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 2s 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 H2 molecules amounting to a gravimetric density of 12.8 wt %.

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 H2 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 produced6 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 H2 by polarizing these molecules. At the end, the storage capacity up to the gravimetric density of 8.4 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 shown8 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 $\hbar^2|\mathbf{k}| + G^2/2m = 380$ eV has been used. In the self-consistent potential and total energy calculations the Brillouin zone has been sampled by $(19 \times 19 \times 1)$ and $(9 \times 9 \times 1)$ special mesh points in $\mathbf{k}$ space for $(2 \times 2)$ and $(4 \times 4)$ 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 $(4 \times 4)$ 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 2s 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 $q \sim 0.35$ electrons (but $q \sim 0.9$ electrons according to Bader analysis11). 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 $\Delta Q =0.35$ 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 $(2 \times 2)$ pattern. Owing to the repulsive interaction between positively charged Li atoms, the binding energy of Li atom is smaller than that of the $(4 \times 4)$ 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 $(4 \times 4)$ 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 $(2 \times 2)$ cell is $\Theta=12.5\%$ (i.e., one Li for every eight carbon atoms) for H1 geometry and $\Theta=25\%$ 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 $\Theta=25\%$ 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 $(2 \times 2)$ cell...
with the H1+H2 (H1+H3) geometry corresponding to Θ=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 Θ=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 Θ=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, Δρ∗, display positive values. As a result of Li adsorption, the charge donated by Li is accumulated between graphene and Li atom and is accommodated by 2π∗-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. 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 Eads=1.09 eV at H1 site. However, the energy difference between top, bridge and H1 sites is 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 H2 molecules. Two dimensional BN-honeycomb structure, being as a possible alternative to graphene, has very weak binding to Li (∼0.13 eV) and hence it is not suitable for hydrogen storage.

The absorption of H2 molecules by Li+graphene in H1, H1+H2, and H1+H3 geometries. A summary of our results about the H2 absorption are presented in Fig. 2. The binding energy of the first absorbed H2, which prefers to be parallel to graphene, is generally small. However, when two or more H2 molecules are absorbed by the same Li atom, the binding geometry and mechanism change and result in a relatively higher binding energy. All H2 molecules are tilted so that one of two H atoms of each absorbed H2 molecule becomes relatively closer to the Li atom. A weak ionic bond forms through a small amount change (∼0.1 electrons) transferred from Li and graphene to nearest H atoms of absorbed H2 molecules. At the end, H atoms receiving charge from Li becomes negatively charged and the covalent H2 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 H2 molecules and Li+graphene complex. Here the bonding interaction is different from the Dewar–Kubas interaction found in H2 −Ti +C60 or carbon nanotube complexes. As the number of absorbed H2, n, increases, the positive charge on Li as well as the minimum distance between H2 and Li slightly increases. No matter what the initial geometry of absorbed H2 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 H2 molecule approaching the absorbed H2 when n≤4. Note that the dissociative absorption of H2 molecules do not occur in the present system. The energy barrier for the dissociation of H2 near Li and H–H bond is ~2 eV. Moreover, dissociation of H2 to form two C–H bonds at the graphene surface is energetically unfavorable by 0.7 eV.

Maximum number of absorbed H2 per Li atom is four, and the maximum gravimetric density corresponding to H1 +H2 geometry at Θ=25% coverage is gH2=12.8 wt %. This is much higher than the limit (gH2=6 wt %) set for the feasible H2 storage capacity. Note that only for n=4, H1+H2 absorption geometry has slightly lower energy than H1+H3 geom-
binding energy of \( E_{L} \) 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 energy of the first H2 absorbed by each Li atom; \( E_{n} (n=2–4) \) is the binding energy of the last \( n \) H2 molecule absorbed by each Li. Shaded panel indicates the most favorable H2 absorption configuration.

In conclusion, two crucial features of Li covered graphene revealed in this paper may be of technological interest. These are high metallicty 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 functionalized by Li atoms are expected to yield higher surface/volume ratio and hence to provide efficient H2 storage in real applications.

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