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グラフェン上へのガス吸着特性に及ぼすひずみの影響：第一原理解析
Effect of Strain on the Gas Adsorption of Graphene: A First Principle Study

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The graphene based gas sensor was proposed as the next generation sensor which have the high sensitivity to detect gases with concentration smaller than 1 p.p.m, along with fast response time and low thermal noise. At the same time, the strain effect on graphene have been studied in detail. In this research, the topic "Strain effect on gas adsorption of graphene" was proposed and it is one potential to find a new way to further enhance the sensitivity and help build selectivity for graphene based gas sensor. The first principle calculation was applied and the analysis of band structure, charge transfer under strain and adsorption condition was studied.

Key Words : Graphene, Adsorption, Strain, First-Principle

1. Introduction

Graphene is an ideal material for use as the channel material in field-effect transistor (FET) devices because of its flatness (high surface to volume ratio), high mobility charge carriers and ballistic transport at the micron level. Those properties are essential for making gas sensors with excellent sensitivity. In previous researches, NO_2, NH_3, H_2O , and CO in concentrations of 1 part per million (p.p.m.) have been shown to be detectable by graphene based FET. [1] It is reported even single molecular adsorption could be detected. And the graphene based gas sensor made by Fujitsu Laboratories Ltd. is able to detect concentrations lower than tens of parts per billion (ppb) of nitrogen dioxide (NO2), which has improved sensitivity more than tenfold. [2] However, the flat graphene is inert to chemical reaction and gas molecules are binding to the surface by physisorption, which is confirmed by first-principles calculations. [3] [4]

On the other hand, graphene is also sensitive to strain. The applied tensile strain in graphene changes the band structure and its density of states. [5] Some researchers reveal that the physical adsorption of molecules on waved graphene is greatly enhanced by compression, using first-principle calculation based on the density functional theory (DFT). [6] In reference 6, the author has stated that elevated chemical potential and strain energy at high local curvature locations (crest and trough of waved graphene) can strongly accelerate activity in chemical reactions (such as catalytic performance) and promote sensitivity in molecule adsorption. Therefore, the effect of tensile strain on flat graphene is expected to affect the adsorption of gas molecules according to those reports. In this research, we focused on a bare graphene with gas molecules put on stable initial positions, which were reported to have the more stable adsorption state among different geometries of gas molecules above graphene sheet. [3]

2. Model and Methodology

The properties of adsorption on graphene were studied by using density functional theory (DFT) [7] [8] with generalized gradient approximation (GGA) of the Perdew - Wang91 (PW91) [9] functional implemented by using the Cambridge
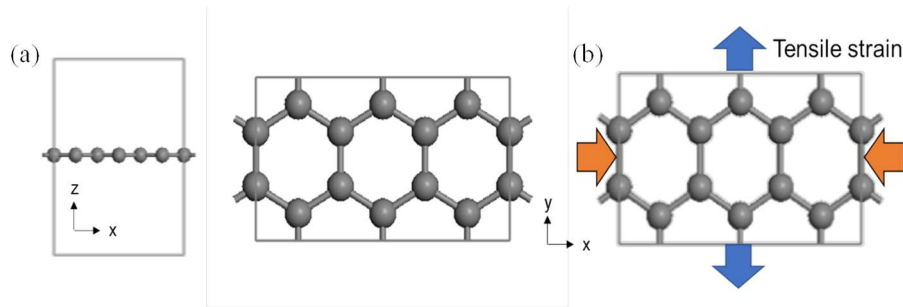
Figure 1(a). The side view and top view of bare graphene. (b). The strain is applied and the structure shrinks after geometry
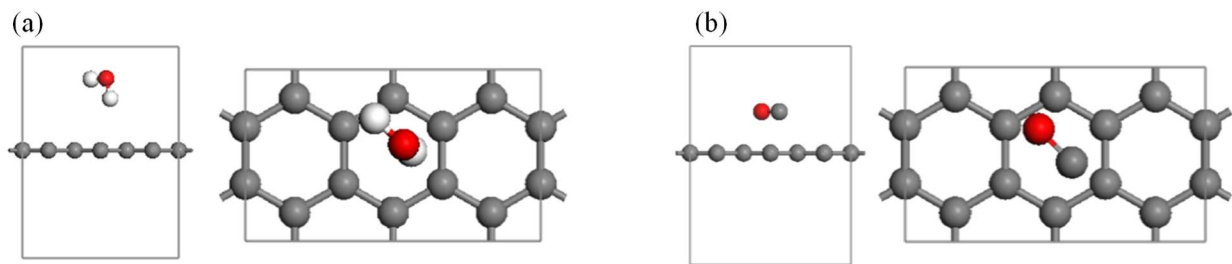

Figure 2(a). The water molecule initial position. (b). The CO molecule initial position

Sequential Total Energy Package (CASTEP) code [10]. Ultra-soft pseudopotential [11] was used to represent the ionic cores. The total energy minimization is performed using convergence tests that include lattice relaxation, energy convergence and k convergence to obtain a stable structure in the ground state. The crystal structures were geometrically optimized using Broyden-Fletcher-Goldfarb-Shanno [BFGS] [12] method with fixed basis quality as in CASTEP.   Total energy is converged to 1×10^{-6} eV and the forces per atom were reduced to 1×10^{-5} eV. The calculations were carried out in the irreducible Brillouin zone with $3 \times 6 \times 2$ k point mesh for geometry optimization and $5 \times 8 \times 1$ k point mesh for Density of States (DOS) calculation with Monkhorst-pack scheme [13]. Kinetic energy plane wave cut off is set at 340 eV for all models. A finite strain is applied to the optimized structure.

The periodic condition was set in x-y plane, in figure 1, and only the atoms in box circled by dashed line were considered. The total number of carbon atoms is 12 in bare graphene. The tensile strain was applied constantly in y direction while the structure was fully-relaxed.

NH3, H2O and CO molecules are put above the hollow of six membrane respectively, represented in figure 2. The gas molecule find its best position after geometry optimization. After the application of strain at each step, the geometry optimization was conducted to investigate the distance change from gas molecules to graphene substrate.

The CO in box was also calculated by deleting the molecules in model in figure 2 to obtain its free energy. Finally, the adsorption energy was calculated by using the formula:

$$E_{\text{ad}} = E_{molecule\ adsorbed\ on\ graphene} - E_{graphene} - E_{molecule} \tag{1}$$

When three energy was obtained as negative value, the negative E_{ad} indicated that adsorption occurs on this system. The smaller the value of E_{ad} indicated more stable adsorption and if the value becomes positive, the gas molecule would no longer be adsorbed on graphene.

3.   Results and discussion

Firstly, the strain effect on DOS was observed, the DOS shrinks to fermi-level as the strain increased. The DOS in HOMO (below the fermi-level), which is close to fermi-level, would have the most possibility to affect the adsorption property of graphene. The peaks shift closer to the fermi-level is observed as well. Therefore, for acceptor molecules such as H2O, the
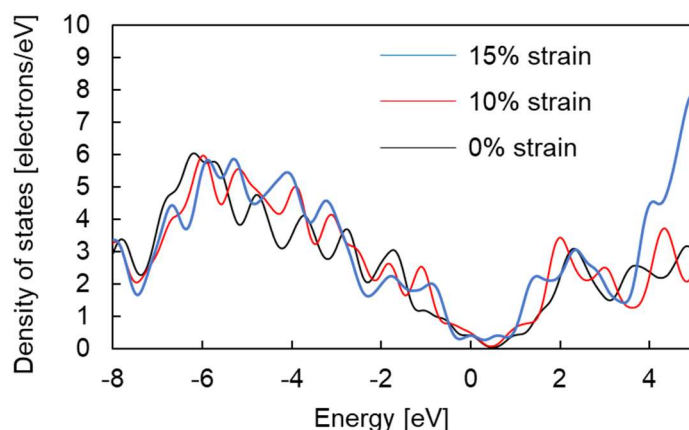
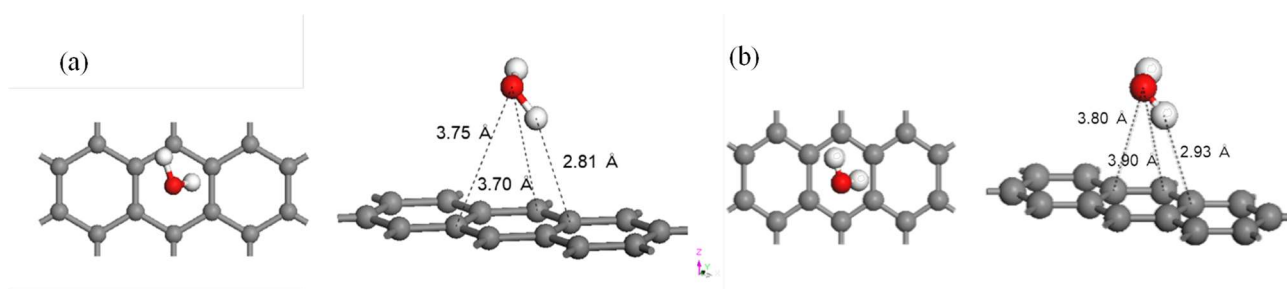Figure 3. The Density of states of bare graphene under strain

Figure 4(a). The optimized structure with H_2O adsorbed on graphene under 0% strain.
(b). The optimized structure with H_2O adsorbed on graphene under 15% strain.

Table 1. The adsorption energy of gas molecules under strain up to 15%

	strain		
	0%	10%	15%
CO	-27.0	-21.9	-17.7
H_2O	-41.2	-16.2	-8.3
NH_3	24.6	23.9	

charge transfer was expected to be easier after applying strain to graphene substrate. The calculated adsorption energies of CO, H_2O and NH_3 on the graphene surface were summarized in table 1. The values of adsorption energy indicated that the adsorption of CO, and H_2O molecules were physical adsorption and NH3 was hard to be adsorbed on a graphene surface. Figure 4(a) shows the adsorption structure of H_2O on the graphene surface after relaxation. The distance between H_2O and the graphene surface was up to 3.70 Å, indicating there was no chemical adsorption between H_2O and the graphene surface. The adsorption energies of CO, CH_4 and H_2O on the graphene surface was increased by applying 10% tensile strain to the graphene. In particular, the adsorption of H_2O behaved relatively large strain dependence. Figure 4(b) shows the adsorption structure of H_2O on the graphene surface with 15% tensile strain. The distance between H_2O and the graphene surface with 15% tensile strain became longer than that in normal graphene surface, indicating the tensile strain should induce desorption of H_2O molecule. These results clearly revealed that the adsorption properties of CO and H_2O change with the tensile strain of graphene, and therefore, it is possible to control the adsorption properties of gas molecules on graphene by applying external tensile strain to a graphene sheet.

4. Conclusion

Firstly, the smooth increasing in free energy indicates a non-cracking stretch under 20% for graphene sheet. Secondly, The DOS in HOMO (below the fermi-level) which is close to fermi-level would affect the charge transfer property of graphene. The peak shift closer to fermi-level is observed as well. Therefore, for acceptor molecules, the charge transfer was expected to be easier after applying strain to graphene substrate. Finally, the adsorption energy increasing indicates the strain will induce desorption of water molecule.

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