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# Mechanical properties of hydrogen functionalized graphene under shear deformation: A molecular dynamics study



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## ABSTRACT

Molecular dynamics simulations have been performed to study the mechanical properties of hydrogen functionalized graphene under shear deformation. It is found that the mechanical properties of graphene greatly depend on the coverage percent of hydrogen atoms. It is shown that the shear modulus, shear strength and fracture strain of graphene can be reduced as much as 50% with increasing hydrogen coverage percent up to 30%. It is also revealed that the distribution of hydrogen atoms would significantly influence on the strength and fracture strain of hydrogen functionalized graphene under shear deformation.

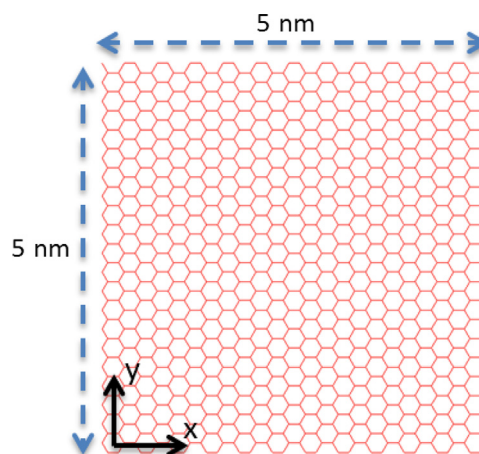
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## 1. Introduction

Graphene-based materials have been attracted much attention due to their exceptional and interesting electronic and thermal properties [1–3]. They have potential for use as chemical sensors because of their extraordinary sensitivity [4]. In addition to electronic, thermal and chemical properties, the mechanical properties of graphene-based materials are also of fundamental and crucial importance. Recent measurements and theoretical studies revealed that Young's modulus of single layer graphene is around 1 TPa [5]. It is also newly shown that shear modulus of single layer graphene film grown on copper is about 280 GPa [6]. These measurements are consistent with theoretical evaluations and predictions from recently carried out simulations [7–10]. These findings suggest graphene-based materials ideal alternatives for nanomechanical applications.

Since tuning mechanical properties of graphene is of great importance in designing and fabrication of nanomechanical systems, there are ongoing scientific works focusing on modification of mechanical properties of graphene by chemical functionalization [7,11,12]. Recent studies have shown that hydrogen functionalization can strongly influence on the mechanical properties of graphene as well as its electronic, chemical and thermal properties [11–16]. The hydrogen functionalized graphene has recently been proposed as a stable structure with interesting properties and

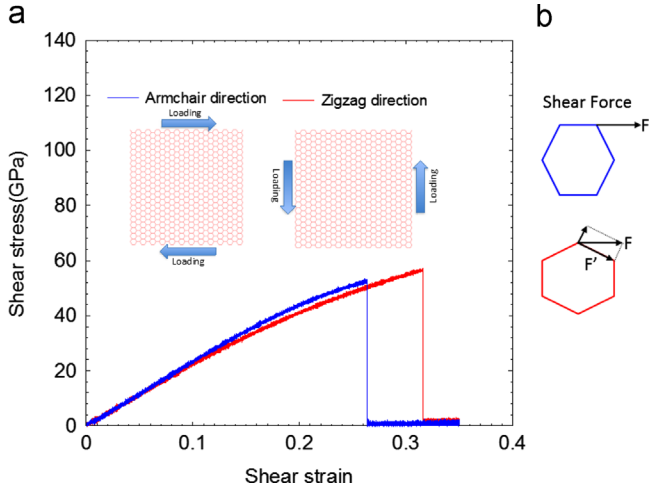
experimentally synthesized by selectively hydrogenating graphene sheets [17]. Therefore, investigation of its mechanical properties would be of potential interest for further applications in nanomechanical systems. Pei et al. have investigated the effect of hydrogen functionalization on mechanical properties of graphene under tensile loading using molecular dynamics simulation [7]. They have shown that Young's modulus, tensile strength and fracture strain of the functionalized graphene decrease with increasing hydrogen coverage percent.



**Fig. 1.** (Color online) Graphene sheet with periodic boundary conditions in both *x* and *y* directions.

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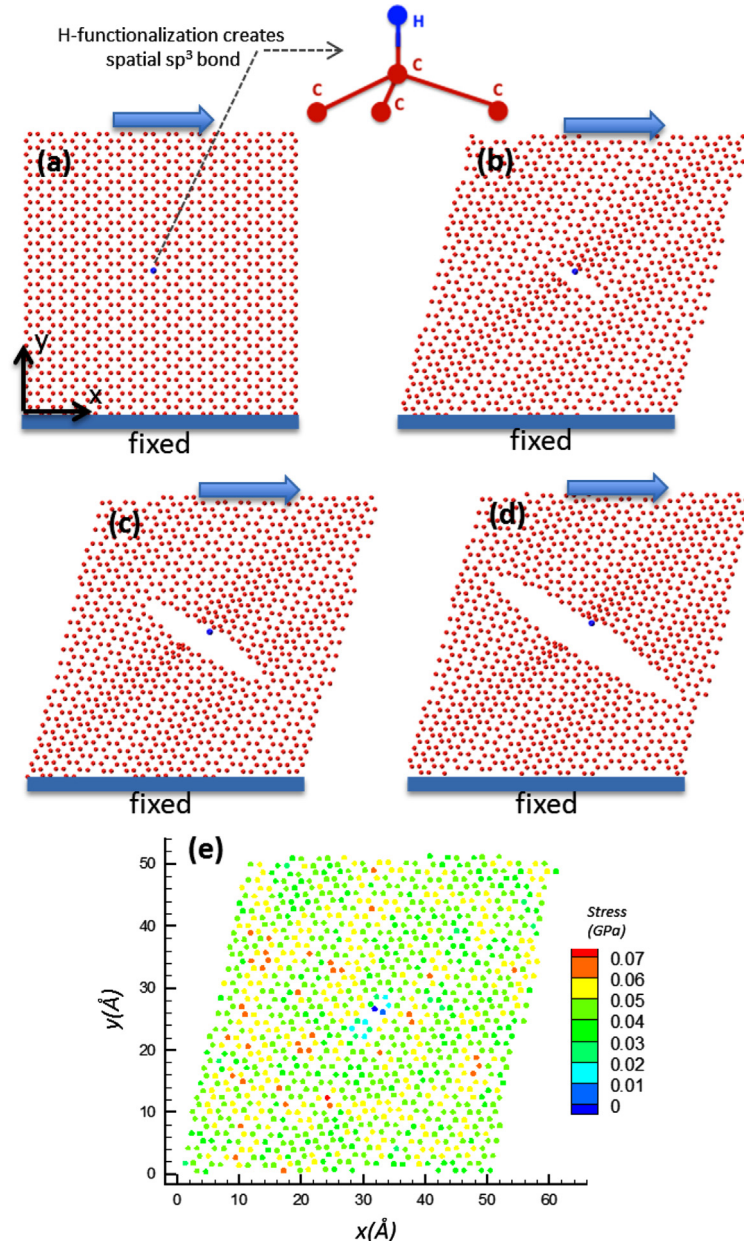


**Fig. 2.** (Color online) (a) The stress–strain curve for pristine graphene under shear loading in armchair and zigzag directions and (b) vector analysis of applied shear force in armchair and zigzag directions.

In this paper using molecular dynamics simulation we investigate the effect of hydrogen functionalization on shear modulus, shear strength and fracture strain of graphene which are important for understanding the advantages and disadvantages of hydrogen functionalized graphene as a nanomechanical material. It is shown that hydrogen coverage (H-coverage) can reduce the shear modulus, shear strength and fracture strain of graphene up to 50%. We also show that the distribution of H-coverage can significantly influence the mechanical properties of graphene.

## 2. Simulation method

All simulations are carried out with LAMMPS package, using adaptive intermolecular reactive bond order (AIREBO) potential which is a suitable potential function for simulation of C–C and C–H bonding interactions [18,19]. Equations of motions are integrated using velocity Verlet algorithm with a time step of 1 fs. The simulated graphene consists of 1008 carbon atoms with a size of 5 nm × 5 nm with periodic boundary conditions applied along two



**Fig. 3.** (Color online) (a–d) Snapshots of functionalized graphene with one attached hydrogen atom (blue-colored) under shear loading, (e) the color plot of the stress distribution when the fracture process started.

planar “x” and “y” directions as schematically shown in Fig. 1. The system is initially relaxed using Nose–Hoover thermostat and barostat to the temperature of 300 K and zero initial stress, respectively. An engineering strain rate of  $0.001 \text{ ps}^{-1}$  is applied along x (y) direction which means the graphene is going under loading in armchair (zigzag) direction. During the loading, the temperature of system is controlled around 300 K and no barostat controlling is applied. The simulation box is continuously deformed using “fix deform” command in LAMMPS and atoms are allowed to move freely in “y” direction due to the periodic boundary condition.

In atomic level, the stress is computed according to the virial theorem [20] as

$$\sigma_{ij} = \frac{1}{V} \sum_{\alpha=1}^N \left( \frac{1}{2} \sum_{\beta=1}^N r_{\alpha\beta}^i F_{\alpha\beta}^j - m^\alpha v_i^\alpha v_j^\alpha \right) \quad (1)$$

where  $ij$  are Cartesian coordinates and  $\alpha$  and  $\beta$  are atom index numbers.  $m$  and  $v$  denotes to the mass and velocity of atom  $\alpha$ .  $r_{\alpha\beta}$  and  $F_{\alpha\beta}$  are respectively the distance and force between two atoms with index of  $\alpha$  and  $\beta$ .  $V$  is also the total volume of the system with thickness of 0.34 nm and with number of total atoms  $N$ .

### 2.1. Determination of shear modulus

Fig. 2(a) shows the stress–strain curve of simulated pristine graphene under shear loading in both armchair and zigzag directions. The shear modulus  $G$ , shear strength  $\tau$  and fracture strain  $\epsilon_f$  can be obtained from the stress–strain curve. The  $G$  is obtained from the linear portion of the curve from zero to 0.01 strain. The  $\tau$  and  $\epsilon_f$  are corresponding values of stress and strain in the curve when it suddenly drops due to the rupture. The shear modulus for armchair and zigzag directions obtained almost the same value since it is a measure of the average deformation of the system in the small strain regime. However, the shear strength and fracture strain are greater for zigzag graphene than those for armchair one. This is because in zigzag graphene there is no C–C bond parallel to the loading direction, while in armchair graphene, some C–C bonds exist. As shown in Fig. 2(b), by a simple vector analysis and decomposition of applied shear forces, it can be found that the applied force in direction of C–C bond of zigzag graphene ( $F'$ ) is less than that of armchair graphene ( $F$ ).

The averaged value of  $G$  for armchair and zigzag directions is 290 GPa. It shows that shear modulus of pristine graphene is high compared to other common materials as well as its tensile properties. In order to validate our results we have found that our predicted shear modulus of graphene is in good agreement with the experimental value of 280 GPa and simulation value of 284 GPa which have been recently reported [6,8].

## 3. Results and discussions

To study the effect of hydrogen functionalization on the mechanical properties of graphene under shear loading, at first a hydrogen atom is attached to the graphene as shown in Fig. 3. When the loading is applied, it is clearly shown that the fracture in graphene occurs exactly in the placement of attached hydrogen atom wherein the planar  $sp^2$  hybridization changes into a spatial  $sp^3$  one. Fig. 3(e) shows a color plot of the stress distribution when the fracture process started. It is shown that the stresses at some other atom places are also high, but the fracture started from the location of attached hydrogen atom that has the weakest C–C bonds. When these bonds are ruptured, then the created defect in graphene leads to rupture other bonds as shown in Fig. 3(a)–(d).

We then increase the number of hydrogen atoms and compute the shear modulus, the shear strength and the fracture strain of

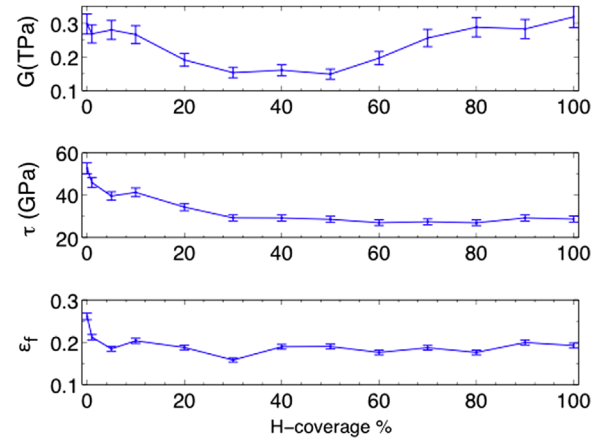


Fig. 4. (Color online) Shear modulus ( $G$ ), Shear strength ( $\tau$ ) and fracture strain ( $\epsilon_f$ ) of hydrogen functionalized graphene in armchair direction versus H-coverage percent.

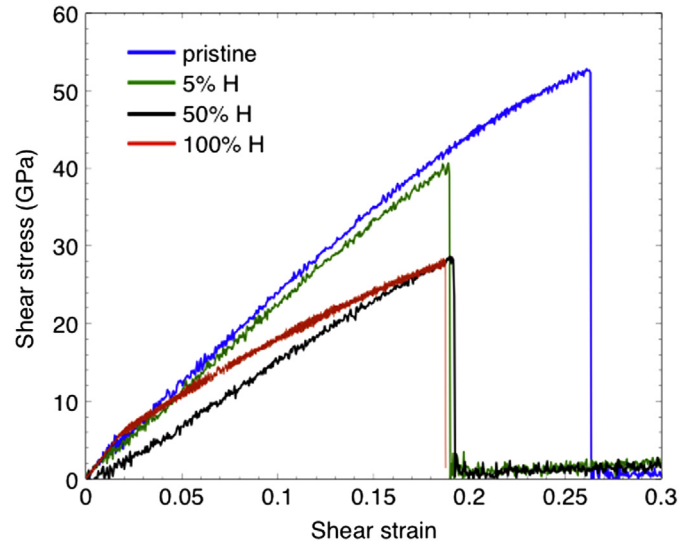


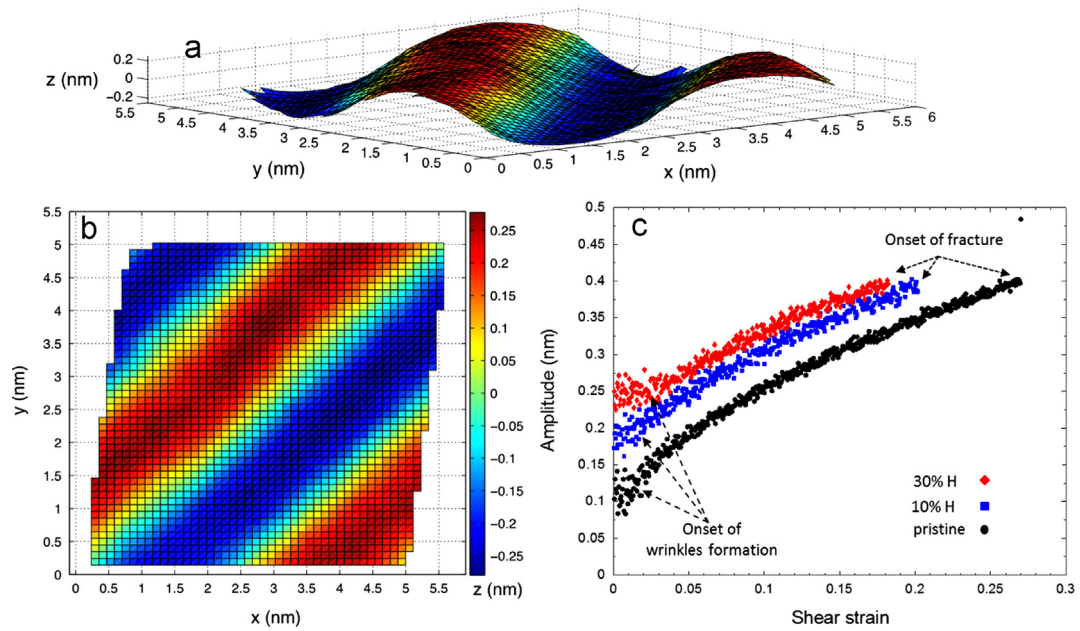
Fig. 5. (Color online) Stress–strain curve for hydrogen functionalized graphene for different percent of H-coverage.

the system. The results are presented in Figs. 4 and 5 for applied loading in armchair direction. As it is shown the shear modulus of graphene is decreased gradually by increasing H-coverage percent up to 50%. Further increase in the H-coverage leads to increase in the shear modulus since the calculated shear stress–strain curve shows a bifurcation behavior for a shear strain of around 0.02 [8]. The shear strength and fracture strain also decrease with increasing H-coverage up to around 30% and 10%, respectively.

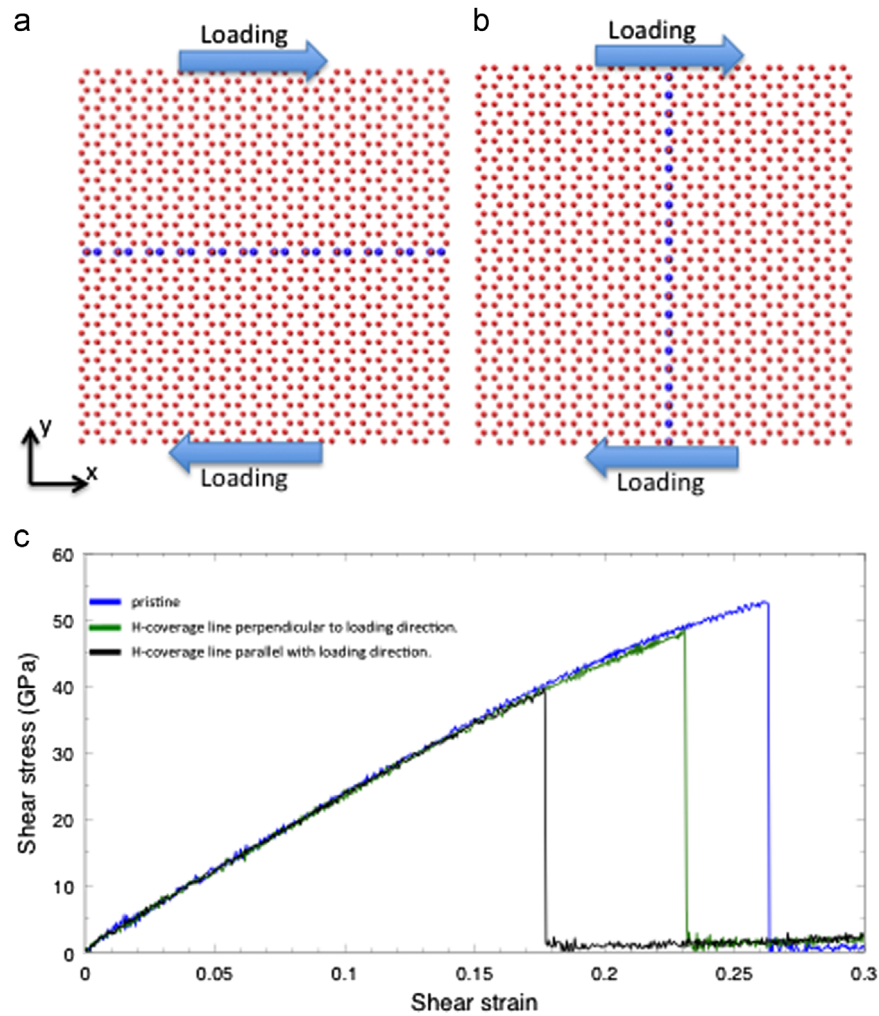
It is worth mentioning that during shear loading wrinkles occurred in graphene as shown in Fig. 6(a) and (b) [21,22]. It is found that the average amplitude of wrinkles is larger in hydrogen functionalized graphene as shown in Fig. 6(c). However, the onset of wrinkle formation and corresponding wavelength are insensitive to hydrogen functionalization percent.

In the above-mentioned results, the H atoms were distributed randomly on the graphene surface. In order to investigate the effect of distribution of H-coverage on the mechanical properties of graphene under shear loading, two different distributions of H-coverage are considered as shown in Fig. 7. The H-coverage in first distribution is parallel to loading direction (Fig. 7(a)) and the second distribution is perpendicular to loading direction (Fig. 7(b)). The shear stress–strain curve is then calculated when the shear loading is applied. As Fig. 7(c) shows, the shear strength in the





**Fig. 6.** (Color online) (a) and (b) Formation of wrinkle in graphene and the corresponding vertical profile of wrinkle at 0.13 strain value, (c) wrinkle amplitude for different percent of H-coverage.



**Fig. 7.** (Color online) Hydrogen functionalized graphene with H-coverage line parallel with loading direction (a) and perpendicular to loading direction (b) and the stress–strain curves for both cases are plotted (c).

parallel case is much smaller than that in the perpendicular case. However, the shear modulus is insensitive to the distribution of H-coverage because it is calculated in small strain regime and it is an averaged value over all bond deformations. The same effect for hydrogen functionalized graphene under tensile loading was observed in reference [12].

#### 4. Conclusion

In conclusion, using molecular dynamics simulation we have calculated the mechanical properties of hydrogen functionalized graphene under shear loading. We have found that H-coverage can reduce the shear modulus, shear strength and shear fracture strain of functionalized graphene. However, the shear modulus will gradually increase for H-coverage larger than 50%. It is also found that the distribution of H-coverage is an important factor in tuning the strength of hydrogen functionalized graphene. Tuning the mechanical properties of graphene-based materials is a key-role parameter in designing and fabrication of nanomechanical systems.

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