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Adsorption of Hydrogen Molecule on the Intrinsic and Al-doped Graphene:A first Principle Study

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Abstract. The adsorption hydrogen molecule on intrinsic and Al-doped graphene was studied by density functional theory calculations. The results show that the intrinsic graphene is not an ideal hydrogen storage material. Compared with the intrinsic, H_2 molecules are stongly adsorbed onto the Al-doped graphene with higher adsorbed energy and shorter distance between H_2 and surface. The band structure and density of states results show that between hydrogen and other atoms, the charge transfers are apparent increased. All are help for hydrogen adsorption. Therefore, Al-doped graphene is a promising candidate for hydrogen storage material.

Introduction

Among alternative energy sources such as solar batteries and fuel cells, hydrogen is an especially promising candidate technology to meet increasing demands for alternatives to environmentally harmful effects of fossil fuel as well as to meet the growing demand for energy. But, how to store hydrogen has become the primary and hot issue. Adsorption is divided into physisorption and chemisorption. The former one is easy to desorbed, which is not helpful hydrogen storage. The latter one is too strong to desorb easily. It is necessary to seek one effective way for hydrogen storage. One of the most promising materials suggested as a potential hydrogen storage media is carbon-based material such as carbon nanotube, fullerenes, and graphene which have a high surface area, thermal stability and easy improvable adsorption capacity by suitable method[1-2]. Among them, graphene has had the focus of research because of its structural, chemical, and electronic properties. Graphene is a planar layer exfoliated from graphite. It was reported that the storage capacity of graphene has been enhanced by doping with lithium and other alkali elements[3]. The alkali atoms seem to have a catalytic effect in dissociating the H_2 molecule and promoting atomic adsorption. Metal-adsorbed graphene also showed very good results [4].in hydrogen storage. In this paper, we report our study on the absorptions of H_2 molecules on surfaces of intrinsic and Al-doped graphene .

Computational method

The calculations are performed using the CASTEP code, which is a plane-wave, pseudo potential program based on density functional theory (DFT).Generalized gradient approximation (GGA) function with the Perdew–Burke–Ernzerhof (PBE) correction is used for the structure optimizations and corresponding total energy calculations of the most stable geometries. A plane-wave basis with a cut-off energy of 280 eV, the K-point is set to 3×3×1.Firstly, we have studied an isolated graphene sheet. Since the computer code uses a periodic supercell method, the cell axis has to be large in the $z-$direction to avoid the interaction between graphene sheets in different cells. Fig.1 gives the calculated energy of the graphene layer as a function of the length c of the unit cell in the $z-$direction. The results show that when $c \geq 14$ À, the energy is well converged for those layer separations. Therefore, $c = 16$ À. The 3×3 intrinsic graphene is shown in Fig.2. the lateral distancce between H_2 molecules of at least 7.4À to eliminate interaction between H_2 molecules in neighboring supercells.

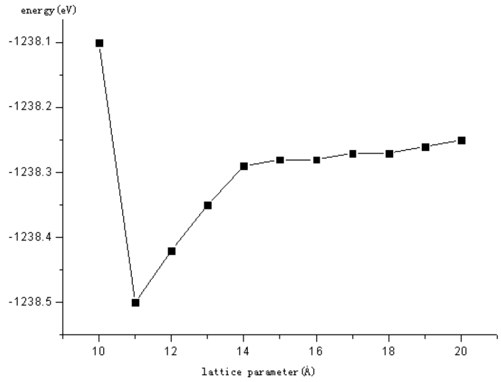

Fig.1. Energy and crystal lattice constant

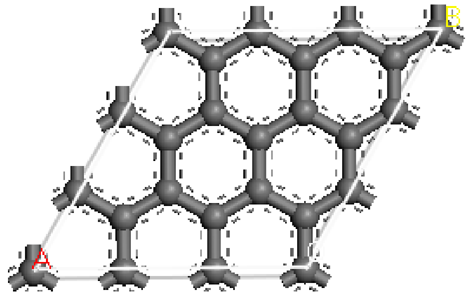

Fig.2. The structure model of graphene

Results and discussion

Stability and geometric structure

We have studied the intrinsic graphene adsorbed system. The optimized structural is shown in Fig.3., the length of C-C bonds are 1.42À which aren't changed. But, the distances of hydrogen molecules and graphene sheets are changed obviously before and after optimizing, which elongate from 1.453À to3.151À and are far more than the length of C-C bonds, indicating that the weak binding between graphene and hydrogen molecules. We also considered several adsorption configurations of hydrogen on graphene surface, including upright, parallel, and angle. Calculated results show that the H_2 molecules prefer the hollow sites above the centers of hexagons, as well as parallel to graphene sheet. Because the background electron density is lower than in channels on top of the skeleton of carbon-carbon bonds. The exchange-correlation contribution provides the weak attraction responsible for physisorption[5] So, we have predicted the adsorption of the H_2 molecule on intrinsic graphene sheet is physisorption.

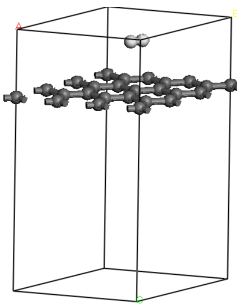

Fig.3. The intrinsic graphene adsorbed syste

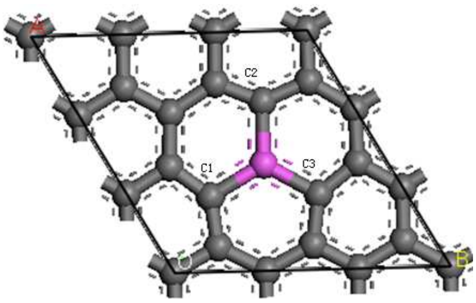

Fig.4. Optimized configurations of Al-dopedgraphene, the atoms around the center (Al) atom are labeled as C1,C2,C3,gray and pink spheres are denoted as C and Al, respectively.

On the other hand, we have studied Al-doped adsorbed system. Its optimized structure is shown in Fig.4. The bonds around the center C (Al) atom are labeled as C1, C2 and C3, when the geometry of graphene is fully relaxed; the Al-C bond length after the Al atom doping is calculated to be1.67À which is larger than the C-C bond length of 1.42À. This is in quite good agreement with Ao's results [6].

Adsorption Energy

To evaluate the interaction between a H_2 molecule and adsorption sheet surface, we have calculated the adsorption energy (E_{ad}) of adsorbed systems, which is defined as

$$E_{ad} = E_{(g+H)_2} - E_g - E_{H_2}$$

Where the $E_{(g+H)}$, E_g and E_{H_2} denote the total energy of intrinsic or Al-doped graphene adsorbed system, isolated graphene or Al-doped graphene and a H_2 molecule, respectively.We also calculated the adsorption energy of (5,5) SWNT in same way. The results are shown in Tab.1

Table 1. Graphene, (5,5) SWNT, adsorb hydrogen molecular

E_{ad}(eV)		Distance(À)	
graphene	(5,5)SWNT	graphene	(5,5)SWNT
0.022	0,032	3.15	2.40

No matter graphene or CNTs, the adsorption energy is range from 0.022eV to 0.032 eV. This is in quite good agreement with Pham Tien Lam's results (0.026 eV)[7].With the increasing of the surface curvature, the adsorption energy also increase. Tab.1 shows the result. Because the surface curvature of CNTS is larger than graphene, the proportion of sp3 and sp2 hybridization is greater. There are more empty P orbital. So, more and more electron of H_2 transfers to the empty P orbital. It enhances the interaction between material and H_2. In any case, the interaction between hydrogen molecule and carbon materials is too weak compared with ideal hydrogen storage materials (0.2 eV~0.4 eV)[8]. Hydrogen molecules and graphene, SWNT surfaces is mainly driven by Van der Waals force. The absorbed hydrogen molecule cannot remain. Therefore, intrinsic graphene is not ideal hydrogen storage materials.

Table 2. The adsorption energy of intrinsic and Al-doped graphene

	E_{ad}(eV)		Distance(À)	
	intrinsic	Al-doped	intrinsic	Al-doped
graphene	0.022	0.294	3.151	1.803

Tab.2 gives the adsorption energy and distance of Al-doped graphene and intrinsic graphene, the former adsorption energy has increased by one order compared with the latter one. Furthermore, the distance of Al-doped grahene is shorter than intrinsic. We predict the adsorption of the hydrogen molecule on intrinsic graphene sheet is chemisorptions. So, doping is one of the most promising methods to increase the adsorption energy and hydrogen storage.

The Energy Band and Densities of States

In an attempt to understand the hydrogen adsorption behavior in graphene, analysis of the electronic properties of Al and H_2 dispersed on graphene with hydrogen adsorption is essential.The band structure of Al-doped graphene (a) and partial density of state (PDOS) for Al(b) are shown in Fig.5 Because Al3+ replaces C4+ after doping Al, systems become Electron-deficient structure. Some impurity level appears near Fermi level. And, Fermi level enter into the valence band after doping (Fig.5 a). Form PDOS (Fig.5.b), we can see impurity levels are mainly composed of 3p electrons of Al (red line), a little 3s electrons (blue line). Near Fermi level, Al 3p electrons compose acceptor levels. The acceptor levels near Femi level induce increase of the charge transfer between H_2 molecule and graphene. Therefore, the blind reaction between H_2 molecule and graphene are enhanced. Doping is good for hydrogen storage.

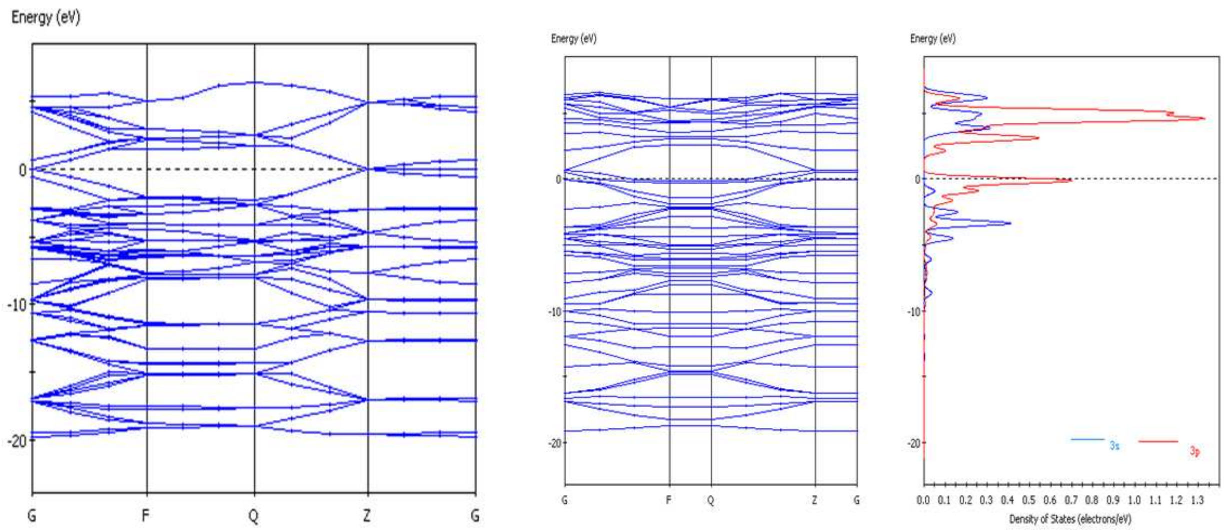

Fig.5.The band structures and partial density of state (PDOS) for Al of intrinsic (a) and Al-doped graphene (b)

Summary

In summary, with DFT calculations, the adsorptions of H_2 on the intrinsic and Al-doped graphene are studied. The former one is physisorption. Desorption of H_2 is so easy. Therefore, intrinsic graphene is not good for hydrogen storage. Compared with the intrinsic, H_2 molecules are stongly adsorbed onto the Al-doped graphene with higher adsorbed energy and shorter distance between H_2 and surface. The band structure and density of states results show that between hydrogen and other atoms, the charge transfers are apparent increased. All are help for hydrogen adsorption. Therefore, Al-doped graphene is a promising candidate for hydrogen storage material.

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