Al doped graphene: A promising material for hydrogen storage at room temperature

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Abstract:

A promising material for hydrogen storage at room temperature–Al doped graphene was proposed theoretically by using density functional theory calculation. Hydrogen storage capacity of 5.13 wt% was predicted at T = 300 K and P = 0.1 Gpa with adsorption energy $E_b = -0.260 \text{ eV/H}_2$. This is close to the target of 6 wt% and satisfies the requirement of immobilization hydrogen with E_b of $-0.2 \sim -0.4 \text{ eV/H}_2$ at ambient temperature and modest pressure for commercial applications specified by U.S. Department of Energy. It is believed that the doped Al varies the electronic structures of both C and H₂. The bands of H₂ overlapping with those of Al and C synchronously are the underlying mechanism of hydrogen storage capacity enhancement.

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I. INTRODUCTION

In recent years, hydrogen-based fuel systems have been considered to be a highly important topic of research for future energy schemes as hydrogen is a more efficient fuel in comparison to the existing carbonaceous fossil fuels. ^{1,2} Despite many recent technological developments in the hydrogen-based fuel systems, it is still an enormous challenge to have a safe and efficient reversible hydrogen storage systems at ambient conditions.² One of the possible ways for such storage is the efficient hydrogen adsorption/desorption in a controllable system. Carbon based materials are candidates for such a purpose. Although several mechanisms of hydrogen storage through both physisorption and chemisorption have been proposed,³⁻⁷ most of these efforts are far to reach the target of 6 wt% and immobilization hydrogen with binding strength of -0.2 ~ - 0.4 eV/H₂ at ambient temperature and modest pressure for commercial applications specified by U.S. Department of Energy (DOE).

With density functional theory (DFT) simulations, it was predicted that a single ethylene molecule can form a stable complex with two transition metals, thus adsorbing ten H₂ molecules and lead to a high storage capacity of ~14 wt%.⁸ In addition, the highest H₂ storage capacity of 13 wt% in a fullerene cage with twelve Li atoms capped onto the pentagonal faces was calculated.⁹ This system has average adsorption energy $E_{\rm b} = -0.075$ eV/H₂. However, all the DFT results are in the ideal condition at the temperature of T = 0 K, their performances at the DOE specified operation conditions are unclear.

Since carbon nanostructures have high surface areas, and thermal stability along with unique mechanical properties, improvement of their adsorption capacity by suitable modification would be of immense interest.³⁻⁹ Thus, the storage of hydrogen molecules

by carbon nanostructures is still an important issue and deserves more attention. For example, the potential of graphene as hydrogen storage materials through doping is investigated. The advantages of graphene are: (1) a large surface for hydrogen adsorption, (2) economical and scalable production,¹⁰ and (3) the strongest material ever measured.¹¹

On the other hand, the prospect of AlH₃ and related aluminum hydrides as hydrogen storage materials have recently become the focus of renewed interest ^{12,13} as their potentially large hydrogen capacity of ~10 wt%. These materials are thermodynamically unstable in ambient, but it is kinetically stable without much lost of hydrogen for years. However, extremely high hydrogen pressure (exceeding 2.5 GPa) is required to load up the hydrogen. While these hydrides possess a small negative enthalpy of formation,¹³ for practical applications there remains the critical issue of a large hydrogen removal energy that hinders the H-desorption process. The origin of this energy barrier lies in the rather strong mixed ionic and covalent bonds ¹³ formed between Al and H. In order for AlH₃ to become a feasible H-storage material, it is essential to develop a technique to significantly reduce the hydrogen removal energy and thus enable a controllable kinetics for hydrogen desorption.

However, there is another way for metallic atoms to storage hydrogen, which is further decreasing the interaction between Al and H. In this way, the weak chemisorption can be changed into strong physisorption. For physisorption of hydrogen storage, it requires a strong interaction between H_2 molecule and the materials on the surface with an area as large as possible. These superior characteristics of graphene and Al for hydrogen storage lead to an attempt of Al doped graphene to consolidate these advantages and to see whether graphene can take the role to weaken the interaction between Al and H or Al can take the role to enhance the adsorption of H_2 on graphene. In this work, the adsorption behavior of H_2 in Al doped graphene was studied by DFT calculation. In addition, we processed the *ab initio* molecular dynamics (MD) calculation to investigate the effects of temperature and pressure on the corresponding adsorption and desorption abilities of this system on hydrogen storage system.

II. CALCULATION METHODOLOGY

All DFT calculations are performed in Dmol³ code.¹⁴ Previous studies ^{15,16} have shown that the local density approximation (LDA) prediction of the physisorption energies of H₂ on the surface of graphite and carbon nanotubes are in good agreement with experiments. The reliability of LDA can be ascribed to the following facts:¹⁵ (1) When the electron densities of H₂ and graphene overlap weakly, the nonlinearity of the exchange-correlation energy density functional produces an attractive interaction even in the absence of electron density redistribution; (2) The overestimated binding energy by LDA ^{17,18} may compensate for the insufficient account of van der Waals interactions.¹⁵ In contrast, DFT calculation using a uniform generalized gradient approximation (GGA) produced a purely repulsive interaction. Using a GGA-PW91 functional, a repulsive interaction between H₂ and a graphene layer and also between H₂ and a (6,6) carbon nanotube was obtained.¹⁹ This contradicts the experimental findings.²⁰ It was noted that LDA calculations well reproduce the empirical interaction potentials between graphitic layers and also in the other graphitic systems for distances near to the equilibrium separation although the LDA is not able to reproduce the long-range dispersion interaction.²¹ Therefore, LDA is used to implement the task of this work. To ensure the calculated results being comparable, the identical conditions are employed for the isolated H₂ molecules and the graphene, and also the adsorbed graphene system. The *k*-point is set to $6\times6\times2$ for all slabs, which brings out the convergence tolerance of energy of 1.0×10^{-5} hartree (1 hartree = 27.2114 eV), and that of maximum force is 0.002 hartree/Å.

In the simulation, three-dimensional periodic boundary condition is taken and H–H bond length is set to $l_{\rm H-H} = 0.74$ Å, which is consistent with the experimental results.²² The graphene used in our simulation consist of a single layer of 3×3 supercell with a vacuum width of 12 Å to minimize the interlayer interaction. Further increasing of the vacuum width has only negligible consequence on the simulated results but is great at the expense of computation. All atoms are allowed to relax in all energy calculations. The adsorption energy $E_{\rm b}$ between the H₂ gas molecule and graphene is defined as,

$$E_{\rm b} = E_{\rm H2+graphene} - (E_{\rm graphene} + E_{\rm H2}) \tag{1}$$

where the subscripts H_2 +graphene, graphene, and H_2 denote the adsorbed system, isolated graphene and H_2 molecules, respectively.

For the Al doped graphene, the concentration of Al is 12.5 at% with the additional constraining that there is only one Al atom per graphene hexagonal ring (Fig. 1) to avoid the doped metal Al atoms clustering on graphene.²³ For H₂ adsorption on the Al doped graphene, there are 4 top sites of T1, T2, T3 and T4, and 3 bridge sites of B1, B2 and B3, and 2 center sites of C1 and C2, as shown in Fig. 1. (In this figure, a larger simulation cell is given in order to better display the different adsorption sites on the Al doped graphene. In actual simulation, the simulation cell is taken as large as Fig. 2.) At each adsorption site, there are two highly symmetrical adsorption configurations, namely H₂ molecule resides parallel or perpendicular to the graphene surface. Therefore, together 18

adsorption configurations for H₂ adsorbed on the Al doped graphene are present.

Due to the periodicity of H_2 adsorbed in intrinsic graphene or Al doped graphene systems, we have selected a unit cell with eight C atoms and one H_2 or seven C atoms, one Al atom and one H_2 (see Fig. 2). If we place a H_2 at any location of the cell, the distance from this H_2 to other H_2 molecules in the nearest cells is 4.920 Å. This large separation, compared to the bond length of H_2 (0.740 Å), would ensure that there is no interaction between H_2 molecules in the different cells.²⁴

To measure H₂ adsorption capability of Al doped graphene at room temperature and modest pressure, we performed *ab initio* MD calculation with CASTEP (Cambridge Sequential Total Energy Package) code based on the structure obtained by DFT above, which utilizes plane-wave pseudopotential to perform first principle quantum mechanics calculations.²⁵ LDA with the Ceperley-Alder-Perdew-Zunger (CAPZ) function ^{26,27} was employed as exchange-correlation functions, cutoff energy $E_c = 280$ eV and *k*-points is $6\times6\times2$. Each MD simulation was performed in *NPT* statistical ensemble, i.e. constant numbers of atoms *N*, pressure *P* and *T*, with T = 300 K and $P = 0.0001 \sim 1$ GPa. Time step of 1 *fs* was selected and simulation time *t* at a particular *T* was 2.5 *ps* where the total energy fluctuation was in the range of 0.01%. The same *t* was selected for H₂S dissociation on the Fe(110) surface.²⁸ A Verlet algorithm ²⁹ was used to integrate the equations of motion, with *T* controlled by algorithm of Nose,³⁰ and *P* was controlled according to the Parrinello-Raham algorithm.³¹

III. RESULTS AND DISCUSSION

After geometry relaxation, E_b values and the corresponding structure parameters of the 18 adsorption configurations for H₂ adsorbed in the intrinsic graphene are listed in Table 1. It was found that the most favorable configuration is H₂ adsorbed on the center site of the carbon ring with $E_b = -0.159$ eV as shown in Fig. 2(a) and the distance between H₂ and the graphene d = 2.635 Å. The results are consistent with other reported results of $E_b = -0.133$ eV and $d \approx 2.8$ Å.¹⁶ The small magnitude of E_b shows that the system is in the weak physisorption region. It indicates that the intrinsic graphene is not suitable for hydrogen storage.

For the adsorption of H₂ in the Al doped graphene, the corresponding results are also listed in Table 1. In light of Table 1, the most favorable position with $E_b = -0.427$ eV for the H₂ molecule is shown in Fig. 2(b). The distance between H₂ and the doped Al, l =2.083 Å while that between H₂ and carbon layer, d = 2.073 Å. As seen from Table 1, the interaction reaches the strongest when both *l* and *d* are minimized. The adsorption of H₂ in the Al doped graphene is much larger than that in other systems, such as $E_b = -0.41$ eV/H_2 in Ti-C₂H₄-graphene system,⁸ and $E_b = -0.08 eV/H_2$ in 12-Li-doped fullerene.⁹ However, it still belongs to the physisorption system as the long distance between the doped graphene and the adsorbed H₂. Therefore, this strong physisorption interaction would be ideal for hydrogen storage, which can adsorb more H₂ molecules.

To understand the enhancement effect of the doped Al on the H₂ adsorption, the projected electronic density of states (PDOS) of the adsorbed H₂, the doped Al and the C atoms in both H₂/graphene and H₂/Al-doped-graphene systems are plotted and shown in Fig. 3. Fig. 3(a) shows the PDOS of H₂/graphene system. The main peaks of H₂ are located at -4.37 eV and 6.92 eV. However, the main peaks of intrinsic graphene are located between 9 and 13 eV. Therefore, the interaction between H₂ molecule and the intrinsic graphene is very weak because of non-overlapping of electrons in these

substances, where E_b is small. On the other hand, for the H₂/Al-doped-graphene system shown in Fig. 3(b), the main peaks of H₂ are located at -8.15 eV, 5.74 eV, 6.52 eV, and 7.51 eV, respectively. The bands of H₂ interact with both the doped Al and the C atoms synchronously at the positions indicated by the dash lines, showing a strong interaction between H₂ and the Al doped graphene where E_b is the largest. In addition, the doped Al changes the electronic structures of both H₂ and the graphene, and both their PDOSs shift towards the lower energy. It exhibits that the H₂/Al-doped-graphene configuration is a much more stable system.

Table 2 shows the charge distribution in both the H₂/graphene and H₂/Al-dopedgraphene systems using Mulliken analysis. Before and after H₂ adsorption, the charge variation for the former is little while it is significant for the latter. In addition, H6 has much more positive charge than H5. Thus, the interaction between H₂ and the Al doped graphene is mainly achieved through H6. The interaction between the band at the location of the highest peak of PDOS plot of H₂ and that of C atoms implies a strong interaction between the H₂ and C atoms, as shown in Fig. 3(b).

The illustrations of electron density distribution for the H₂/graphene and H₂/Aldoped-graphene systems are shown in Fig. 4. In the system of H₂/graphene [Fig. 4(a)], no electron exists in the region between H₂ and C layer while some electrons appear in the region among H₂, Al atom and C layer in the system of H₂/Al-doped-graphene [Fig. 4(b)]. This supports the notion that the H₂/Al-doped-graphene possesses a much stronger H₂ adsorption ability.

After understanding the mechanism of the enhancement for H_2 adsorption in the Al doped graphene, it is important to determine how much H_2 molecules can be adsorbed on

the 3×3 layer surface. We constructed an adsorption configuration with 3 H₂ molecules adsorbed in the three favorable C1 adsorption positions on the topside of the doped system. After geometry relaxation, the atomic structure is shown in Fig. 5(a). It has $E_b = -$ 0.303 eV/H₂, which satisfies the requirement of $E_b = -0.20 \sim -0.40$ eV/H₂ at room temperature ³⁻⁶ set by DOE although the value of 5.1 wt% of H₂ adsorbed is slightly below the DOE's 6 wt% target.

In order to understand the effect of the adsorbed H_2 molecule number on the E_b , the configuration with 6 H_2 molecules adsorbed in the Al doped graphene in the favorable C1 adsorption positions on both sides was calculated. It is found that $E_b = -0.164 \text{ eV}/H_2$, which is much smaller than the E_b for the above case where the Al doped graphene adsorbed 3 H_2 on one side of graphene. In addition, the adsorption with 8 H_2 molecules in the Al doped graphene was also calculated, and it is found 2 H_2 molecules were released. In the other words, the interaction between H_2 molecules would weaken the adsorption and the saturated number of H_2 molecules adsorption is 6.

It is well known that *T* and *P* have essential effects on hydrogen storage, where increasing *P* and decreasing *T* enhance the capacity of hydrogen storage. Thus, most studied systems are either under high *P* or at very low T,²⁰ which may not be viable for mobile applications. For example, a storage capacity of 8 wt% for purified single wall carbon nanotubes (SWNTs) at 80 K with a hydrogen pressure of 13 MPa ³² and a lower hydrogen storage capacity of 2.3 wt% at 77 K were reported.³³ The hydrogen storage capacities in other carbon related materials, such as activated carbon (AC), single walled carbon nanohorn, SWNTs, and graphite nanofibers (GNFs) were also investigated.³⁴ Although the AC had a capacity of 5.7 wt% at 77 K with P = 3 MPa, its capacity is < 1%

at 300 K.34 Recent experimental results demonstrated that the intrinsic graphene has hydrogen storage capacity of 1.7 wt% under 1 atm at 77 K, and 3 wt% under 100 atm at 298 K.35 Thus, to meet the DOE target, it is necessary to study the adsorption and desorption behaviors of H₂ in the Al doped graphene at T = 300 K with different P. Therefore, the adsorption behaviors of 3H₂/Al-doped-graphene and 6H₂/Al-dopedgraphene systems were calculated under 0.0001, 0.01, 0.1 and 1 GPa using ab initio MD simulation. For both the $3H_2/Al$ -doped-graphene and $6H_2/Al$ -doped-graphene systems, we found that all H₂ molecules were released at 0.0001 GPa [Fig. 5(c)]. However, there was only one H₂ molecule adsorbed in both the systems at 0.01 GPa, while the structure of the doped graphene was completely destroyed with H and Al forming covalent bond at 1 GPa [Fig. 5(d)]. When P = 0.1 GPa, there are three H₂ left on the top side of the two Al doped systems [Fig. 5(b)]. Therefore, the Al doped graphene for hydrogen storage capacity at room temperature and 0.1 GPa is 5.13 wt% with $E_b = -0.260 \text{ eV/H}_2$, satisfying the requirements of actual application. In addition, all the adsorbed H_2 molecules can be released when P = 0.0001 GPa.

IV. CONCLUSION

In conclusion, the adsorption behaviors of H_2 in the intrinsic and Al doped graphene were studied using DFT. It is found that the physisorption of H_2 is greatly enhanced by doping Al into graphene. The doped Al varies the electronic structures of both C and H_2 , causing the bands of H_2 overlapping with those of Al and C synchronously. It induces an intensive interaction between H_2 and the Al doped graphene. This was also demonstrated by the electron density distribution. In order to understand the temperature and pressure effects on the H₂ adsorption behavior for actual application, *ab initio* MD calculations for H₂/Al-doped-graphene system were processed. It is found that the system has 5.13 wt% hydrogen storage ability at T = 300 K with P = 0.1 GPa. Therefore, the Al doped graphene would be a promising hydrogen storage material owing to the strong interaction between H₂ and the Al doped graphene.

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Table 1. Summary of results for H_2 adsorption on intrinsic graphene and Al doped graphene on different adsorption sites. For H_2 adsorption on intrinsic graphene, there are 6 different adsorption sites as listed in the table. For H_2 adsorption on Al doped graphene, there are 18 different adsorption configurations as shown in Fig. 1.

Initial binding configuration		Intrinsic graphene		Al doped graphene		
		$E_{\rm b}~({\rm eV})$	d (Å) ^b	$E_{\rm b}({\rm eV})$	$l(\text{\AA})^{a}$	$d (\text{\AA})^{\text{b}}$
H ₂ //graphene	T1	-0.136	2.845	-0.209	2.762	
	T2			-0.34	2.526	2.682
	T3			-0.407	2.588	2.486
	T4			-0.361	2.942	2.537
	B1	-0.139	2.817	-0.21	2.757	
	B2			-0.411	2.527	2.575
	B3			-0.411	2.506	2.563
	C1	-0.159	2.635	-0.427	2.083	2.073
	C2			-0.188		2.657
H₂⊥graphene	T1	-0.141	2.615	-0.153	2.622	
	T2			-0.284	2.427	2.749
	Т3			-0.406	2.367	2.524
	T4			-0.33	2.976	2.179
	B1	-0.142	2.620	-0.206	2.271	3.732
	B2			-0.412	2.468	2.595
	B3			-0.426	3.196	2.074
	C1	-0.148	2.425	-0.426	2.092	2.104
	C2			-0.24	3.117	2.468

a. Distance between Al and H₂.

b. Distance between H₂ molecule and graphene or Al doped graphene layer.

Table 2. Charges of atoms in H_2 adsorbed in graphene system as well as charge transfer Q between graphene and H_2 molecule, obtained by Mulliken analyse. The unit of the atom charge is one electron charge e, which is elided here for clarity.

Atom	intrinsic graphene	Al doped graphene		
Al1(C1)	0.001	0.292		
C2	-0.002	-0.228		
C3	0	-0.193		
C4	0	-0.193		
H5	-0.001	-0.001		
H6	-0.001	0.021		
Q	-0.002	0.019		

Captions:

FIG. 1. Nine different adsorption sites on Al doped graphene. The gray and pink balls are respectively C and Al atoms.

FIG. 2. The favorite adsorption configurations with 1 H_2 molecule adsorbed in intrinsic graphene (a), and in Al doped graphene (b). The gray and pink balls have the same meaning in Fig. 1, and the white balls are H atoms.

FIG. 3. The projected electronic density of states (PDOS) of adsorbed H_2 , doped Al and graphene for both the H_2 /graphene and H_2 /Al-doped-graphene systems as shown in panel (a) and panel (b), respectively. Fermi level is set to 0.

FIG. 4. Electron density distributions in the H₂/graphene [panel (a)] and H₂/Al-dopedgraphene [panel (b)] systems.

FIG. 5. Atomic configurations $3H_2/Al$ -doped-graphene system at different temperature and pressure. (a) In the ideal condition with T = 0 K, (b) in the condition with T = 300 K and P = 0.1 GPa, (c) in the condition with T = 300 K and P = 0.0001 GPa, and (d) in the condition with T = 300 K and P = 1 GPa.



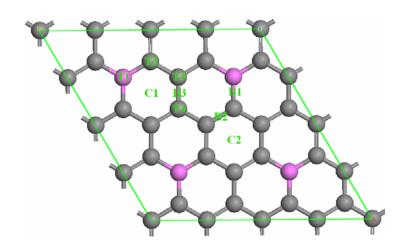


FIG. 2

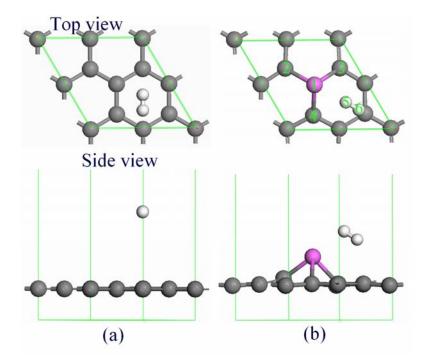


FIG. 3

