Theoretical study of H₂ adsorption on metal-doped graphene sheets with nitrogen-substituted defects

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ABSTRACT: In the present work, we perform a theoretical study of light metal (Li, Na, and Ca) doping and H₂ adsorption on graphene sheets with N-substituted defects. Through density functional theory calculations, the adsorption energies, density of states, and extent of charge transfer in systems featuring H₂ adsorption on metal-doped species (ideal, pyridinic, and pyrrolic graphene sheets) are obtained, and we determine that both N and metal atoms play important roles in H₂ adsorption. In addition, molecular dynamics simulations are employed to evaluate the nature of H₂ adsorption at room temperature. All computational results indicated that Ca-doped pyrrolic graphene could be expected as a promising candidate for H₂ storage.

KEYWORDS: defective graphene, N substitution, metal doping, H₂ adsorption, density functional theory, molecular dynamics

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1. Introduction

As an ideal carrier of energy, H₂ has attracted considerable attention because of its merits of being clean, renewable, abundant, and having a high energy density. Nevertheless, the automotive applications of this energy carrier are limited because it is difficult to store both safely and economically. To realize the extensive commercialization of H₂, in recent years, many scientific researchers have attempted to overcome this bottleneck.[1-3] Unfortunately, to the best of our knowledge, in spite of several theoretical works,[4, 5] no materials for H₂ storage experimentally meet the requirements for practical application set by the U.S. DOE,[6] that is, 5.5 wt% in gravimetric density and 40 g/L in volumetric density under ambient temperatures and safe operating pressure (≤ 100 bar). Therefore, it is essential to identify new materials that are capable of storing H₂ for hydrogen-powered vehicles.

In the laboratory and even in industry, graphene and its derivatives have been widely applied to design new functional materials. For example, graphene-based structures have been functionalized as gas storage media,[7-9] gas purification membranes,[10-12] and materials for the electrodes in batteries [13-15]. For H₂ storage, experimental studies show that few-layer graphene can store 3.0 wt% H₂ at 298 K,[16] whereas single-layer graphene has achieved only 0.2 wt% H₂ uptake at 290 K and 60 bar[17], and 0.9 wt % H₂ at room temperature. [18] These differences can be attributed to the weak interaction between the graphene sheet and the H₂ on single-layer graphene and the stronger interaction between the sheet and the H₂ that is located on the interlamination of few-layer samples. Differences in storage ability can also arise from variations in the morphology of graphene[19], atoms-doping[20], vacancy[21] and other inconsistencies among experimental methods. Regardless of the variations in methodology, the H₂ adsorption capacities of graphene under ambient temperatures are too low for practical

applications. Recent theoretical works have unambiguously explained the poor capacity for H₂ adsorption on monolayer graphene, that is, the adsorption energy (E_{ad}) of H₂ on graphene is only approximately 5 kJ/mol,[22-24] which is far from the suggested E_{ad} (20~40 kJ/mol or 0.2~0.4 eV/molecule) for practical application.[25] Therefore, enhancing the E_{ad} of H₂ on graphene could improve the uptake of H₂ at room temperature.

The most common method to enhance the adsorption energy of H₂ on carbon materials is the introduction of defects or heteroatoms. Previous experimental and theoretical studies have, without exception, demonstrated that metal doping can enhance H₂ uptake.[4, 9, 26-28] Nevertheless, the low binding energy for metal atoms on carbon structures and the overly strong interaction between transition metals and H₂ both greatly affect H₂ adsorption. For light metal doping, for instance, with Li, the weak binding energy on graphene will lead to a well-known metal clustering problem.[29] When doping with transition metals, these heavy metal atoms will increase the total mass of the host materials, hence reducing the gravimetric density of H₂. Moreover, the very high E_{ad} of H₂ around transition metals can cause H₂ to dissociate and can influence the dynamics of H₂ during the process of release.[30] Thus, dispersing light metals on a graphene surface and strengthening their binding to the surface would be promising methods for improving H₂ storage.

Pioneering theoretical works have demonstrated that B or N substitution on graphene, porous graphene, and carbon nanotubes can increase the binding energies of metals, and these substituted materials have been further tested as H₂ storage media.[31-35] In particular, metal decoration on N-substituted graphene (M@N-graphene) can enhance H₂ adsorption.[36-38] Unfortunately, the H₂ capacities of these materials cannot fully satisfy what is demanded for the portable utilization of practical hydrogen storage devices. For example, the E_{ad} of H₂ on Li@N-

graphene is in the range of 0.12~0.20 eV/H₂,[36] however, only the E_{ad} of the first adsorbed H₂ molecule meets the minimum demand (0.20 eV) for practical application.[25] Even for Pd-doped N-graphene, the 1.99 wt% H₂ uptake found by experiments and calculations [37, 38] is still far from the DOE target.[6]

In this study, we suggest that the theoretical studies examining high performance H₂ storage materials should be based on the structures obtained from experiments. Interestingly, using hydrothermal or chemical vapor deposition methods, N-substituted defective graphene (including pyridinic and pyrrolic) can be easily synthesized.[39, 40] To further explore H₂ adsorption on N-doped graphene sheets, pyridinic and pyrrolic graphene containing N-edge defects, named PIG and PRG, respectively, are considered and displayed in **Fig. 1**. Ideal graphene (IG) is also studied for comparison. In terms of metal doping, Li, Ca, and Na are chosen. In addition to the use of density functional theory (DFT) calculations of geometric and electronic properties to reveal the H₂ adsorption mechanism, molecular dynamics (MD) simulations are performed to examine the thermal stability of the structures and evaluate the capacity for H₂ adsorption under realistic conditions.

Fig. 1 — (a) Graphene (IG) and its N-substituted defective structures, (b) PIG and (c) PRG.

2. Computational methods

All calculations in this work were performed using Vienna Ab-initio Simulation Package.[41] To precisely describe the weak dispersion interactions, the Grimme DFT-D2 dispersion correction method[42] was employed. To explore thermal stabilities, we examined the geometries at ambient temperatures from first-principles MD simulations, in which Nosé's algorithm was used to control the temperature and atomic motion for 4.5 ps with a time step of 1.5 fs. Ion-electron interaction was described with the projected augmented wave[43, 44] method and the Perdew-Burke-Ernzerhof exchange correlation functional was used in the generalized gradient approximation. The k -mesh grids were $5 \times 5 \times 1$, and the supercell size was 5×5 based on IG structure. The vacuum space was set to 20 Å, which was sufficiently large to avoid the interaction of periodic images. Numerical calculations were accomplished with the following criteria: the convergence thresholds were set to 10^{-5} eV of energy and 10^{-2} eV/Å of force with a cutoff energy of 500 eV.

The average binding energy of metal atoms on host materials is defined as $E_b = (E_{M-G} - E_G - mE_M)$, where E_{M-G} , E_G , and E_M represent the total energies of the metal-loaded graphene-based structure, pristine graphene-based structure, and metal atom, respectively, and m is the number of metal atoms. Similarly, the average adsorption energies of H_2 on the metal-loaded host materials are calculated with the equation $E_{ad} = (E_{nH_2@M-G} - E_{M-G} - nE_{H_2})/n$, where $E_{nH_2@M-G}$ and E_{H_2} are the total energies of the H_2 -adsorbed structure and the single H_2 molecule, respectively, and n is the number of adsorbed H_2 molecules.

3. Results and Discussion

3.1 Metal doping

The graphene and its N-substituted models with defects are built by simplifying a real sample with local defects containing pyrrolic or pyridinic N (**Fig. 1**). The optimized lattice parameters of 5×5 supercells are 14.81 Å, 14.80 Å, 14.79 Å, respectively for IG, PIG and PRG, which means that the N-edged defects do not change the layered geometry of the graphene sheet.

As mentioned above, the aggregation of doped metals has negative effects on the ensuing H₂ adsorption, and it is expected that the N-edged defects could enhance the binding of the metals and prevent them from clustering. Therefore, two metal atoms adsorbed on either side of IG, PIG and PRG are optimized and displayed in **Fig. S1 in the Supplementary Material**.[†] The metal atoms are found to be located above the center of a hexagonal ring on IG, which is consistent with the literature.[45] For PIG and PRG, metal atoms are located at both sides of defected sites, as determined in previous theoretical works.[46, 47] In fact, we demonstrate that the N-substituted vacancies are electron-deficient sites that can attract the electrons of electron-rich metals, causing strong interactions.[46]

In **Table 1**, we present the binding energy of metals on IG, PIG, and PRG. Obviously, the E_b of each of the three metals are greatly increased on graphene sheets with N-edged defects, with E_b that are much higher than the corresponding cohesive energies of the metals, which are 1.63 eV, 1.13 eV and 1.84 eV for Li, Na and Ca, respectively.[48] These data indicate that the aggregation of metals (Li, Na and Ca) can be avoided on PIG or PRG surfaces, thereby enhancing the capacity for H₂ storage. Interestingly, the E_b of Ca on PRG is higher than that on PIG, which is most likely the result of the reconstituted pentacyclic ring in PRG. This energy difference can also be explained by an analysis of the local density of states (DOS) of metals and their neighboring atoms. As seen from **Fig. 2**, there are more overlaps among metal, C, and N atomic orbitals in the defected graphene sheets with N edge than there are in IG. In other words,

hybridization between metal atoms and PIG or PRG is responsible for the enhancement of metal binding. In the case of Ca, specifically, the overlaps between atoms of Ca@PIG are less extreme than those of Ca@PRG, leading to a smaller interaction stemming from the hybridization mechanism.

Table 1 — The average binding energies (in eV) of two metal atoms on either side of IG, PIG, and PRG

	Li	Na	Ca
IG	1.34	0.74	0.55
PIG	4.04	2.74	3.52
PRG	3.71	2.48	3.72

Fig. 2 — Local DOS of metals and its neighboring atoms (Fermi energy is zero), in which C1 and C2 represent carbon atoms at different sites of PRG, more details are in **Fig. S2**.[†]

Fig. 3 — Top and side views of the charge density difference of metals on IG, PIG and PRG. Blue, charge depletion; and yellow, charge accumulation.

Additionally, there is another explanation for the higher E_b values on PIG and PRG,[46] that is, the introduction of N and defects breaks the π -bond of graphene, leading to a significant attraction of electrons to N defects and causing the defects to adsorb electrons from other atoms, such as metals. In other words, electrons could be transferred from metal to N-substituted

defective graphene, leading to a strong charge polarization and electrostatic interaction between metals and host materials. To investigate this possibility, we calculated the charge density differences and plotted the polarized charge distributions in **Fig. 3**. Clearly, significant charge polarization and charge transfer from metals to host materials can increase the electrostatic interaction between metals and defected graphene sheets with N edges, resulting in a high binding energy of metal atoms. Interestingly, the charge redistribution of Ca is different from those of Li and Na. Specifically, charge depletes from the outer area of Li (or Na) atoms away from the layer while charge accumulates between Li (or Na) and the layer. However, for Ca-doped structures, charge depletion is clearly observed between Ca and the host materials, and the charge accumulation is primarily in the plane of the host materials, which is similar to the charge distribution of a neutron,[49] a stable uncharged particle which has an accumulation of negative charge at its center. Therefore, the Ca-doped system should be stable because of its specific charge distribution and the strong internal interactions that exist inside these Ca-doped structures.

H₂ adsorption

The E_{ad} of H₂ is the factor that determines the capacity for the physisorption of hydrogen by storage materials, and a value in the range of 0.2~0.4 eV/H₂ is desirable for practical applications.[25] Next, we optimized adsorption sites of nH_2 ($n=1, 2, 3$) around each metal atom on graphene-based materials. The average adsorption energies of H₂ are listed in **Table 2**. On the metal-doped graphene sheets with N-edged defects, the E_{ad} values of H₂ are found to be lower compared to those of pristine graphene, which is expected because the strong binding of metals on N-edged defects weakens charge polarization when H₂ molecules are adsorbed, as is described in our previous work.[33] Despite the decrease of E_{ad} of H₂ on PIG and PRG, the absolute values are important for evaluating the potential application of metal-doped PIG and

PRG in hydrogen storage devices. For 4H_2 and 6H_2 adsorbed on Ca-doped PIG and PRG, the average E_{ad} values are larger than 0.2 eV.

Hereafter, we primarily investigate H_2 adsorption on Ca-doped sheets. In **Fig. 4**, partial DOS plots are provided to show the hybridization of the σ orbitals of H_2 and the $3s$ orbitals of Ca. For Li- and Na-doped sheets, the results can be found in the SI. The overlaps between Ca and H_2 orbitals are distributed over a broad range that nearly encompasses $-0.5\sim 4$ eV for IG and $0.5\sim 4\text{eV}$ for N-substituted graphenes, suggesting stronger interactions with H_2 and stronger adsorption on Ca-doped IG, in accordance with the findings arrived at from the analysis of E_{ad} . Moreover, upon increasing the number of hydrogen molecules, the DOSs of Ca- s and H_2 - σ , as well as the overlap areas between them are changed, which means that the added H_2 can influence the Ca-doping and H_2 adsorption. This phenomenon can be attributed to Kubas interactions,[50,51] which can slightly increase the binding energy for multiple H_2 adsorption. For example, in PRG, we observed that the energy range of overlap between Ca- s and H_2 - σ is narrow for single H_2 adsorption whereas it is wider for two- H_2 adsorption owing to the interaction from the extra H_2 . From DOSs in **Fig. 4**, the interaction between H_2 and H_2 is observable, which is very similar to the statement about multipole Coulomb interaction and Kubas interaction responsible for the nonmonotonic variation of H_2 adsorption energy in Table 2.[50,51]

In **Fig. 5**, charge density differences are presented to analyze the electrostatic polarization induced by the adsorption of H_2 . The E_{ad} of H_2 can be influenced by the redistribution of charge density. Several works[4, 33, 34] have demonstrated that the charge transfer between doped metals and host materials generates an induced electric field, which can polarize the adsorbed H_2 molecules and strengthen their interactions. By calculating how the charge distribution on Ca

changes as more H_2 molecules are adsorbed, we found that the charge accumulation between Ca and H_2 becomes significant with the addition of H_2 molecules, implying stronger electrostatic interactions and thus an enhancement of the E_{ad} with more hydrogen molecules. Consequently, the synergistic effect of Ca and the adsorbed H_2 is influential when there are multiple H_2 adsorptions. Consistent with the data in **Fig. 4**, the charge polarization of Ca is much more pronounced on IG than it is on N-substituted graphenes.

Table 2 — Average adsorption energies (in eV) of H_2 on metal-doped graphene and N-substituted ones

Metals	H_2	IG	PIG	PRG
2Li	2 H_2	0.304	0.237	0.234
	4 H_2	0.283	0.218	0.171
	6 H_2	0.262	0.143	0.152
2Na	2 H_2	0.211	0.191	0.150
	4 H_2	0.234	0.181	0.160
	6 H_2	0.233	0.173	0.173
2Ca	2 H_2	0.268	0.179	0.194
	4 H_2	0.285	0.207	0.216
	6 H_2	0.264	0.202	0.210

Fig. 4 — The partial DOS of H₂ adsorption on Ca doped structures: (a) 1H₂ (b) 2H₂ and (c) 3H₂ around each Ca on IG; (d) 1H₂ (e) 2H₂ and (f) 3H₂ around each Ca on PIG; (g) 1H₂ (h) 2H₂ and (i) 3H₂ around each Ca on PRG.

Fig. 5 — The charge density differences of H_2 adsorption on Ca doped structures: (a) $2H_2$, (b) $4H_2$, and (c) $6H_2$ on $2Ca@IG$; (d) $2H_2$, (e) $4H_2$, and (f) $6H_2$ on $2Ca@PIG$; (g) $2H_2$, (h) $4H_2$, and (i) $6H_2$ on $2Ca@PRG$. Blue, charge depletion; yellow, charge accumulation.

All the above results and analyses are from standard DFT calculations, which cannot accurately describe H_2 adsorption under realistic conditions. Several previous works involved carrying out grand canonical Monte Carlo simulations to predict the H_2 storage capacities at

certain temperatures and pressures, nevertheless, this force-field-based approach employs the optimized host structure and does not consider the thermal stabilities of materials at ambient temperature. In an effort to account for the variable of temperature, we performed first-principles MD simulations to study the stability of geometric structures and adsorption properties at room temperature, and the data from the MD simulation can provide straightforward reference for practical hydrogen uptakes. **Fig. 6** shows the structures with 6H₂ adsorbed on Ca-doped IG, PIG and PRG after 4.5 ps MD simulations at 300 K. It is clear that all host structures are stable with Ca doping and H₂ adsorption. The influences of Ca doping and N-edged defects on H₂ adsorption are remarkable. In **Fig. 6 (a)**, 4 H₂, 3 H₂, and 4 H₂ are efficiently adsorbed on 2Ca@IG, 2Ca@PIG, and 2Ca@PRG, respectively. This extent of binding is consistent with the average binding energies of H₂ on 2Ca-doped samples. One should note that for doping with more Ca atoms, the binding energy of Ca on IG is not sufficiently high to prevent the clustering of Ca atoms, which is a phenomenon that can negatively influence H₂ adsorption. Despite the metal clustering, present MD results indicate that Ca doping can enable more H₂ molecules to be held (around the Ca atoms) at room temperature. By comparing the DFT binding energy of H₂ and the MD results for Ca-doped PIG and PRG, we can infer that the PRG sheet with Ca doping is likely to be more suitable as a potential H₂ storage material.

Fig. 6 — The side and top views of first-principles MD results for 6H₂ adsorbed on Ca-doped IG (a, d), PIG (b, e) and PRG (c, f) at 300 K.

Conclusions

By means of DFT calculations, we have studied metal-doped N-substituted defective graphene and its potential application in H₂ storage. We determined that the N-edged defects in graphene can enhance the binding energy of metals because the defect with N-substitution is electron-deficient, which can prevent the metals from clustering on graphene sheets. In regard to H₂ adsorption, It is demonstrated that the capacity for H₂ adsorption is influenced by metal doping and by the quantity of H₂ that is present. Additionally, in 2Ca@PRG, the average binding energy for 6 H₂ adsorption is higher than 0.2 eV, and the MD results for 2Ca@PRG show 4 H₂ molecules held around the two Ca atoms at room temperature, a result which suggests that the Ca doped PRG could be a promising candidate for H₂ storage.

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Supplementary Material[†]

Supplementary Material associated with this article can be found, in the online version, at <http://dx.doi.org/xxx>.

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Graphical Abstract

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N-substituted defects are studied through density functional theory calculations, and we found that both N and metal atoms play important roles in H₂ adsorption properties. Additionally, the performance of H₂ adsorption at room temperature has been evaluated by using molecular dynamics simulations. All data demonstrated that Ca-doped pyrrolic graphene could be a promising candidate for H₂ storage.