High-capacity hydrogen storage by metallized graphene

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First-principles plane wave calculations predict that Li can be adsorbed on graphene forming a uniform and stable coverage on both sides. A significant part of the electronic charge of the Li 2*s* orbital is donated to graphene and is accommodated by its distorted π^*-bands. As a result, semimetallic graphene and semiconducting graphene ribbons change into good metals. It is even more remarkable that Li covered graphene can serve as a high-capacity hydrogen storage medium with each adsorbed Li absorbing up to four H_2 molecules amounting to a gravimetric density of 12.8 wt %. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2963976]

Developing safe and efficient hydrogen storage is essential for hydrogen economy.[1] Recently, much effort has been devoted to engineer carbon based nanostructures,[2–5] which can absorb H_2 molecules with high storage capacity, but can release them easily in the course of consumption in fuel cells. Insufficient storage capacity, slow kinetics, poor reversibility, and high dehydrogenation temperatures have been the main difficulties toward acceptable media for hydrogen storage.

Recently, graphene, a single atomic plane of graphite, has been produced[6] showing unusual electronic and magnetic properties. In this letter, we predict that metallized graphene can be a potential high-capacity hydrogen storage medium. The process is achieved in two steps. Initially, graphene is metallized through charge donation by adsorbed Li atoms to its π^*-bands. Subsequently, each positively charged Li ion can absorb up to four H_2 by polarizing these molecules. At the end, the storage capacity up to the gravimetric density of g_d=12.8 wt % is attained. These results are important not only because graphene is found to be a high capacity hydrogen storage medium, but also because of its metallization through Li coverage is predicted.

Our results have been obtained by performing first-principles plane wave calculations using ultrasoft pseudopotentials.[7] We used local density approximation (LDA), since the van der Waals contribution to the Li-graphene interaction has been shown[8] to be better accounted by LDA. Numerical results have been obtained by using VASP,[9] which were confirmed by using the PWSCF code.[10] A plane-wave basis set with kinetic energy cutoff $\hbar^2|\mathbf{k}+\mathbf{G}|^2/2m$=380 eV has been used. In the self-consistent potential and total energy calculations the Brillouin zone has been sampled by $(19\times19\times1)$ and $(9\times9\times1)$ special mesh points in $\mathbf{k}$ space for (2×2) and (4×4) graphene cells, respectively. Atomic positions in all structures are optimized using the conjugate gradient method. Convergence is achieved when the difference of the total energies of last two consecutive steps is less than 10^{-6} eV and the maximum force allowed on each atom is less than 10^{-2} eV/Å. All configurations studied in this work have also been calculated by using spin-polarized LDA, which were resulted in nonmagnetic ground state.

Adsorption of a single (isolated) Li atom on the hollow site of graphene (i.e., H1 site above the center of hexagon) is modelled by using (4×4) cell of graphene with 1.70 Å minimum Li-graphene distance and with a minimum Li–Li distance of 9.77 Å, resulting in a binding energy of E_L =1.93 eV. Upon adsorption, Li atom donates part of the charge of its 2*s* state to the more electronegative carbon atoms at its proximity. Despite the ambiguities in determining the atomic charge, Löwdin analysis estimates that Li becomes positively charged by donating $q\sim0.35$ electrons (but $q\sim0.9$ electrons according to Bader analysis[11]). The energy barrier to the diffusion of a single Li atom on the graphene sheet through top (on top of carbon atoms) and bridge (above the carbon-carbon bond) sites are calculated to be ΔQ =0.35 and 0.14 eV, respectively.

Lithium atoms can form a denser coverage on the graphene with a smaller Li–Li distance of 4.92 Å forming the (2×2) pattern. Owing to the repulsive interaction between positively charged Li atoms, the binding energy of Li atom is smaller than that of the (4×4) cell. For H1 adsorption site [see Fig. 1(a)], the binding energy is calculated to be E_L=0.86 eV. The binding energies are relatively smaller at the bridge and top sites, and are 0.58 and 0.56 eV, respectively. The binding energy of the second Li for the double sided adsorption with H1+H2 and H1+H3 configurations described in Fig. 1(a), are E_L=0.82 and 0.84 eV, respectively. The same binding energies for H1+H2, and H1+H3 geometries on the (4×4) cell are relatively larger due to reduced repulsive Li–Li interaction, namely E_L=1.40 and 1.67 eV, respectively. The coverage of Li on the (2×2) cell is Θ=12.5% (i.e., one Li for every eight carbon atoms) for H1 geometry and Θ=25% for either H1+H2 or H1+H3 geometries. Metallic charge accumulated between Li and graphene weakens the interaction between Li atoms which are adsorbed at different sites of graphene. Further increasing one-sided coverage of Li to Θ=25% with H1 geometry (or two-sided coverage to 50% with H1+H2 or H1+H3 geometries) appears to be impossible due to strong Coulomb repulsion between adsorbed Li ions and results in a negative binding energy ($E_L\sim-2.5$ eV). On the other hand, the total binding energy of all Li atoms adsorbed on a (2×2) cell

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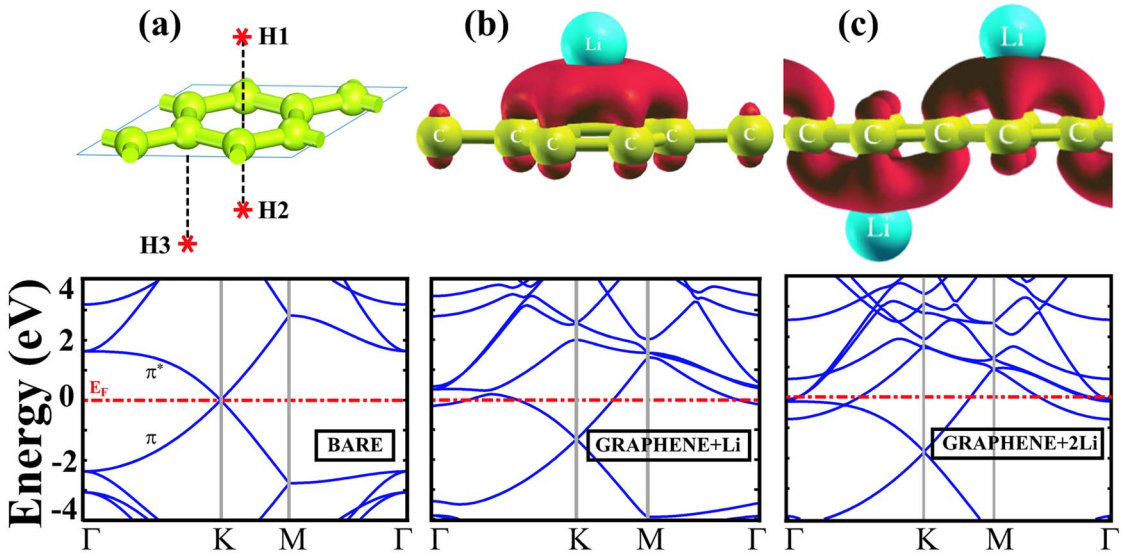

FIG. 1. (Color online) (a) Various adsorption sites H1, H2 and H3 on the (2×2) cell (top panel) and energy band structure of bare graphene for the same size of cell (bottom panel). (b) Charge accumulation, $\Delta\rho^+$, calculated for one Li atom adsorbed to a single side specified as H1 (top) and corresponding band structure. (c) Same as (b) for one Li atom adsorbed to H1 site, second Li adsorbed to H3 site of the (2×2) cell of graphene. Zero of band energy is set to the Fermi energy, E_F.

with the H1+H2 (H1+H3) geometry corresponding to $\Theta=25\%$ is 3.23 eV (3.12 eV) higher than that of Li atom adsorbed on the (4×4) cell with the same geometry corresponding to $\Theta=6.25\%$. Hence, since the cluster formation is hindered by the repulsive interaction between the adsorbed ions, a stable and uniform Li coverage on both sides of graphene up to $\Theta=5\%$ can be attained.

The charge accumulation and band structure calculated for the H1 and H1+H3 adsorption geometries are presented in Figs. 1(b) and 1(c), respectively. Isosurface plots of charge accumulation obtained by subtracting charge densities of Li and bare graphene from that of Li which is adsorbed to graphene, $\Delta\rho^+$, display positive values. As a result of Li adsorption, the charge donated by Li is accumulated between Li and graphene and is accommodated by $2p\pi^*$-bonds of carbons. The empty π^*-bands become occupied and eventually get distorted. Occupation of distorted graphene π^*-bands gives rise to the metallization of semimetallic graphene sheets. By controlled Li coverage, one can monitor the position of Fermi energy in the linear region of bands crossing at the *K* point of the Brillouin zone. Metallization is also important for zigzag and armchair graphene nanoribbons, since both are semiconductors with their energy gaps depending strongly on the widths of these ribbons.[12] Segments of these ribbons metallized by Li adsorption may be interesting for their electronic and spintronic applications. For example, a junction of two nanoribbons with and without Li adsorbed segments can serve as a Schottky barrier.

Sodium, a heavier alkali metal, can be bound to graphene with $E_b=1.09$ eV at H1 site. However, the energy difference between top, bridge and H1 sites are minute due to relatively larger radius of Na. Upon adsorption, graphene and graphene nanoribbon are metallized. Nevertheless, Na is not suitable for hydrogen storage because of its heavier mass and very weak binding to H_2 molecules. Two dimensional BN-honeycomb structure, being as a possible alternative to graphene, has very weak binding to Li ($\sim$0.13 eV) and hence it is not suitable for hydrogen storage.

The absorption of H_2 molecules by Li+graphene in H1, H1+H2, and H1+H3 geometries. A summary of our results about the H_2 absorption are presented in Fig. 2. The binding energy of the first absorbed H_2, which prefers to be parallel to graphene, is generally small. However, when two or more H_2 molecules are absorbed by the same Li atom, the binding geometry and mechanism change and result in a relatively higher binding energy. All H_2 molecules are tilted so that one of two H atoms of each absorbed H_2 molecules becomes relatively closer to the Li atom. A weak ionic bond forms through a small amount change ($\gtrsim$0.1 electrons) transferred from Li and graphene to nearest H atoms of absorbed H_2 molecules. At the end, H atoms receiving charge from Li becomes negatively charged and the covalent H_2 bond becomes polarized. Weak ionic bond, attractive Coulomb interaction between positively charged Li and negatively charged H and weak van der Waals interaction are responsible for the formation of mixed weak bonding between H_2 molecules and Li+graphene complex. Here the bonding interaction is different from the Dewar–Kubas interaction[13] found in H_2-Ti+C_{60} or carbon nanotube complexes.[3] As the number of absorbed H_2, *n*, increases, the positive charge on Li as well as the minimum distance between H_2 and Li slightly increases. No matter what the initial geometry of absorbed H_2 molecules would be, they are relaxed to the same final geometry presented in Fig. 2 for any given *n*. We found no energy barrier for a H_2 molecule approaching the absorbed H_2 when $n\leqslant4$. Note that the dissociative absorption of H_2 molecules do not occur in the present system. The energy barrier for the dissociation of H_2 near Li to form Li–H bond is $\sim$2 eV.[14] Moreover, dissociation of H_2 to form two C–H bonds at the graphene surface is energetically unfavorable by 0.7 eV.

Maximum number of absorbed H_2 per Li atom is four, and the maximum gravimetric density corresponding to H1+H2 geometry at $\Theta=25\%$ coverage is $g_d=12.8$ wt %. This is much higher than the limit ($g_d=6$ wt %) set for the feasible H_2 storage capacity. Note that only for $n=4$, H1+H2 absorption geometry has slightly lower energy than H1+H3 geom-

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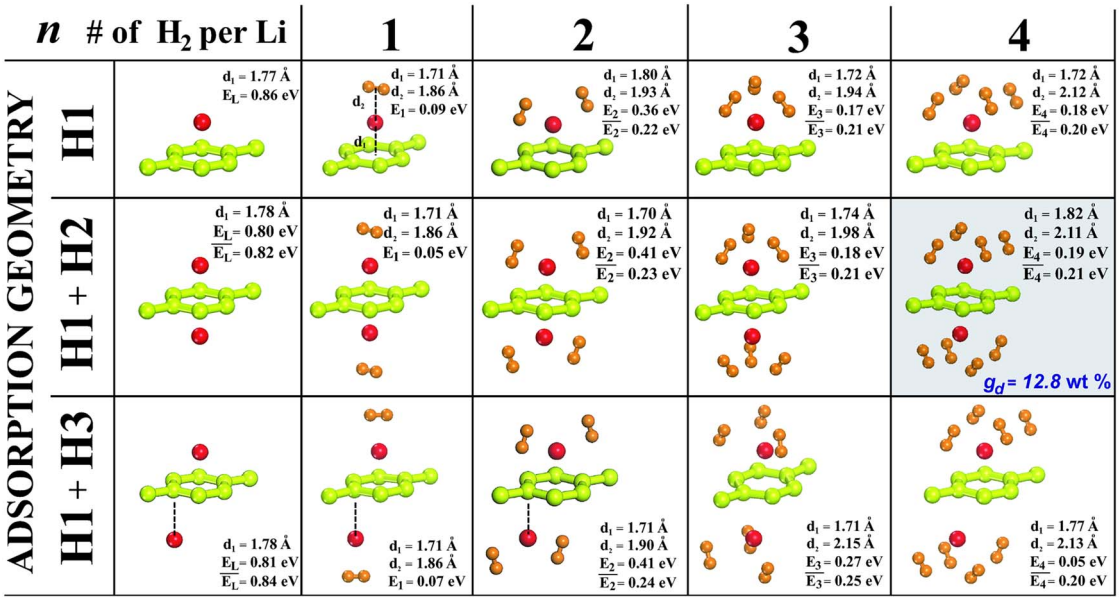

FIG. 2. (Color online) Adsorption sites and energetics of Li adsorbed to the (2×2) cell of graphene and absorption of H_2 molecules by Li atoms. E_L is the binding energy of Li atom adsorbed to H1 site, which is a minimum energy site. For H1+H2 or H1+H3 configuration corresponding to double sided adsorption, E_L is the binding energy of second Li atom and $\bar{E}_L$ is the average binding energy. For H1, H1+H2 and H1+H3 configurations, E_1 is the binding energy of the first H_2 absorbed by each Li atom; E_n $(n=2-4)$ is the binding energy of the last nth H_2 molecule absorbed by each Li atom, and $\bar{E}_n$ is the average binding energy of n H_2 molecules absorbed by each Li. Shaded panel indicates the most favorable H_2 absorbtion configuration.

etry. This is a remarkable result indicating another application of graphene as a high capacity storage medium. Here Li+graphene complex is superior to Ti+C_{60} or carbon nanotube complexes since Li is lighter. Even though graphene by itself is stable,[15,16] more stable form is obtained by Li adsorption on graphene due to strong Coulomb repulsion between adsorbed Li atoms. Moreover, Li covered graphene is resistant to clustering of adsorbed Li atoms. Earlier, Durgun *et al.*[5] has predicted that ethylen+Ti complex can store H_2 up to g_d=14.4 wt % per molecule. Later, their results have been confirmed experimentally.[17] We believe that hydrogen storage by the Li covered graphene is interesting, since it may not require encapsuling and hence may yield even higher effective g_d.

In conclusion, two crucial features of Li covered graphene revealed in this paper may be of technological interest. These are high metallicity and high hydrogen storage capacity of graphene functionalized by Li atoms. Graphene nanoribbons metallized through adsorbed Li atoms can be used as interconnects between graphene based spintronic devices. Graphene functionalized by Li can also serve as a medium of hydrogen storage. As far as efficiency in storage is concerned, graphene may be superior to carbon nanotubes because both its sides are readily utilized. Cell configurations formed by different junctions of graphene[18] functionalized by Li atoms are expected to yield higher surface/volume ratio and hence to provide efficient H_2 storage in real applications.

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