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Citation: *Applied Physics Letters* **94**, 173102 (2009); doi: 10.1063/1.3126450

View online: <http://dx.doi.org/10.1063/1.3126450>

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Effect of vacancy defects in graphene on metal anchoring and hydrogen adsorption

Gyubong Kim,¹ Seung-Hoon Jhi,^{1,a)} Seokho Lim,² and Noejung Park²

¹Department of Physics, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea

²Department of Applied Physics, Dankook University, Yongin, Kyunggido 448-701, Republic of Korea

(Received 23 January 2009; accepted 3 April 2009; published online 27 April 2009)

The dispersion of transition and alkaline-earth metals on defective graphenes is studied using first-principles calculations. The effect of vacancy defects on binding properties of metal atoms to the graphene and with hydrogen molecules is particularly investigated. It is shown that vacancy defects enhance efficiently the metal binding energy and thus its dispersion, particularly for alkaline-earth metals. Mg on vacancy defects shows a substantial increase in its binding energy and hydrogen uptake capacity. Among metals considered, Ca-vacancy complexes are found to exhibit the most favorable hydrogen adsorption characteristics in terms of the binding energy and the capacity. © 2009 American Institute of Physics. [DOI: 10.1063/1.3126450]

Hydrogen is one of the most-sought renewable energy sources.^{1,2} Serious bottleneck for full usage of hydrogen energy includes the lack of efficient energy conversion technology and storage systems that can operate at ambient conditions. The operation at room-temperature and low pressures require that hydrogen be stored in nondissociative forms rather than atomic hydrogen. 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.^{3–8} It was shown 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 %.^{3–8} The Kubas interaction between TM atoms and hydrogen molecules was shown to be responsible for enhanced hydrogen adsorption energy.⁹ Unfortunately, subsequent studies raised a question of TM clustering that causes degradation of storage capability.^{10,11} While many studies have been reported on TM-dispersed medium for hydrogen storage, non-TMs are less motivated for dispersion. Here, we carried out first-principles calculations based on the density functional theory for a comparative study on the dispersion of TM atoms (Sc, Ti, and V) and alkaline-earth metal (AEM) atoms (Mg and Ca) and also on the hydrogen adsorption on these metals. The effect of vacancy defects in graphenes on metal binding and hydrogen adsorption is particularly investigated.

The binding of metal atoms and hydrogen adsorption are investigated by using pseudopotential density functional method. All calculations are performed with the spin-polarized first-principles total energy method as implemented in the Vienna *ab initio* simulation package.¹² The electron exchange correlation is treated within local density approximation (LDA)¹³ which is reliable for covalent bonding and static Coulomb interactions.^{5,14,15} For a cross check, we repeated part of calculations with the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof form.¹⁶ The GGA calculations give similar trends as those obtained with LDA, while the adsorption energies of H₂ on TMs are half

the LDA values.^{5,14,15} As the LDA (GGA) gives an upper (lower) bound of van der Waals type binding of hydrogen compared to the highly correlated methods,⁵ we give the readers a caveat that our calculated results should be interpreted in such context. 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 intercell interactions. For simulating isolated graphene, 4 × 4 supercell is used. The adsorption energy per H₂ on metal was sequentially calculated as $E_b = E_{\text{tot}}[M + n\text{H}_2] - E_{\text{tot}}[M + (n-1)\text{H}_2] - E_{\text{tot}}[\text{H}_2]$, where $E_{\text{tot}}[\bullet]$ is the total energy of the system [\bullet].

TM atoms can hold up to five hydrogen molecules without a significant dissociation of the molecules (the first hydrogen molecule tends to dissociate).^{3–8} Once dispersed on carbon nanostructures or polymers, the storage capacity can reach up to 6 wt % at ambient conditions according to theoretical simulations.^{3–7} However, the metal atoms are shown to have a strong tendency of clustering that deteriorates the storage capability. The origin of such clustering is the large cohesive energy of TM, and thus chemically active sites are required to hold TM atoms so strongly as to overcome the metal cohesion. Otherwise, less cohesive metals should be considered. Here, we introduce vacancy defects, which generate acceptorlike states that will enhance the charge transfer and hence the Coulomb interaction between metal and graphene.⁷ Compared to substitutional doping by boron or nitrogen, vacancy provides more localized acceptor states. 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.

Table I shows the calculated results. We observe that metal binding energy on pristine graphene is significantly smaller than its cohesive energy, which results in 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. On the other hand, our calculations show that the vacancy increases the metal binding energy so

^{a)}Electronic mail: jhish@postech.ac.kr.

TABLE I. Calculated cohesive energy (E_c , eV/atom) and binding energy of metal atoms (eV/atom) on pristine or defective graphenes with vacancy. For comparison, calculated values on PNG are also shown.

Metal	E_c	Pristine	Vacancy	PNG
Sc	4.83	2.08	7.08	7.26 ^a
Ti	6.50	2.73	9.03	7.54 ^a
V	6.66	2.00	8.29	7.01 ^a
Mg	1.78	0.18	2.34	3.96
Ca	2.21	1.10	4.14	5.46

^aReference 8.

significantly as to exceed the cohesive energy. Also, the increase is larger than that by boron doping.⁷ This indicates that clustering of metal atoms will be less likely if such defects are available for metal binding. Similar effects are also expected for carbon nanotubes or graphene-based nanostructures.^{10,11}

Next we attached hydrogen molecules to metal-vacancy complexes in graphene and calculated the adsorption energy. Sc and Ca exhibit the best H_2 adsorption characteristics among TM and AEM considered here, respectively, in terms of hydrogen binding energy and uptake capacity. As shown in Fig. 1, four and six H_2 s can adsorb on Sc and Ca, respectively. Interestingly, the vacancy retains its atomic structure upon metal binding except Ca which induces a reconstruction to 5–9 carbon rings [see Fig. 1(b)]. Figure 2(a) shows the calculated hydrogen adsorption energy on Sc, Ti, and V bound to vacancy sites 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 by about 0.2–0.3 eV.⁷ The effect of vacancy on metal binding and hydrogen adsorption is, in fact, very similar to that observed for pyridinelike nitrogen doped graphene (PNG) (one carbon vacancy with three neighboring carbon atoms replaced by nitrogen).⁸ We note that both the carbon vacancy and the pyridinelike nitrogen doping result in electron depletion in graphenes. The acceptorlike states generated by vacancy or pyridinelike defects enhance the charge transfer from metal to graphene, which provides a stronger Coulomb interaction between the metal and graphene.⁸ Experimentally, the single atomic vacancies in graphene were also directly observed.¹⁷

Lochan and Head-Gordon¹⁸ showed that bare ionized AEM can bind hydrogen molecule very effectively. Also recently, it was reported that Ca-dispersed fullerenes can be plausible hydrogen storage materials.¹⁹ We considered Mg

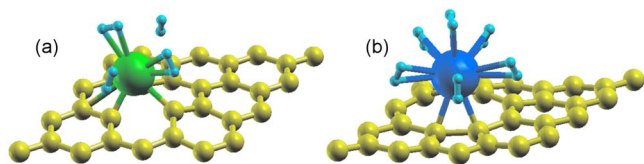


FIG. 1. (Color online) Hydrogen molecular adsorption on (a) Sc and (b) Ca bound to vacancy site of graphene. Four and six H_2 molecules adsorb on Sc and Ca, respectively, without dissociation. On pristine graphene, the first H_2 molecule dissociates into two hydrogen atoms upon adsorption (see Ref. 7), which reduces the storage capacity. The vacancy undergoes a reconstruction to 5–9 carbon rings only upon Ca binding, as shown in (b).

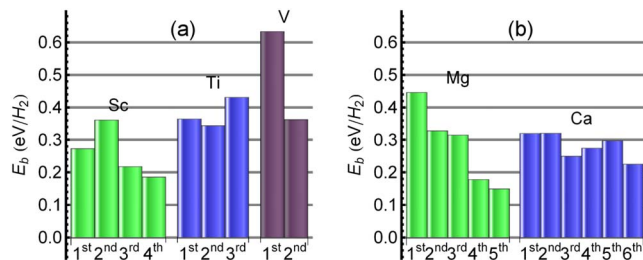


FIG. 2. (Color online) Calculated adsorption energy (eV/ H_2) of hydrogen molecules on (a) TM and (b) AEM bound to vacancy defects in graphene. The abscissa denoted the order of attached H_2 . We observe relatively uniform adsorption energy on Ca compared to that on Mg, which indicates that Ca can provide better hydrogen adsorption sites than Mg once dispersed on defective graphenes.

and Ca, which are found to be better than other non-TM atoms such as Be or Al (both Be and Al on defective graphene are capable of binding only one H_2). As shown in Table I, 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, has strong binding energies, particularly for the Ca case that shows an almost twofold increase from its bulk cohesive energy. Five and six H_2 s can adsorb on Mg and Ca, respectively, as shown in Fig. 2(b), which is one more than corresponding number in PNG according to our calculations (not shown here). We note that Mg-pristine graphene does not bind hydrogen at all. Figure 2 indicate that Ca is superior to other metals in terms of the uptake capacity and the uniformity in binding energy (again care should be taken in interpreting the hydrogen binding energies obtained with LDA or GGA as mentioned above). The later is related to the width of desorption temperature that determines the usable number of H_2 s.^{4,7} The hydrogen uptake capacity of Ca-dispersed graphenes is estimated to reach about 6–7 wt % depending on available Ca binding sites. This simple estimation suggests that Ca-dispersion in graphitic materials will be a very promising approach for developing hydrogen storage materials.

The origin of the enhancement in metal binding in vacancy site is attributed to the charge transfer from metal to graphene as mentioned above. The strong static Coulomb interaction between the metal and graphene results in the enhanced binding energy. Figure 3 shows the calculated density of states of graphene with vacancy defects. Similar to PNG,⁸ we observe the acceptorlike states near the Fermi level. Once metal atoms are bound, the electron from metal

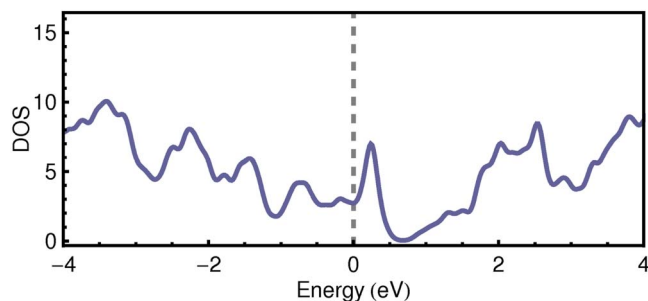


FIG. 3. (Color online) Calculated density of states of graphene with vacancy. The Fermi level (set at the zero of energy) shifts down by about 0.5 eV from the original position (a dip near 0.5 eV) due to electron depletion upon vacancy formation.

transfers to graphene, filling the acceptorlike states. As the electron depletion (acceptorlike states) increases, more electrons would transfer to graphenes. The decrease in the number of electrons occupying metal d level (for TM case), on the other hand, reduces the back-donation and thus weakens the adsorption energy,⁷ which is the case in our calculations. For AEM, such decrease in hydrogen binding energy is not observed while the metal binding energy increases. The multiple Coulomb interaction is dominant between ionized AEM and H_{2s} ,¹⁸ whereas the orbital interaction is responsible for TM-hydrogen binding. Mg atoms in pristine graphene do not bind hydrogen at all, whereas, on vacancy defects, they are ionized and bind hydrogen. For Ca, its low-lying empty d orbitals also play some roles for hydrogen adsorption. On vacancy defects, Ca d orbitals are split and partially occupied due to the hybridization with graphene π orbitals. Hence the orbital interaction between Ca d and hydrogen σ^* states comes to contribute to hydrogen adsorption. Ca-vacancy has more uniform hydrogen adsorption energy than Ca-pristine graphene. The splitting and occupation of Ca d orbitals due to ligand fields was also discussed in Ca- C_{60} systems.¹⁹

In summary, we studied the dispersion of transition and alkaline-earth metal atoms on pristine and defective graphenes. It was found that vacancy defects provide stronger binding sites of metal atoms, particularly Ca. With caution given in comparing LDA/GGA values of hydrogen binding energies to experiment, our calculations showed that AEMs can hold more hydrogen than TMs. Also AEM is expected to be easily dispersed in atomic forms in defective graphenes since its binding energy on vacancy defects is much larger (by almost two times) than the cohesive energy. Our study suggests that metal-vacancy complexes can be ac-

tive hydrogen adsorption sites to be utilized for hydrogen storage and metal catalysts.

This research was performed for the Hydrogen Energy R&D Center, one of the 21st Century Frontier R&D Program, funded by the Ministry of Science and Technology of Korea. This work was also supported by Grant No. KSC-2007-S00-2004 from KISTI.

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