

Computational study of defective graphenes dispersed with metal atoms for hydrogen storage

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ABSTRACT: The dispersion of transition metals and alkaline earth metals on prisitine and defective graphenes is studied with the use of first principles calculations. The effect of vacancy on binding properties of metal atoms to the graphene and with hydrogen molecules is particularly investigated. It is found that pure carbon sp^2 -bonded surfaces are ineffective for holding metal atoms without clustering and thus for hydrogen adsorption. The vacancy defect is shown to enhance the metal binding energy and thus its dispersion and also improve the hydrogen adsorption, particularly for Ca. The hydrogen storage capacity is estimated from the maximal number of hydrogen molecules adsorbed on such metal atoms.

Keywords: hydrogen storage, metal dispersion, calculations

1. INTRODUCTION

Traditional energy media such as coal and petroleum have been considered as a major source that accelerates climate change and deteriorates environmental conditions. Yet rapidly increasing demand of those materials is driving up their price, which is affecting everyday life of people around the world. Developing alternative and renewable energy sources is thus becoming the central issue in many areas of research more than ever. Hydrogen is one of the most-sought such energy sources, and its production, transportation, storage, and conversion to energy are all greatly challenging topics that still do not have adequate solutions for commercial purpose

[1-2]. A serious bottleneck for full usage of hydrogen energy is the lack of storage systems that can operate at ambient conditions. Operations at room-temperature and low pressure require that hydrogen be stored in non-dissociative forms rather than atomic hydrogen that usually makes chemical bonding with host materials. However, most materials studied so far can hold hydrogen molecules at very low temperature or/and high pressure and do not meet such requirements. Recently, several computational studies proposed that transition metal (TM) dispersed in nanomaterials or polymers can bind hydrogen molecules with appropriate strength so that the storage system filled with such TM complexes can operate at ambient conditions with enough storage capacities [3-7]. Quantum mechanical

simulations showed that the hydrogen binding energy ranges from 0.3 to 0.7 eV depending on the metal type, and that the effective storage capacity can reach as high as about 6 wt% [3-5]. The Kubas interaction between TM atoms and hydrogen molecules was shown to be responsible for enhanced hydrogen adsorption energy [8]. Unfortunately, subsequent studies raised a question of TM clustering that causes degradation of storage capability [9, 10]. While many studies have been reported on transition metal-dispersed medium for hydrogen storage, non-transition metals are less motivated for dispersion. Here, we carried out first principles calculations based on the density functional theory (DFT) for a comparative study on the dispersion of transition metal atoms (Sc, Ti, and V) and alkaline earth metal atoms (Mg and Ca) and also on the hydrogen adsorption on these metals. The effect of vacancy defects on metal binding and hydrogen adsorption is particularly investigated.

2. COMPUTATIONAL METHOD

The binding of metal atoms and hydrogen adsorption are investigated by using pseudopotential density functional method, which has been accepted as a standard model for calculating ground state properties of solids and many particle systems. All calculations are performed with the spin-polarized first-principles total energy method as implemented in the Vienna ab-initio simulation package [11]. The projector augmented wave pseudopotentials are used as provided in this package. The electron exchange-correlation is treated within local density approximation (LDA) [12] which is reliable for covalent bonding and static Coulomb interactions [6, 13, 14]. For a cross check, we repeated part of calculations with the generalized gradient approximation (GGA) of Perdew-Burke-Enzelhof form [15]. The GGA calculations give similar trends as those obtained with LDA while the adsorption energies of H₂ on

transition metals are half the LDA values [6, 13, 14]. Presented below are the LDA results unless specified otherwise. The cutoff energy for the planewave-basis expansion is chosen to be 400 eV and the atomic relaxation is carried out until Hellmann-Feynman forces acting on atoms are less than 0.01 eV/Å. The distance between individual graphene sheets are chosen to be about 15 Å to minimize artificial inter-cell interactions. For simulating vacancy or pyridine-like nitrogen defect in graphene, 4×4 supercell is used. The adsorption energy per H₂ on metal was sequentially calculated as $E_b = E_{tot}[M+nH_2] - E_{tot}[M+(n-1)H_2] - E_{tot}[H_2]$, where $E_{tot}[\bullet]$ is the total energy of the system [$\bullet$].

Table I: Calculated cohesive energy (E_c , eV/atom), binding energy of metal atoms (eV/atom) on pristine or defective graphenes with vacancy. For comparison, the values on pyridine-like nitrogen doped graphene are also shown.

Metal	E_c	pure	vacancy	PNG
Sc	4.87	2.08	7.08	7.26 ^a
Ti	6.57	2.73	9.03	7.54 ^a
V	6.77	2.00	8.29	7.01 ^a
Mg	1.78	0.18	2.34	
Ca	2.21	1.10	4.14	

^a Ref. [7]

3. RESULTS AND DISCUSSIONS

It was shown that transition metal atoms can hold up to five hydrogen molecules without a significant dissociation of the molecules (the first hydrogen molecule tends to dissociate) [3-5]. Once dispersed on carbon nanostructures such as carbon nanotubes, fullerenes, or covalent bonded graphenes, or polymers, the storage capacity can reach up to 6 wt% at ambient conditions according to theoretical simulations [3-5]. However, the metal atoms are shown to have a strong tendency of clustering that

deteriorates the proposed storage capability. The origin of such clustering turns out to be the large cohesive energy of TM, and thus strong chemically active sites are required to hold TM atoms so strongly as to overcome the metal cohesion. Or less cohesive metals should be considered. In this study, we introduce vacancy defects, which generate acceptor-like states that will enhance the charge transfer and hence the Coulomb interaction between metal and graphene. We calculated the binding energy of TM and AEM on both pristine and defective graphenes to investigate such effects on metal dispersion and hydrogen binding affinity.

3.1 Transition metal

Table 1 shows the calculated cohesive energy and metal binding energy on pristine and defective graphenes. We observe that metal binding energy on pristine graphene is significantly smaller than its cohesive energy, which is the origin of metal clustering as mentioned above. Since the energy gain from cohesion is much larger than that from binding to graphene, TM would aggregate instead of existing as individual and well-dispersed atomic form, which is critical for the desired hydrogen adsorption.

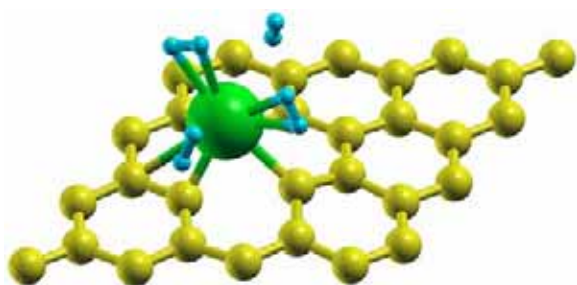


Figure 1: Hydrogen molecular adsorption on Sc bound to vacancy site of graphene. We observe four H_2 molecules adsorbed on Sc without dissociation. On pristine graphene, the first H_2 molecule is dissociated into two hydrogen atoms upon adsorption, reducing the storage capacity.

This behaviour is also true for carbon nanotubes. As the dispersion of TM is not favourable in pristine graphene, we considered vacancy defects that can provide strong metal binding sites. Our calculations show that the vacancy increases the metal binding energy as to exceed the cohesive energy. This indicates that clustering of transition metal atoms can be significantly reduced once such defects are generated upon metal dispersion. Similar effects are also expected for carbon nanotubes or graphene-based nanostructures [6, 7].

Next we attached hydrogen molecules on TM that is bound to vacancy defects in graphene and calculated their adsorption energy.

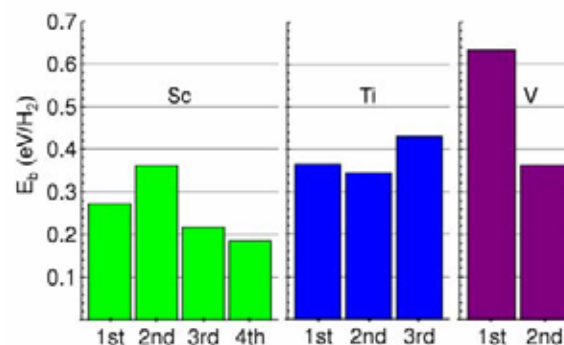


Figure 2: Calculated adsorption energy (eV/ H_2) of hydrogen molecules on TM bound to vacancy defects in graphene. The abscissa denoted the order of attached H_2 . Sc is shown to adsorb more hydrogen molecules than Ti or V.

Figure 2 shows the calculated hydrogen binding energy on Sc, Ti, and V bound to vacancy site of graphenes. Compared to pristine graphenes, the hydrogen adsorption shows two characteristics: first there is no dissociation of hydrogen molecules, particularly first hydrogen and second, the adsorption energy is smaller (but the value is within a range for ambient operation) than that in pristine graphene. The effect of vacancy on metal binding and hydrogen adsorption is, in fact, very similar to that observed for pyridine-like nitrogen doping (one carbon vacancy with three neighboring carbon atoms replaced by nitrogen) in

graphene [7]. Both carbon vacancy and pyridine-like nitrogen doping result in electron depletion in graphenes. This indicates that the acceptor-like states generated by vacancy or pyridine-like defect enhance the charge transfer from metal to graphene, which results in the strong Coulomb interaction between the metal and graphene [7].

3.2 Alkaline earth metal

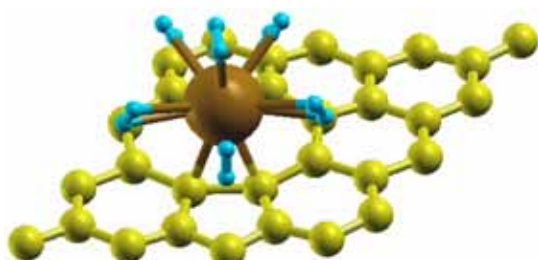


Figure 3: Hydrogen molecules adsorbed on Ca, which is bound to a reconstructed vacancy defect in graphene. A single vacancy is reconstructed to 5-9 carbon rings. Six hydrogen molecules are adsorbed on Ca, which is significantly larger than those on TM.

Alkaline earth metals are chemically easy to process compared to transition metals. As AEM can exist in ionized form, it would be interesting to consider them as hydrogen adsorption centers. Head-Gordon *et. al.* showed that bare ionized AEM can bind hydrogen molecule very effectively [16]. And recently, it was reported that Ca on fullerene can be effective hydrogen binding centers [17]. In this study, we considered Mg and Ca, which are found to be better than other non-transition metal atoms such as Be or Al.

Similar to TM cases, we first calculated the binding energy of AEM on pristine and defective graphenes with results shown in Table 1. The binding energy of AEM on pristine graphene is very small, similar to TM case, indicating that it would not be stabilized even at moderate temperatures. AEM on vacancy defects, on the other hand,

is shown to have strong binding energy, particularly for Ca case.

Another interesting observation is that the vacancy undergoes a reconstruction to form 5- and 9-carbon rings, which is not the case for Mg or TM. This may explain the large increase in binding energy compared to other metals.

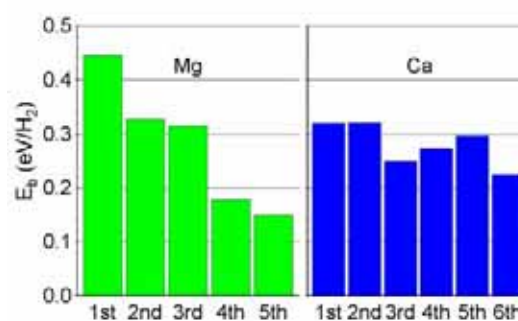


Figure 4: Hydrogen adsorption energy on AEM bound to vacancy defect in graphene. We observe relatively uniform adsorption energy on Ca compared to that on Mg, which indicates that Ca atoms can provide better hydrogen adsorption sites than Mg once dispersed on defective graphenes.

The storage capacity of Ca-dispersed graphenes is estimated to reach about 6~7 wt% depending on available Ca binding sites. While this estimation is a simple guide, it suggests that Ca-dispersion in graphitic materials including carbon nanotubes, fullerenes, or porous 3D structures [6] can be a very promising approach for developing hydrogen storage materials.

3.3 Analysis

The origin of the enhancement of metal binding in vacancy site is attributed to the charge transfer from metal to graphene. The strong static Coulomb interaction between the metal and graphene results in the enhanced binding energy. Figure 5 shows the calculated density of states of graphene with vacancy defects. Similar to PNG [7], we observe the acceptor-like states near the Fermi level. Once metal atoms are bound, electron from metal transfers to graphene, filling the acceptor-like states.

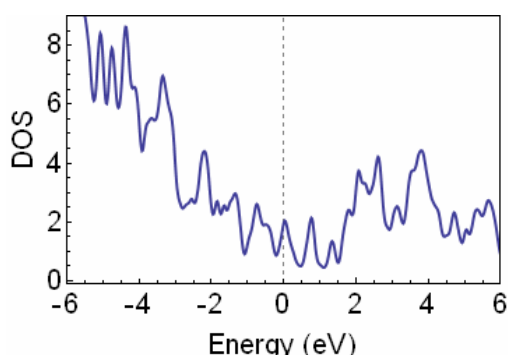


Figure 5: Density of states of graphene with vacancy. The Fermi level (set at zero of energy) is shifted to lower energy by about 0.5 eV due to electron depletion by vacancy formation.

As the electron depletion (acceptor-like states) increases, more electron charges would transfer to graphenes. The decrease of electrons occupying metal *d*-level (for transition metal case), on the other hand, reduces the back-donation and thus weakens the adsorption energy, which is the case in our calculations. Such a tendency is not observed for AEM except the enhanced metal binding energy.

4. CONCLUSION

We studied the dispersion of transition metal and alkaline earth metal atoms on pristine and defective graphenes. It was found that vacancy defect sites provide stronger binding of metal atoms, particularly for Ca atom. Calculated hydrogen adsorption showed that AEM is better in dispersion and holds more hydrogen than TM. Our study suggests that AEM can be used as active components of hydrogen storage materials, providing efficient adsorption sites.

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