-induced structural transformation that involves the breaking of C-C bond adjacent to Ni atoms, the formation of Ni-C bonds and a resultant jump in the strain.

1. Introduction

Graphene, the monolayer graphite sheet, is one of the most promising materials for post-silicon nano-electronics devices and nano-sensors for its characteristic properties [1-3]. The honeycomb structure of graphene is built up of very strong sp² covalent bonding and the π bonding between carbon atoms, thus this thinnest membrane is the most stable allotrope of carbon with extremely high tensile strength along the sheet. In fabrications of nano-sized graphene such as the graphene ribbons, the development of new techniques to perform a cutting as designed in atomic scale are desired and are a challenging problem.

Researchers have experimentally and theoretically investigated the mechanical property of pristine graphene [4-6], and also the graphene with vacancies [7-9] or Stone-Wales defect [8,9]. It has been found that the introduction of defects promotes bond breaking and degrades the tensile strength of the graphene. Similar effects may be expected for catalytic 3d-transition metal atoms, which are known to exhibit strong adsorption to graphene and carbon nanotubes [10,11]. Ci et al. has reported a pioneering study that a Ni nanoparticle can be used to cut graphene in pieces with discrete armchair or zigzag edges [12].

In the present study, we examine the effect of the adsorption of a line of Ni atoms on atomic structures and mechanical properties of graphene using density functional calculations. The total energy, stress and bond lengths are calculated as functions of strain. The calculated tensile strengths and stress-induced structural transformation will be discussed.

2. Methods

The present calculations have been performed on the basis of the density functional theory using the VASP code [13]. The Kohn-Sham wave function is represented in the planewave basis with the
projector augmented wave (PAW) method [14,15]. An optimized cut-off kinetic energy of 400 eV is used for plane-wave basis throughout the present study. The generalized gradient approximation with Perdew-Burke-Ernzerhof functional [16,17] is employed for the exchange-correlation energy. Three kinds of orthorhombic unit cells with different periodicities in $x$ (zigzag) direction are considered in order to examine systematically the effect of adsorption of Ni atoms. Figure 1 shows the initial structures containing one Ni adatom in (a) the eight C atoms unit cell (referred to as Period 1), (b) the sixteen C atoms unit cell (Period 2), and (c) the twenty four C atoms unit cell (Period 3). Along the $c$-axis, a vacuum separation, $Z$ (> 10 Å), that is large enough to eliminate interactions between graphene layers was used in each unit cell. The $k$-points meshes of $18 \times 5 \times 1$, $9 \times 5 \times 1$, and $6 \times 5 \times 1$ are employed in the cases of period 1, 2 and 3, respectively.

Structures are relaxed using the conjugate gradient (CG) algorithm until the interatomic forces are less than 0.05 eV/Å. We first optimized the equilibrium structure with no strain for each unit cell. Then, structural relaxation was performed for given strains starting from the initial structures depicted in figure 1, uniformly expanded only in the $y$ (armchair) direction. The cell size along $x$ direction was kept at the equilibrium value ($\varepsilon_{ex}=0$). Following the commonly used prescription [4], the stress of monolayer graphene is defined by rescaling the supercell stress by $Z/3.34$ Å (interlayer distance of graphite). Tensile strength was determined from the maximum value of the calculated stress.

3. Results and discussions

3.1. Tensile test of graphene with a line of adsorbed Ni: Period 1

Figure 2 shows (a) the calculated stress $\sigma_{yy}$ and total energy, (b) the lengths of C-C bonds adjacent to the Ni atom (denoted as C5-C6) and the distance between the Ni and the nearest C atoms (denoted as C-Ni), (c) the lengths of other C-C bonds in $y$ direction (denoted as C1-C2, C3-C4, C7-C8) versus strain $\varepsilon_{yy}$ in $y$ direction.

As the strain increases from zero, the stress, total energy and C-C bond lengths increase and the stress takes the maximum value at $\varepsilon_{yy}=0.123$, giving the tensile strength of 82.64 GPa. A drastic change takes place on going from $\varepsilon_{yy}=0.127$ to 0.128. We see discontinuous change in figures 2(a) and (b) that the stress and total energy decrease and the C5-C6 bond length increases significantly.
whereas the C-Ni distance shrinks to create C-Ni bonds. Figure 2(c) shows that the other C-C bonds recover the bond length at the equilibrium. Figures 2(d) and (e) visually illustrate the change occurred between $e_{yy}=0.127$ and $0.128$. We see a distinct reduction in bond charges when C5-C6 bonds break to cut the graphene sheet apart. At the same time, the sheet warps so that C atoms move in closer alignment with adjacent Ni atom to create C-Ni bonds and the other stretched C-C bonds in the sheet are virtually relaxed.

It should be noted that this warped structure exhibits a negative stress and therefore it is unstable. The instability however is to be dissolved spontaneously by further increase in the strain, which brings the total energy to the local minimum at $e_{yy}=0.209$, forming a zero stress, metastable planar structure as shown in the figure 2(g). Therefore, a stress-induced structural transformation, in which the line of Ni atoms adsorbed on graphene in zigzag direction cuts into and is embedded in the sheet to form an overstretched structure, will take place when an applied stress reaches the tensile strength. When a further increase in strain is given, C-Ni bonds are to be stretched predominantly as we see in figure 2(b), and the total energy starts to increase again, giving a positive stress. The stiffness in this high strain phase is much weaker than that in the original phase, since the average gradient of the stress around $e_{yy}=0.209$, 0.45 TPa, is nearly a half of the Young's modulus 1.03 TPa around zero strain.

Figure 2. Calculated results for Period 1. (a) The stress $\sigma_{yy}$ and total energy measured from that at zero strain. (b) The C-C bond length adjacent to Ni atom and the distance between a Ni and the nearest C atoms. (c) Lengths of the other C-C bonds in $y$ direction versus strain in the $y$ direction. (d)-(g) illustrate the structure and isosurface (at 0.1 electrons/Å$^3$) of the charge density projected on $x$-$y$ (left) and $z$-$y$ (right) plane, each corresponding to the data points indicated by arrows in panels (a)-(c).
3.2. Tensile test of graphene with a line of adsorbed Ni: Period 2

Next we show the results of calculated tensile test for the case of a halved density of Ni atoms in the line. Figure 3 shows (a) the calculated stress $\sigma_{yy}$ and total energy, (b) the lengths of C5-C6, C13-C14 and C-Ni bonds, (c) the lengths of C1-C2, C3-C4, C7-C8, C9-C10, C11-C12 and C15-C16 bonds versus strain in y direction. The tensile strength in this case is calculated to be 87.62 GPa at $e_{yy}=0.131$, which is slightly higher than in the case of Period 1 reflecting the reduced density of the Ni adatoms.

The optimum structure as a function of the strain exhibits a discontinuous change between $e_{yy}=0.139$ and 0.140, where the stress drops to be negative and C-C bonds adjacent to Ni atom, i.e. C5-C6 and C13-C14, break and the bonding between C and Ni is created as we see in figures 3(a)-(e). The negative stress is to be dissolved spontaneously by flattening the sheet as depicted in figures 3(f) and (g). Thus, in common with the case of the Period 1 model, a stress-induced structural transformation is predicted to occur when an applied stress in the armchair direction reaches the tensile strength. Further increase in the strain causes predominantly a stretching of C-Ni bonds. The stiffness in this high strain phase is 83% of that in the previous case of Period 1, reflecting the less number of C-Ni bonds.
Finally the results of calculated tensile test are shown for the case that Ni atoms are adsorbed on only one in every three hollow sites in the line. Figure 4 shows (a) the calculated stress $\sigma_{yy}$ and total energy, (b) the lengths of C5-C6, C13-C14, C21-C22 and C-Ni bonds, (c) the lengths of C1-C2, C3-C4, C7-C8, C9-C10, C11-C12, C15-C16, C17-C18, C19-C20 and C23-C24 bonds versus strain in the $y$ direction. Tensile strength is evaluated to be 92.05 GPa at $e_{yy}=0.145$. As a function of the strain, the stress shows a steep drop between $e_{yy}=0.147$ and 0.150, but it does not overshoot to negative value, unlike in the previous cases of more Ni atoms. The breaking of C-C bonds along $y$ direction and formation of C-Ni bonds are illustrated in figures 4(d)-(g). When going from $e_{yy}=0.147$ up to 0.148, the Ni adatom comes closer to the graphene plane to create bonds with nearest C atoms, breaking the C-C bonds i.e. C5-C6 and C13-C14, that are adjacent to the Ni adatom. It follows that the remaining C-C bond, i.e., C21-C22, breaks on going from $e_{yy}=0.149$ to 0.150. These calculated results indicate the stress-induced structural transformation that involves the formation of C-Ni bond and successive breaking of the stretched C-C bonds. Further increase in the strain causes predominantly a stretching of C-Ni bonds.
The stiffness in this phase at high strains is only 41% of that in the case of Period 1, reflecting a very low line density of Ni atoms that join the discrete zigzag edges.

**Figure 5.** Comparison of the strain-stress curves for three patterns of Ni-adsorbed and pristine graphene.

3.4. Comparison of tensile strength

Table 1 with figure 5 summarizes tensile strengths for three cases of adsorption patterns we have shown and that for a pristine graphene. It is clearly shown that presence of a line of adsorbed Ni weakens the tensile strength monotonically depending on the line density of Ni. The tensile strength shows decrease by 21.0% (Period 1), 16.2% (Period 2), and 12.0% (Period 3) compared with that for the pristine graphene. The effect is more prominent for higher density of adsorbed Ni atoms in the line. The breaking of C-C bonds adjacent to Ni atom occurs between \( \varepsilon_{yy} = 0.127 \) and \( 0.128 \) (Period 1), \( \varepsilon_{yy} = 0.139 \) and \( 0.140 \) (Period 2), and \( \varepsilon_{yy} = 0.147 \) and \( 0.148 \) (Period 3). Table 1 also shows the predicted strain, which is the result of the jump in strain caused by the predicted stress-induced structural transformation.

**Table 1.** Comparison of the tensile strengths in pristine graphene and each adsorption patterns. In the second column, the strain corresponding to the tensile strength is given. The third column shows the strain at the lowest non-negative stress after the stress-induced structural transformation.

|                  | Tensile strength (GPa) | Strain tensile strength | after structural transformation |
|------------------|------------------------|-------------------------|-------------------------------|
| Ni/Graphene (Period 1) | 82.64                  | 0.123                   | 0.209                         |
| Ni/Graphene (Period 2) | 87.62                  | 0.131                   | 0.185                         |
| Ni/Graphene (Period 3) | 92.05                  | 0.145                   | 0.150                         |
| Pristine graphene  | 104.55                 | 0.189                   | –                             |
4. Conclusions

Using the density functional calculations, we have performed uniaxial tensile tests of the graphene that is modified by adsorption of a line of Ni along zigzag direction. For three different cases of Ni line densities, the structure and total energy, stress and bond lengths are calculated as functions of strain in armchair direction. The calculated tensile strengths exhibited reduction of 21%, compared with that of the pristine graphene, for the case of highest Ni line density.

It is predicted that when the stress reaches the tensile strength, the system will undergo a stress-induced structural transformation, in which the graphene is disjoined to create zigzag cut edges along the line of Ni by the breaking of stretched C-C bonds adjacent to Ni atoms, and at the same time the zigzag cut edges are re-joined by Ni-C bonds. These calculated results should be useful in further understanding and exploring of new techniques for catalyst-assisted cutting of the graphene and graphene-based materials. Simulated tensile test for larger strains is under progress. VESTA [18] was used for visualization of structures and charge density.

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