Hydrogen storage of calcium atoms adsorbed on graphene: First-principles plane wave calculations

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(Dated: January 14, 2009)

In this paper, we showed that Ca atoms, in fact, can be bound on both sides of graphene plane and each Ca atom absorbing four H₂ results in a medium of high-capacity hydrogen storage of 8.4 wt %. In the present case the binding energy of the fourth H₂ absorbed by Ca atom is still significant and is ∼300 meV. While each Ca atom donates part of its charge to the graphene layer, graphene, by itself, having Fermi surface consisting of six points at the corners of the hexagonal Brilloiun zone, is metalized. These results are obtained from our study based on first-principles calculations.

We first consider the adsorption of a single Ca on the graphene as the substrate material. This is modeled by one Ca atom adsorbed on the hollow site (namely H₁ site above the center of hexagon) for each (4×4) cell of graphene (namely one Ca atom for every 32 carbon atoms). The Ca-Ca interaction is indeed negligible owing to large distance of ∼9.84 Å between them. A chemical bonding occurs between Ca and C atoms with a binding energy of 0.99 eV and Ca+graphene distance of 2.10 Å. Similar to the bonding mechanism of Ca on C₆₀, Ca atom donates part of its charge from 4s-orbital to the π*-bands of graphene. Due to the formation of an electric field between Ca atom and the graphene layer, part of this charge is then back-donated to the unoccupied 3d-orbitals of Ca through their hybridization with π*-states. The resulting positive charge of Ca atom is calculated to be ∼0.96 electrons. The diffusion of the single Ca atom adsorbed on the graphene has to overcome relatively small energy barriers of Q = 118 meV and 126 meV to diffuse to the top site (i.e. on top of C atom) and bridge site (on top of the C-C bond), respectively. Ca atom adsorbed on the top or bridge sites becomes less positively charged (∼0.89 and ∼0.92 electrons, respectively).

A denser Ca coverage, which is energetically more favorable, is attained, if one Ca is adsorbed on each (2×2) cell of graphene with Ca-Ca distance of 4.92 Å. Ca atom adsorbed on the top and bridge sites has a binding energy of 0.86 and 0.89 eV, respectively. However, energetically most favorable adsorption site is found to be the H₁ site, which is 2.15 Å above the graphene with a binding energy of 1.14 eV. Here, the Ca-Ca coupling is subtracted from the calculated binding energy. In this dense (2×2) coverage, a stronger electric field is induced between Ca atoms and the graphene layer, which, in turn, leads to a larger back-donation of charge from the graphene layer to 3d-orbitals of Ca atom. Hence by increasing Ca coverage from (4×4) to (2×2), adsorbed Ca atoms become less positively charged, but their binding energy increases. As demonstrated in Fig.1 even if it is energetically more favorable, the clustering of adsorbed Ca atoms is hindered by the Coulomb repulsion.

We next consider the double sided adsorption of Ca. The binding energy of second Ca atom for the double sided adsorption with H₁+H₂ and H₁+H₃ configuration indicated in Fig.2 (c), is 1.27 and 1.26 eV, respectively. Since the repulsive Coulomb interaction between Ca atoms on the upper and lower part of the plane is screened by the negative charge around graphene, the binding energy of Ca atom in the double sided adsorption is larger than that in the single sided adsorption. It is also found that 3d-orbitals of both Ca atoms have higher...
occupancies as compared with Ca atom in the single sided adsorption. It is noted, however, that the partial occupancy of 3$d$-orbitals of Ca atom does not cause any magnetic properties in the system. Our results indicate that a stable and uniform Ca coverage up to $\Theta=12.5\%$ ($\Theta=25\%$) can be attained for single sided (double sided with H1+H2 or H1+H3) adsorption forming a $(2\times2)$ pattern.

Finite-temperature ab initio molecular dynamics simulations have also been carried out for Ca adsorbed on the $(2\times2)$ graphene unit cell for H1 geometry. Simulations are performed by normalizing the velocities of the ions and increasing the temperature of the system gradually from 0 K to 900 K in 300 time steps. The duration of time steps are intentionally taken as 3 fs, which is relatively longer for a MD calculation. If the system is unstable, the geometry of the structure can be destroyed much easier in long time steps. While the bonding between adsorbed Ca atom and the graphene layer is sustained, the adsorbed $(2\times2)$ Ca layer begins to diffuse on the graphene layer as the temperature of the system rises over $\sim 300$ K. However, no structural deformation is observed indicating that the Ca+Graphene system is found to be stable up to 900 K within 300 time steps.

Other alkaline-earth metals, such as beryllium and magnesium do not form strong bonds with graphene. Since Be has ionization potential of 9.32 eV\(^{11}\) which is much higher than that of Ca atom (6.11 eV), the charge of its 2$s$-orbital cannot easily transferred to the graphene layer. A similar situation occurs also with Mg having an ionization potential of 7.64 eV. Besides, the hybridization of $\pi^*$-orbitals of graphene with the $d$-orbital of Ca atom, which is absent in both Be and Mg plays an essential role in strong binding of Ca to graphene. However, Ti and Co form strong bonds (with binding energies 1.58 and 1.20 eV for the $(2\times2)$ adsorption pattern, respectively\(^{12}\)). The binding energies of Fe, Cr and Mo are rather weak.

The above arguments related with the binding of Ca to graphene are confirmed by examining the band structure and the charge difference isosurfaces presented in Fig. 2. Both H1+H2 and H1+H3 adsorption configurations are included in our calculations because there is a small energy difference (H1+H2 structure is 26 meV more energetic.) between them. Hence, both adsorption configurations should be observable at room temperature conditions. Charge difference isosurfaces are obtained by subtracting charge densities of Ca and bare graphene from that of Ca+graphene, namely $\Delta \rho = \rho_{\text{Ca+Gr}} - \rho_{\text{Ca}} - \rho_{\text{Gr}}$. It is seen that there is a significant charge accumulation between the adsorbed Ca atom and graphene, which forms the ligand field. Partial occupation of 3$d$-orbitals of Ca can be most clearly demonstrated by the projected density of states in Fig. 2(b). The empty $\pi^*$-bands become occupied through charge transfer from 4$s$-orbitals of adsorbed Ca and eventually get distorted due to 3$d$-$\pi^*$ hybridization between 3$d$-orbitals of Ca and the states of $\pi^*$-bands as a result of the charge back-donation process. Occupation of distorted graphene $\pi^*$-bands gives rise to the metallization of semi-metallic graphene sheets for all adsorption sites. It is also seen that charge density around graphene layer increased significantly as a result of double sided adsorption of Ca. The increase of charge back-donation to 3$d$-orbitals becomes clear by the increased 3$d$-projected density of states below the Fermi level. Changing the adsorption configuration from H1+H2 to H1+H3 does not make any essential changes in the electronic structure. One notes that the position of Fermi energy and hence electron density can be monitored by the controlled doping of Ca atoms. Metallization process is also important for graphene nanoribbons, which form conductive interconnects and spintronic devices in the same nanostructure\(^{12,13}\). It might be an interesting study to investigate the magnetic and electronic properties of Ca adsorption on graphene nanoribbons due to its different bonding mechanism.

We next study the absorption of hydrogen molecules by Ca atoms. A summary of energetics and geometry related with the absorption of molecular H\(_2\) for H1,
H1+H2, and H1+H3 sites for the (2×2) and H1 site for the (4×4) coverage are given in Fig.3. The binding mechanism of H2 invokes not only the adsorbed Ca atom, but also the graphene layer. In the case of single and double H2 absorption, the absorbed molecules are parallel to graphene and all hydrogen atoms are equidistant from Ca atom. As a result, both hydrogen atom of each absorbed H2 have the same excess charge of ∼0.08 electrons. Once the number of H2 absorbed by each Ca atom exceeded two, absorbed H2 molecules tent to tilt towards Ca atom because of increased positive charge of Ca atom and the symmetry of the bonding configuration of H2 molecules. The charge of Ca, H atom closer to Ca, H atom farther from Ca and graphene are calculated for 8H2+2Ca+Graphene system corresponding to H1+H2 configuration in Fig.3 to be ∼+1.29, ∼−0.06, ∼−0.11 and ∼−1.23 electrons. One hydrogen atom of tilted H2, which is closer to Ca has more excess charge than the other one. It is important to note that charges transferred to absorbed H2 are not only from Ca atom. Graphene atoms at close proximity also supply charge through back-donation process. At the end, ionic bonding through attractive Coulomb interaction between positively charged Ca and negatively charged H and weak van der Waals interaction are responsible for the formation of mixed bonding between H2 molecules and Ca adsorbed on graphene. The above discussion is substantiated by the partial density of states in Fig.3(d). The excess charge on H-s and Ca-3d orbitals and their contribution to the states below the Fermi level increase with increasing number of H2 molecules. Broadening of the molecular level of H2 at ∼−9 eV indicates significant H2-H2 interaction, that in turn increases the binding energy. In fact, the binding energy of the first H2 molecule to Ca atom which prefers to be parallel to the graphene layer is generally small. Whereas the average binding energy for two H2 molecules which are again located parallel to the graphene layer, and for three or more H2 molecules which are tilted around Ca atom are larger. We note that the adsorption of Ca atoms and also H2 molecules slightly affect the underlying graphene lattice and C-C distance. The average C-C distance of bare graphene is increased from 1.41 Å upon adsorption of Ca and absorption of H2 to dC, values indicated in all (2×2) structures in Fig.3. Since Ca-Ca interaction is negligible in (4×4) structures, there is no variation in average C-C distance.

Maximum number of absorbed H2 per adsorbed Ca atom is four for the (2×2) coverage yielding a H2 storage capacity of 8.4 wt % and five for the (4×4) coverage of graphene. The reason why we include the (4×4) coverage even if the resulting gravimetric density is very low (∼%2.3 wt), is to mimic the Ca-H2 interaction in the absence of H2-H2 interaction occurring in the (2×2) coverage. Fifth H2 molecule can be bound to the top of Ca atom in the (4×4) coverage with a significantly high binding energy. Other 4 H2 molecules remain in quadrilateral positions around Ca. When we compare graphene with C60, we can conclude that C60 with a single Ca ad-
FIG. 3: (Color online) Sites and energetics of Ca adsorbed on graphene with the (2×2) coverage and absorption of H₂ molecules by Ca atoms. \( d_c \) is the average C-C distance in the graphene layer. \( E_L \) is the binding energy of Ca atom adsorbed on H1-site, which is a minimum energy site. For H1+H2 or H1+H3 configurations corresponding to double sided adsorption, \( E_L \) is the binding energy of the second Ca atom and \( E_n \) is the average binding energy. For H1, H1+H2 and H1+H3 configurations, \( E_1 \) is the binding energy of the first H₂ absorbed by each Ca atom; \( E_n \) (\( n=2-5 \)) is the binding energy of the last \( n^{th} \) H₂ molecule absorbed by each Ca atom. Last row indicates the sites and energetics of one Ca atom adsorbed on each (4×4) cell of graphene and absorption of H₂ molecules by each Ca atom. Only the (4×4) coverage can absorb 5 H₂ molecules. The shaded panel indicates energetically the most favorable H₂ absorption configuration.

Absorption on the surface yields similar results with the (4×4) coverage on graphene. However, increasing Ca coverage adsorption results in lower binding energies of absorbed H₂ molecules in the present case. Unfortunately, we cannot comment on the case of high Ca coverage of C₆₀, since Yoon et al. did not give details on the energetics of H₂ molecules in denser Ca adsorption. They have just emphasized that adsorption of 32 Ca results in full coverage of C₆₀ surface and this structure can absorb up to 92 H₂ molecules with binding energy of ~0.4 eV. Under these circumstances, single Ca atom can hold only 3 H₂ molecules. In graphene structures, while the charge on (i.e. charge depletion or positive charge) Ca increases with increased number of the absorbed H₂ molecules, the electric field around Ca increases. This, in turn, results in a decrement in the distance between adsorbed Ca and polarized H₂ molecules. The charge on graphene decreases, as well.

In conclusion, this paper deals with two different subjects which are of current interest; namely graphene and hydrogen storage. Firstly, we showed that recently synthesized graphene with carriers behaving as if massless Dirac fermions can be metallized as a result of the adsorption of Ca atoms. Electrons donated by Ca is accommodated partly by the \( \pi^* \) bands of graphene, partly back donated to its 3d-orbitals. Ca atoms can be bound to both sides of graphene and can attain 25% coverage without clustering. Secondly, we found that each adsorbed Ca can absorb up to four hydrogen molecules. At full coverage this yields a storage capacity of ~8.4 wt%, which is higher than the value set for feasible gravimetric density of hydrogen storage. The calculated bonding energies of hydrogen molecules are suitable for room temperature storage; while above the room temperature hydrogen molecules are released, Ca atoms remain adsorbed on graphene for further recycling. Even though storage capacities higher than the present case is achieved in different nanostructures, our results may be important for efficient hydrogen storage since graphene flakes are now easily available.

This work is supported by TUBITAK through the grant TBAG104536. Part of the computational resources for this study has been provided through Grant No. 2024-2007 by the National Centre for High Performance Computing of Turkey, Istanbul Technical University.
We have performed first-principles plane wave calculations within Density-Functional Theory using PAW potentials [P.E. Blöchl, Phys. Rev. B 50, 17953 (1994)]. We used Local Density Approximation (LDA), since the van der Waals contributions are generally better accounted. We also calculated binding energies by using Generalized Gradient Approximation (GGA). We found that GGA binding energy for \( n = 1 \) is 120 meV smaller than the LDA binding energy for H\(_1\) adsorption site. However for \( n = 2 \), the binding energy becomes \( \sim 210 \) meV smaller than LDA because the H\(_2\)-H\(_2\) interaction is neglected in the former. Hence GGA and LDA result in very close atom configurations. Numerical results are acquired by using VASP [G. Kresse and J. Hafner, Phys. Rev. B 47, R558 (1993)]. A plane-wave basis set with kinetic energy cutoff \( \hbar^2 |\mathbf{k} + \mathbf{G}|^2 / 2m = 900 \text{ eV} \) has been used. The Brillouin zone has been sampled by (19x19x1) and (9x9x1) special mesh points in \( \mathbf{k} \)-space for (2x2) and (4x4) graphene cells, respectively. In the course of structure optimizations, the convergence for energy is chosen as \( 10^{-6} \text{ eV} \) between consecutive steps, and the maximum force allowed on each atom is less than \( 10^{-2} \text{ eV/Å} \). The pressure on the system is kept smaller than \( \sim 0.1 \text{ KBar per unitcell} \).

Charge transfer values are calculated according to the Bader analysis. See G. Henkelman, A. Arnaldsson, H. Jonsson, Comput. Mater. Sci. 36, 254-360 (2006).

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